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STRUCTURE AND PROPERTIES OF POLYURETHANES

by

Yu. S. Lipatov, Yu. Yu. Kercha, and L. M. Sergeyeva

UNEDITED MACHINE TRANSLATION

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STRUCTURE AND PROPERTIES OF POLYURETHANES

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L. M. Sergeyeva

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

Page 1.

STRUCTURE AND PROPERTIES OF POLYURETHANES.

Yu. S. Lipatov, Yu. Yu. Kercha, L. M. Sergeyeva.

Page 2.

In the book are examined the basic properties of class it is polyurethane[1], bonded with the specific character of the structure of polymeric molecules and their intermolecular interactions.

This book - the first in world literature, dedicated structure and properties of one of the most important classes of high-molecular compounds - it is polyurethane. The analysis of the special feature/peculiarities of the flexibility of chains, nature of bonds, effect of the chemical nature of chains on the phase and physical transitions, physicomechanical and other properties makes it possible to set the basic reasons for manifestation by polyurethane of that combination of properties which determines their wide practical application/use in the form of rubbers and rubbers, coatings, fibers and other materials.

Monograph is calculated in scientific workers, aspirants and workers of industry, who specialize in the region of chemistry, the physical chemistry and technology of polymeric materials.

---

[1] NOTE TO THE READER: Throughout this document, whenever the terms "it is polyurethane" or "is polyurethane" appears, please read "of polyurethanes," when applicable. END NOTE.

Page 3.

PREFACE.

Among a large number of polymeric materials, utilized in national economy, special position they occupy polyurethanes. This is determined by the very valuable and specific combination of the properties, developed by polymers, which makes possible their application/use in the most different branches of industry and in private life. Really/actually, we do not know another class of polymers on basis of which it is possible to obtain virtually all technically valuable polymeric materials - rubbers and rubbers, sealing compounds and sealing compounds, rigid and elastic synthetic fibers, glues and coatings, foamed plastics and many others. The possibilities of obtaining the such different materials are laid with the special feature/peculiarities of chemical structure it is polyurethane and not limited the possibilities of the regulating of their structure.

In world literature is known a large number of investigations, in which are examined questions of synthesis, technology and processing/treatment it is polyurethane. These works are generalized in the monograph of Saunders and Frisch, translated into the Russian language.

As a result of the conducted investigations, are created ten and hundreds of polyurethane connections and numerous technically valuable materials on their basis. However, to these ones on we have available the very limited information about the bond between the chemical structure and properties it is polyurethane, but some most important special feature/peculiarities it is polyurethane which determine the special value of these connections, until now, they are investigated very little. In the literature there are no generalizing data according to the relationship/ratios between the structure and properties it is polyurethane, but the majority of the investigations of the physicochemical and physical character devoted to the properties of foamed plastics on basis is polyurethane. On separate questions of the physical chemistry, it is polyurethane (flexibility of chains, property of solutions and fusion/melts, etc.) there is very few investigations in comparison with data for other classes of polymers.

Everything presented determined that problem which the authors placed before themselves in present monograph. It consists in the generalization of existing knowledges about structure and properties it is polyurethane and explanation on this basis of the reasons for the specific properties of this class of polymeric materials, what is very essential both from the point of view of their utilization in practice and from the point of view of finding the correct ways of the synthesis of polymers with preassigned combination of physicochemical properties.

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Primary task of physics and physical chemistry it is polyurethane - the establishment of the basic regularities, which join properties and structure with their specific special feature/peculiarities and which are determining the ways of their application/use to the study of these problems is dedicated this work.

As the basis of monograph, are assumed the data, published in world literature, and the results of the investigations, conducted in the section of physical chemistry of the polymers of the institute of the macromolecular chemistry of AS UkSSR by the authors and their coworkers.

Chapters I-III are written by Yu. S. Lipatov, Chapter IV - by Yu. Yu. Kercha, Chapter V - by L. M. Sergeyeva, Chapter VII - by Yu. S. Lipatov and L. M. Sergeyeva.

The problems of the bond between the conditions of the synthesis reaction of polyurethanes and the supermolecular structures, which appear with synthesis, were studied by T. E. Lipatova, who wrote chapter VI.

Page 5.

CHAPTER 1.

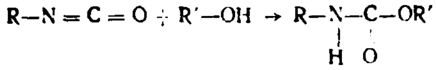
BASES OF THE CHEMISTRY CF POLYURETHANES.

Physical and chemical properties it is pclyurethane they are determined by the presence in the polymer chains of different types of chemical bonds and functional groups. This is caused by the fact that for synthesis it is polyurethane and polyurethane materials it is used considerably more initial of connections, than for other classes of polymers. Therefore it is, first of all, necessary to examine the basic methods of synthesis it is polyurethane and obtaining on their basis of different technical materials, in order to connect their properties with the conditions of synthesis and processing/treatment.

GENERAL PRINCIPLES OF SYNTHESIS OF POLYURETHANES.

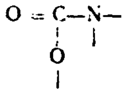
At the basis of obtaining, it is polyurethane it lie/rests the reaction of the step polymerization, by which is understood the reaction as a result of which during the addition of di- or polyfunctional reactants are formed the macromolecules without the splitting of the fragments of the reacting groups. For this type of reactions, is characteristic the migration of the atom of hydrogen at each step/stage, which gives grounds to call reaction also migration polymerization [47].

Formation it is urethane bonded with the addition reactions of isocyanates, described long ago by Wurtz [345],



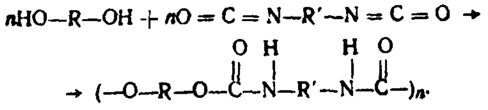
$$R{-}N{=}C{=}O + R'{-}OH \rightarrow R{-}\underset{H}{\underset{|}{N}}{-}\underset{O}{C}{-}OR'$$

For it is urethane it is characteristic the grouping of the atoms



$$O{=}\underset{\substack{|\\O\\|}}{C}{-}\underset{|}{N}{-}$$

The method of obtaining ~~is~~ polyurethane it is developed in Germany [286] and by the USA [285] simultaneously it is based on the reaction of isocyanates with glycols, as a result of which occurs the formation of linear polyurethane by the overall diagram



$$nHO{-}R{-}OH + nO{=}C{=}N{-}R'{-}N{=}C{=}O \rightarrow$$
$$\rightarrow ({-}O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R'{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-})_n.$$

Page 6.

The polymers of this structure have many common/general/total properties with polyamides and other linear polymers, which predetermine the potential possibilities of their application/use. With the aid of the selection of components (diisocyanates and hydroxyl-containing connections) it is possible over wide limits to vary their properties. Specifically, the possibility of the active regulating of the structure of polymer chain makes it possible to obtain on basis it is polyurethane materials with the most different properties.

For obtaining the high-molecular products, it is necessary to take the initial components of the high degree of purity in strictly equimolecular quantities. If one of the components is used in excess, this leads, as in the case of polycondensation, to the decrease of molecular weight. The component, undertaken in excess, forms predominantly end groups. The high reactionary character of diisocyanates makes it possible to carry out the reaction at low temperatures (in the case of the catalyzable reactions - with room ones). Under soft conditions occur/flow/lasts less than side reactions, which makes it possible to avoid branchings as a result of the reaction of diisocyanates with the formed urethane groups.

The examined above method of obtaining is polyurethane is most common it is used on industrial scale. There are also many other methods of their synthesis, one of which is based on the reaction of the polycondensation of dichlorocarbon ether/esters of glycols with diamines [267]:

$$n\mathrm{ClCOOR{-}OOCCl} + n\mathrm{NH_2{-}R'{-}NH_2} \rightarrow$$
$$\rightarrow [\mathrm{-R-OOCNH-R'-NH-COO-}]_n + \mathrm{HCl}.$$

Dichlorocarbon ether/ester of glycol is obtained during reaction with phosgene. Thus, this method includes the reaction of some component with phosgene as obtaining diisocyanates, based on the reaction of amines with phosgene, but it not found wide acceptance. It is necessary to note that the searches of the ways of synthesis it is polyurethane without the application/use of isocyanates and synthesis of isocyanates without the collaboration of phosgene they are of great practical interest; however, at present these methods cannot compete with the basic method of synthesis it is polyurethane, presented it is above.

The examined reactions are the basis of the synthesis of linear ones it is polyurethane.

By essential difference it is polyurethane from all other polymers it is the presence in the polyurethane chains also of other types of chemical bonds. Specifically, the diversity of the latter in many respects determines chemical and physical property it is polyurethane and their structure.

Polyurethane chain/network depending on molar ratio of the components, undertaken for synthesis, can have different terminal reactive groups.

Page 7.

On their reactionary character are based the methods of the elongation of chains or obtaining of the block copolymers. So, during the reaction of two molecules it is polyurethane, obtained with the excess of diisocyanate and having terminal isocyanate groups, with water occurs the elongation of chain and the emergence of the uric bond

$$2OCN\cdots NCO + HOH \rightarrow OCN\cdots NH-CO-NH\cdots NCO + CO_2.$$

The analogous elongation of chains with the formation of uric grouping occurs during the reaction of this polyurethane with diamines

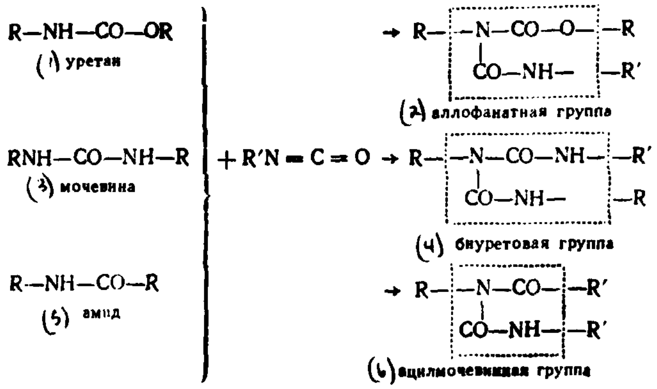
$$OCN\cdots NCO + H_2NRNH_2 + OCN\cdots NCO \rightarrow OCN\cdots NHCONH-R- \\ -NHCONH\cdots NCO.$$

So are obtained high-molecular polyurethane, in main chain of which are alternated urethane and uric groupings.

During obtaining of concrete polyurethane materials, especially three-dimensional structure, in the main chain of polymer can be present other types of bonds. This is explained by the fact that during formation it is polyurethane they occur/flow/last and other reactions, which have the technical value

$$R-N=C=O+\begin{cases} R'NH_2 \rightarrow R-NH-CO-NH-R' \\ R'COOH \rightarrow R-NH-CO-R'+CO_2 \\ HOH \rightarrow RNH-COOH \rightarrow RNH_2+CO_2 \rightarrow \\ \xrightarrow{R-N=C=O} R-NH-CO-NH-R. \end{cases}$$

The initial materials of addition have in uric, urethane, amide and other groups the reactive atoms of hydrogen which with increased temperatures interact with isocyanates with the formation of the new groupings



Key: (1). urethane. (2). allophanate group. (3). urea. (4). biuret group. (5). amide. (6). acylurea group.

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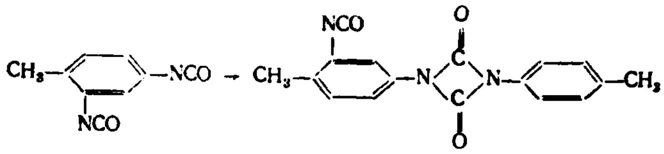
Further diversity introduces the reactions of the dimerization of diisocyanates, which lead to the formation of the uretdione ring



Thus, polyurethane in contrast to other classes of polymers are not the connections in chain of which is only one characteristic type of bonds. In a number of cases the concentration of urethane bonds in polymer can be compared with the concentration of the bonds of other types. In spite of this, fundamental characteristics of this class of polymers they are determined by the collaboration of isocyanates in synthesis reactions, and therefore all polymers of this form are related to class it is polyurethane.

For synthesis it is polyurethane three-dimensional structure they are used the trifunctional connections, which contain either three hydroxyl groups (for example, glycerin), or triisocyanate. These methods widely are used during obtaining of polymeric materials on basis it is polyurethane.

During the study of structure, it is polyurethane necessary to bear in mind the kinetic special feature/peculiarities of reaction. Their bond with structure we will examine separately. However, it should be noted that diisocyanates depending on their chemical structure possess varying reactivity - with minimum speed enter into reaction aliphatic diisocyanates, while the aromatic, especially containing electron-acceptor substituents (nitro-, nitrile, halide groups), they possess the increased reactionary character.

The reaction rate of isocyanates with alcohols falls upon transfer from primary ones to the secondary hydroxyl groups and from those saturated to unsaturated aliphatic glycols. Aliphatic primary and secondary amines react with isocyanates virtually instantly. If at temperatures of 20-80°C in essence occur the reactions of diisocyanates with glycols, water and diamines, then at the temperatures of higher than 100°C occur the side reactions, which lead to the formation of branchings and cross-linkings. The rate of these reactions grow/increases with a temperature rise in greater degree than basic ones.

To the rate of the various reactions, which lead to formation it is polyurethane, affect numerous catalysts - organic basis/bases, diamines, piperidine, piperazine, hydroxide of alkali metals, acetyl acetonates of copper, beryllium and vanadium, naphthenate of lead and cobalt, tributylol and many others.

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The action/effect of catalysts is propagated not only to the main reaction of diisocyanates with glycols, but also to the side reactions, bonded with the formation of urea, allophanat, biuret groups, with the polymerization of isocyanates into isocyanurate, etc. [333]. All this leads to the great variety of reaction products.

From short survey/coverage of the basic principles of synthesis, it is polyurethane evident that it is based on the application/use of connections with the isocyanate groups, which are characterized by unique reactionary character and capability for many chemical reactions. Macromolecular chemistry are not known other monomers, except isocyanates, capable of such a large number of different chemical reactions. This specific character of basic monomer determines the diversity of the types of chemical bonds in chains and of chemical transformations it is polyurethane. This creates possibility within the limits of one class of connections - it is polyurethane - to obtain materials with quite diverse properties. The more detailed information about the chemistry of isocyanates and the mechanism of formation it is polyurethane they are represented in works [114, 262, 333].

OBTAINING POLYURETHANE CAOUTCHOUCS [NATURAL RUBBER] AND RUBBERS.

Urethane caoutchoucs are very promising in the region of practical utilization it is polyurethane. Polyurethane elastomers are characterized by unique properties - extremely high strength for tear and abrasion, by high strength and elasticity.

Polyurethane elastomers obtain on the basis of oligomeric polyether/polyesters, which contain the terminal hydroxyl groups, and diisocyanates. Term "oligomer" designates the low molecular polymer, obtained during the reactions of radical telomerization or with the polycondensation, conducted with large excess of one of the components. Oligomers are viscous liquids, and their molecules are the basic building block of linear high-molecular chain. Common molecular weight of oligomeric polyesters, used for synthesis is polyurethane, it composes 1000-2000.

For the synthesis of polyurethane elastomers, can be used both simple and polyesters. In the case of simple polyesters, use extensively different copolymers - oxide of ethylene and propylene, their copolymers with tetrahydrofuran and so forth, etc. From polyesters are most common polyether/polyesters on the basis of different glycols (ethylene glycol, diethylene glycol, etc.) and of adipic acid. Basic diisocyanates, which are used for synthesis, are toluene-2,4-diisocyanate (2,4-TDI), 1,5-naphthylenediisocyanate, 4,4'-diphenylmethanediisocyanate, 1,6-hexamethylenediisocyanate (GMDI), etc.

The synthesis of polyurethane elastomers occur/flow/lasts in two stages [297].

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During the first stage from 2 moles of oligomeric polyether/polyester and 3 moles of diisocyanate obtain so-called macro-diisocyanate, or prepolymer:

$$\begin{array}{c}\mathrm{OCN{-}R{-}NCO + HO{\cdots}OH + OCN{-}R{-}NCO + HO{\cdots}OH + OCN{-}R{-}NCO} \\ \downarrow \\ \mathrm{OCN{-}R{-}NH{-}CO{-}O{\cdots}OCONH{-}R{-}NHCOO{\cdots}OCONH{-}R{-}NCO,}\end{array}$$

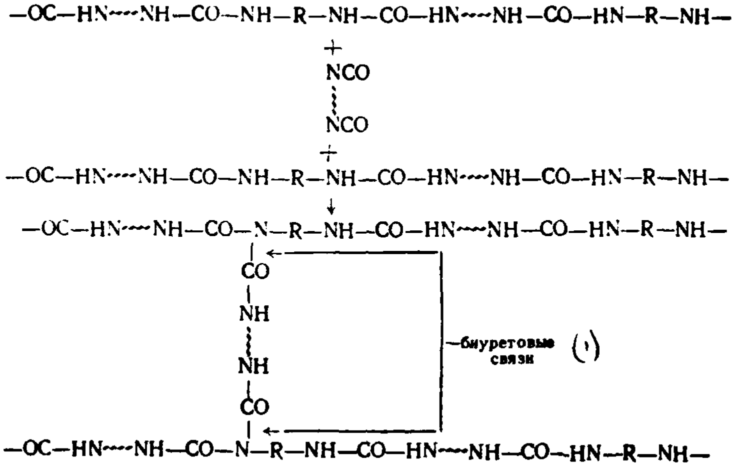
where surging line designates the molecule of oligoester or oligourethane (macro-diisocyanate).

Prepolymer - viscous liquid or easily softened solid. Terminal isocyanate groups make it possible to elongate chain with the aid of it is diamine or glycols (butanediol, triethylene glycol, etc.).

During the reaction of macro-diisocyanates it is diamine initially are obtained linear polyurethaneurea

$$\begin{array}{c}\mathrm{OCN{\cdots}NCO + H_2N{-}R{-}NH_2 + OCN{\cdots}NCO + H_2N{-}R{-}NH_2} \\ \downarrow \\ \mathrm{{-}OC{-}NH{\cdots}NH{-}CO{-}HNR{-}NH{-}CO{-}HN{\cdots}NH{-}CO{-}NH{-}R{-}NH{-}}\end{array}$$

The excess of macro-diisocyanate, which did not enter the reaction, causes the cross-linking of chains. During this cross-linking macro-diisocyanate is added according to the preliminarily formed uric bonds which are sufficiently reaction with respect to diisocyanate groups. As a result of this in the cross-linked rubbers, appears one additional type of bonds - biuret:



Key: (1). biuret bonds.

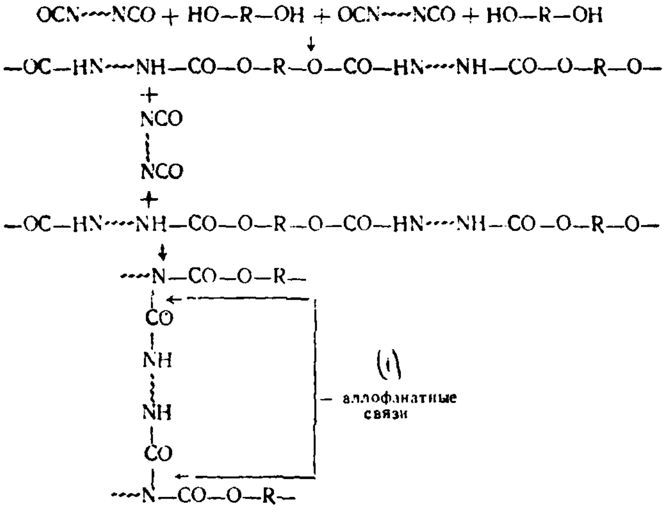
One and the same macro-diisocyanate serves both for the construction of chains and for their cross-linking, which is determined, in particular, the almost identical size/dimensions of mesh. In this, consists, obviously, one of the reasons high strength and small abradability is polyurethane.

Page 11.

Elastomers with analogous properties are formed also when instead of diamine for cross-linking is taken water. With splitting

CO_2, initially is formed linear polyurethaneurea, which, interacting with the excess of macro-diisocyanate, leads to lengthening of chains and their cross-linking with the formation of biuret bonds.

During obtaining of high-molecular products for cross-linking, can be also used the reaction of the reaction of macro-diisocyanates with diatomic alcohols, for example by butanediol,



Key: (1). allophanate bonds.

Glycol in this case is taken somewhat less than it is required for full/total/complete saturation diisocyanate. The excess of macro-diisocyanate cross-links polymer chains because of reaction with the atoms of hydrogen of urethane groups. In this case, appears one additional type of bonds in chains - allophanate.

Combination of the examined methods gives the possibility to widely vary the structures of the grid of rubbers and, thus, to change their physicomechanical of characteristic, especially if one considers that as the variables, which are determining properties, it is possible to select oligomers of different chemical structure and molecular weight and different diisocyanates.

There is also yet another possibility of obtaining the cross-linked polyurethane elastomers the single-stage method. It consists in the fact that into oligoester with its synthesis is introduced a small quantity of triatomic alcohol, for example trimethylol propane. in this case, is formed branched polyether/polyester.

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In the course of its reaction with diisocyanates simultaneously with a chain growth occurs the cross-linking of the free hydroxyl groups of the introduced triatomic alcohol.

From that presented it is evident that the chemistry of polyurethane elastomers has in effect unlimited possibilities of changing the chemical structure of polyurethane elastomers. Common for all, however, remains the presence of four basic types of bonds (urethane, uric, biuret and allophanate) and the alternating in the chain of the blocks of oligomeric component - oligoester or other hydroxyl-containing connections - and the blocks, introduced by diisocyanate component.

POLYURETHANE FIBERS.

Fibers on basis it is polyurethane they are separated into two basic classes. The first includes the fibers, analogous to other thermoplastic fibers of the type poliamide, polyether/polyester, etc. This of fiber not to basis linear thermoplastic crystalizing it is polyurethane. the chemistry of obtaining such fibers consists in the synthesis of linear products during the reaction of the dihydroxyl-containing short-chain connections (ethylene glycol, di-, triethylene glycol, 1,4-butanediol) with different diisocyanates. The most widely used type of polyurethane fibers - perlon U - is obtained during the reaction of butanediol-1,4 with hexamethylene diisocyanate. Varying the components, used for the synthesis of the fibre-forming polymers, it is possible to change the melting points of polymers and their physicomechanical of characteristic [23].

The second class of polyurethane fibers includes the elastomeric fibers, which possess linear or three-dimensional three-dimensional/space structure. This group of fibers is unique in its properties and does not have analogs among other classes of polymeric compounds. The elastomeric fibers into which enters not less than 85o/o it is polyurethane, there were for the first time published in the USA at the end of 1960 because of their chemical structure they they possess high extension at break (500-800o/o), by low module/modulus of elasticity and high elastic deformation.

The chemism of the formation of elastic three-dimensional polyurethane fibers and three-dimensional polyurethane rubbers is analogous. In present time there are various forms of polyurethane elastomeric fibers, known under different firm designations (Lycra, Spandex, Virayn) [48]. For their obtaining are used different polyether/polyesters with terminal hydroxyl groups (simple and complex) and diisocyanates - toluenediisocyanate, diphenylmethane-4,4'-diisocyanate, 1,5-naphthalenediisocyanate, etc., i.e., the compounds utilized also during obtaining of polyurethane rubbers and rubbers.

Page 13.

Differences in the methods of obtaining bear not so much chemical as technological nature and are associated with special spinning conditions of the filament which can be realized by the wet and dry method. Highly elastic polyurethane fibers depending on the type of the reactions, utilized for their obtaining, have three-dimensional and linear structure. The vital difference for these fibers and polyurethane elastomers, from other rubbers is in the large role of physical nodes in grid.

The basic special feature/peculiarity of the structure of polyurethane elastomeric fibers is alternating the blocks of different chemical nature, which makes it possible to give to fiber the necessary textile and mechanical properties. In detail questions of the chemistry of elastomeric polyurethane fibers are examined in works [48, 298, 303].

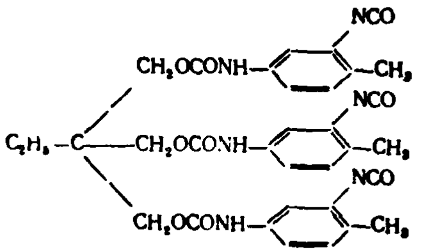
The formation of the hydrogen bonds between groups CO and NH of adjacent chains to a certain extent replaces chemical cross-linking. The rigid segments, which contain urethane bonds, are the nodes of the three-dimensional physical grid whose elastic properties are determined by pure/clean polyether/polyester blocks.

POLYURETHANE COATINGS.

By by of trial and error of the components, used for synthesis it is polyurethane, to them it is possible to give the most different properties. from three-dimensional ones it is polyurethane, in which the blocks of hydroxyl-containing component sufficiently rigid in comparison with the same in rubbers, it is possible to obtain three-dimensional polyurethane films and coatings. The presence of a large number of polar groups provides the high adhesion of coatings to surfaces, and specific properties it is polyurethane - high physicomechanical properties of coatings. The basic principle of obtaining coatings is based on the utilization of polyfunctional connections, which ensure the formation of three-dimensional three-dimensional/space grid. As polyfunctional connections are used ter- and tetratomic alcohols, branched polyether/polyesters and their combinations. During the formation of polyurethane coatings, occur virtually the same reactions, that during obtaining of rubbers, i.e., in reaction products are besides urethane ones also uric, biuret and allophanate bonds. From a chemical point of view, are very important the reactions with water, since the solidification of varnish coatings on basis it is polyurethane usually it occurs under conditions for contact with moisture of air.

Page 14.

Since the poly-functionality of initial compounds is the necessary condition of obtaining the three-dimensional coatings, then as one of the components of reaction is used the adduct toluenediisocyanate with trimethylol propane and diethylene glycol



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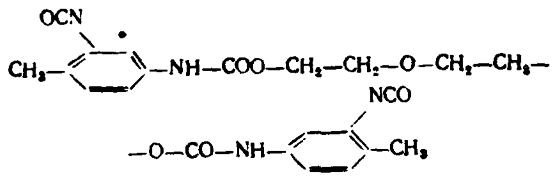

Is known at present a large number of most different compositions, used for obtaining the polyurethane coatings, which make it possible to obtain the coatings, which correspond to the most varied requirements. however, at the basis of all methods, lie/rest one and the same chemical principles of obtaining three-dimensional structures.

Obtaining the polyurethane adhesive compositions virtually in no way differs from the principles of obtaining coatings. In each individual case the chemical nature of components and the conditions of the solidification of composition select so as to ensure the necessary viability of compositions, the temperature conditions of solidification, rate of processes, etc.

From that presented it is evident that the diversity of chemical structure it is polyurethane it is determined by application/use for their synthesis of the connections of the most varied classes, beginning with low-molecular glycols and finishing with numerous oligoesters and other oligomeric compounds with the terminal hydroxyl groups.

The presence in the chains of different types of bonds does not make it possible to already consider polyurethane the single class of polymers as, for example, polyamides or polyacrylates. Really/actually, by the only common/general/total sign, which gives the basis to relate polymers to polyurethane, in many instances can serve only presence of urethane grouping.

Thus, the special feature/peculiarity of chemical structure it is polyurethane and diversity of their properties they are determined by the fact that for synthesis are used the initial connections, which relate to different classes. In this sense there is no problem it is polyurethane as such, but there is a problem of initial connections for the synthesis of the polymers, which contain urethane groups.

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Chapter II.

THERMODYNAMIC PROPERTIES OF SOLUTIONS OF POLYURETHANES.

In the examination of the special feature/peculiarities of physical and molecular structures, it is polyurethane, first of all, necessary to dwell on the flexibility of molecular chains. The flexibility of chains as the characteristic, which is inherent only in high-molecular compounds, determines the basic physicomechanical and physical properties of polymers. The information about flexibility can be obtained either during the analysis of the properties of dilute polymer solutions or from the investigations of the sorption of vapors by polymers, or from data in mechanical and relaxation properties.

PROPERTIES OF DILUTE SOLUTIONS OF POLYURETHANES.

By the specific line of structure it is polyurethane, caused by the chemism of their formation, is alternating in the polymer chain of the sections of different chemical nature - residue/remainders of the molecules of glycol or polyether/polyester and diisocyanate. Thus, in linear polymer chain are located heterobonds of different nature, besides carbon-carbon ones, bonds of the type C-O-C in glycol and simple polyether/polyesters, bond C-O- in polyesters, bond

$$\begin{array}{c}\| \\ \mathrm{O}\end{array}$$

-NH-CO-O- and so forth. The diversity of heterobonds must significantly affect the flexibility of polyurethane chain. The flexibility of chain determines the basic physicochemical and physicomechanical properties of polymers. It is known that the reason for the flexibility of chain is the presence of the known freedom of rotation around the valent atomic bonds, which generate molecules. This rotation to a greater or lesser extent is braked both by intramolecular and intermolecular forces. The potential threshold of rotation depends on the type of valence bond and nature of substituents in the appropriate atoms of polymer chain. The examination of data according to internal rotation in organic molecules [16] shows, in particular, that the internal rotation around bond C-O is facilitated in comparison with rotation around bond C-C. Therefore it is possible to assume that the polymer chains with heterobonds of the type polyethers will possess the increased flexibility.

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On the other hand, the presence of the strongly interacting polar groups in chain had to cause an increase in the barriers of internal rotation and stiffening of chain. Combination in one polymeric molecule of different types of bonds determines the complex character of the dependence of the flexibility of chains it is polyurethane on their chemical nature.

On the basis of the data on size/dimensions and geometric form of macromolecules in solutions, can be determined the thermodynamic (equilibrium) flexibility of polymer chain, which is characterized by ratio/relation of the not disturbed by reaction with the solvent size/dimensions of chains $(\bar{h}_0^2)^{1/2}$ to the size/dimensions which would have the polymeric ball during completely free running of all links $(\bar{h}^2_{\text{св}})^{1/2}$. For determining this value, it is necessary to know the size/dimensions of chain in ideal (noninteracting) solvent. Value $(\bar{h}^2_{\text{св}})^{1/2}$ is usually determined by calculation, also, for the chain, which consists of n of valence bonds, by length l with constant valency angle $\pi-\theta$ and free running,

$$\bar{h}^2_{\text{св}} = nl^2\frac{1+\cos\theta}{1-\cos\theta}.$$

The immediate determination of these values for it is polyurethane hinder/hampered on two reasons. As a rule, linear polyurethane comparatively low molecular polymers, which limits the possibility of applying the method of light scattering for determining of the dimensions of chain. They possess the limited solubility in many organic solvents, which decreases with an increase in molecular weight, which creates difficulty during the selection of ideal solvent.

On the other hand, the size/dimension of chain under the condition for free running cannot be determined from the equation, which considers only C-C-bond in main circuit. Sizing of the chains, in which are alternated two or considerably more than the types of bonds as in polyurethane, is more complex [16]. The absence in a number of cases of precise data on a system of alternating and a quantity of heterobonds in chain makes such calculations with those difficultly attained. Therefore for obtaining the information about the flexibility of polyurethane chains, it is necessary to use indirect methods.

Let us examine this question based on the example of the investigation of prepolymers on the basis of polydiethyleneglycoladipate (molecular weight 4100) and toluenediisocyanate, and also polyurethane on the basis of butanediol and toluenediisocyanate [96].

For low-molecular prepolymers it is not possible to directly determine value $(\bar{h}^2)^{1/2}$ therefore they were applied the graphic method, proposed by Stockmayer and Fixman [323].

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They showed that the known equation of Flory, joining intrinsic viscosity with molecular weight and size/dimensions of chain,

$$[\eta] = \Phi (\bar{h}^2)^{3/2}/M$$

easily is converted:

$$[\eta] = \Phi (\bar{h}_0^2/M)^{3/2} M^{1/2} + 0{,}51 \Phi B M,$$
$$B = \bar{v}^2 (1 - 2\chi_1)/V_1 N_A,$$

where $\bar{v}$ - a partial specific volume of polymer in solution, V_1 - molar volume of solvent, χ_1 - the thermodynamic parameter of reaction.

This relationship/ratio makes it possible to determine $(\bar{h}_0^2/M)^{1/2}$ and B by initial ordinate and slope/inclination of direct dependence $[\eta]/M^{1/2}$ on $M^{1/2}$ (Fig. 1). After assuming that Flory's constant does not depend on the quality of solvent, and after accepting $\Phi = 2{,}8 \cdot 10^{21}$, we find value $(\bar{h}_0^2/M)^{1/2}$ in benzene and acetone, equal to 0.9 and 0.86, but value $(\bar{h}_0^2/\bar{h}_{\text{св}}^2)^{1/2} - 1{,}57$ and 1.50 respectively. During such a calculation of value $(\bar{h}_{\text{св}}^2)^{1/2}$ was not considered the effect of urethane bonds and benzene rings on the size/dimensions of chain, since bulk of chain consists of polyether/polyester segments. That establish/installed for the prepolymers of different molecular weight in by the dissimilar relationship/ratio of urethane groups linear dependence $\lg[\eta]$ on $\lg M_w$ shows that $[\eta]$ the investigated specimen/samples is really/actually determined only by glycol component that it makes possible calculation $(\bar{h}_0^2/M)^{1/2}$.

On the basis of the theory of Stockmayer and Fixman [323] are investigated the solutions of the polyurethane, obtained from polyoxyethyleneglycol (mol. weight 2000 and 1000) and toluylenediisocyanate it was established that value $(\bar{h}_0^2/\bar{h}_{\text{св}}^2)^{1/2} = 1{,}54$, is comparable with the appropriate values for it is polysiloxane and rubbers [153].

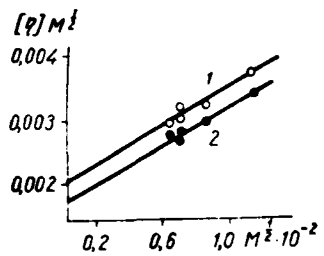

Fig.1

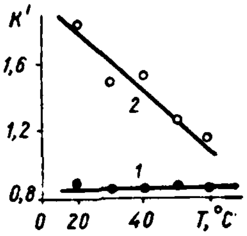

Fig.2.

Fig. 1. Dependence $[\eta]M^{1/2}$ on $M^{1/2}$ for prepolymers in benzene (1) and acetone (2).

Fig. 2. Dependence of constant of Huggins (K') on temperature in benzene (1) and methylethylketone (2).

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For calculation $(\overline{h_0^2}/M)^{1/2}$ it is possible to also apply the equation of Flory, if is known value $[\eta]_\theta$. Data [96] showed that in equation $[\eta] = KM_w^a$ parameter a has a value, common for the solutions of pliable macromolecules in good solvents (0.5<a<0.8) 237]. Calculated according to slope/inclinations of straight lines $[\eta]/M^{1/2} = f(M^{1/2})$ and known to values $\bar{v}$=0.900 (for benzene) and 0.887 cm³/g (for acetone) value χ_1 composes 0.163 and 0.228 respectively. Since $[\eta] \sim M^{1/2+3\varepsilon/2}$ [211] (ε - parameter, bonded with volume effects), then the degree of swelling α can be determined by equation

$$\varepsilon = (\alpha^2 - 1)(5\alpha^2 - 3).$$

In our case for both of solvents $\varepsilon = 0{,}133$, which brings to $\alpha=1.33$. Knowing α, it is possible to calculate [257] $[\eta]_\Theta$ and, consequently $(\bar{h}_0^2/M)^{1/2}$ from the ratio/relations

$$\alpha = ([\eta]/[\eta]_\Theta)^{2,43},$$

$$(\bar{h}_0^2/M)^{1/2} = \left(\frac{[\eta]_\Theta M}{\Phi}\right)^{1/3} M^{1/2}.$$

Calculations give $(\bar{h}_0^2/M)^{1/2} = 0{,}88$ and 0.84, which agrees well with value $(\bar{h}_0^2/\bar{h}_{\text{св}}^2)^{1/2}$.

Thus, corrected value $(\bar{h}_0^2/\bar{h}_{\text{св}}^2)^{1/2}$ shows that the flexibility of the chain/networks of low-molecular prepolymers exceeds the flexibility of vinyl polymers and is comparable with flexibility it is polysiloxane and rubbers [257].

For a prepolymer with $M_w = 1{,}35 \cdot 10^4$ is also measured the temperature dependence of intrinsic viscosity in benzene and methylethylketone. As can be seen from Fig. 2, the intrinsic viscosity of prepolymer in benzene falls from an increase in the temperature. The value of temperature coefficient $\frac{1}{[\eta]} \cdot \frac{d[\eta]}{dT} = -1{,}09 \cdot 10^{-3}$ is characteristic for polymers in the good solvents where the thermodynamic reaction of polymer with solvent insignificantly is changed with temperature, and basic effect on ductility/toughness/viscosity exerts a change in the close-range interaction. In methylethylketone $[\eta]$ calculation with an increase in the temperature and $\frac{1}{[\eta]} \cdot \frac{d[\eta]}{dT} = 4{,}16 \cdot 10^{-3}$. It is obvious that methylethylketone is poor solvent. Attention is drawn to also the high value of the constant of Huggins K' (Fig. 2) which in benzene in the investigated temperature interval is not virtually changed, but in methylethylketone sharply it falls from a temperature rise.

Transition to linear polyurethane in which glycol component has a small size/dimension, must, obviously, lead to stiffening of chain. For linear ones it is polyurethane on the basis of butanediol and toluenediisocyanate (mol. weight 0.2-0.96•10^{4}) this same by method are determined the values of the equilibrium flexibility of chains. It was established that $(\bar{h}_0^2/M)^{1/2} = 1{,}03$, and corresponding to it value $(\bar{h}_0^2/\bar{h}_{св}^{2}) = 2{,}0$.

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This indicates that an increase in the concentration of urethane groups in chain leads to significant lowering in its flexibility, which in this case is comparable with the flexibility of the chains of common vinyl polymers.

The given data really/actually make it possible to consider that the flexibility of the polyurethane chains is characterized in essence by the flexibility of oligomeric polyether/polyester component. In connection with this arises a question concerning the flexibility strictly of oligomeric molecules. The study of the behavior of oligomers in solutions is very important, since gives the possibility to judge also the properties and the flexibility of the chains of those three-dimensional polymers which are obtained on their basis. With the aid of the hydrodynamic characteristics of oligomers, it is possible to determine their size/dimension, configuration and reaction with solvent.

Works on the investigation of diffusion and ductility/toughness/viscosity of oligomers it is very little, but information about the properties of the oligomers of the esters, which are of greatest interest for synthesis it is polyurethane, they are absent. In connection with this it is expedient to dwell on those carried out by Nesterov and Lipatov studies of diffusion and ductility/toughness/viscosity of oligomers on the basis of diethylene glycol and adipic acid with a molecular weight of from 2000 to 430 [97]. The curves of the dependences of the coefficients of diffusion and intrinsic viscosity on molecular weight have a slope/inclination, close to 0.5. The corresponding data are represented in Table 1, from which it is evident that the absolute values of ductility/toughness/viscosity in acetone are somewhat more than in ethanol. This, probably, it is caused by different effect of solvents on the skeletal/skeleton hardness (close-range interaction) of chains, but not to volume effects (remote action). Values a, close to 0.5, indicate that the parameter of swelling A approaches unity.

Table 1. Hydrodynamic characteristics of oligomers.

M	[η], дл/г (3)		D·10⁶, см²/сек (4)		$(\bar{h}^2)^{1/2}$, Å		$A_0 \cdot 10^{10}$, эрг/град (5)	
	(1) Ацетон	(2) Этанол	(1) Ацетон	(2) Этанол	(1) Ацетон	(2) Этанол	(1) Ацетон	(2) Этанол
430	0,0360	0,0300	10.0	3,04	23.0	21.0	2.78	2,89
600	0,0386	0,0350	8,9	2,48	26.0	25,8	2.85	2,78
800	0,0463	0.0400	7,45	2,22	31,0	29,0	2.80	2.85
1200	0,0550	0.0485	6,3	1.86	36,6	34,5	2.86	2,92
2000	0.0737	0,0610	5.1	1.39	45,5	46.0	3,03	2.80

Note. $A_0 = \frac{D\eta_0}{T}(M[\eta])^{1/3}$ where η_0 - viscosity of the solvent.

Key: (1). Acetone. (2). Ethanol. (3). dl/g. (4). cm²/s. (5). erg/deg.

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Probably, with low molecular weight the reaction polymer - solvent does not exert a substantial influence on the conformation of molecules. The absence of an increase in the exponent with M with the decrease of molecular weight speaks that for the chain molecules even of this light molecular weight is characteristic small hydrodynamic flowability. This differs them from semirigid molecules of the type of derivatives of cellulose [148]. In that case of the property of molecules, it is possible to describe by the theories, which consider only hydrodynamic reaction. According to [225], application/use of persistent model in the hydrodynamic theory of Kirkwood-Riseman [247] makes it possible to determine the persistent length of molecule, which characterizes its flexibility. The conducted for the oligomers in question calculations showed that for the chains of oligodiethyleneglycoladipate the persistent length is 8-8.6 A. Findings also attest to the fact that the behavior of the molecules of oligomers is similar to the hydrodynamic behavior of Gaussian balls with a small hydrodynamic reaction.

Table 2. Characteristics of oligomers in acetone and ethanol.

(1) Олигомер	$M \cdot 10^{-3}$	(2) $[\eta]$ в ацетоне, дл/г	(3) $[\eta]$ в этаноле, дл/г	$D \cdot 10^6$ в ацетоне, (4) $см^2/сек$	$D \cdot 10^6$ в этаноле, (5) $см^2/сек$	(6) $(\bar{h}^2)^{1/2}$ в ацетоне, Å	(7) $(\bar{h}^2)^{1/2}$ в этаноле, Å	a, Å	$(\bar{h}_0^2/\bar{h}_{св}^2)^{1/2}$	$K \cdot 10^4$	m
(8) Полиэтиленгликольадипинат (ПЭГА)	1,00	0,060	—	5.90	—	40,0	—	9,3	2,15	17.8	0,5
	2,00	0,086	—	4,15	—	57,0	—	—	—	—	—
(9) Полидиэтиленгликольадипинат (ПДЭГА)	0.43	0.035	0.03	10.00	3,04	23,0	21.0	8,0	1.8	16.2	0.5
	0.60	0.0386	0,035	8,90	2.48	26,0	25,8	—	—	—	—
	0.80	0,0463	0.040	7.45	2,22	31,0	29,0	—	—	—	—
	1,20	0,055	0.0485	6.30	1,86	36,6	34,5	—	—	14,1	0,5
	2.00	0.0737	0,061	5,10	1,39	45.[illegible]	46,0	—	—	—	—
(10) Политриэтиленгликольадипинат (ПТЭГА)	0,90	0,055	—	6,15	—	39,0	—	8.0	2,0	17,4	0,5
	2,02	0.078	—	4,30	—	55,0	—	—	—	—	—
11 Полиокситетраметиленгликоль (ПОТМГ)	1,00	0.0765	—	5,67	—	42,0	—	11,5	2,25	23,0	0,5
	2,00	0,113	—	58,50	—	58,5	—	—	—	—	—

Key: (1). Oligomer. (2). in acetone, dl/g. (3). in ethanol, dl/g. (4). in acetone, cm²/s. (5). in ethanol. (6). in acetone. (7). in ethanol. (8). Polyethyleneglycoladipate (PEGA). (9). Polydiethyleneglycoladipate (PDEGA). (10). Polytriethyleneglycoladipate (PTEGA). (11). Polyoxytetramethyleneglycol (POTMG).

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This gives the possibility to use the relationship/ratios, which join the diffusion coefficient and the size/dimensions of the diffusing particles

$$(\bar{h}^2)^{1/2} = \frac{2.6 \cdot 10^{-17} T}{\eta_0 D},$$

for determining of the dimensions of the molecules of oligomers. Calculated values $(\bar{h}^2)^{1/2}$ for the oligomers of diethyleneglycoladipate are represented in Table 1. Value $(\bar{h}^2)^{1/2}$ in ethanol is somewhat less than in acetone, which will agree with differences in the ductility/toughness/viscosity. Ratio/relation $(\bar{h}_0^2/\bar{h}_{\text{св}}^2)^{1/2}$, equal respectively in acetone and ethanol 1.83 and 1.76, is close to the values, obtained for common high-molecular rubbers.

Thus, the investigation of diffusion and intrinsic viscosity of oligomers they showed that the hydrodynamic characteristics of these molecules will agree well with the same for the model of the non-proceeding Gaussian balls, although this and not Gaussian balls in their common form due to an insufficient number of links in molecular chain.

In work [98] is undertaken the more detailed investigation of the properties of different oligomers and low-molecular it is polyurethane, obtained on their basis, by the methods of diffusion and intrinsic viscosity. Were studied oligomers of ethyleneglycoladipate, diethyleneglycoladipate, triethyleneglycoladipate, hydroxytetramethyleneglycol and polyurethane on the basis of these oligomers and toluene-2,4-diisocyanate. Tables 2 and 3 depict the characteristics of the investigated objects and the obtained results. From dependence $\lg[\eta]$ on lg M (Fig. 3) it is evident that the slope/inclinations of straight lines for all oligomers are equal to 0.5. For a comparison this same figure, gives dependence $\lg[\eta] - \lg M$ for polyurethane on the basis of diethyleneglycoladipate and 2,4-TDI.

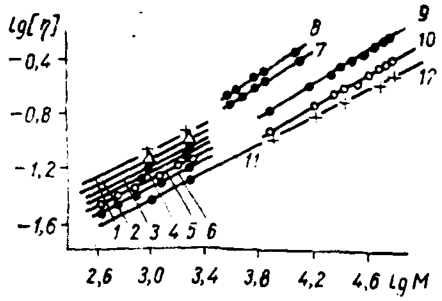

Fig. 3. Dependence $\lg[\eta]$ on lg M for the solutions of the oligomers of hydroxytetramethyleneglycol in acetone (1) and methylethylketone (2); PEGA in acetone (3); PTEGA into acetone (4); PDEGA in acetone (5) and standard (6); polyurethane on the basis of diethylene glycol and 2,4-TDI in acetone (7) and benzene (8); polyurethane on the basis of POPG and 2,4-TDI in benzene (9) and methanol (10); POPG (11) and polyurethane (12) in θ-solvent.

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The values of the intrinsic viscosity of oligomers depend on the nature of solvent. This, probably, it is caused by the effect of solvent on the skeletal/skeleton hardness of molecular chain, but not volume effects, since the value of the exponential in equation of type $[\eta]=KM^{a}$ (equal to 0.5) shows that the parameter of thermodynamic swelling α=1, and testifies to small hydrodynamic flowability of all investigated molecules. From the calculations of persistent length [98] it follows that the flexibility of the chain of oligomers has a tendency toward growth with an increase of the number of oxygen atoms in chain in accordance with determining of the dimensions of chains from the coefficients of diffusion (see Table 2 and 3).

Upon transfer to polyurethane (see Fig. 3) a change in the intrinsic viscosity by whole depends on structure and properties of oligomeric component. The value of exponent with M in the equation of Mark-Hewing is more than 0.5, which is caused by the effect of volume effects on intrinsic viscosity, but not by an increase in the partial flowability of balls upon transfer from oligomer to polyurethane. The points of dependence $\lg[\eta]$ on lg M for oligomers it is polyurethane in θ-solvent they are stacked to one straight line (see Fig. 3). This confirms the absence of the effect of urethane groups on the thermodynamic flexibility of chain for the case it is polyurethane on the basis of oligomers. The thermodynamic flexibility of chains was determined according to the method of Stockmayer-Fixman, value $(\bar{h}_0^2/\bar{h}_{\text{св}}^2)^{1/2}$ were given in Table 3.

Table 3. The characteristics of solutions it is polyurethane in acetone and benzene.

(1) Полимер	(2) M олигомера	(3) M полимера	(4) [η] в ацетоне, дл/г	(5) [η] в бензоле, дл/г	(6) $D \cdot 10^6$ в ацетоне, $см^2/сек$	$(\bar{h}^2)^{1/2}$, Å	NCO : OH	$K \cdot 10^4$	m
ПЭГА — ТДИЦ	1000	4700	0,243	—	2.70	88.0	1,1	—	—
	2000	4400	0,234	—	2.80	84,5	1,1	—	—
ПДЭГА — — ТДИЦ	4000	13 500	0,390	0.440	—	—	0,75	(7) 5.05 (ацетон)	0,7
	4000	7500	0.260	0.280	—	—	0.5	—	—
	800	6600	0.234	—	2,44	98,0	1.1	—	—
	1700	5200	0.200	—	2.80	82,5	1,1	(8) 5.5 (бензол)	0,7
	4000	5100	0.190	0,230	—	—	1,1	—	—
	4000	5000	0,186	0,218	—	—	1,33	—	—
	4000	4350	0.185	0,195	—	—	2.0	—	—
ПТЭГА — — ТДИЦ	900	5000	0.230	—	2.90	82.0	1.1	—	—
	2020	4700	0.200	—	3.32	70.0	1.1	—	—
ПОТМГ — — ТДИЦ	2000	15 600	0.630	—	1,31	181,0	1.1	—	—
	1000	6700	0,380	—	2,02	118.0	1.1	—	—

Key: (1). Polymer. (2). oligomer. (3). polymer. (4). in acetone, dl/g. (5). in benzene, dl/g. (6). in acetone, cm²/s. (7). acetone. (8). benzene.

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During calculation $(\bar{h}^2_{св})^{1/2}$ they disregarded the contribution of urethane groups on the basis of the fact that the points in direct/straight 7 Fig. 3 were obtained for polyurethane from diethyleneglycoladipate and 2,4-TDI whose oligomeric components have different molecular weight (from 800 to 4000) and nevertheless they are stacked well to one straight line. As another confirmation serves the fact that dependence $\lg[\eta]$ on lg M for polyurethane on the basis of polyoxypropyleneglycol and 2,4-TDI is described by one straight line for oligomer and polyurethane.

The method of Stockmayer-Fixman is applied also for evaluating the undisturbed size/dimensions for linear PU on the basis of ethylene glycol and 4,4'-diphenylmethanediisocyanate according to the data of viscosimetry at θ-point which was created with the aid of binary solvent [172]. In this case for nine fractions, is found relationship/ratio $[\eta]\ 3{,}64\cdot10^{-4}M^{0{,}71}$, which is very close to the results, presented above. Index a=0.62-0.66 for linear PU on the basis of 4,4'-diphenylmethanediisocyanate and polycaprolactone is determined in [298]. The results of the investigation of those branched it is polyurethane [304] they will agree with general laws governing the properties of solutions of PU.

The flexibility of polyurethane chain is determined in essence by the properties of units - oligoesters, and therefore the study of their behavior in solutions and in mass has important value for understanding of structure of PU.

Are studied some parameters (intrinsic viscosity, specific volume and second virial coefficient) of polypropylene glycols depending on the molecular weight, which lies within the limits from 300 to 5000 [310]. For finding of constants in θ-point, is used the equation of Stockmayer-Fixman. According to ductility/toughness/viscosity and molecular weight, are determined the size/dimensions of the balls of the branched and linear molecules which in tetrahydrofuran do not depend, but in toluene they depend on branching.

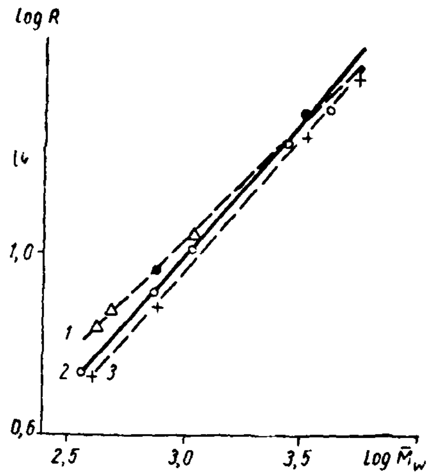

Fig. 4. The dependence of the size/dimensions of the balls of polypropylene glycols on molecular weight: 1 - on the basis of 2,3-propyleneglycol in tetrahydrofuran, 2 - propyleneglycol and glycerin in tetrahydrofuran, 3 - 2,3-propyleneglycol in toluene.

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So, Fig. 4 gives dependence on molecular weight of the size/dimensions of balls in toluene and tetrahydrofuran during sizing according to the equation $h = \left(\frac{[\eta] M}{\Phi(\varepsilon)}\right)^{1/3}$,

in which

$$\Phi = \Phi\,(1 - 2{,}67\varepsilon + 2{,}86\varepsilon^2), \quad \Phi = 2{,}84 \cdot 10^{23}, \quad \varepsilon = 2/3\,(a - 0{,}5),$$

where a - an exponent of the equation of Mark-Hewing. In this case, it was reveal/detected that upon transfer from the low- to high-molecular products occurs a change in the conformation of molecules. Is very important, from our point of view, the molecular association in toluene with molecular weight of less than 800, which was reflected in the dependences of the constants of Huggins on degree of association. Is shown also the possibility of describing the behavior of low-molecular oligomers from the point of view of the theories, developed for high-molecular chains. To accurate account chain conformations, it is necessary to conduct strict sizing of chains, under the condition for free running, with the for accurate estimation of all types of bonds both in the oligomeric unit and in diisocyanate. Such calculations are sufficiently difficult. The examination of configuration statistics of the poliamide chains, simpler in comparison with polyurethane which, however, contain a large number of different bonds within each monomer unit, it showed the contribution of these bonds to the size/dimensions of chains [216]. Subsequently it is expedient to transfer the proposed in this work calculation methods on polyurethane. Given data make it possible to consider that for obtaining the information about the properties of oligomers and prepolymers it is possible to use the existing statistical theories, developed for pliable macromolecules. This shows that comparatively low-molecular units possess their own flexibility as linear high-molecular chains. From this, manifestation of the flexibility of macromolecules in the grids of polyurethane elastomers on the basis of prepolymers not only the result of their cross-linking into the long sequence of comparatively short oligomeric cuts, but also the result of its own flexibility of the molecules of oligomers. The flexibility of polyurethane chain is really/actually determined in essence by glycol component, since its properties can be well explained independent of a number of short rigid units in molecules by the theories, developed for linear networks.

SORPTION PROPERTIES OF POLYURETHANES.

Oligomeric molecules with comparatively low molecular weight possess their own flexibility, and therefore the flexibility of polyurethane chain is determined by three basic factors - its own flexibility of oligomeric units, their concentration in chain and number of urethane groups in chains. The latter influence the equilibrium flexibility of chain, also, to greater degree - to the mobility of macromolecules in the condensed phase, since the flexibility of macromolecules depends not only on intramolecular, but also on intermolecular interaction, which cannot be taken into account during the estimation of flexibility according to this with the properties of dilute solutions.

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Is feasible also the thermodynamic approach to the estimation of the flexibility of chains, which consists in the calculation of the value of the segments of chain molecule. By value of segment, is understood the value of molecular weight, which they must have molecules of polymer so that the polymeric system would be subordinated to common for low-molecular bodies thermodynamic law [132]. Finding the value of segment from thermodynamic data is based on the measurement of the sorption of vapors of solvents by polymers and determination according to the law of Raoult of the effective (seeming) molar fraction of polymer in solution, whence is calculated effective molecular weight of polymer or segment. A. A. Tager and coworkers for it is polyurethane different degree of reticulation, but with the identical concentration of urethane groups, were studied the sorption isotherms of dioxane, in which the investigated polyurethane were dissolved or swelled athermically [131]. Findings showed that the sorption capacity of those investigated was polyurethane and the thermodynamic affinity for them of solvent they depend only on chemical nature, but not from the degree of reticulation, which was regulated in such a way that molecular weight of the cut of the chain between network points varied from 2000 to 27000.

Are studied polydiethylenesuccinate urethane, polydiethyleneglycoladipinate urethane and polybutyleneglycoladipinate urethane with application/use for synthesis is polyurethane 2,4-TDI [131]. The flexibility they judged by the calculations of change of entropy of mixing for different systems (Fig. 5). The course of changing the entropy indicates a regular increase in the flexibility of chains with an increase in the number of methylene groups between ester bonds. The authors [131] set/assume, that this conclusion/derivation is confirmed by the values of thermodynamic segments, equal for polydiethylenesuccinate 600, polydiethyleneglycoladipate 400 and polydiethyleneglycolsebacate 300. These values are less than the size/dimensions of the thermodynamic segments of polyisobutylene, polyethylene, etc., which indicates the great flexibility of chains it is polyurethane, caused by the presence of flexible members C-O-C.

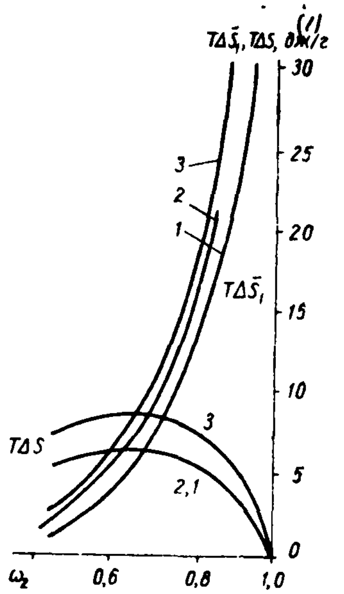

Fig. 5. The dependence of entropy of mixing on the composition of the solution: 1 - polyurethanesuccinate; 2 - polyurethaneadipate; 3 - polyurethanesebacate.

Key: (1). J/g.

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The thermodynamic parameters of grids do not depend on their denseness, and the authors this join with the low value of thermodynamic segment, since the minimum distance between network points composed 2300, which considerably exceeded the size/dimensions of thermodynamic segment. However, they did not use their data for calculating the value of the segment of chain in grid, but actually was conducted the correlation of data on the thermodynamics of sorption and flexibility of the chains of polyether/polyesters, entering the grid.

Thus, the presentation/concepts of the flexibility of the chains of linear polyether/polyesters are unjustifiably postponed by the flexibility of chains it is polyurethane in grid. Furthermore, it is well known that by the specific line of structure is polyurethane it is the large contribution of physical reactions to effective network density, as a result of which the effective network density, calculated by physical methods, always considerably more than that that is determined from the stoichiometric relationship/ratio of the components, undertaken for synthesis. Therefore the results of this work it is not possible to consider sufficiently reliable.

Meanwhile is of interest precisely the flexibility of polymer chains in three-dimensional grid and change in the flexibility of chain with its entry into grid, since flexibility depends on intermolecular interactions and bond between chains.

For explaining this question, are investigated sorbing vapors by polyurethane on the basis of different oligomers and toluenediisocyanate (Table 4) [71].

Network density was evaluated in contrast to [131] on the basis of data according to equilibrium elasticity modulus, which made it possible to consider chemical and physical network points. As can be seen from Fig. 6, the sorption isotherms of dioxane by the studied polyurethane take the S-shaped form and differ from those obtained in work [131].

Table 4. Characteristics it is polyurethane, investigated by sorption method.

(1) Образец	(2) Полиэфир	(3) Сшивающий агент	(4) Мольное соотношение	(5) M_c экспериментальное
1	(6) Диэтиленгликольадипинат-1600	(7) Триэтаноламин + диэтаноламин (1,5 : 1)	1 : 1; 1 : 0,035	3700
2	(8) Диэтиленгликольадипинат-1600	То же (9)	1 : 1,2 : 0,100	2600
3	(10) Олигобутадиендиол-1600	(11) Триэтаноламин	1 : 1,68 : 0,4	2400
4	(12) Олигоизопрендиол-2000	То же (13)	1 : 1,68 : 0,4	3200

Key: (1). Specimen/sample. (2). Polyether/polyester. (3). Cross-linking agent. (4). Molar ratio. (5). experimental. (6). Diethyleneglycoladipate-1600. (7). Triethanolamine + diethanolamine. (8). Diethyleneglycoladipate-1600. (9). the same. (10). Oligobutadienediol-1600. (11). Triethanolamine. (12). Oligoisoprenediol-2000. (13). The same.

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The analysis of isotherms shows that for polyurethane 1 with the greatest M_c (see Table 4) is observed the greatest sorption. For the specimen/sample of the same nature, but with smaller M_c the value of sorption is smallest. It should be noted that the value of the sorption of dioxane by polyurethane 3 and 4, in spite of their different nature, they are close to each other with comparatively small pressures of vapors (to 50o/o). With P_1/P_0=50o/o value of the sorption of dioxane these polyurethane they are characterized by.

For the investigation of temperature effect on sorption, are obtained the isotherms at 25 and 40°C (Fig. 7). In all cases the initial sections of isotherms with 40°C lie/rest above the same with 25°C, i.e., in this case with an increase in the temperature, occurs the increase in the sorption of dioxane which usually is observed for polymers and is explained by an increase in the mobility of the segments of macromolecules. With the large vapor pressures the sections of isotherms with 25°C lie/rest above than at 40°C. This can be caused by existence in solid polyurethane of the conformational transition near 40°C, which is caused by the partial destruction of intermolecular hydrogen bonds. It is obvious, with the vapor pressure of approximately 50o/o, concentrations of dioxane in system reach its critical value, after which occur the changes in the structure of those cross-linked it is polyurethane.

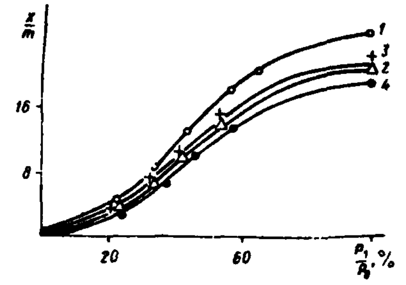

Fig. 6. Isotherms of sorption of dioxane of polyurethane on the basis of DEGA and TDI (1, 2), oligobutadienediol and TDI (3) and oligoisoprenediol (4) at 25°C.

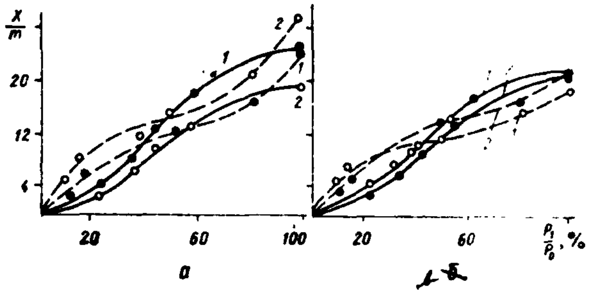

Fig. 7. Sorption isotherms of dioxane of polyurethane with 25°C (unbroken curves) and 40°C (dotted curves). a) polyurethane 1 (1); polyurethane 2 (2); b) polyurethane 3, (1); polyurethane 4 (2).

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Since polyurethane are characterized by the presence of a large number of physical bonds, it can be assumed that during selective reaction with solvent (with its specific concentration) occurs the redistribution of physical bonds in the three-dimensional/space grid of polyurethane. This leads to the appearance of a structure, which differs from initial, and to a change in its behavior during sorption. This mobility and lightness/ease of the rearrangement of three-dimensional/space grid - one of the specific special feature/peculiarities of the structure of three-dimensional one. it is polyurethane. Thus, during the sorption of vapors of solvent, as with swelling it is polyurethane (70), the network density of physical bonds it is changed. Therefore for the calculations of thermodynamic functions, are used only the sections of isotherms to 50o/o of relative vapor pressure which corresponds to the beginning of a change in structure [71] (Table 5).

In connection with the fact that a change of the enthalpy in the investigated cases is considerable in its value, the determination of the segment, which characterizes the flexibility of chain, from sorption data [132] erroneously, since the value of sorption here is determined not only from a change in the number of chain conformations, but also from a change of the energy barrier of the rotation of the cuts of chains in grid, that is reflected in ΔH. Therefore a change in the flexibility of chains, can be judged from a change in the partial specific entropy of polymer $T\Delta S_2$ (Fig. 8). For polyurethane on the basis of oligodiethyleneglycoladipate, a change in the entropy depends on the degree of the cross-linking: $T\Delta S_2$ is more for polyurethane with the smaller degree of cross-linking. This indicates an increase of the flexibility of the cuts of chains in grid during the decrease of the effective density of cross-linking.

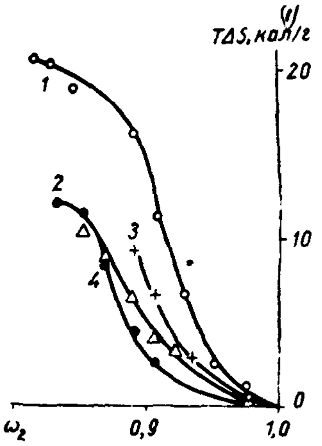

Fig. 8. A change in the partial specific enthropy it is polyurethane during the sorption (designations see in Table 3).

Key: (1). cal/g.

Table 5. Changes in the thermodynamic functions during the sorption of vapors by polyurethane.

x/m	ω_2				$\Delta F_{1уд}$, кал/г (1)				$\Delta F_{2уд}$, кал/г (1)				$\Delta H = \omega_1 \Delta H_1 + \omega_2 \Delta H_2$, кал/г (1)				$T\Delta S_2$, кал/г (1)			
	1	2	3		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
0.025	0,975	0,976	0,975	0,976	—[illegible]89	—11,23	—12,39	—13,80	—0,03	—0,05	—0,07	—0.06	3,71	3,73	2,73	3.40	1,09	0.96	0,74	1,09
0,050	0,953	0,952	0,952	0,953	—9,37	—7,92	—8,85	—9.37	—0,16	—0,12	—0,18	—0,24	—	6,64	—	—	2.67	—	—	—
0,075	0,930	0,930	0,930	0,930	—7,70	—6.56	—6,89	—7,10	—0,27	—0,21	—0,26	—0,34	4.89	9,48	6,57	5.97	6.64	—	3,56	2,87
0,100	0.910	0,909	0,909	0,908	—6.53	—5,38	—5,78	—4,94	—0,37	—0,31	—0,39	—0.46	5.33	12,05	6,30	8,64	11,20	2,53	4,08	6,70
0.125	0,881	0,889	0,889	0,888	—5,86	—4,42	—4,69	—4,82	—0,45	—0,46	—0,54	—0,61	5,21	14,23	6.90	10,71	16,27	4,70	6,29	9,18
0,150	0,870	—	—	—	—4,83	—	—	—	—0,56	—	—	—	5,68	—	—	—	19,19	—	—	—

Key: (1). cal/g.

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The dependence of flexibility on the nature of oligomer can be traced based on example it is polyurethane on the basis of oligodienediols which are characterized by only the nature of oligomers. Change $T\Delta S_2$ for it is polyurethane on the basis of oligoisoprenediol less than for oligobutanedienediol, i.e., the flexibility of chain is less for the three-dimensional/space grid of polyurethane on the basis of oligoisoprene. This can be explained by the presence in the chain of oligoisoprene of methyl group, which purely geometrically limits the flexibility of chain. However, the effect of the nature of oligodienediol the degree of flexibility affects not as strongly, as a change in the degree of cross-linking for it is polyurethane on the basis of esters.

Thus, the conducted investigations showed that the flexibility of the cuts of chains in the three-dimensional/space grid of polyurethane is defined by both the chemical nature of unit and by degree of the cross-linking of grid. Hence it follows that the estimation of the flexibility of chains, produced for linear molecules, cannot be transferred to the systems, in which the molecules are cross-linked and will form three-dimensional grid. Really/actually, the more number of conformations accepts chain, is those more it pliable. It is logical that with entry into grid a number of possible conformations is limited. In the case in question the presence of intermolecular interactions, which depend on chemical network density, changes the potential threshold of rotation and, correspondingly, the flexibility of the cuts of the chains between nodes even when the distance between them exceeds the value of the thermodynamic segment, found for the uncombined in grid high-molecular chains. It is implied that the chain/network as is uniform in the ratio/relation to flexibility, i.e., is not examined separate effect on the sorption of rigid and pliable units. This approach is permissible for obtaining the common picture of behavior it is polyurethane during the investigation of the sorption of the substances, which are solvents for both of units of chain.

More strictly one should examine and demarcate sorption by separately rigid and pliable sections. Such data can be obtained during the study of the gas diffusion or permeability of vapors.

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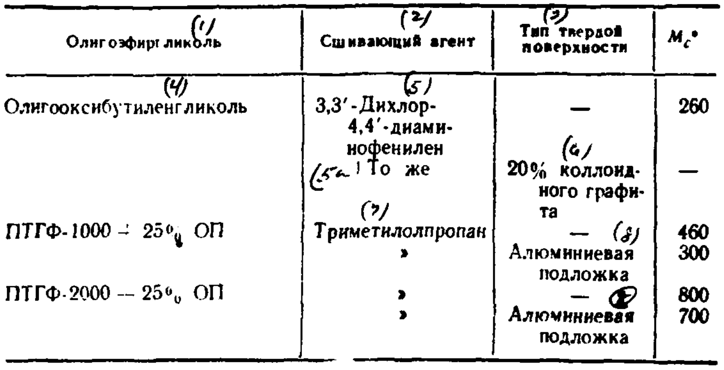
For example, during diffusion CO_2 in polyurethane [178] it is establish/installed, that the diffusion coefficients in them are considerably lower than in other rubbers. This is bonded with the fact that, in spite of significant flexibility of the individual sections of chains, strong intermolecular interaction as a result of the formation of hydrogen bonds is led to more tight packing of chains. This effect prevails above the effect of the flexibility of the separate cuts of chains.

Analogous conclusions are made during the study of the transfer of the water through polyurethane films with different nature of pliable unit [311].

It is necessary to note that in the examination of the properties of polyurethane materials we we can clash with the case when the flexibility of polymer chains in material is determined also by the special feature/peculiarities of material, for example for those filled it is polyurethane or polyurethane coatings. In work [47] are investigated changes in the thermodynamic functions of polyurethane coatings on the basis of polyetherglycol (tetrahydrofuran +25o/o propylene oxide) of mol. weight 2000 and 1000 and of adduct of trimethylopropane with 2,4-TDI, and also polyurethane on the basis of oligohydroxybutyleneglycol and TDI, obtained during the reaction of TDI with tetrahydrofuran also of filled with 20o/o colloidal graphite (Table 6).

Table 6. The characteristics of some it is polyurethane.



(1) Олигоэфиргликоль	(2) Сшивающий агент	(3) Тип твердой поверхности	M_c*
(4) Олигооксибутиленгликоль	(5) 3,3'-Дихлор-4,4'-диаминофенилен	—	260
	(5a) То же	(6) 20% коллоидного графита	—
ПТГФ-1000 + 25% ОП	(7) Триметилолпропан	— (8)	460
	»	Алюминиевая подложка	300
ПТГФ-2000 — 25% ОП	»	— (8)	800
	»	Алюминиевая подложка	700

Key: (1). Oligoetherglycol. (2). Crosslinking agent. (3). Type of rigid surface. (4). Oligchydroxybutyleneglycol. (5). Dichloro-4,4'-diaminophenylene. (5a). The same. (6). colloidal graphite. (7). Trimethylol propane. (8). Aluminum base.

FOOTNOTE *. Value M_c is determined according to swelling. ENDFOOTNOTE.

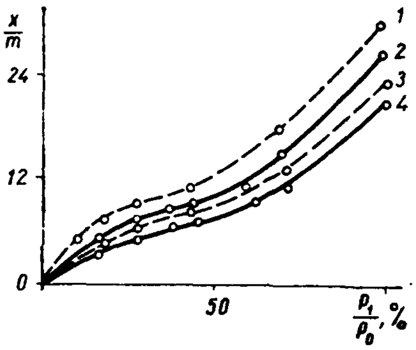


Fig. 9. Sorption isotherms it is polyurethane on the basis of oligohydroxybutyleneglycol and toluenediisocyanate with 30°C (2, 4) and 40°C (1, 3): 1, 2 - filled with 20o/o of colloidal graphite; 3, 4 - not filled.

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Isotherms of the sorption of toluene by the studied polyurethane are represented in Fig. 9. The isotherms, which characterize sorption with 40°C, lie/rest in entire interval of the relative pressures of the vapors higher than analogous isotherms with 30°C. A similar increase of sorption with an increase in the temperature is characteristic for polymers and it is caused by an increase in the mobility of the segments of macromolecules.

We noted that during the sorption of vapors of dioxane by some polyurethane at different temperatures was observed the intersection of isotherms at 40 and 25°C with the specific pressure of the vapors of dioxane. Taking into account that the fact that dioxane is capable to form hydrogen bonds with urethane groups [12], is made the assumption about the redistribution of physical bonds in the three-dimensional/space grid of polyurethane as a result of reaction with solvent with its specific concentration, which leads to the emergence of the effective three-dimensional/space grid, different from initial, to a change in the behavior during sorption. Toluene, in contrast to dioxane, is latent solvent with respect to polyurethane, that, probably, it affects the character of isotherms.

Introduction to polyurethane on the basis of oligohydroxybutyleneglycol and toluenediisocyanate 20o/o graphite as filler leads to an increase in the sorption of toluene (Fig. 9, 1, 2). From the comparison of the sorption isotherms of toluene by free polyurethane films and films on the aluminum foil it is evident that the presence of rigid surface contributes to the decrease of sorption (Fig. 10).

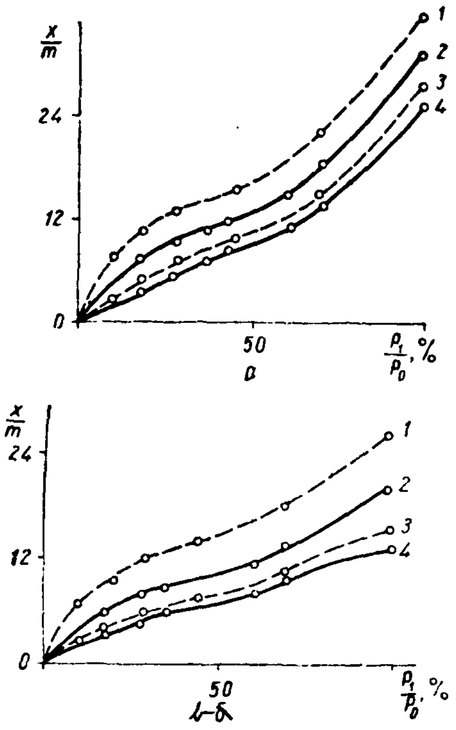

Fig. 10. The sorption isotherms of toluene by polyurethane on basis TGF-1000-25o/o OP (a) and TGF-2000-25o/o OP (b) at 30°C (2, 4) and 40°C (3): 1, 2 - free film; 3, 4 - film on foil.

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On the basis of sorption data, are calculated changes in the thermodynamic functions - partial free energy of polymer and solvent, enthalpy and entropy of polymer and solvent. On a change of the flexibility of polymer in this case, they judged by a change in the entropy of polymer $T\Delta S_2$ (Fig. 11). Changes in the partial specific enthropy of polymer are more for the filled with graphite specimen/sample, than for that not filled (Fig. 11a). On the other hand, $T\Delta S_2$ is greater for free films, than for the films, molded in the presence of rigid surface (Fig. 11b). Consequently, the effect of rigid surface the flexibility of chains in grid dissimilarly affects in the described cases. For the explanation of this effect, it is necessary to take into consideration following: the introduction of filler to polymerization limits the mobility of polymer chains and, therefore, must decrease their conformational collection and change in the entropy during sorption. But the limitation of the mobility of the growing polymer chains as a result of their reaction with filler leads to the emergence of the more defective grid, which is characterized by a smaller number of chemical nodes in comparison with the grid, formed in the absence of filler [63, 68], which causes an increase in the entropy of polymer. It is obvious, when strongly extended surface of filler is present, an increase in the entropy of polymer due to the defectiveness of the generating grid prevails above its decrease, caused limitation of mobility of chain in grid, bonded with their reaction with filler. Therefore the sorption of toluene by the filled polymer in comparison with that not filled is increased and simultaneously less is changed $T\Delta S_2$. With the formation of polyurethane film on smooth rigid surface, the formation of physical bonds polymer - surface prevails above the possibility of the emergence of defective structure, which conditions an increase in the effective density of the cross-linking of film on surface in comparison with free film. The latter leads to an increase in the sorption of toluene with free polyurethane film. At the same time, change $T\Delta S_2$ is greater in free film, than in the same on base (Fig. 11c).

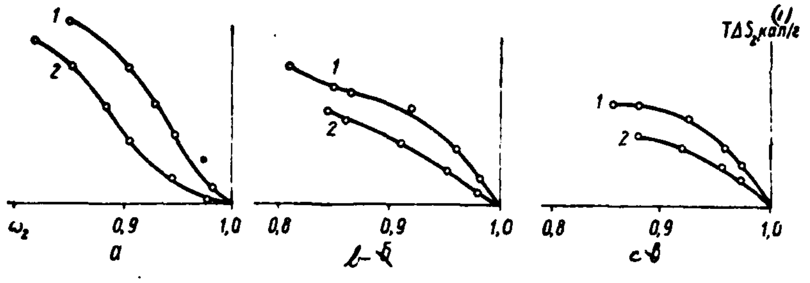

Fig. 11. A change in the partial specific enthropy it is polyurethane on the basis of oligohydroxybutyleneglycol and toluenediisocyanate (a), TGF -1000 25o/o OP (b) and TGF-2000-25o/o OP (c): 1 - free film; 2 - film on foil.

Key: (1). cal/g.

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Findings tell about the fact that the presence of hard surface with shaping of polyurethane three-dimensional grid affects the structure of the latter and conditions a change in the flexibility of the cuts of the chains between network points. Consequently, the mechanical properties of those filled it is polyurethane one should compare with the flexibility of chains, determined in the presence of rigid surface, and it is not possible to transfer the data on the flexibility, obtained for the unfilled polymers, to filled.

SOME PROPERTIES OF THE MONOMOLECULAR LAYERS OF OLIGOMERS OF POLYURETHANES.

It is known that at present from the data on the properties of the monomolecular layers of polymers on liquid bases it is possible to obtain the essential information about the structure of chains, their flexibility and the character of packing [99]. This is assumed as the basis of the theory of Singer [3, 4], which examines the state of macromolecules on the phase boundary, on the basis of the theory of the solutions of the polymers of Huggins [233]. Singer introduced the equation

$$\pi = \frac{xKT}{A_0}\left[\ln\left(1-\frac{A_0}{A}\right)-\left(\frac{x-1}{x}\right)\frac{Z}{2}\ln\left(1-\frac{2A_0}{ZA}\right)\right],$$

where Z - coordination number of monomer units in chain; A_0 - value of the specific surface area of monomolecular layer at a zero pressure; x - degree of polymerization; A - surface area at surface pressure π. Equation is modified by Davis [200], who introduced into it the conventional characteristic of the flexibility of chain ω, taking values from 0 to 2 upon transfer from rigid to the completely flexible chain:

$$\pi = -\frac{KT}{A_0}\left[\ln\left(1-\frac{A_0}{A}\right)-\frac{x-1}{x}\,\frac{\omega+2}{2}\ln\left(1-\frac{2}{\omega+2}\,\frac{A_0}{A}\right)\right].$$

Davis's method is used during the estimation of the flexibility of the chains of polymers [296], and also with the characteristic of the flexibility of the chains of oligomers it is polyurethane on the phase boundary and the explanation of its dependence on reaction with base [140].

For investigation were undertaken low-molecular polydiethyleneglycoladipate of different molecular weights and polyurethane, obtained during the reaction of these oligomers with 2,4-TDI. In such chains are contained the groupings, capable of the formation of hydrogen bonds. The properties of monomolecular layers are studied in four types of the bases: distilled water (base 1), 3-n solution HCl (base 2), 40o/o solution $(NH_4)_2SO_4$ (base 3) and mixed solution of 30o/o of sulfate ammonium and 10o/o HCl (base 4). The selection of bases is bonded with the fact that base 2 can form strong hydrogen bonds with monomolecular layer when, in the polymer chain, corresponding groups are present, [346]; on base 3, is raised the common/general/total adhesive reaction due to an increase in the surface tension of solution [157], and finally base 4 must cause the summary effect of bases by 3 and 4 (Fig. 12, Table 7).

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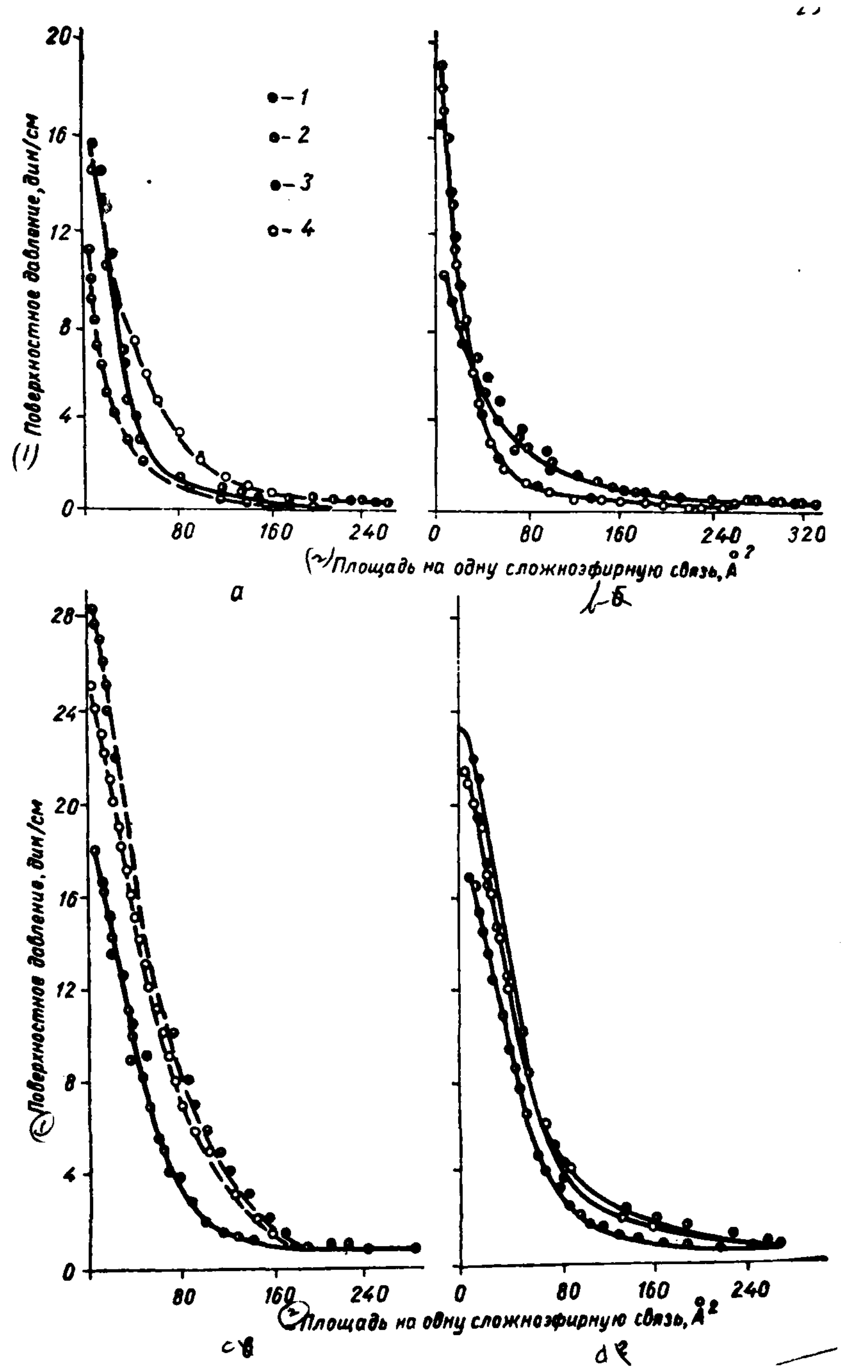
20
16
12
8
4
0
(1) Поверхностное давление, дин/см
●- 1
●- 2
●- 3
○- 4
80
160
240
0
80
160
240
320
(2) Площадь на одну сложноэфирную связь, Å²
a
b б
28
24
20
16
12
8
4
0
(1) Поверхностное давление, дин/см
80
160
240
0
80
160
240
(2) Площадь на одну сложноэфирную связь, Å²
c в
d г

Fig. 12. The isotherms of the compression of the monomolecular layers of polymers on water (a), 3-n hydrochloric acid (b), 40o/o solution of sulfate ammonium (c) and in the mixed solution of 30o/o of sulfate ammonium and 10o/o of hydrochloric acid (d): 1 - polyurethane 1 $(\bar{M}_\omega = 12\,200)$; 2 - polyurethane 2 $(\bar{M}_\omega = 6400)$; 3 - polyether/polyester 1 $(\bar{M}_n = 640)$; 4 - polyether/polyester 2 $(\bar{M}_n = 2500)$.

Key: (1). Surface pressure, dyn/cm. (2). Area to one complex-ester bond, $Å^2$.

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Monomolecular layers it is polyurethane the length of polyether/polyester unit they independent of give the identical isotherms of compression, and only on base 4 these polyurethane have somewhat different isotherms. At the same time the isotherms of the compression of the monomolecular layers of polyether/polyesters on all bases very differ during a change in the length of chain [141]. During the comparison of the isotherms of the compression of monomolecular layers, it is polyurethane on bases, which contain hydrochloric acid (bases 2 and 4), and acid-free (base 1 and 3) it is evident that in the first case are formed the more elongated monomolecular layers.

The identity of the isotherms of the compression of monomolecular layers it is polyurethane, just as smaller protracted length in comparison with the same for the monomolecular layers of initial polyether/polyesters, is explained, obviously, by the fact that the length of polyether/polyester unit does not affect density of the packing of molecule in mono-layer. An increase in the reaction between chains is revealed also by direct measurement of surface tension is polyurethane by the method of hanging drop [158], since these products are high-viscosity fluids. Measurements showed that if the surface tension of polyether/polyesters composes value on the order of 40-42 dyn/cm [142], then it is polyurethane - 46-47 dyn/cm, in spite of a small concentration of urethane groupings in chain (one urethane bond to 7.4 ester bonds for a polyether/polyester unit with $\bar{M}_n = 800$ and one to 15.7 for a unit with $\bar{M}_n = 1700$).

Table 7. The density of packing and the flexibility of chains it is polyurethane and polyether/polyesters on different bases.

(1) Характеристика цепей в монослоях	(2) Образец	(3) Поверхность			
		H$_2$O	3-н. HCl	40%-ный (NH$_4$)$_2$SO$_4$	30% (NH$_4$)$_2$SO$_4$ + +10%, HCl
(4) Площадь плотной упаковки, Å^2	(5) Полиуретан 1	25,5	25	40	40
	Полиуретан 2	25,5	25	40	38
	Полиэфир 1 (6)	10,0	25	37	22
	Полиэфир 2	40,0	40	46	38
(7) Гибкость цепи	Полиуретан 1 (5)	0,12	0,28	0,28	0,56
	Полиуретан 2	0,12	0,28	0,28	0,88
	Полиэфир 1 (6)	—	—	1.00	0
	Полиэфир 2	0,20	0,30	1,00	0,47

Key: (1). Characteristic of chains in monomolecular layers. (2). Specimen/sample. (3). Surface. (4). Area of tight packing, Å^2. (5). Polyurethane. (6). Polyether/polyester. (7).

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The protracted length of monomolecular layers it is polyurethane on the bases, which contain acid, it makes it possible to unambiguously establish that the strong interaction between chains, caused by the appearance of urethane groupings, presents reaction of the type of hydrogen bond [268].

Especially clearly these regularities are developed in the examination of the density of packing and and the flexibility of chain it is polyurethane on different bases. Monomolecular layers it is polyurethane they have the different density of packing on bases with the weak and strong interaction (see Table 6), moreover the density of packing is changed almost double, although this difference for it is polyurethane with the different length of polyether/polyester unit it is absent. At the same time the density of the packing of the monomolecular layers of polyether/polyesters is changed both from the length of chain and from the type of base.

These changes just as change in the flexibility of chain, are explained as follows. An increase in the flexibility of polyurethane chain on base 2 is bonded with the fact that the strong hydrogen bonds of base partially eliminate a similar reaction between chains in mono-layer. In this case, there is in mind lateral cohesion between the molecules of polymer and flexibility of this molecule in the plane of monomolecular layer. Certain increase in the flexibility of polyether/polyester is caused by an insignificant increase in the adhesion bond with the end groups of polymer. An increase in the adhesion of the monomolecular layer of polyurethane to base 3 sharply decreases the density of packing; however, the presence of the hydrogen bond between chains leads to the fact that the flexibility of chain remains the same as on base 2. At the same time the flexibility of the chain of polyether/polyesters where are absent similar bonds, grow/increases very considerably. It hence follows that monomolecular layer it is polyurethane on bases 1 and 2 have higher ordering which is caused by the complex interaction of all means of Van der Waals bonds. In this case, stiffening of chain due to the presence of urethane grouping is so strong that to the packing of molecules in mono-layer does not affect different length of polyether/polyester unit. Only by mixed base 4 flexibility of polyurethane chains grow/increases so, that is revealed different behavior of molecules depending on the length of the polyether/polyester unit: chains with the smaller concentration of urethane groups are more pliable, since the hydrogen bonds of base eliminate the reaction between chains in mono-layer. The absence of this bond in polyether/polyesters leads to another behavior of their monomolecular layers on base 4: falls flexibility, grow/increases the density of packing due to the decrease of adhesion bond monomolecular layer - base.

Consequently, the density of packing and the flexibility of polymer chain in surface layer can be substantially changed, selecting different bases. Energy factor has strong effect on the conformation of polymer chain in surface layer moreover to flexibility and density of the packing of polymeric molecule it affects not only the value of reaction the phase boundary, but also the nature of this reaction.

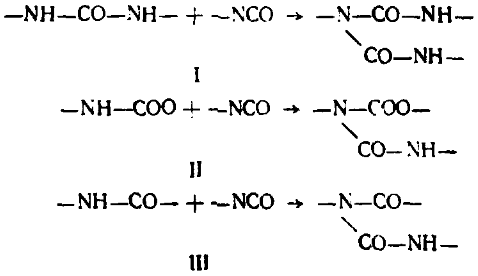
Chapter III. NATURE OF CHEMICAL AND PHYSICAL MOLECULAR BONDS IN POLYURETHANES.

The flexibility of chains is polyurethane - one of the factors, which are determining the fundamental characteristics of polymer. However, it is necessary to consider during the study of the properties of polymers the nature of the molecular bonds between the polymer chains which determine the physical and phase state of polymer and its basic mechanical properties. The diversity of functional groups in chain it is polyurethane creates great possibilities for the emergence of the molecular bonds of different energy and chemical nature - from hydrogen ones to van der Waals ones. The role of intermolecular interactions especially important to consider in the examination of three-dimensional cross-linked ones it is polyurethane, in which, in contrast to the majority of other cross-linked rubberlike materials, these bonds have fundamental importance. They determine also the possibilities of crystallization it is polyurethane, the temperature ranges of melting or transitions of one physical state tc another and the like.

In present chapter we will examine the existing data by the nature of chemical and physical bonds in polyurethane, bearing in mind that the collaboration of one or the other groups of chain in the formation of chemical cross connections limits their collaboration in the formation of physical bonds.

Types of chemical bonds in chains.

During the reaction of those obtaining at the first stages of the reaction of urethane, uric and amido groups with isocyanates, is possible the formation of biuret (I), allophanate (II) and acylurea groupings (III)



$$-NH-CO-NH- + -NCO \rightarrow -N(-CO-NH-)-CO-NH- \quad \text{I}$$

$$-NH-COO + -NCO \rightarrow -N(-CO-NH-)-COO- \quad \text{II}$$

$$-NH-CO- + -NCO \rightarrow -N(-CO-NH-)-CO- \quad \text{III}$$

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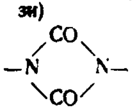
It is most convenient to identify different types of bonds in the cross-linked polyurethane with the aid of infrared spectroscopy. This method is applied for the analysis of the types of chemical bonds in expanded polyurethanes of different chemical structure [268].

Different structural units in polyurethane give in IR spectra the characteristic frequencies of oscillations, known for the appropriate low-molecular analogs. Therefore via the selection of the adequate/approaching low-molecular connections (for example, N,N'-diphenylurea, N,N',N"-triphenylisocyanurate, etc.) it is possible to obtain the information about characteristic strips. For the characteristic of the corresponding groups, one should select only such characteristic strips which possess sufficient intensity and least undergo the effect of other groups. The authors [268] examine the strips which are given in Table 8 and give the typical spectrum of the solidified expanded polyurethane on the basis of desmophen and Desmodur with the addition of other components (Fig. 13).

These data indicate the complexity of conducting the quantitative analysis it is polyurethane in the intensities of characteristic frequencies. Really/actually, if the first two groups to identify is sufficiently easy, then to distinguish ester, urethane, allophanate and other bonds by the oscillations of carbonyl is virtually impossible, since the simultaneous presence of different groups leads to the expansion of the strip of the oscillations of carbonyl group. Therefore the results of work [268] can be applied only for the establishment of the presence of one or the other groups only when on the basis of the chemical composition of composition is expected the appearance of the specific groups.

Table 8. Characteristic strips of structural groups in polyurethane.

(1) Структурная группа	(2) λ, мк	ν, см$^{-1}$
(3) —N=C=O (кумулированные двойные связи)	4,40—4,46	2270—2240
—N=C=N— (кумулированные двойные связи)	4,72	2120
 (4) Уретдионовое кольцо (карбонил)	5,62—5,72	1780—1755
(5) NH—CO—O Сложноэфирная группа (карбонил)	5,71—5,83	1750—1717
(6) Уретановая группа, изоциануратное кольцо, биуретовая группа (карбонил)	5,81—5,92	1720—1690
(7) Аллофанатная группа (карбонил)	5,71—6,06	1750—1658
(8) Мочевинная и амидная группы (карбонил)	6,10—6,20	1640—1610
(9) Уретдионовое кольцо (колебания кольца)	7,04—7,14	1420—1410
(10) Изоциануратное кольцо (колебания кольца)	7,00—7,11	1428—1406

Key: (1). Structural group. (2) μ. (3) cumulative double bonds. (4). Uretedione ring (carbonyl). (5). Ester group (carbonyl). (6). Urethane group, isocyanourate ring, biuret group (carbonyl). (7). Allophanate group (carbonyl). (8). Uric and amido groups (carbonyl). (9). Uretedione ring (oscillations of ring). (10). Isocyanourate ring (oscillations of ring).

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Another work [269] for purpose of approach to quantitative analysis gives the IR spectra of model substances (phenylurethane and diphenylurea, polyurethane and poly-urea, etc.). On their basis/base in certain cases it is possible to in more detail determine the position of separate functional groups in the spectra of low-molecular model substances and polymers. However, to distinguish separate strips is difficult, that together with the unsatisfactory reproducibility of intensities does not make it possible to conduct quantitative estimation, but the obtained material gives the possibility to trace only qualitatively the chemical changes in the course of reaction of formation it is polyurethane, i.e., to explain in general terms the effect of prescription factors, temperature and time.

Zharkov investigated IR spectra it is polyurethane and them derivatives [32] and for their more full/total/complete interpretation studied the absorption spectra in the homologous series of alkyl-N-phenylurethane and some of them derivatives (table 9). Are calculated frequencies and forms of normal oscillatory mode for purpose of the identification of the structural units in polyurethane. The selection of alkyl-N-phenylurethane was determined those that in the majority of the cases the polyurethane, which are of practical use, are obtained on the basis of arylisocyanate.

It is establish/installed, that in dilute solutions all alkyl-N-phenylurethane have a strip with 3446 cm^{-1}. The out-of-plane deformation vibration N-H is characterized by strip with 535 cm^{-1}. The strip of the stretching vibration of the carbonyl group of alkyl-N-phenylurethane has frequency 1745 cm^{-1}, sensitive to the formation of hydrogen bond.

As a result of the calculations conducted and analysis of the spectra of model substances, the conclusion is made that by the most constant sign of urethane group it is possible to consider the strips of ester fragment 1730-1750 and 1210-1230 cm^{-1} together with intensive strip in region 1515-1540 cm^{-1}, the corresponding to deformation vibration group N-H.

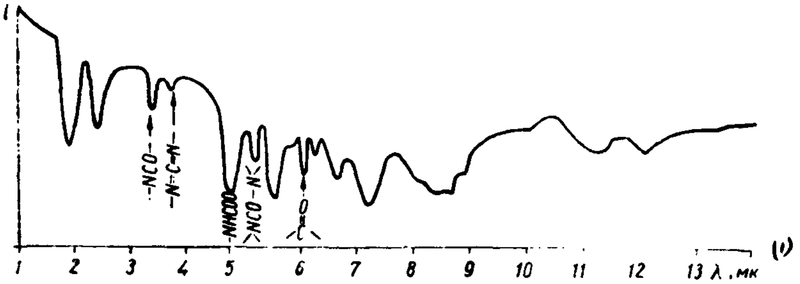

Fig. 13. IR spectrum of polyurethane foam on the basis of the mixture of polyether/polyesters and 4,4-diphenylmethanediisocyanate.

Key: (1) μ.

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Are selected analytical strips for the identification of allophanate and biuret groups. In the spectra of polymers, allophanate structures are masked with the bonded NH-groups of urethane. On model of allophanates it is shown [to 49], that their spectra are different from the spectra of appropriate it is urethane. The appearance of allophanates in spectra it is polyurethane bonded with strips 1280, 1310 and 1965 cm^{-1}.

Thus, on model substances it is possible to identify different types of bonds, but their determination in polymers remains the yet not solved problem.

To considerably more easily determine by the method of IR spectroscopy isocyanate group, which allows according to its disappearance in the course of reaction to investigate kinetics formation it is polyurethane. This reaction was investigated on the absorption band of the isocyanate group of 2270 cm^{-1} [169, 279] and urethane of 6750 cm^{-1} [259], and also on the disappearance of hydroxyl groups [50]. The mechanism of the reactions of formation of polyurethane elastomers by the method of IR spectroscopy is studied also in work [59], and polyurethane coatings - in work [101].

Until now, the method of IR spectroscopy does not give the possibility to quantitatively determine the relationship/ratio of the types of bonds in the cross-linked polyurethane.

Table 9. The normal bands of absorption, in reference to the oscillation/vibrations of urethane group in alkyl-N-phenylurethane (Ph-HCOO-R).

(1) Индекс полосы	(2) Частота колебаний, $см^{-1}$			
	$-CH_3$	$-C_2H_5$	$-CH(CH_3)_2$	$-C(CH_3)_3$
ν_0'	3446	3446	3446	3446
ν_1'	1750	1745	1743	1742
ν_2'	1529	1582	1528	1520
ν_3'	1450	1445	1443	1443
ν_4'	1312	1312	1311	1312
ν_5'	1213	1210	1212	1222
ν_6'	1068	1068, 1097*	1048, 1113*	1055, 1171*
ν_7'	770	770	765	770
ν_{11}'	538	537	540	545

*Strip is disintegrated because of reaction with the skeletal/skeleton oscillation/vibrations of alkyl radical.

Key: (1). Index of strip. (2). Frequency.

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From this point of view great interest are of works [283, 324], in which conducted detailed investigation of the resonance region of protons for the nitrogen-bearing bonds in polyurethane by the method of NMR of high resolution. It is establish/installed, that all connections, which have such bonds, give sharp signals of NMR in polar solvents of the type of dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), pyridine, etc. Is synthesized the series/number of the special connections, which contain such types of the bonds which can be present in polyurethane, and is carried out their detailed analysis by method of NMR. For the model substances (table 10) of the intensity/strength of the fields, by which appear the signals of NMR, strongly they differ for different types of bonds. This makes it possible to use a method for the quantitative determination of bonds in polyurethane. Really/actually, the analysis of the prepolymers, obtained from polypropylene glycol and diphenylmethane diisocyanate, it showed, that is observed the good agreement between the NMR spectra of model substances and investigated prepolymers (table 11). During the comparison of data for prepolymers on the basis of polypropylene glycol and toluenediisocyanate with data for the model substances (see Table 11) are evident that in the spectra of this prepolymer are three signals that correspond to groups N-H, two of which (9.43 and 8.55 m.d.) are related to the N-H-proton of 2,4-diurethane, and the third - to the protons of 4-urethane (a). The relative intensities of signals depend on the conditions of the synthesis reaction of prepolymer.

For the analysis of the types of bonds, the authors [283, 324] used the method, based on the destruction of those cross-linked was

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polyurethane with the aid of amines. Were investigated the polyurethane, obtained on the basis of polypropylene glycol (mol. weight 1000) and diphenylmethane-4, 4'-diisocyanate.

Are studied also the model substances, which contain substituted urethanes, ureas, allophanates and biurets. The authors in this case proceeded from the fact that under the influence of amines on the cross-linked polyurethane the allophanate and biuret bonds disintegrate considerably faster than uric or urethane ones.

Table 10. The magnetic nuclear resonance of group N-H in model substances.

(1) Связь	(2) Химический сдвиг, м. д.	
	(3) в ДМСО	(3) в ДМА
(4) Мочевинная	5,70—8,58	5,93—8,77
Уретановая (5)	8,60—9,70	8,57—9,88
Биуретовая (6)	9,60—10,25	9,85—10,55
Аллофанатная (7)	10,62—10,67	10,70—10,87

Key: (1). Bond. (2). Chemical shift/shear, m.d. (3) in (4). Uric. (5). Urethane. (6). Biuret. (7). Allophanate

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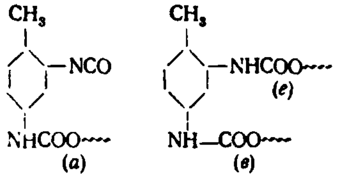
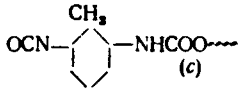
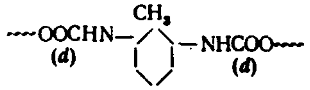
This makes it possible to convert the cross-linked polymer into the soluble state and according to the analysis of the formed end groups to conduct the quantitative estimation of the content of one or the other types of bonds.

Considerably simpler the same analysis is carried out for the soluble prepolymers. For a prepolymer and cross-linked it is polyurethane, obtained during different relationship/ratios of the undertaken for synthesis components and under the varied conditions of cross-linking specifically percent ratio of allophanate and biuret groups to a total number of nitrogen-bearing functional groups in polymer is establish/installed that in certain cases it reaches 15-20o/o. Thus, is shown the possibility of determining these types of bonds quantitatively for those cases when their content comprises not less than one group by 30 urethane and uric ones, or one cross connection in the cut of the polymer chain of molecular weight of approximately 10 000 (with accuracy of analysis 10-20o/o).

Conducted detailed investigation of the IR spectra of polyurethane oligomers on the basis of hexamethylene diisocyanate and 1,4-butanediol [351] (table 12).

Table 11. NMR of group N-H ot prepolymers is polyurethane.

(1) Форполимер	Молярное отношение изоцианата к ППГ (2)	(3) Структура	(4) Химический сдвиг, м. д. (5) в ДМСО	(4) Химический сдвиг, м. д. (6) в ДМА
ППГ-1000—МДИ	1,9 2,0 2,1	$—OOCHN—C_6H_5—CH_2—C_6H_5——NHCOO\sim$	9,41	9,47
			9.51 (a) 9,33 (в) 8.83 (c) 8,57 (e) 9,51 (a)	9,60 (a) 9,43 (в) 8,92 (c) 8,57 (e) 9,60 (a)
ППГ*-ТДИ**	2,0 1,5		9,33 (в) 8,83 (c) 8,70 (d) 8,55 (e)	9,43 (в) 8,92 (c) 8,72 (d) 8,55 (e)
ППГ*-2,4 ТДИ	2,0			9,60 (a) 9,43 (в) — (c) — (d) 8,55 (e)

* Среднечисленный мол. вес 1000. (6)
** Смесь 80 : 20 2,4- и 2,6-изомера. (7)

Key: (1). Prepolymer. (2). molar ratio of isocyanate to PPG. (3). Structure. (4). Chemical shift/shear, m.d. (5) in (6). * Numerical average mol. weight 1000. (7). ** Mixture 80:20 2.4- and 2,6-isomer.

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It should be noted that already monomeric diols give absorption bands in the same regions that and polymers, being characterized by only presence of the characteristic strips, which relate to end groups. Consequently, by the method of infrared spectroscopy thus far it is possible to only qualitatively analyze the structure of three-dimensional ones it is polyurethane and to quantitatively determine changes in the concentration of urethane groups during the cross-linking and other chemical transformations. However, method is not suitable for the establishment of the relationship/ratio between the structure and properties it is polyurethane, or by a number and the type of cross connections.

Hydrogen bond in polyurethane.

The chemical structure of polyurethane chains and the presence of different functional groups determine great possibilities for formation in polyurethane of molecular bonds, including hydrogen ones. It is well known that the intra- and molecular bonds in polymers have noticeable effect on structure and entire combination of the physicomechanical properties. Is especially great the role of hydrogen bonds in polyurethane, since the proton-donor grouping N-H in urethane group and the proton-acceptor atoms of oxygen (in the form of ether/ester oxygen in simple ether/ester bond and in carbonyl group) determine the possibilities of hydrogen joining.

Table 12. Reference of frequencies in oligourethane.

ν, см$^{-1}$	(1) Интенсивность	(2) Колебания
3325	Сильная (3)	N—H-валентные (4)
3060	Очень слабая (5)	(6) Амид II в резонансе Ферми с NH-группой
2945	Сильная ③	Антисимметричные CH$_2$-валентные (13)
2860	Средняя (7)	Симметричные CH$_2$ (8)
1690	Очень сильная (9)	Амид I } (10)
1540	» »	Амид II }
1474—1414	Средняя до слабой (11)	CH$_2$-деформационные (12)
1340	Средняя ⑦	ОС-деформационные ⑫
1265	Очень сильная ⑨	Амид III ⑩
1244	Сильная ③	Антисимметричные СОС-валентные (14)
1180	Очень слабая ⑤	Симметричные СОС-валентные (15)
1137	Сильная ③	CN-валентные (16)
1065	»	
995	Средняя ⑦	С—С-валентные ⑯
783	»	С—О-деформационные ⑫
748	Слабая (17)	CH$_2$-маятниковые, цепи (CH$_2$)$_4$ (18)
730	»	CH$_2$-маятниковые, цепи (CH$_2$)$_6$

Key: (1). Intensity. (2). Oscillation/vibrations. (3). Strong. (4). N-H-valent. (5). Very weak. (6). In resonance Fermi's amide II with NH-group. (7). Average. (8). Symmetrical CH$_2$. (9). Very strong. (10). Amide. (11). Average to weak. (12) deformation. (14). Antisymmetric COC-valent. (15). Symmetrical COC-valent. (16) valent. (17). Weak. (18). ~~cdh~~ CH$_2$-pendulum, chain.

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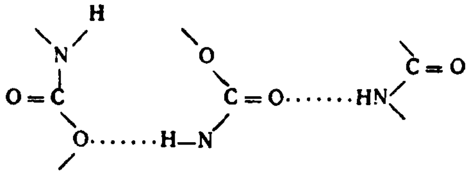
Schematically three basic types of hydrogen bonds can be presented as follows:



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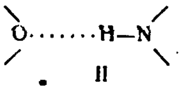

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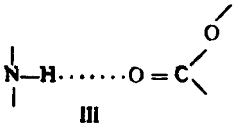

III

As is evident, this of the bond between urethane groups or urethane and ester group and simple ether/ester oxygen of contiguous chains.

Realization in polyurethane of one or the other type of hydrogen bonds depends on the hardness of molecule, determined by the length of oligomeric unit or chain/network of glycol, the concentration of urethane groups in chain, density of the three-dimensional/space grid, which limits the mobility of the cuts of the chains between the nodes of chemical grid. Zharkov [32] assumes that since elastomeric polyurethane can be considered as the peculiar "solution" of urethane groups in polyether/polyester, the predominant type of hydrogen bonds will be form II.

For the investigation of hydrogen bonds, is used the method of IR spectroscopy, since during the formation of the hydrogen bonds of the frequency of the stretching of groups N-H and C=O they are shift/sheared to the side of lower frequencies. A number of works in this direction is small.

With the aid of IR spectroscopy are studied the hydrogen bonds in the urethane elastomers, obtained on the basis of complex and simple polyether/polyesters, and also on model substance - N-phenylurethane [12].

For evaluating the probability of forming one or the other type of bond, was determined the relative electron-donor capacity of proton-acceptor groups during the comparison of the constants of the molecular association of those N-monosubstituted was urethane, modelling the urethane link of polymer, with the molecules of the connections, containing the proton-acceptor groups, similar to the same in polymer chains (methylethylketone, ethylacetate, isobutylbutyrate, tetrahydrofuran, dioxane, etc.).

From the IR spectra of urethane elastomers in region 3200-3500 and 1600-1800 cm^{-1} (Fig. 14) it is evident that for all elastomers are observed the wide absorption bands (3300, 3310 and 3347 cm^{-1}), the relating to absorption groups N-H, by the excited hydrogen bond. Strips 3450 and 3445 cm^{-1} are related to free N-H--group.

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The data [12] on the equilibrium constants of the formation of the hydrogen bond of N-phenylurethane with the molecules, which contain proton-acceptor groups (carbonyl of urethane group, ester group and oxygen of simple ester group) (table 13), made it possible to estimate energy of hydrogen bond in associates (2-3 kcal/mole); however, due to small differences in the equilibrium constants, it is not possible to draw a conclusion about preferred formation of any specific type of bond. Obviously, durable bond it will be hydrogen with the collaboration of oxygen of simple ester groups.

For model substances different types of hydrogen bonds considerably differ by the amount of the frequency switch of the stretching vibration N-H. So, during the formation of hydrogen bond urethane - ester is observed the shift of strip ν(N—H) to the side of lower frequencies on 80-90 cm^{-1}, and for a bond urethane - ether shift is 120-140 cm^{-1}. The preferred type of hydrogen bond in polymers depends on the relative content of different proton-acceptor groups and their three-dimensional/space arrangement in chain.

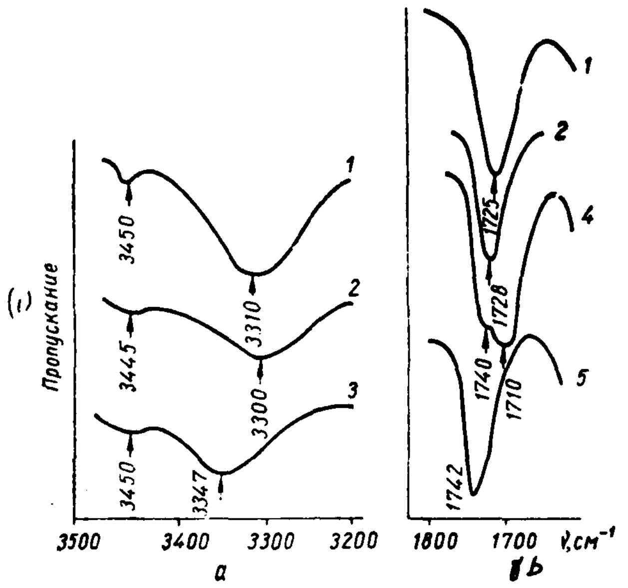

Fig. 14. The IR spectra of urethane elastomers in region 3200-3500 (a) and 1600-1800 cm^{-1} (b): 1 - polyoxypropylurethane; 2 - polyoxytetramethylurethane; 3 - polydiethyleneadipinate urethane; 4, 5 - solution of N-phenylurethane in CCl_4 (C=3.0 and 0.1 mole/l respectively).

Key: (1). Passing.

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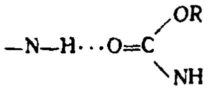
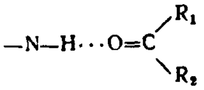
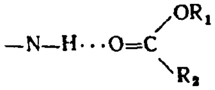
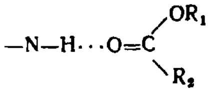
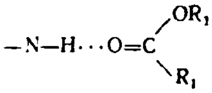
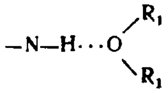
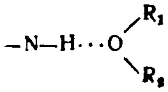
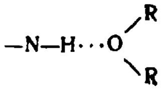
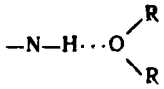
Table 13. Equilibrium constants and frequency switch (Δν) N-H during the formation of hydrogen bond by N-phenylurethane.

(1) Раст-воритель	Соединение, содержащее протоноакцепторные группы (2)	(3) Система водородной связи	K, л/моль (4)	Δν, см⁻¹
CCl_4	(5) Фенилуретан		2,0	—
	(6) Метилэтилкетон		1,5	88
	(7) Этилацетат		1,5	88
	(8) Изобутилбутират		1,7	89
C_6H_{14}	(9) Диметиладипинат		1,2 *	81
CCl_4	(10) Дибутиловый эфир		1,1	140
C_6H_{14}	(11) Диметиловый эфир диэтиленгликоля		0,7 *	126
	(12) Тетрагидрофуран		4,3	142
	(13) Диоксан		3,0	128

*Corrected values correspond to K, divided into a number of acceptor groups in molecule.

Key: (1). Solvent. (2). Connection, which contains proton-acceptor groups. (3). System of hydrogen bond. (4) l/mole. (5). Phenylurethane. (6). Methylethylketone. (7). Ethylacetate. (8). Isobutylbutyrate. (9). Dimethyladipinate. (10). Dibutyl ether/ester. (11). Dimethyl ether of diethylene glycol. (12). Tetrahydrofuran. (13). Dioxane.

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The comparison of spectra it is urethane on the basis of simple and polyesters shows (Fig. 14a) large difference in the frequencies of the absorption of N-H--group, agitated by hydrogen bond, which indicates different forms of communication in these systems. In ester polyurethane, obviously, the basic means of hydrogen bond is the bond with carbonyl of ester group. The formation of hydrogen bond is accompanied also by the shift of strip C=O into the region of low frequencies, that it is possible to use for evaluating the collaboration of group C=O in hydrogen bond. This strip has maximums 1725 and 1728 cm^{-1} (polyoxypropylene urethane and polyoxytetramethylene urethane). The shift of maximum into the region of lower frequencies indicates the collaboration of C=O -group in hydrogen bonds. Thus, it is possible to make a conclusion about preferred formation in ester polyurethane of the hydrogen bond between N-H of urethane link and ester group, but in elastomers on the basis polyethers - between N-H and C=O of urethane links. The small role of bonds N-H with C=O urethane groups is explained by their low content, and the insignificant portion/fraction of bonds with simple ether/ester oxygen - by steric factors.

The investigation of hydrogen bonds in the polyurethane, obtained on the basis of diisocyanates with the mixtures of high and low-molecular diols [32], made it possible to establish/install one additional interesting special feature/peculiarity of these bonds in polyurethane. The collaboration of diols in reaction disturbs the regular arrangement of urethane groups in the chains of the obtained polymer. An effective change in the concentration of these groups is accompanied not only by a change in the total quantity, but also the means of hydrogen bonds, which are generated during the reaction of the proton of NH-COO -group with the included in polymer chain proton-acceptor groups. It is shown [to 32], that with the high concentrations of urethane groups the specific reactions between them differ from reactions in polymers with the smaller content of such groups, i.e., depending on conditions, urethane groups can form two forms of complexes with the hydrogen bonds whose relationship/ratio can depend on the chemical nature of polymer. This fact once again underscores the diversity of the types of hydrogen bonds in polyurethane.

For purpose of obtaining the information about the role of hydrogen bond in polyurethane elastomers [326] by the method of IR spectroscopy is investigated the reaction between N-phenylurethane (I) and diphenylamine (II) as proton donors and by di-n-butyl ether/ester and polyoxyethyleneglycol (mol. weight 6000) as by proton acceptors in solution CCl_4.

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With the aid of Wilson-Wells's method [339] are determined the integral coefficients of absorption of free N-H--group in the solutions of different concentrations for both of components. The formation of hydrogen bond shift/smears the absorption band of the deformation vibrations N-H to the side of low frequencies.

On the basis of experimental spectra with the utilization of integral absorption coefficients, are calculated the concentrations of free N-H--group in all investigated systems in dependence on the summary and separate concentration of the investigated components. Was also examined a question concerning equilibrium in the solutions between bonded and free N-H--group and were determined the apparent equilibrium constants. Actual equilibrium constants cannot be determined due to different degrees of association of molecules with joining by hydrogen bond.

It is establish/installed [326], which N-H in I and II can form the hydrogen bond with simple ether/ester oxygen, which, however, is characterized by the low value of equilibrium constant and therefore it is weak in comparison with bond N-H with carbonyl group. Hydrogen joining in system I - ether is complicated by the presence of two types of the acceptors: -O- and C=O. Findings showed that in dilute solutions is formed the hydrogen bond with simple ether/ester oxygen, if its concentration in system is sufficiently great. With an increase in urethane, concentration becomes possible the association of its molecules on C=O--group, and with the high concentration of urethane, is realized only last/latter interaction mode. On this basis/base is made the conclusion that in polyether urethane occurs the complex equilibrium of the hydrogen bonds between N-H and C=O of urethane groups and -O- polyether/polyester chain. If concentration N-H in polyurethane is small, their large part forms hydrogen bonds with ether/ester oxygen. In that case secondary interchain bonds are scattered throughout entire volume of polymer. If the concentration of N-H-group in low-molecular polyether/polyester is great, then are localized bonds of the type N-H..C=O. Hence is created the possibility of changing the chain configuration in grid during a change in the concentration of urethane groups. In ester systems predominates the strong acceptor C=O and here again appears probability that bonds NH... C=O are not localize in volume even with the high concentration of urethate groups.

With purpose of the investigation of the nature of hydrogen bond in polyurethane, some manifestations of this bond are studied on the model as which is undertaken N-ethylurethane [181]. On the basis of the analysis of the IR spectra of N-ethylurethane and its solutions in the solvents, which contain simple and ester bonds, and also investigations of ductility/toughness/viscosity and dielectric polarization the conclusion is made that in polyurethane as a result of the high content of simple and complex ester groups reaction are determined predominantly by the reaction of urethane groups with ether/ester ones, but not with each other.

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For it is polyurethane by the method of IR spectroscopy studied absorption in the region of the oscillations of group N-H [327]. It occurs in region $\lambda=3$ μ, which is interpreted as absorption by N-H-group, bonded by hydrogen bonds, and free groups N-H. The large part of N-H--group participates in hydrogen bonds independent of the structure of polyurethane itself (ether/ester or ester type, linear or cross-linked).

Investigated also the effect of solvents on the spectra of absorption of linear ones it is polyurethane and it is establish/installed, that during dilution occurs the dissociation of hydrogen bonds. For those cross-linked it is polyurethane the insignificant dissociation of hydrogen bonds it is noted in the range of temperatures of 20-100°C. Partial dissociation was observed also with the stretching of specimen/samples.

In connection with the fact that many properties it is polyurethane they are explained precisely by difference to the degree of the hydrogen joining of macromolecules with each other, this question it was specially investigated [by 220].

Are studied series/numbers it is polyurethane the general formula

$$[-(CH_2)_y-OCONH-(CH_2)_6-$$
$$-NHCOO-]_n$$

with y=4-10, including the linear and cross-linked polymers, and also their models - diurethane. The free oscillation/vibrations of N-H--group occur, as it was shown above, with 2.9 μ (3448 cm-¹). Typical spectrum in this region for 6,8-polyuret on is given in Fig. 15. Spectra are removed in the range of temperatures of 20-300°C.

The intensity of the oscillations (Fig. 15) of free N-H--group grow/increases with a temperature rise (spectrum 2). However, the authors did not find differences in the degree of hydrogen joining for even and odd was polyurethane, or polyamides. At room temperatures in linear ones, it is polyurethane less than 1o/o free N-H--group (0.8o/o for 6,8- and 6,9-homologs and 1.5o/o for 6,6- and 6,10-copolyurethanes). It is interesting that the cross-linked polyurethane do not show the greater intensity of the oscillations of free N-H~~Y~~-group, i.e., even in irregular systems is observed virtually full/total/complete joining. For 6,8-polyurethane with 175°C, the content of the uncombined groups composes only 15o/o. Thus, the explanation of a difference in the properties it is polyurethane by the different degree of hydrogen joining it cannot be plausible as a result of the fact that virtually in all cases the free NH-groups in system are absent.

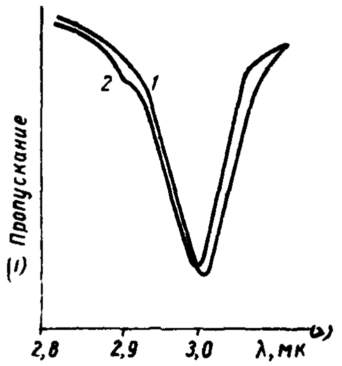

Fig 15. Spectrum of polyurethane in the region of oscillations N-H at 22°C (1) and 100°C (2).

Key: (1). Passing. (2) μ.

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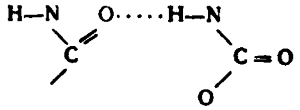
For the examination of the role of hydrogen bond in polyurethane there is great interest in a question concerning the possibility of evaluating energy of this bond. For this estimation it is possible to use the absorption of groups N-H. The corresponding calculations are given in [32]. Equilibrium constant between the uncombined and bonded hydrogen bond group N-H is determined by the expression

$$K = \frac{l_m}{l_a} \cdot \frac{D_a}{D_m},$$

where l_a and l_m - molar absorption coefficients, D_a and D_m - optical densities of absorption bands of bonded and free N-H-group.

Calculated from values K at two different temperatures, energy of hydrogen bond (ΔH) in polyurethane was 4.8+-1 kcal/mole. According to [220], this value for bond ~~H~~N-H... OC is equal to 8.36+-1.6 kcal/mole. It is interesting to note that in polyurethane on basis 2,4- and 2,6-toluenediisocyanate the urethane groups are arrange/located nonequivalently with respect to aryl radical, as a result of which formed by these urethane groups the hydrogen bonds must be distinguished by their energy. Absorption band (N-H) with frequency 3444 cm^{-1} is related to the urethane group whose three-dimensional/space arrangement contributes to the formation of hydrogen bond, while strip 3460-3463 cm^{-1} answers the urethane group whose three-dimensional/space arrangement impedes the formation of such bonds. Because of this in polyurethane elastomers, can exist uncombined by the hydrogen bond of N-H~~°~~-group. The study of the problem concerning association as a result of the emergence of hydrogen bonds in model urethanes and some polyurethane led to the conclusion about the fact that the auto/self-association of urethane groups cannot be the determining factor in the formation of hydrogen bonds in polyurethane on the basis polyethers [32]. High value has a bond between urethane group and ether/ester oxygen.

In real polyurethane elastomeric systems must be observed more complex picture. On one hand, the presence only of uric groups leads to the possibility of the formation of the hydrogen bonds between the uric groups



The formation of allophanate and other groups even more greatly changes conditions and the possibility of the formation of hydrogen bonds.

On the other hand, their emergence depends substantially on the chemical nature of polyurethane in that sense, that the length of glycol units, the type of diisocyanate and other chemical factors affect the mutual arrangement of the groups, capable of forming hydrogen bonds, and on their mobility. So, work [324] shows the possibility of the formation of intramolecular hydrogen bonds for allophanates and it is biuret and it is establish/installed, that the hydrogen joining is more intensive in biuret.

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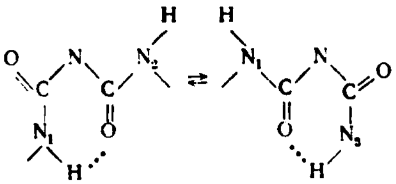

These conclusions are made on the basis of the analysis of the NMR spectra of high resolution. For it is biuret the authors they give the following diagram of the formation of the hydrogen bonds: .th the allowed transitions between two structures.

The information about hydrogen bonds in polyurethane thus far are still limited both according to a number of investigated systems and on their chemical structure. The investigation of this question is very important for the detailed understanding of the properties of polyurethane materials. So, in work [12] is assumed that different means of hydrogen bonds can lead to the specific differences in the packing of molecular chains in complex ester polyurethane and polyurethane on the basis polyethers. The authors proposed the diagram of the formation of hydrogen bonds in urethane elastomers (Fig. 16). The bond between urethane and ester links is set no limitations on the mutual arrangement of the urethane sections of chains (Fig. 16a). The emergence of the hydrogen bonds between two urethane links requires their specific mutual arrangement in chain (Fig. 16b), which can lead to partial ordering.

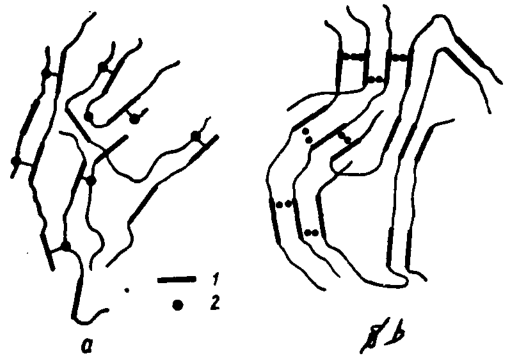

Fig. 16. The diagram of H-bond in the urethane elastometers: a - polymers on the basis of polyesters; b - polymers on the basis polyethers; 1 - urethane sections of polymer chain; 2 - ester groups.

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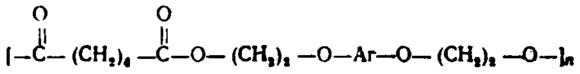
In the study of the problem concerning the role of hydrogen bonds, one should, according to our opinion, bear in mind, that their value in the physicomechanical properties of polyurethane elastomers is small. This is bonded with the fact that in elastomeric systems the relative concentration of the capable of formation hydrogen bonds of urethane groups is small and descends with an increase in molecular weight of polyether/polyester. At the same time, the common/general/total contribution of physical reactions to the effective network density of polyurethane elastomers is essential. This is caused by the fact that the presence of many functional groups in polyurethane chain leads to the significant van der Waals reactions between chains, considerably greater than in the case of common (nonpolar) rubbers. Therefore there is great interest in the investigation of intermolecular interaction between the component units of polyurethane chain and common van der Waals reactions. The given by us data on the flow properties of oligomers, which are used for synthesis it is polyurethane, distinctly they show, what important role in the common/general/total combination of properties play the common van der Waals reactions (see pg. 216).

Different picture is observed for crystalline ones it is polyurethane. The formation of hydrogen bonds has vital importance for those crystallizing it is polyurethane, especially on the basis of low-molecular units. These bonds define both the crystal lattice and other properties of polymers. However, in contrast to polyamides, for crystalline ones it is polyurethane investigations in hydrogen bonds carried out little.

The IR spectra of polyether/polyesters it is polyurethane they are described in works [81, 82]. These objects are capable of existing in two crystalline forms, if in the chain/network of the structure



$$[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-(CH_2)_2-O-Ar-O-(CH_2)_2-O-]_n$$

Ar-m- or n-phenylene. For different polymers are determined the strips of crystallinity in different modifications. Depending on crystalline form, can be formed the hydrogen bond. The appearance of hydrogen bonds is capable of stabilizing crystalline modifications. These works indicate the value of hydrogen bonds in the crystallized polymers of urethane series/number.

For capable of crystallization polyamidourethanes the IR spectra are compared with roentgenographic investigations [29]. Taking into account that the hydrogen bonds between separate molecules affect both the conformation of molecules themselves and their packing in crystal structures, and that besides the principle of tight packing must be observed the principle of the maximum saturation of hydrogen bonds, is proposed the probable model of the arrangement of macromolecules in the crystalline regions of polyamideurethane.

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In the literature there are some data according to intermolecular interactions in the connections, which are components it is polyurethane. Are investigated intra- and intermolecular hydrogen bonds in glycols [255, 256], with the aid of spectroscopy are studied the intramolecular bonds in some polyoxyalkylenediols [31]. For polyoxypropyleneglycol and poly-tetrahydrofuran of absorption band 3480 and 345~~6~~7 cm^{-1}, they are referred to the oscillations of the OH-groups, included in hydrogen bond, but 3640

cm^{-1} - to free OH-group in poly-tetrahydrofuran. From the temperature dependence of the absorption coefficients for the strips of the free and bonded by hydrogen bond OH-groups, is calculated the energy of intramolecular hydrogen bond according to method [33]. It is establish/installed, that this energy for the investigated systems is 2.1-2.8 kcal/mole. However, it is necessary to bear in mind, that these reactions are determined in essence by end groups.

Thus, the application/use of spectroscopic methods to investigation it is polyurethane it makes it possible to give the qualitative characteristics both of the chemical structure of grid and some types of intermolecular interactions in polyurethane amorphous and crystalline structure. Nevertheless, the creation of the ordered theory of properties it is polyurethane, that is based on detailed qualitative and quantitative spectral analysis, it remains the business of the future.

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Chapter IV. VITRIFICATION AND PHASE TRANSFORMATIONS IN LINEAR AND THREE-DIMENSIONAL POLYURETHANES.

VITRIFICATION OF AMORPHOUS POLYURETHANES.

It is known that the temperature of vitrification (T_c) of polymers is defined by both the internal mobility or flexibility of polymer chains and by forces of intermolecular interaction, to a considerable degree which depend on the presence in the chains of polar groups. Thus, T_c polymers depends on length, nature and structure of their chains (speech it goes about amorphous the not modified by fillers or plasticizers polymeric systems).

All factors indicated for it is polyurethane they are determined by the properties of their initial components, i.e., by the properties of glycols (ether glycols) and of diisocyanates. Consequently, the properties of initial components their relationship/ratio in polymer chain in essence must determine T_c it is polyurethane.

Is studied dependence T_c of polyester-urethane elastomers on the structure of initial glycols, in particular, from the presence of simple ether/ester bonds in main chain and its lateral suspensions, and also from a number of methylene groups in glycol [93].

Together with T_c, which determined on the tool, described in [113] on pendulum elastomer KS [52], investigated elasticity of polyurethane elastomers on the basis of complex oligoester and toluene-2,4-diisocyanate with an average molecular weight of approximately 20 000. According to the minima of the curves of the temperature dependence of elasticity, they calculated the temperature of the minimum of elasticity ($T_{мин}$) (table 14).

From the data of table 14, it is evident that the increase of the concentration of C-O-C--group in the main chain of polymer leads to successive reduction T_c. The constant for this series/number of polymers difference between T_c and $T_{мин}$ testifies to the clearly expressed quantitative bond between these two values.

Table 14. Temperatures of the transitions of polyurethane elastomers.

(1) Полимер	T_c	$T_{мин}$
Полидиэтиленадипинатуретан (2)	—39	—13
Политриэтиленадипинатуретан (3)	—42	—16
Полигексаэтиленадипинатуретан (4)	—44	—18

Key: (1). Polymer. (2). Polydiethyleneadipinate urethane. (3). Polytriethyleneadipinate urethane. (4). Polyhexaethyleneadipinate urethane.

Note: For all polymers $\Delta T = T_c - T_{мин} = 26^\circ$ C.

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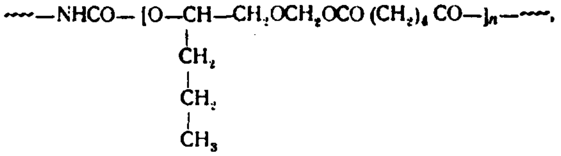
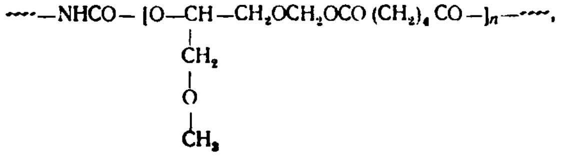
The observed character of change T_c is explained by weakening intermolecular interaction as a result of the decrease of the concentration of strongly polar complex ester groups in polymer chain with an increase in the length of the monomer unit of initial glycol.

Based on the example of polydiethylene- and polypentmethyleneadipateurethane, which are characterized by only the presence in the glycol links of CH_2—group instead of ether/ester oxygen, it is shown, that absence of C-O-C—group leads to reduction T_c. This is explained by the possibility of the joining of ether/ester oxygen by hydrogen bonds, that leads to a reduction in the mobility of chain.

At the same time for polypropyl- and polymethoxymethylethyleneadipateurethane, which are characterized by only the structure of the lateral groups



$$\sim\sim-NHCO-[O-\underset{\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}}{\underset{CH_2}{\underset{|}{CH}}}-CH_2OCH_2OCO(CH_2)_4CO-]_n-\sim\sim,$$



$$\sim\sim-NHCO-[O-\underset{\underset{\underset{CH_3}{|}}{\underset{O}{|}}}{\underset{CH_2}{\underset{|}{CH}}}-CH_2OCH_2OCO(CH_2)_4CO-]_n-\sim\sim,$$

the absence in the side chain of ether/ester oxygen does not affect vitrification temperature which for both of polymers is identical.

Study T_c it is polyurethane, obtained on basis glycols with the even and odd sequences of methylene groups with the general formula

$$\sim\sim-NHCO-[O(CH_2)_nOCO(CH_2)_4CO]_x-\sim\sim,$$

where n=2, 3, 4, 5, it showed that the polymers with odd number n have lower T_c, than with even (Fig. 17).

Is investigated dependence T_c of polyurethane elastomers on the basis of polyoxypropyleneglycol and toluene-2,4-diisocyanate or hexamethylenediisacyanate on the mole concentration of urethane groups [317] (Fig. 18).

As can be seen from Fig. 18, T_c for both it is polyurethane linearly it increases with an increase in the concentration of urethane groups. For an elastomer on the basis of toluene-2,4-diisocyanate, the slope angle is direct/straight greater than for an elastomer on the basis of hexamethylene diisocyanate, which is caused by a simultaneous increase in the concentration both of urethane and phenylene groups; the latter also increase rigidity of chains. However, extrapolation to curve T_c-C to C=0 for both of elastomers gives T_c, the appropriate same for high-molecular polyoxypropyleneglycol.

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Analogous dependence T_c on C is found for polyurethaneacrylate [128] on the basis of oligohydroxypropyleneglycol, toluene-2,4-diisocyanate and mono-methacrylic ether/ester of ethylene glycol. However, in this case slope angle straight line T_c-C is more than for the given above elastomer with analogous oligoester and diisocyanate units. This is explained by the presence in polyurethaneacrylate of the strongly polar complex ester groups, which condition the lower mobility of polymer chains with the same concentration of urethane groups, as in the compared elastomer.

We investigated T_c in the series/number: oligodiethyleneglycoladipate (OE), linear oligourethane (prepolymer) and cross-linked polyurethane elastomer [65]. As diisocyanate component served the mixture of isomers 2.4- and of 2,6-toluenediisocyanate (TDITs), but by the crosslinking agent - an equimolar mixture of di- and triethanolamine. Vitrification temperature was defined by the differential-thermal analysis as in [38].

The influence of molecular weight of oligoester on T_c is shown on Fig. 19, from which it is evident that higher than molecular weights 4000 T_c is not practically changed.

If we, according to [36], consider that constancy T_c is reached at molecular weight, which corresponds to such for a mechanical segment chain, then it is possible to assume that for polydiethyleneglycoladipate mechanical segment is the cut of chain with a molecular weight of approximately 4000.

Were studied prepolymers and elastomers whose oligoester units had molecular weight 1600 (OE-1) and 4100 (OE-2) (Table 15).

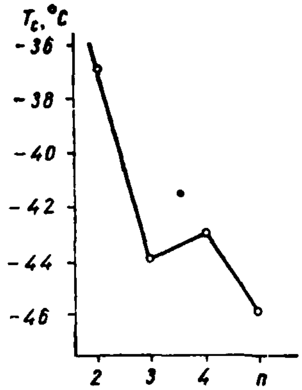

Fig. 17. Dependence T_c on a quantity of CH_2—group in the glycol segment of polyurethane chain.

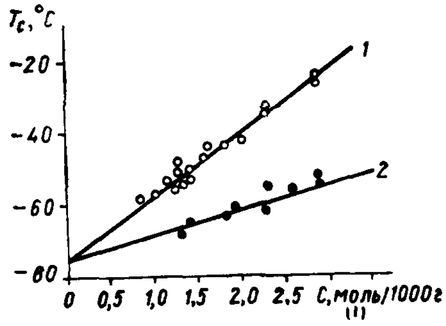

Fig. 18. Dependence T_c on mole concentration of urethane groups (C) of polyurethane elastomers on basis of oligohydroxypropyleneglycol with toluene-2,4-diisocyanate (1) and oligohydroxypropyleneglycol with 1,6-hexamethylene diisocyanate (2).

Key: (1). mole/1000 g.

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Consequently, in one of them molecular weight corresponds to the length of mechanical segment, but in another it is more than twice less.

From the data of table 15, it is evident that the presence in the chain of prepolymer and cross-linked elastomer of urethane groups together with complex ester groups leads to significant increase T_c in the latter in comparison with initial oligoesters. In this case, T_c prepolymers (Fig. 20) with the identical length of oligoester units linearly grow/increases not with an increase in molecular weight, but with an increase in the molar fraction of diisocyanate component in the molecule of prepolymer.

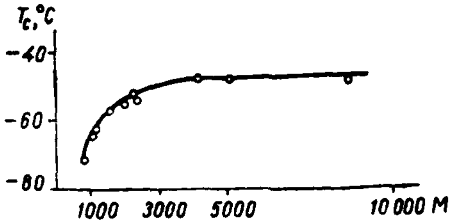

Fig. 19. Dependence T_c on molecular weight (M) of polydiethyleneglycoladipate.

Table 15. Relationship/ratio of initial components and characteristic of the specimen/samples of oligoester, prepolymers and elastomers.

(2) Номер образца	(3) Образец	(1) Мольная доля компонентов ОЭ	 ГДИЦ	 (4) Сшиватель	$m_{\text{ТДИЦ}}$ / $m_{\text{ОЭ}}$	M	(5) T_c' (начало), °C	(6) T_c'' (конец), °C	(7) T_c (средняя), °C	$\Delta T = T_c'' - T_c'$
1	(8) Олигоэфир 1	—	—	—	—	1600	—60	—51	—55,5	9
2	(8) Олигоэфир 2	—	—	—	—	4100	—50	—45	—47,5	5
3	Форполимер на олигоэфире 1	2,0	1,00	—	0,50	3430	—46	—38	—42	8
4	(9)	2,0	1,50	—	0,75	3500	—43	—33	—38	10
5		1,0	1,00	—	1,00	6300	—42	—31	—36,5	11
6		1,5	2,00	—	1,33	4500	—39	—26	—32,5	13
7	(9)	1,0	2,00		2,00	1990	—33	—20	—26,5	13
8	Форполимер на олигоэфире 2	2,0	1,00	—	0,50	7500	—50	—40	—45	10
9	Форполимер на олигоэфире 2	2,0	1,50	—	0,75	13500	—45	—38	—41,5	7
10	(9)	1,0	1,00	—	1,00	5500	—45	—38	—41,5	7
11		1,5	2,00	—	1,33	5000	—46	—35	—40,5	9
12	(10)	1,0	2,00	—	2,00	4800	—44	—35	—39,5	9
13	Эластомер на олигоэфире 1	1,0	1,07	0.017	1,07	—	—44	—26	—35	18
14		1,0	1,10	0,035	1,10	—	—41	—25	—33	16
15		1,0	1,15	0.070	1,15	—	—40	—24	—32	16
16	(10)	1,0	1,20	0.100	1.20	—	—39	—24	—31,5	15
17	Эластомер на олигоэфире 2	1,0	1.15	0,070	1,15	—	—45	—34	—39,5	9
18		1,0	1,20	0,100	1,20	—	—45	—34	—39,5	9

Key: (1). The mole fraction of components. (2). Number of specimen/sample. (3). Specimen/sample. (4). Cross-linking agent. (5). start. (6). end. (7). average. (8). oligoester. (9). Prepolymer on oligoester. (10). Elastomer on oligoester.

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At the same time curve 1 lie/rests above and has greater slope angle, than curve 2. This phenomenon is explained by the higher concentration of urethane groups per unit of volume of prepolymer, which contains the oligoester units of smaller molecular weight, and by a more significant increase in the concentration of these groups in this same prepolymer in proportion to an increase in the share of diisocyanate.

It is substantial that extrapolation of both of curves to the zero value of the mole fraction of diisocyanate gives $T_c = -47^\circ C$, which corresponds such mechanical segment of polydiethyleneglycoladipate (see Fig. 19).

The curve of dependence T_c on the mole concentration of urethane groups for prepolymers (Fig. 21) has the same character, as analogous curved for it is polyurethane another nature (see Fig. 18). In this case, data of both of prepolymers lie down on one and the same curve, which indicates the dominant role of the concentration of urethane groups in change T_c in polyetherurethane.

In turn, the transition from prepolymer to the cross-linked elastomer is not accompanied by this significant increase T_c, as transition from oligoester to the prepolymer (see Table 15). Hence follows the conclusion that the transition from oligoester to prepolymer leads to a sharp qualitative change in the properties of the molecule, in which the properties of initial units seemingly partially are lost. New molecule (molecule of prepolymer) is the independent kinetic unit/one, which is characterized by its own mobility.

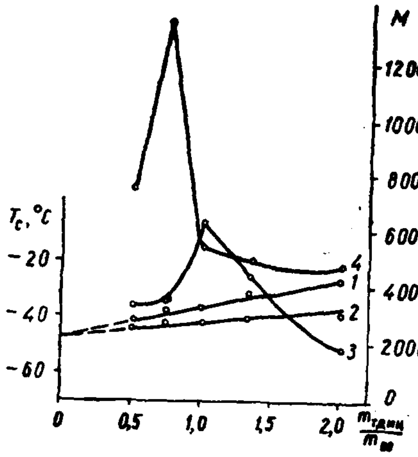

Fig. 20. Dependence T_c (1 and 2) and molecular weight (3 and 4) from molar ratio of oligoester and diisocyanate for prepolymers on the basis of oligoester with M=1600 (1, 3) and 4100 (2, 4).

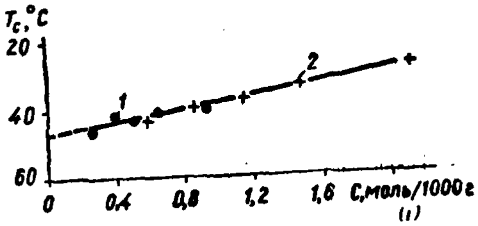

Fig. 21. Dependence T_c on mole concentration of urethane groups (C) of prepolymers on basis of OE with M=4100 (1) and 1600 (2).

Key: (1). mole/1000 g.

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Otherwise the loss of mobility by such system would occur into two stages - first mobility fell because of the joining of the sections of chains of polar urethane groups, but from the preservation/retention/maintaining of the mobility of oligomeric unit; further at lower temperature occurred the loss of the mobility of oligomeric units. In this case, we must cbserve two T_c, as for block copolymers [159].

From the value of the difference between T_c oligoester and prepolymer, prepolymer and elastomer (table 16) is evident that the dominant role in increase T_c, and it means in a reduction in the mobility of oligoester units into elastomer, plays not crosslinking agent, i.e., not transverse bonds, but polar urethane groups or physical cross connections. Consequently, the basic contribution to the three-dimensional/space grid of polyurethane elastomers introduce not chemical, but physical cross connections [115].

An increase in prepolymers of molecular weight of the oligoester units (see Table 15) is accompanied together with reduction T_c by narrowing the temperature interval of this process, which is explained by the decrease of the mean relaxation time of polymer chains as a result of an increase in their mobility.

To analogous conclusion/derivations about T_c are given the thermomechanical investigations of the systems (Fig. 22) indicated. As can be seen from the character of thermomechanical curves, either oligoester, or prepolymer is not revealed highly elastic strain and above T_c they are in the viscous flow state. Only cross-linking into three-dimensional/space grid adds to the obtained systems highly elastic properties. The comparison thermomechanical curve elastomers on the basis of oligoesters with different molecular weights shows that for an elastomer on the basis of oligoester with large molecular weight it is observed together with highly elastic and certain plastic deformation, which is explained by the smaller concentration of chemical and physical cross connections in specimen/sample.

Table 16. Contribution of diisocyanate and crosslinking agent to an increase in the temperature of the vitrification of oligoester.

(1) Номер образца	$\frac{m_{ТДИЦ}}{m_{ОЭ}}$	(2) Количество сшивателя	(3) T_c форполимера (рассчитано), °C	(4) T_c эластомера, °C	ΔT ТДИЦ	(5) ΔT сшивателя
13	1,07	0,017	—36,0	—35,0	19,5	1,0
14	1,10	0,035	—35,5	—33,0	20,0	1,5
15	1,15	0,070	—35,0	—32,0	20,5	3,0
16	1,20	0,100	—34,5	—31,5	21,0	3,0
17	1,15	0,070	—41,5	—39,5	6,0	2,0
18	1,20	0,100	—41,0	—39,5	6,5	5,0

Key: (1). Number of specimen/sample. (2). Quantity of cross-linking agent. (3). prepolymer (calculated), of °C. (4). elastomer, °C. (5). Cross-linking agent.

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Entirely another picture we observe in the case of polyurethane elastomers with carbon-chain (oligoisoprene and oligobutadiene) oligomeric units [127] (table 17). With the synthesis of the elastomers indicated as diisocyanate component, was used toluenediisocyanate, and as the crosslinking agent served triethanolamine.

It is very substantial, that the elastomers, synthesized both on oligoisoprene and on oligobutadiene begin to devitrify at the same temperature, as their component oligomers, only in the wider temperature range.

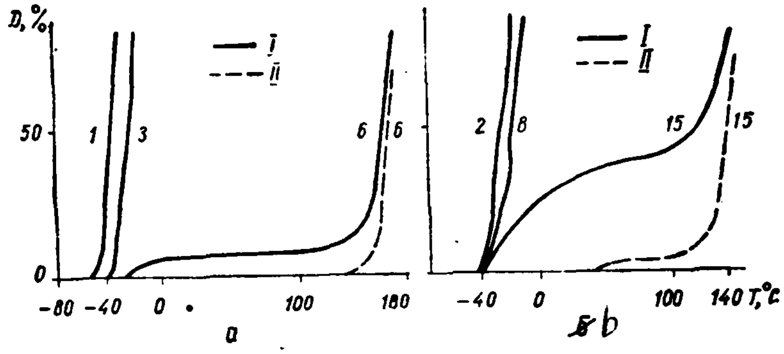

Fig. 22. Thermomechanical curve of oligoesters with M=1600 (a) and 4100 (b) and synthesized on their basis prepolymers and elastomers: I - common/general/total deformation; II - irreversible deformation (number they correspond to the numbers of specimen/samples table 15).

Table 17. The temperature characteristic the vitrification of polyurethane elastomers and their oligomeric components.

(2) Вещество	(1) Соотношение исходных компонентов			(5) T_c' (начало), °C	(6) T_c' (конец), °C	$\Delta T = T_c' - T_c'$
	ТДИЦ	(3) Олигомер	(4) Сшива-тель			
(7) Олигоизопрен-1 ($M = 2000$)	—	—	—	—60	—50	10
(8) Эластомер на ОИ-1	1	1,68	0,4	—60	—34	26
(7) Олигоизопрен-2 ($M = 5500$)	—	—	—	—61	—50	11
(8) Эластомер на ОИ-2	1	1,68	0,4	—60	—45	15
(9) Олигобутадиен ($M = 2000$)	—	—	—	—80	—61	18
(8) Эластомер на ОБ	1	1,68	0,4	—80	—60	20

Key: (1). Relationship/ratio of initial components. (2). Substance. (3). Oligomer. (4). Crosslinking agent. (5). it began. (6). end. (7). Oligoisoprene. (8). Elastomer on. (9). Oligobutadiene.

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The comparison of the data of Table 15 and 17 shows that the replacement into the elastomer of the oligomeric unit of ester nature to hydrocarbon leads to the essential difference for the character of vitrification of these forms of polyurethane elastomers. Difference is in an intermittent increase in vitrification temperature upon transfer from the esterglycols to polyurethane elastomers, which indicates a sharp reduction in the mobility of oligoester unit in the composition of elastomer. Transition from oligodiene glycols to polyurethane elastomer is not accompanied by an abrupt change in the mobility of oligomeric units, about which tell the identical temperatures of the beginning of the devitrification of oligodiene glycols and elastomers.

An increase in the interval of the vitrification of the investigated elastomers with respect to initial oligoglycol is explained by the presence in them of the rigid cuts of the polymer chain, formed by the diisocyanate component, which, interacting with each other, increase the hardness of system, impeding the course of relaxation processes. All this in the final analysis affects also the relaxation time of polymer chains. An increase of the relaxation time in turn, leads to the expansion of an interval of the vitrification of elastomer. This explanation of an increase in the interval of vitrification in elastomers is confirmed by the fact that an interval of vitrification in elastomers is lowered with an increase in the length of oligomeric unit, i.e., with a reduction in the share of diisocyanate component per unit of volume of the elastomer (see Table 17).

The special feature/peculiarity of the behavior of polyurethane elastomers on the basis of oligodiene glycols one should explain by the ne-polarity of oligodiene units. The absence of polar groups in the chain of oligodiene units make it (possible for them) to enter into strong interaction with diisocyanate units and friend with other. As a result the possibility of formation of stable physical bonds is insignificant. Therefore a sharp reduction in the mobility of oligomeric unit in the composition of elastomer, as this occurred for the case of the ester nature of unit, is not observed.

The comparison of the temperature intervals of the vitrification of the elastomers, obtained on oligoisoprene with molecular weights of 2600 and 5500, shows that the elastomer with the units of larger molecular weight has the smaller temperature interval of devitrification.

Transition from glassy state to highly elastic for polyurethane elastomers with oligodiene units occur/flow/lasts in the wider temperature interval (see Table 17), than in elastomers with the units of the ester nature (see Table 15). This, obviously, it is possible to explain by the homogeneity of basic physical bonds in the elastomers, which contain the units of ester nature, and by the heterogeneity of the same in elastomers with the units of hydrocarbon nature.

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In the first intermolecular interaction because of the presence of polar complex ester groups is determined mainly by the hydrogen bonds which as a result of identical intensity for entire extent/elongation of macro-chains dissociate in sufficiently narrow temperature interval. In the second because of nonpolar nature units intermolecular interaction is realize/accomplished in essence by the dispersion forces.

The wide collection of the interatomic distances of adjacent macromolecules, caused by their relatively small polarity, causes formation between the chains of polyurethane of the dispersion bonds of different intensity whose destruction must occur/flow/last in significant temperature interval. In connection with this we assume that the differences in change T_c upon transfer from oligomeric units to the cross-linked elastomers for polyurethane elastomers with ester and hydrocarbon nature are explained by a difference in the character of the physical grid, which is generated in polyurethane elastomer. In turn, in polyurethane elastomers with the ester nature of oligomeric units the predominant contribution to the effective density of the physical grid should be played by hydrogen bonds.

Thus, T_c amorphous is polyurethane it is predetermined by both the chemical nature, structure and molar fraction of components of polyurethane diisocyanates and glycols and by molecular weight of the latter. The basic contribution to increase T_c cross-linked is polyurethane in comparison with initial oligoglycol it introduces not spatial structure it is polyurethane, but the presence in them of the urethane groups, which play the dominant role in the formation of secondary physical bonds.

PHASE TRANSFORMATIONS AND VITRIFICATION OF LINEAR ALIPHATIC POLYURETHANES ON THE BASIS OF LOW-MOLECULAR GLYCOLS.

Properties it is polyurethane they depend substantially on that, will be it glycol comprised monomer or oligomer. In the case of monomeric glycols, the generating polyurethane in essence are crystallized, whereas capability for crystallization it is polyurethane with oligoglycol units it is not the necessary result of the chemical nature of chain. Therefore it is expedient to examine the questions, bonded with phase transformations, for each form it is polyurethane separately.

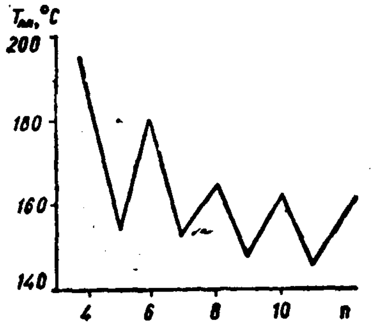

Fig. 23. The dependence of melting point it is polyurethane on the basis of butanediol and linear aliphatic diisocyanates from a number of carbon atoms for target/purpose (n) the latter.

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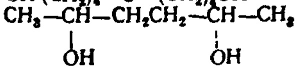
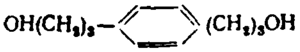
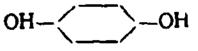
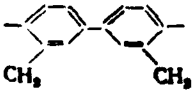
Table 18. Some characteristics of linear ones it is polyurethane.

(1) Диизоцианат	(2) Гликоль	$T_{пл}$, °C	(3) Свойства
$-(CH_2)_4-$	1,4-Бутандиол (4)	193	Очень хорошо вытягивается в нить (5)
	1,6-Гександиол (6)	180	То же (7)
	1,10-Декандиол (8)	171	» »
	1,3-Пропандиол (9)	167	» »
	1,5-Пентандиол (10)	151	» »
	1,9-Нонандиол (11)	147	» »
	$OHCH_2CH_2-O-CH_2CH_2OH$	120	» »
	$OH(CH_2)_4-O-(CH_2)_4OH$	124	» »
	 $CH_3-\underset{OH}{\underset{\mid}{CH}}-CH_2CH_2-\underset{OH}{\underset{\mid}{CH}}-CH_3$	104	» »
		158	» »
	$OH(CH_2)_2S(CH_2)_2OH$	129—134	» »
	$OH(CH_2)_4S(CH_2)_4OH$	120—125	» »
$-(CH_2)_6-$	1,4-Бутандиол } (4)	160	» »
	1-3-Бутандиол	77—82	Рогоподобный (12)
	1,6-Гександиол (6)	153	Очень хорошо вытягивается в нить (5)
	 (13) (транс, цис)	215—220	Хорошо вытягивается в нить, хрупкий (14)
	 (15) (транс)	250—255	Разлагается (16)
		168	Плохо вытягивается в нить (17)
		208—212	Вытягивается в нить (18)
$-(CH_2)_8-$	1,4-Бутандиол (4)	136—140	Очень хорошо вытягивается в нить (5)
$-(CH_2)_{11}-$	1,4-Бутандиол (4)	121—125	То же
	1,5-Пентандиол (10)	143—146	» »
— —	1,4-Бутандиол (4)	260	Разлагается (16)
$-(CH_2)_{12}-$	1,12-Додекандиол (19)	128	Очень хорошо вытягивается в нить (5)
	1,10-Декандиол (8)	215—219	Волокнообразующий, хрупкий (20)
$-(CH_2)_3S(CH_2)_3-$	1,4-Бутандиол (4)	126—133	То же (7)

Key: (1). Diisocyanate. (2). Glycol. (3). Properties. (4). Butanediol. (5). Very well it is pulled out. (6). Hexanediol. (7). The same. (8). Decanediol. (9). Propanediol. (10). Pentanediol. (11). Nonanediol. (12). Horn-like. (13). trans-, cis-. (14). Well ropy, brittle. (15). trans-. (16). It is decompose/expanded. (17). Badly/poorly ropy. (18). Ropy. (19). Dodecanediol. (20). Forming fiber, brittle.

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Linear polyurethane on the basis of low-molecular glycols have much in common with analogous polyamides. So, this form is polyurethane it possesses the capacity to ropy, and therefore is of interest as the fiber-forming material. For it is polyurethane just as for polyamides, is observed a zigzag change in the melting point with a change in the number of methylene groups between the polar groups of chain (Fig. 23). Melting point it is polyurethane with even number of methylene groups higher than in their nearest polymer homologs, which contain the odd number of methylene groups in hydrocarbon chain/network.

The properties of linear ones it is polyurethane strongly they depend on nature and structures from components, which can be judged according to data table 18 [170].

Let us pause at the presentation of existing in literature information which concern separate aliphatic ones it is polyurethane.

Polyurethane on the basis of 1,6-hexamethylenediisocyanate and 1,4-tetramethyleneglycol (perlon-U).

Known a significant quantity of crystallizing aliphatic ones it is polyurethane, but is solidly studied the structure of polyurethane on the basis of 1,6-hexamethylenediisocyanate and 1,4-butanediol (perlon-U or 4.6-PU). This is explained by the fact that this polyurethane already found practical application/use as the fiber-forming material.

For the first time structure of 4,6-PU described Brill [177], then Zahn and Winther [349, 350], and also Borchert [174].

Diagrammatic representation of the structure of unit cell of 4,6-PU, proposed by Brill, is given in Fig. 24. The authors indicated assign to this polyurethane anorthic lattice with the following parameters of unit cell:

a, Å	b, Å	c, Å	α°,	β°,	γ°,	
9,5	19,10	8,4	90	63—65	77	[349, 350]
4,95	10,10	8,23	90	60,2	73	[174]
9,56	19,10	8,23	90	63	73	[243, 244]

Triclinic crystal lattice of 4,6-PU consists of the "flat/plane grids" [147, 170] whose adjacent macromolecules are connected through (dotted line). In turn the "plane grids" are stacked on the regularly repeated sections by N-bridges (Fig. 25, A each other, is formed three-dimensional lattice.

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Thus, 4,6-PU it is packed according to the type of layer lattice. In this case, at the direction of chains (axis c) lie/rest main valence bonds, in "flat/plane grid" (axis a) act the hydrogen bonds. Between "flat/plane grids" the bond is realize/accomplished by van der Waals forces (axis c).

The usually crystallizing polymers do not form ideal crystalline systems and always contain sections with mono-, two- and three-dimensional by the disturbance/breakdowns of crystal lattice. Crystal structures with mono- and two-dimensional lattice imperfections call pseudo- or paracrystalline ones. Similar structures can be formed also in polyurethane, especially in the initial (primary) stage of crystallization.

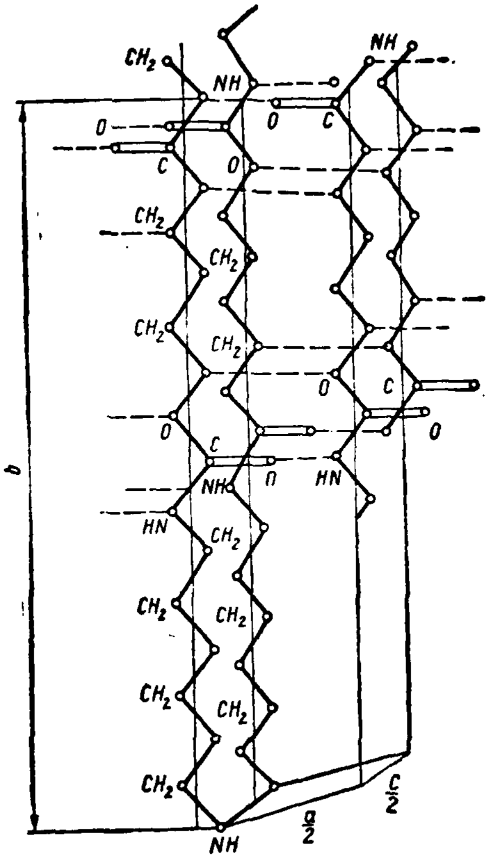

Fig. 24. Diagram of the part of elementary cells of 4,6-polyurethane.

For determining the degree of order (crystallinity) in 4,6-PU according to the data of X-ray studies Kilian and Yenkel [243, 244] calculated the integral degree of the crystallinity

$$\alpha = \frac{1}{I} \int_{2\theta_1}^{2\theta_2} I_c d\Theta, \qquad \text{(IV.1)}$$

the partial crystallinity, characterizing the hydrogen bonds

$$\alpha_{\text{н}} = \frac{1}{\bar{I}} \int\limits_{200} I_{c_1} d\Theta, \quad \text{(IV,2)}$$

and the partial crystallinity, characterizing the van der Waals bonds

$$\alpha_V = \frac{1}{\bar{I}} \int\limits_{(002)} I_{c_2} d\Theta, \quad \text{(IV,3)}$$

where $\bar{I}$ - the total intensity of interference, Θ_1 and Θ_2 - angles of reflection of interference (200) and (002) respectively; I_{c_1} and I_{c_2} - intensity of the interference of the crystalline part of the spectrum when Θ_1 and Θ_2.

The diffraction curves of 4,6-PU (Fig. 26) show that with a temperature rise the intensity of van der Waals bonds is lowered and their characteristic peak practically disappears at the melting point of polymer. The intensity of hydrogen bonds practically does not change up to melting point.

This phenomenon very visually reflect/represents the character of the curves of the dependence of the integral and partial degrees of crystallinity of 4,6-PU on temperature (Fig. 27), calculated by formulas (IV.1; IV,2 and IV,3).

Thus, is observed different temperature dependence of the intensity of interference (200), that corresponds to Van der Waals bonds. This dependence testifies to the strength of "flat/plane grids" and about the fact that crystal structure, caused by hydrogen bonds, remains unchanged up to melting point.

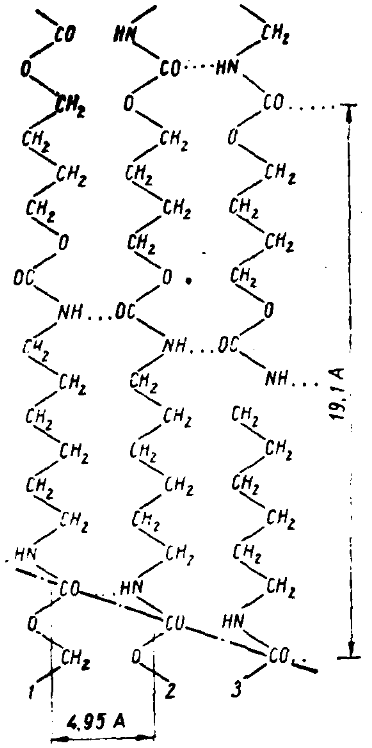

Fig. 25. Structure of the "flat/plane grid" of 4,6-polyurethane.

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Simultaneously with the decomposition of "flat/plane grids" occurs the spontaneous decomposition of interplanar van der Waals bonds; however, a gradual reduction in their intensity with a temperature rise is observed already considerably lower than the melting point (~0°C).

The diffraction curves of the exposed/persistent at different temperatures hardened/tempered specimen/samples of 4,6-PU (Fig. 28) show not the identical temperature dependence of hydrogen and van der Waals bonds in the course of its crystallization from highly elastic state. The integral and partial crystallinity, which are characterized by Van der Waals bonds, in the range of temperatures of 0-100°C coincide (Fig. 29). Higher than 100°C integral crystallinity sharply grows on because of an increase in the partial crystallinity, caused by the emergence of hydrogen bonds. However, splitting of the maximum of the diffraction curve (see Fig. 28) is observed at lower temperatures, which is especially clearly evident from the curves, given for 4,6-PU [14]. This phenomenon indicates the emergence of three-dimensional crystalline formations already at the lower temperatures (see Fig. 29).

At the same time crystallization of 4,6-PU from highly elastic state bears in stages character. To temperature of 100°C, macromolecules are stacked in essence into two-dimensional pseudocrystalline structure and only higher than this temperature is formed modern crystal structure with intermolecular hydrogen bonds.

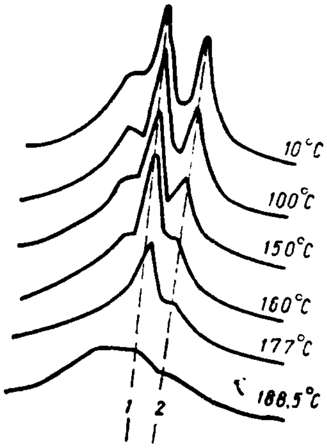

Fig. 26. The diffraction curves of the thermalization/heat-treated at high temperatures specimen/sample of 4,6-polyurethane: 1 - N-bond; 2 - van der Waals bonds.

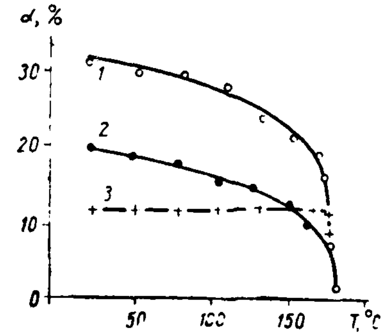

Fig. 27. Temperature effect on degree of crystallinity of 4,6-polyurethane: 1 - integral; 2 - partial according to van der Waals bonds; 3 - partial on N-bond.

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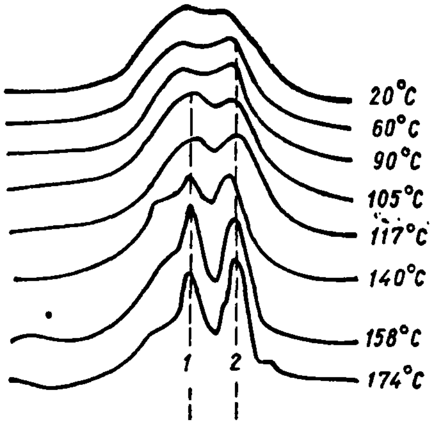

Fig. 28. Diffraction curves of thermalization/heat-treated at different temperatures hardened/tempered specimen/sample of 4,6-polyurethane: 1 - N-bond; 2 - van der Waals bonds.

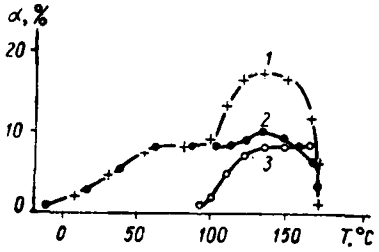

Fig. 29. Temperature effect on degree of crystallinity of hardened/tempered 4,6-polyurethane: 1 - integral; 2 - partial according to van der Waals bonds; 3 - partial on N-bond.

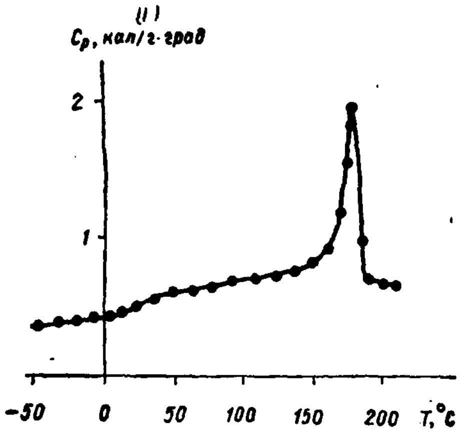

Fig. 30. Temperature dependence C_p for 4,6-polyurethane.

Key: (1). cal/g•deg.

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The influence of thermal effect on structural transformations in 4,6-PU is investigated [39, 43] by the method of differential-thermal analysis (DTA) and of differential micro-calorimetry [19].

Figure 30 gives temperature dependence C_p for a crystalline (annealed) specimen/sample of 4,6-PU in the range of temperatures from -50 to 200°C. Is below given C_p (cal/g•deg) in the investigated temperature interval:

(1) от −50 (2) до −10°C $C_p = 0{,}422 + 1{,}5 \cdot 10^{-3}\,T$
от 45 до 120°C $C_p = 0{,}495 + 1{,}85 \cdot 10^{-3}\,T$
от 195 до 210°C $C_p = 0{,}665$

Key: (1). from. (2). to.

In the range of temperatures of 10-40 °C in the curve of heat capacity (Fig. 31) is observed the lift, caused by the emergence of the segmental mobility of macromolecules, the caused by transition amorphous parts of the polymer from glassy into highly elastic state. Higher than 120°C increase in the heat capacity significantly is accelerated and temperature course C_p describes the peak, which corresponds to melting the crystalline formations the melting point of which 183°C.

Calculated according to the data of the micro-calorimetry of heat of fusion of 4,6-PU (without the account to the degree of crystallinity) is equal to 20.7 cal/g. The heat of fusion, determined by method of DTA for a specimen/sample of 4,6-PU with lower melting point (173°C), render/showed 22.3 cal/g. This divergence/disagreement can be explained by the greater crystallinity of the last/latter specimen/samples of the polyurethane, which possesses smaller molecular weight, and also greater error for the quantitative definitions, conducted by method of DTA.

Heat of crystallization of fusion/melt of 4,6-PU (per data of DTA) at rate of cooling of 4°C per minute is 19.8 cal/g.

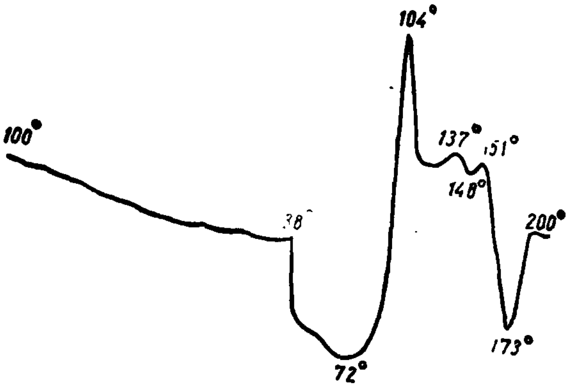

Fig. 31. Thermogram of heating amorphous 4,6-polyurethane.

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The thermal behavior amorphous specimen/sample of 4,6-PU, obtained by the quenching of small quantities (0.05d) of fusion/melt by liquid nitrogen, can be judged also from thermogram (Fig. 31).

At temperature of 38°C in differential curve, is revealed the jump to the side of endothermal effects, which testifies to a sharp increase of the heat capacity of polymer as a result of the appearance of a segmental mobility of polymer chains (devitrification). Further increase in the temperature adds optimal for crystallization mobility, and they are crystallized, to which testifies the presence in the curve of sharp exothermic peak with apex/vertex with 104°C. Melting formed crystal structure is characterized in essence by the subsequent endothermal peak with apex/vertex with 173°C. The which precedes it small endothermal peak with apex/vertex with 148°C also characterizes of melting, but less modern crystalline formations whose emergence is caused by the rigorous conditions for crystallization. This phenomenon indicates both the commensurability of the areas of the exothermic peak of crystallization from such both or endothermal peaks of melting and coincidence of the temperatures of the beginning of small peak (137°C) with the temperature of the beginning of melting the initial crystalline specimen/sample, which has the same character as the peak (see Fig. 30) [39]. Consequently, the data of micro-calorimetry and DTA are in good agreement with the data of X-ray analysis. So, for a crystalline specimen/sample of 4,6-PU in region of 130-160°C heat capacity initially relatively slowly, and then sharply it is raised (see Fig. 30). This behavior is explained by the anisotropic character of crystal lattice for which the first region of increase C_p corresponds to the gradual disappearance of van der Waals bonds, and the second - to relatively rapid decomposition of the hydrogen bonds, which unite macromolecules into "flat/plane grids".

Fig. 31 also shows well the mechanism of crystallization of 4,6-PU from highly elastic state. The sharp exothermic maximum of higher than 100°C reflect/represents the formation of modern crystal structure with intermolecular hydrogen bonds. The beginning of maximum characterizes the emergence of the pseudocrystalline structures whose part does not manage to be organized in three-dimensional structure and subsequent melting of which it is record/fixed with endothermal peak with 148°C.

However, all thermograms of heating indicate the higher temperatures of vitrification of 4,6-PU, than this escape/ensues from X-ray data, in particular from Fig. 29.

Kinetics of the crystallization of 4,6-polyurethane. Essential interest are of data on kinetics of the isothermal crystallization of 4,6-PU, which make it possible to draw conclusions both about the temperature dependence of the crystallization rate and about the character of structurization in polymer.

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Kinetics of the crystallization of many homopolymers is completely satisfactorily described by equation of Abrami [88]

$$\alpha = 1 - e^{-K_v t^n}, \qquad (IV,4)$$

where α - a share of the substance, which was subjected to phase transformation for time t; n - constant, which characterizes for this substance the type of nuclei forming and the type of the growing structures, is taken value from 1 to 4; K_0 - rate constant.

Kinetics of the isothermal crystallization of 4,6-PU from fusion/melt was studied by the method of veighing the "weights of density" [300] and differential micro-calorimetry [21]. The procedure of the micro-calorimetric studies of kinetics of the crystallization of polymers is described in [17, 18]. Figure 32 in semilogarithmic coordinates depicts the isotherms of crystallization of of 4,6-PU, the constructed according to data micro-calorimetry.

However in order to judge kinetics and type of the growing structures, one should determine K_0 and n. The latter are determined via the presentation/concept of experimental results in the proposed by Abrami coordinates

$$\lg[-\lg(1-\alpha)] - \lg t.$$

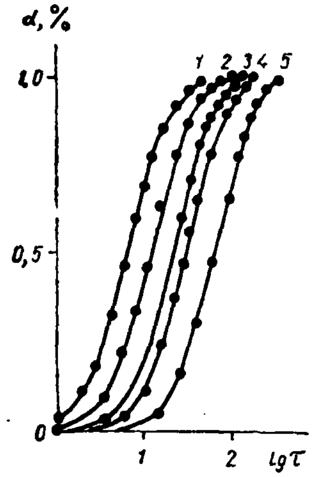

Fig. 32. The dependence of the degree of the perfection of the thermal effect of the crystallization of 4,6-polyurethane on the logarithm of the time of crystallization at temperatures (°C): 1 - 162; 2 - 163; 3 - 165; 4 - 167; 5 - 169.

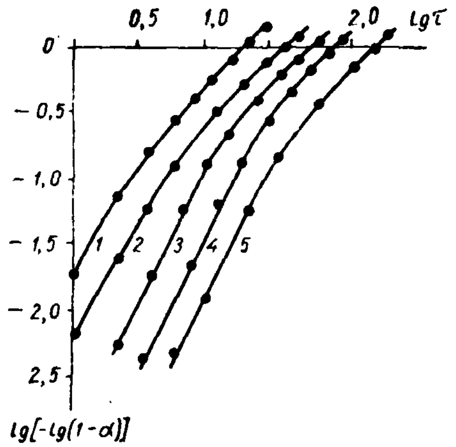

Fig. 33. Isotherms of crystallization of 4,6-polyurethane in

coordinates of Abrami at temperatures (°C): 1 - 162; 2 - 163; 3 - 165; 4 - 167; 5 - 169.

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After the dual logarithmic operation of equation (IV, 4) we have

$$\lg[-\lg(1-\alpha)] = \lg 0{,}434K_0 + n\lg t.$$

On slope/inclination toward the axis of abscissas by the obtained in the coordinates indicated straight line is easy to determine value n, while according to cutting off intercept/detached by it on the axis of ordinates - value K_0.

Kinetics of crystallization 4.6-PU is described by equation (IV, 4) only in range of values α not higher than 0.25, after which are observed systematic deviations from theories. Really/actually, the observed degrees of transformation are less than theoretical (Fig. 33).

Values n, determined on the basis of the straight [88] corresponds to the formation either of flat/plane structural cell/elements on heterogenic embryos or linear structures on homogeneous embryos (Table 19).

On the bases of the contemporary concepts about lamellar character of crystallites in polymers and possibility of existence in fusion/melt 4.6-PU of heterogenic formations (the individual sections of the piles of macromolecules) it is possible to assume that value n=2 answers the course crystallization with the formation of lamellar crystallites. This will agree well with electron-microscope [206] and X-ray ones to investigations [245], from which it follows that crystallites in 4,6-polyurethane really/actually flat/plane.

As a result of the investigation of kinetics of crystallization 4.6-PU with the aid of weighing, the authors [300] come to the conclusion that n=2.3 which contradicts other data [21].

Polyurethane on the basis of hexamethylene diisocyanate and ethylene-, diethylene- and triethylene glycols.

As a result of their fiber-forming properties are of interest and linear aliphatic polyurethane on the basis of ethylene glycols.

Table 19. Characteristics of crystallization for 4,6-polyurethane.

$T_{кр}$, °C	$\Delta T = T^{\circ 1}_{пл} - T_{кр}$	lg K_0	n	(1) $\tau_{0,5}$, мин
162	21	−1,51	1,95	6,0
163	20	−1,99	1,88	10,5
165	18	−2,60	2,00	18,5
167	16	−3,10	2,06	27,5
169	14	−3,61	2,08	59,0

Key: (1). min.

FOOTNOTE [1]. Melting point 4.6-PU of 183°C.

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So, X-ray diffraction analysis investigated of melting and crystallization it is polyurethane on the basis of hexamethylene diisocyanate and ethylene-, diethylene-, triethylene glycols [14].

The authors [14] come to the conclusion that changes in nature and structure of glycol do not change the character of melting and crystallization it is polyurethane on their basis, i.e., in these polyurethane as in 4.6-PU, of melting and crystallization two-stage. Are different only temperature intervals of these processes which depend on nature and length of the composing polyurethane units. However, in [14] the data on the character of crystal structure of separate forms it is polyurethane they are not given; by analogy with 4.6-PU they ascribed anorthic lattice.

These authors in [15] note that depending on crystallization conditions polyurethane on the basis of ethylene- and diethylene glycol are capable of forming different crystalline modifications. on the characteristic features of crystallization and melting, it is polyurethane on the basis of diethylene- and of triethylene glycols testify the data of differential-thermal analysis [43, 45] and of micro-calorimetry [19, 20].

In contrast to 4.6-PU for is polyurethane on the basis of diethylene- (PUDEG) and of triethylene glycols (PUTEG) in the region of melting is observed the complex course C_p, which is evinced by the presence of two maximums (Fig. 34). This form to curve C_p in the region of melting indicates the course of two successive processes to each of which corresponds the specific thermal effect. In the case of PUDEG these thermal effects divided could not be, and in sum they were equal to 19.8 cal/g. The sum of the thermal effects of melting PUTEG 15.3 cal/g from which 12.8 cal/g answer the first, and 2.5 cal/g - to the second thermal effect.

Heat were calculated according to the data of the heat capacity which for the crystalline annealed specimen/samples varied within the limits:

(1) Для ПУДЭГ
(2) от −50 (3) до −5° C $C_p = 0{,}422 + 1{,}5 \cdot 10^{-3}\,T;$
(2) от 50 (3) до 100° C $C_p = 0{,}512 + 1{,}5 \cdot 10^{-3}\,T;$
(2) от 140 (3) до 160° C $C_p = 0{,}623;$
(4) Для ПУТЭГ
(2) от −50 (3) до −20° C $C_p = 0{,}422 + 1{,}5 \cdot 10^{-3}\,T;$
(2) от 0 (3) до 60° C $C_p = 0{,}308 + 2 \cdot 10^{-3}\,T;$
(2) от 120 (3) до 135° C $C_p = 0{,}631.$

Key: (1). For PUDEG. (2). from. (3). to. (4). For PUTEG.

It should be noted that on the curved temperature dependence of the heat capacity of the annealed specimen/sample of PUDEG in the temperature range of vitrification are visible two distinctly expressed lifts: the first in the range of temperatures from -5 to +10°, by the second from 30 to 45°C. For PUTEG is observed only one lift in region from -15 to -10°C.

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The curve of the temperature dependence of the heat capacity of the hardened/tempered (amorphous) specimen/sample of PUDEG (Fig. 34, curves 2) shows that in range from -50 to -5°C temperature course C_p analogous such of crystalline (annealed) specimen/sample. In range from -5 to 10°C, the heat capacity sharply grow/increases, which is caused by the transition of specimen/sample from glassy state to highly elastic. After 20°C is observed the sharp decrease of heat capacity. This is bonded with the crystallization of the sections of macromolecules, sufficiently pliable ones for the course of this process. On completion of the process of crystallization C_p becomes somewhat less than for the same temperatures in crystalline specimen/sample, after 85°C again it begins to decrease, passing through the minimum at temperature of 103°C.

On the basis of the shape of the curve of heat capacity, is made the assumption that in temperature interval of 50-100°C proceeds the slow crystallization process, which after 85°C becomes completely noticeable. Higher than 110°C formed in the course of heating crystal structure begins to be decomposed; in this case, as in the case of crystalline specimen/sample, melting occur/flow/lasts in two stages.

Very essential is the equality of the values of heat capacity in fusion/melt and highly elastic state, which testifies to the uniformity of the character of intermolecular interaction in these two states.

Given data of distances to the authors [19] basis/base for

following conclusions in the ratio/relation to to crystallization and melting PUDEG.

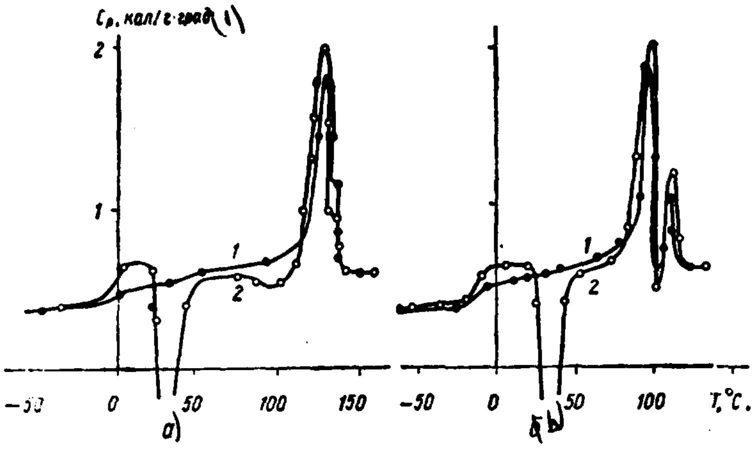

Fig. 34. Temperature dependence C_p

for PUDEG (a) and PUTEG (b): 1 - crystalline specimen/sample; 2 - hardened/tempered specimen/sample.

Key: (1). cal/g•deg.

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Is higher than vitrification temperature in the temperature range of 20-45°C crystal structure is formed in essence because of the emergence of hydrogen bonds in planes (emergence of pseudocrystals). Higher than 50°C order in pseudocrystals is increased, and in interval of 85-110°C are crystallized the ether/ester links, which up to this torque/moment acquired sufficient mobility. simultaneously begins the gradual decomposition of crystal lattice. The first peak in fusion curve of Fig. 34 corresponds to the decomposition of bulk of crystals, while by the second is bonded with the decomposition of the crystalline sections, formed by ether/ester links.

The complex character of crystallization and melting can be explained by the tendency of PUDEG toward the formation of polymorphic crystal structure as this assumed in work [43]. However, for final conclusion/derivations are necessary detailed structural investigations.

Are of interest results on the investigation of the effect of the depth of crystallization of PUDEG on the character of a change of heat capacity in the region of vitrification. Specimen/samples with various depth of crystallization are obtained as follows. The fusion/melt PUDEG was hardened, then at temperature of 29°C they crystallized during the specific time under isothermal conditions and again they hardened.

During the analysis the vitrification of the specimen/samples, subjected to dual quenching, besides the temperature dependence of heat capacity (Fig. 35a) are examined the change with temperature and functions C_p/T (Fig. 35b), for which Dol and the coworkers [156] proposed the name encraty and designated through L. Values Q indicate the values of thermal effect (cal/g), fixed before the second quenching.

Table 20 gives the maximum values of a change of encraty in the region of vitrification ΔL, and also T_c, which defined as the temperatures by which encraty accepted the half its maximum value and ΔC_p during vitrification.

From the data of table 20, it is evident that with an increase in the depth of crystallization of PUDEG the temperature of its vitrification somewhat is misaligned into the region of higher values, and the temperature interval of vitrification is expanded. For the annealed specimen/sample (see Table 19) are obtained results separately for the first and second lifts on the temperature dependence of the heat capacity (see Fig. 34). For the completely amorphous specimen/sample, in which Q=0, is calculated the value of a change in the heat capacity during vitrification to 1 mole of links in accordance with [343]. In the case C_p in question with vitrification, it was 0.196 cal/g•deg. Molecular weight of the repeated section of the macromolecule of PUDEG is equal to 274.3. According to [343], this section contains 17 kinetic links, whence $\Delta C_p' = (M/17) \times \Delta C_p' = \overline{M} \cdot \Delta C_p = 16{,}3 \cdot 0{,}196 = 3{,}16$ cal/mole•deg, where M - average molecular weight of kinetic link.

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Calculated value $\Delta C_p'$ will agree well with theoretical (2.97 cal/mole X deg), obtained on the basis of the hole theory of vitrification and with the value of 2.7 cal/mole•deg, found during the analysis of these for a large number monomeric and organic glasses [230, 243].

It should be noted that the shift T_c of PUDEG with an increase of the depth of crystallization into the region of higher temperatures and the expansion of the temperature interval of this process they indicate constant change in the structure of amorphous zones. Together with completely amorphous sections, apparently, appear the mesomorphic regions, which condition the character of transition indicated.

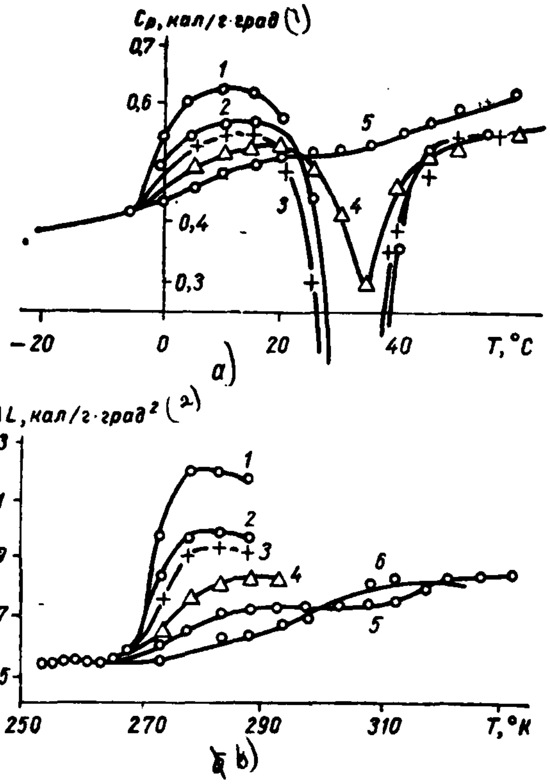

Fig. 35. Temperature dependence C_p (a) and ΔI (b) for specimen/samples PUDEG in the temperature range of vitrification after dual quenching at Q (cal/g): 1 - 0; 2 - 7.6; 3 - 9.5; 4 - 14.35; 5 - 16.3; 6 - 4.6=PU.

Key: (1). cal/g•deg. (2). cal/g•deg^2.

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The fact that in the specimen/sample, to annealed, the first lift in the curve of heat capacity is observed in the same temperature range, as in that harden/tempered, testifies to the presence in it of noncrystalline regions. The second lift in the curve of heat capacity of the annealed specimen/sample in field of 30-45°C is explained by the additional mobility of the individual sections of macromolecules PUDEG. Since in 4.6-PU is observed one lift approximately in this same temperature range, is made assumption about the fact that the two-stage character of the vitrification of PUDEG in a some manner is bonded with the presence in its macromolecules of ether/ester oxygen.

The experimental data, obtained for PUTEG, also indicate the separate crystallization of the diisocyanate and ethyl glycol sections of polymer chains. However, an increase in the length of ethyl glycol unit causes the considerably larger difference between the temperatures of the maximums of peaks in fusion curves and somewhat changes the relationship/ratio of the temperatures of the maximums (see Fig. 34). For PUTEG this relationship/ratio depends on the heat treatment of specimen/sample.

The temperature dependence of heat capacity and encraty in the temperature range of the vitrification of the subjected to dual quenching specimen/samples PUTEG is given in Fig. 36. The basic quantitative data, which characterize the vitrification of PUTEG, are given in Table 21. Calculated value $\Delta C_p'$ comprised for PUTEG of 3.42 cal/mole•deg.

For the specimen/samples PUTEG, obtained from fusion/melt, in contrast to PUDEG on the curved temperature dependence of heat capacity in the temperature range of the vitrification (see Fig. 34) is observed only one lift. This fact did not thus far obtain satisfactory explanation.

Isothermal crystallization from fusion/melt and solution. The isotherms of the crystallization of fusion/melts PUDEG and PUTEG in coordinates Avrami are represented in Fig. 37, 38. The calculated on their basis values $\lg K_0$ and n, are given in tables 22.

Table 20. Characteristics of the vitrification of PUDEG.

(1) Q, кал/г	T_c, °C	(2) $\Delta L \cdot 10^3$, кал/г·град²	(3) ΔC_p, кал/г·град
0	—1	6,6	0.196
7,60	—1	4,6	0.144
9,50	0	4.1	0.131
14.35	2	3,1	0.108
16,30	4	1,9	0.091
	43	1,1	0,054

Key: (1). cal/g. (2). cal/g•deg². (3). cal/g•deg.

Table 21. Characteristics of the vitrification of PUTEG.

(1) Q, кал/г	T_c, °C	(2) $\Delta L \cdot 10^3$, кал/г·град²	(3) ΔC_p, кал/г·град
0	—13	7,3	0,215
6.2	—13	5,8	0,178
10,3	—13	4,9	0.153
15.3	—13	3,15	0,107

Key: (1). cal/g. (2). cal/g•deg². (3). cal/g•deg.

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From the character of isotherms and data of Table 22, it is evident that for both of polymers kinetics of crystallization in entire temperature interval is subordinated to equation of Avrami. In this case, for PUTEG in entire temperature interval, constant n is in effect equal to two, which gives grounds to assume about an increase in the lamellar crystallites during the crystallization of this polyurethane from fusion/melt.

Value n=3 for PUDEG formally indicates an increase in the flat/plane structural cell/elements on homogeneous embryos or volumetric ones on heterogenic ones.

In one of works [242] it was established that polyurethane on the basis of hexamethylene diisocyanate and diethylene glycol reveals the clearly expressed high period of order 70Å. On basis of this, the conclusion is made that crystals in this polyurethane are formed by macromolecules with folding structure. Consequently, it is possible to assume that value n=3 corresponds to the formation of lamellar crystallites by the mechanism of homogeneous nuclei forming. An increase in three-dimensional structures on heterogenic embryos is less probable, on thus far still it is not possible to give simple answer/response to a question, what structure is formed in crystallizing PUDEG.

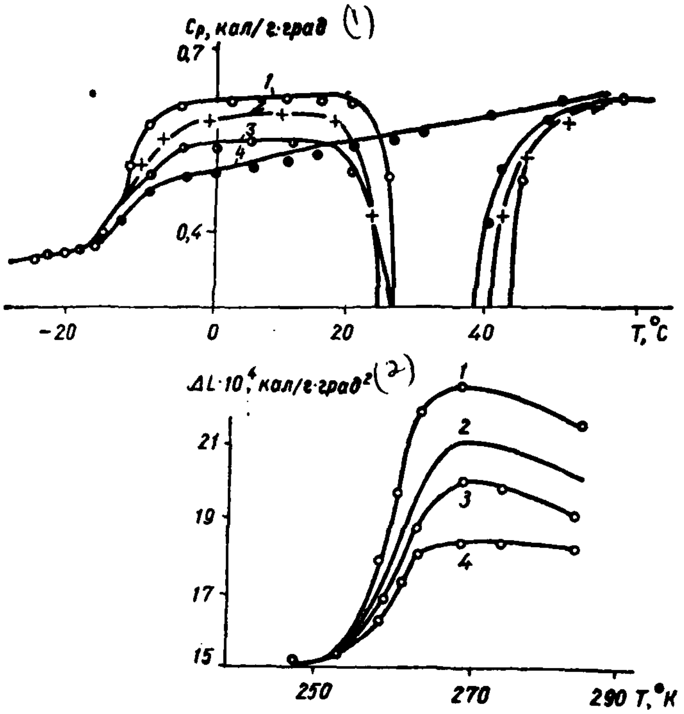

Fig. 36. Temperature dependence C_p and ΔL for specimen/samples PUTEG in the temperature range of vitrification after dual quenching at Q (cal/g): 1 - 0 2 - 6.2; 3 - 10.3; 4 - 15.3.

Key: (1). cal/g•deg. (2). cal/g•deg².

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They were conducted optical-microscopic investigations of spherulitic structure of PUTEG [206]. Were studied the films, obtained by isothermal crystallization from the 1o/o solution of PUTEG in the mixture of dimethyl formamide with acetone, and also from fusion/melt. Spherulitic crystallization from solution was realize/accomplished in the range of temperatures of 80-40°C. It is shown, that in interval of 80-60°C increase the ring spherulites, which have the single rings of extinction, moreover the sign of the double refraction (DL) of ring is positive. At temperature of 55°C, increase the ring spherulites, which have the dual rings of extinction and alternating/variable sign DL along the radius of the spherulite: wide bright ring has positive sign, and narrow bright ring - negative (Fig. 39a, cm gluing-in). With a temperature decrease of crystallization to 50°C, sharply is changed the picture of spherulitic crystallization - they appear the mixed spherulites. At $T_{кр}$~50°C increase predominantly the spherulites with ring center and radial periphery (Fig. 36.b), while at $T_{кр}$ ~40°C - the mixed spherulites whose center takes the spherulite-like form, and periphery radial (Fig. 39c). At this same temperature increase the virtually completely radial spherulites, in which fairly often is observed the vividly glowing center (Fig. 39d). Sign DL of radial spherulite negative, and center is predominantly positive.

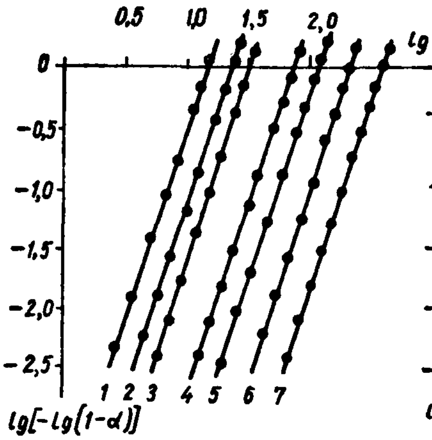

Fig. 37.

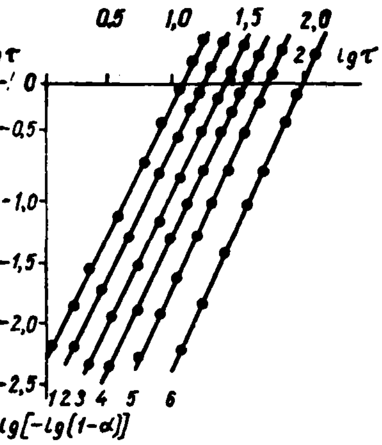

Fig. 38.

Fig. 37. Isotherms of the crystallization of PUDEG from fusion/melt in coordinates of Avrami. 1 - 95; 2 - 98; 3 - 100; 4 - 103.5; 5 - 105; 6 - 107.7; 7 - 109°C.

Fig. 38. Isotherms of crystallization of PUTEG from fusion/melt in coordinates of Avrami: 1 - 69; 2 - 72; 3 - 75; 4 - 78; 5 - 81; 6 - 85°C.

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Isothermal crystallization from fusion/melt was conducted in the range of temperatures from 99 to 75°C. It is reveal/detected that in temperature range from 99 to 93°C increase the spherulites, which do not have the cross of extinction (Fig. 40a, see insert). In the cell/elements, directed along the radius of spherulite, positive or negative sign DL almost all its over length. The regular arrangement of radial structural cell/elements is not observed.

Abrupt changes in morphology of spherulites occur during further temperature decrease of the crystallization in all on several degrees. In this case, occur the following two phenomena: first, the structural elements of spherulites seemingly begin to be collected into "sheaves"; in the second place, DL of spherulites it becomes predominantly positive. Most clearly this is developed at $T_{кр} \sim 90°C$ (Fig. 40b).

A temperature decrease of crystallization to 89°C leads to engendering of the rings of extinction and appearance of a cross. More regularly the rings of extinction in spherulites are observed at crystallization temperatures from 85 to 80°C. The cross of extinction in these spherulites has zigzag form (Fig. 40c). At 75°C rings of extinction, apparently, are so narrow that they are not permitted in optical microscope, but the cross of extinction becomes straight line. According to their appearance these spherulites (Fig. 40d) are similar to radial ones, obtained by crystallization from solution, but in contrast to the latter they have positive sign DL.

Table 22. Characteristics of the crystallization of PUDEG and PUTEG from fusion/melt.

$T_{кр}$, °C	$\Delta T = T_{пл}^{\circ}$[1] $- T_{кр}$	lg K_0	n	$\tau_{0,5}$, мин (1)
ПУДЭГ				
95	38	—3,24	3,02	10.5
98	35	—3,82	3,00	16,0
100	33	—4,17	2,97	23,0
103,5	29,5	—5,20	2,95	51,0
105	28	—5,90	3,00	81,0
107	26	—6,73	3,02	148,0
109	24	—7,54	3,00	288,0
ПУТЭГ				
69	44	—1,86	2,02	7.0
72	41	—2,13	1,97	10,5
75	38	—2,51	2,00	15,5
78	35	—2,84	2,00	22,5
81	32	—3,33	2,04	36,0
85	28	—3,79	1,99	71,0

Key: (1). min.

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[1] FOOTNOTE ¹. Melting point of PUDEG 133, of PUTEG of 113°C.

Page 80a.

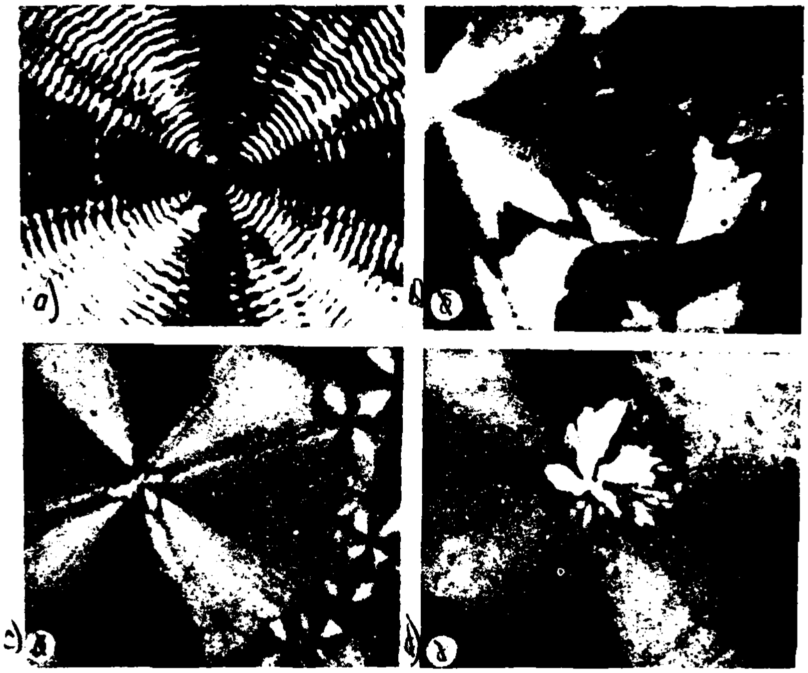

Fig. 39. Supermolecular structures in thin gauge sheets of PUTEG, obtained from solution at crystallization temperature: a) 55; b) ~~50,~~ 40
c
d) 50°C (x750).

Page 80b.

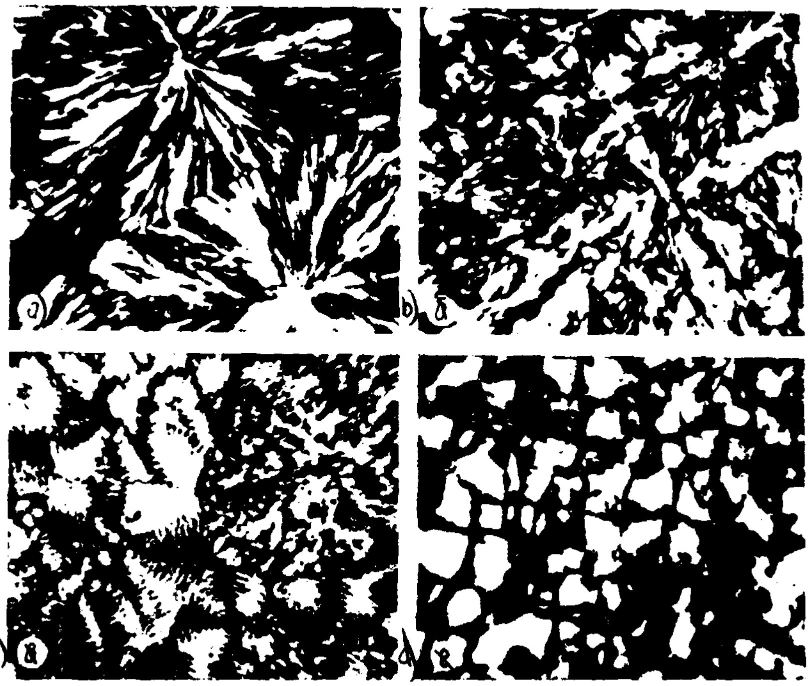

Fig. 40. Supermolecular structures in thin gauge sheets of PUTEG, obtained from fusion/melt at crystallization temperature: a) 93; b) 90; c) 89-80; d) 75°C (x280).

Page 80c.

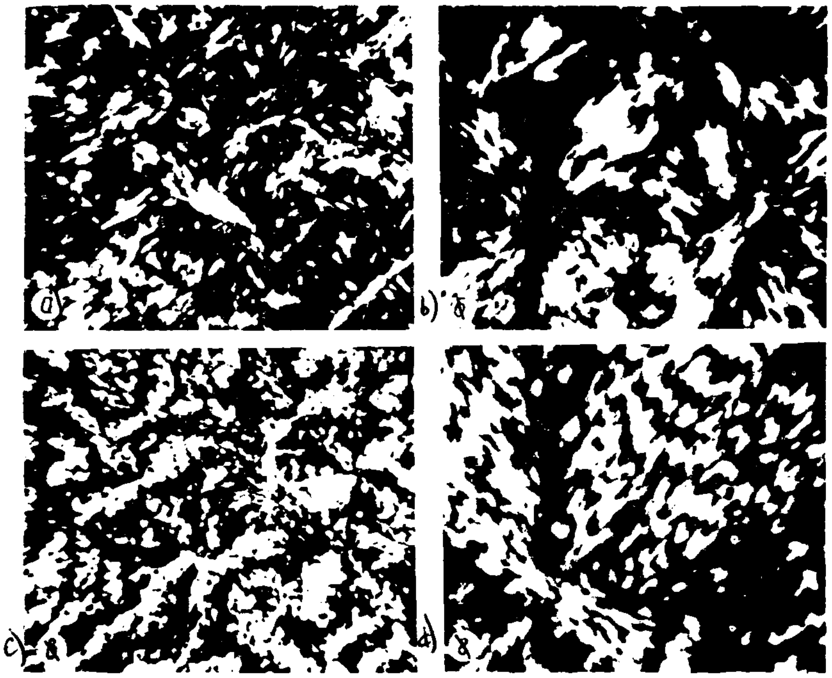

Fig. 41. Supermolecular structures in thin gauge sheets of PUTEG, obtained at temperature of crystallization of 89°C in dependence on the thickness of film: a) 10; b) 20; c) 30(x280); d) 30 μ; (x750).

Page 80d.

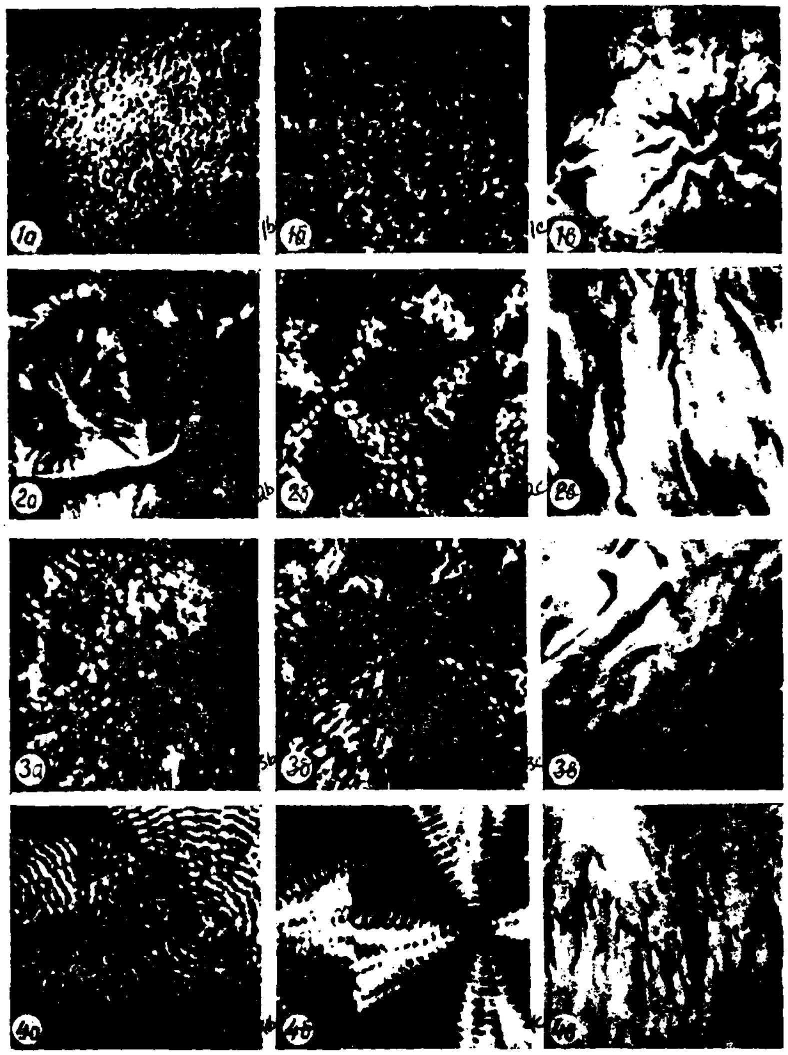

Fig. 53. Structure of spherulites OEA. a) in reflected light (x200); b) the same section in the passing polarized light; c) electron microphotography of replicas (1-3 - x30000, 4 - x20000): 1 - fine-crystalline structure; 2 - radial spherulites; 3 - acicular

spherulites; 4 - annular spherulites.

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Together with that presented work [206] gives the results of the investigations of the effect of the thickness of films (10; 20 and 30 μ) on the generating supermolecular structure at temperature of 89°C, by which increase ring spherulites.

With the thickness of film 10 μ, are observed in essence the "sheaves", which have positive sign DL (Fig. 41a, cm gluing-in). "sheaves" are oriented by ratio/relation to each other in essence at angle 90°. For the treatment of this phenomenon they are necessary additional electron-microscopic examinations.

With an increase in the thickness of film to 20 μ "sheaves" begin to form spherulites, moreover in some of them is developed the sufficiently developed cross of extinction (41b). In separate "sheaves" begins the irregular torsion of fibrils. Sign DL remains previous.

Basic changes in the structure of spherulite occur in the films with a thickness of 30 μ. As can be seen from Fig. 41c, d ring spherulite consists as of several "sheaves", moreover in the center of spherulite one of the "sheaves" is located above others.

Thus, the structure of ring spherulite depends on the thickness of film. The last/latter series of photographs allowed the authors [206] to assume that the "sheaf" is the laminated flaky pseudocrystal, which possesses the properties of unitary single crystal.

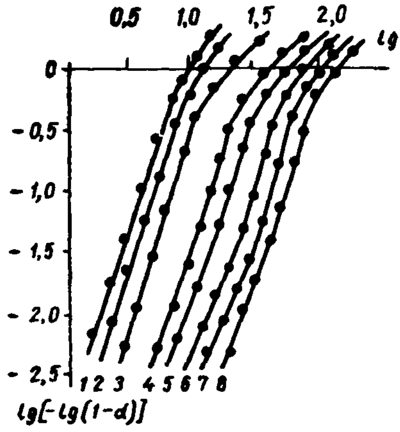

Fig 42.

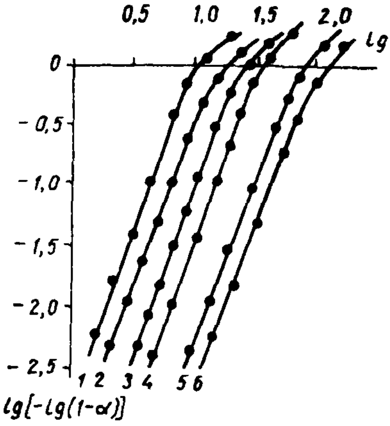

Fig 43.

Fig. 42. The isotherms of crystallization from the highly elastic state of PUDEG in coordinates of Avrami: 1 - 28.2; 2 - 27.2; 3 - 25.6; 4 - 22.3; 5 - 20.3; 6 - 17.8; 7 - 16.2; 8 - 14.2°C.

Fig. 43. Isotherms of crystallization from highly elastic state of PUTEG in coordinates of Avrami: 1 - 26; 2 - 24.5; 3 - 22; 4 - 19; 5 - 16.1; 6 - 13.6°C.

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It is obvious, analogous "sheaves" compose "spherulite-like" centers of the radial spherulites, having grown from the solution (see Fig. 39), and positive on sign DL the radial cell/elements of the spherulites, obtained from fusion/melt in the temperature range of 94-93°C (Fig. 40). Negative on sign DL the radial elements of the structure of these spherulites are the same "sheaves", but oriented so that the plane of hydrogen bonds is approximately parallel to the plane of specimen/sample. With a temperature decrease of crystallization, predominate the structures, positive on sign DL, and, finally under specific conditions appear more or less correct ring spherulites with the zigzag cross of extinction. The results of calorimetric and optical-microscopic investigations are in good accord, and it is possible with confidence to speak that during the crystallization of PUTEG from fusion/melt occurs an increase in the lamellar crystallites.

Isothermal crystallization from highly elastic state. The accord of theory with experiment in the case of the isothermal crystallization of PUDEG and PUTEG of the highly elastic state is considerably worse than for crystallization from fusion/melt (table 23).

So for PUDEG crystallization occur/flow/lasts into three stages (Fig. 42). In the initial sections of isotherm, they are described by equation of Avrami with the fraction values (in range from two to three) of constant n.

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STRUCTURE AND PROPERTIES OF POLURETHANES. PART 1,(U)
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Table 23. Characteristics of the crystallization of PUDEG and PUTEG from highly elastic state.

[1] $T_{кр}$, °C	$\Delta T = (T_{кр} - T_c^*)$	lg K_0	n	(1) $\tau_{0,5}$, мин
		ПУДЭГ		
28.2	24,2	—2,40	2,82	5,5
27.2	23,2	—2.72	2,80	7.2
25.6	21,6	—3,20	2,86	10
22.3	18,3	—33,79	2,44	22
20,3	16,3	—4,00	2,38	32,4
17,8	13,8	—4,32	2,31	50
16.2	12.2	—4.77	2,36	66
14.2	10.2	—5,07	2,38	93
		ПУТЭГ		
26.0	39	—2.498	2,86	6,5
24,5	37,5	—2,81	2,62	10
22.5	35	—3.48	2,78	16
19.0	32	—4.04	2,78	22
16.0	29,1	—4,61	2.64	49
13,6	26,6	—4,79	2,55	66

Key: (1). min.

FOOTNOTE 1. Temperature of the vitrification of PUDEG-4, of PUTEG of -13°C.

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With α=0.05 occurs the acceleration of crystallization, and after α

it reaches value by 0.7 sets in the retarding/deceleration/delay of the process whose degree depends substantially on temperature. If at the relatively high temperatures, sufficient distant from vitrification temperature, retarding/deceleration/delay not such sharp, then in proportion to a temperature decrease it becomes significant. This bears out the fact that the crystallization in this case occur/flow/lasts much more complexly than this is provided for by theory.

The analogous character of kinetics of the crystallization is observed also for PUTEG (Fig. 43); however, systematic deviation from theory is expressed much weaker, so that the observed mechanism of crystallization to a certain degree is caused by the specific character of the molecular structure of data it is polyurethane, that contain in polymer chain the sections of different flexibility. This concerns first of all the abrupt deceleration of the crystallization rate, which, probably, is bonded with the fact that in the temperature interval indicated are not crystallized the ethyl glycol sections of the chains of investigated it is polyurethane.

Copolyurethanes on the basis of hexamethylene diisocyanate, diethylene- and triethylene glycol.

Copolymers on the basis of hexamethylene diisocyanate, diethylene- and triethylene glycol, i.e., such initial homopolymers of which are PUDEG and PUTEG, were investigated by differential-thermal, thermomechanical and infrared-spectroscopic methods [46].

Thermograms are obtained for the specimen/samples of initial homopolymers and some copolymers (Fig. 44), crystallized from fusion/melt by cooling with a velocity of 1°C per minute.

The thermograms of PUDEG and PUTEG have the same character, as the thermogram of already described homopolymers [19, 20, 43]. In this case for PUDEG, is observed one peak of melting, which precedes the exothermic peak, which characterizes crystallization before the melting. For PUTEG there is no clearly expressed effect of crystallization before the melting; however, is developed the complex character of the melting: on thermogram there is two endothermic peaks in the region of melting polymer.

In the character of the thermograms of copolymers, are developed their special feature/peculiarities, which depend on the relationship/ratio of homopolymers in copolymer. As can be seen from differential curves 2 and 3 (see Fig. 44), introduction to PUDEG to 30 mol. o/o PUTEG it leads to a sharp increase in the exothermic peak of crystallization before melting of copolymer. simultaneously is observed a temperature decrease and areas of the peaks of melting. An increase in the portion/fraction of PUTEG to 40 mol. ones o/o leads to an abrupt change in the character of thermograms and a temperature decrease and area of the basic peak of melting copolymer. Thermogram has the same character as the thermogram initial of PUTEG: the exothermic peak of crystallization before melting is absent; besides the basic peak of melting, are present other, higher-temperature endothermal peaks.

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However, with further increase in the portion/fraction of PUTEG, the high-temperature peaks indicated no longer are developed. In this case, minimum temperature of melting is observed in copolymers from 70 and 80 mol. o/o PUTEG, but in copolymer from 90 mol. o/o PUTEG melting point above approaches in its value a melting point pure/clean of PUTEG.

The sharper presentation/concept of the effect of the composition of copolymers on their melting points can be obtained from Fig. 45. The "phase diagram", given on this figure, resembles diagram with eutectic minimum. Let us note that the "eutectic minimum" in this case has diffusion character. Furthermore, to "eutectic" point with 30 and 90 mol. o/o PUTEG to curve are bends which are absent from similar curves, given in the literature [88].

For the study of the character of crystal lattice in the series/number of copolymers, are removed at room temperature the infrared spectra.

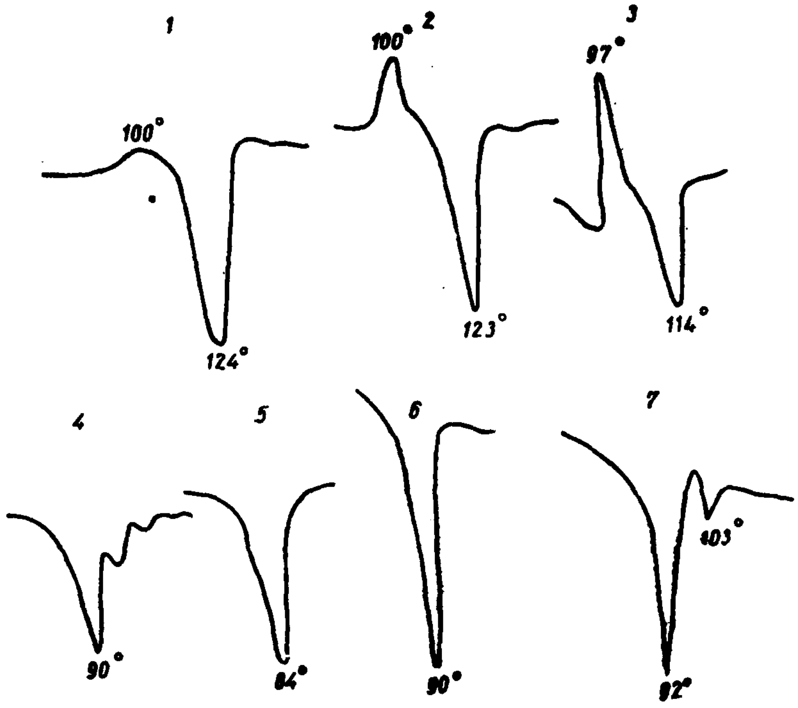

Fig. 44. Thermograms of heating PUDEG (1), PUTEG (7) and their copolymers, which contain 90 (2), 70 (3), 60 (4), 50 (5) and 10 (6) mol. o/o PUDEG.

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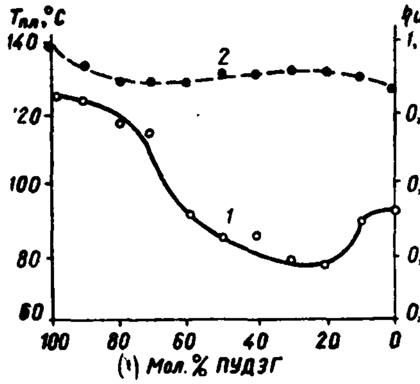
Specimen/samples took in the form of the films, obtained from the solutions was polyurethane in dimethyl formamide at 55-60 and 40-42°C, and also films from fusion/melts.

The comparison of the spectra of fusion/melts and crystalline films PUDEG and PUTEG made possible to ascribe to crystal structures of these was polyurethane the characteristic crystalline strips: for PUTEG strip 860 cm^{-1}, for PUDEG - 830 cm^{-1}.

Is establish/installed, that the strip 830 cm^{-1} is retained in copolymers with a reduction in the content of PUDEG, molar relationship/ratio PUTEG: PUDEG= 0.6:0.4, after which occurs the jump: strip 830 cm^{-1} disappears and appears the strip 860 cm^{-1}, which is retained in the spectra of all remaining copolymers.

On the basis of the dependence of melting point on composition and change of crystal lattice in the series/number of copolymers expressed specific judgment about the character of distribution in the macro-chain of the copolymer of sections with different chemical structure. taking into account, which on the "phase diagram" of the investigated system of copolymers is observed "eutectic minimum", on the one hand of which are crystallized only first type polymeric sections, but on the other hand - only second, and also by the fact that in copolymer with molar relationship/ratio PUTEG:PUDEG=0.6:0.4 is crystallized the second component, is made the assumption about the approach/approximation of the behavior of system in the region of average/mean compositions to the behavior of the random copolymer.



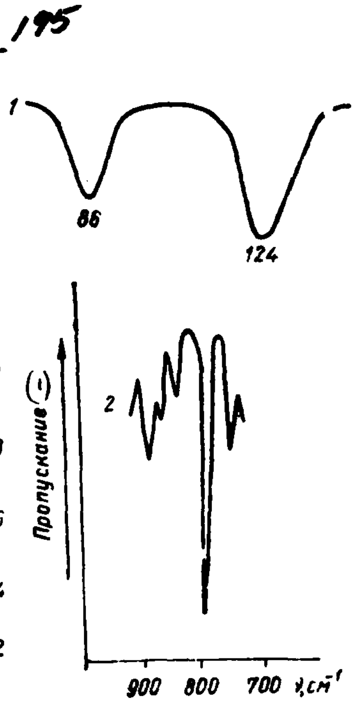


Fig. 45. Dependence of the melting point (1) and of logarithmic viscosity number (2) of the 0,5o/o solution of copolymers in m-cresole on the relationship/ratio in them of glycols.

Key: (1). mole.

Fig. 46. Differential curve of thermogram of heating (1) and section of IR spectrum of passing (2) for physical mixture (0.5:0.5) of PUDEG and PUTEG.

Key: (1). Passing.

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In the similar cases usually "eutectic" point is misaligned to the side of the component, which possesses lower melting point, that also is observed in the system indicated.

The crystallization rate pure/clean of PUDEG is more than PUTEG. Assuming that this is correct for the forming part macro-chains of the copolymer of sections PUDEG and PUTEG, the authors [21] explain the absence of the "crystalline" strips of PUTEG in the copolymer, which contains 0.6 mole fractions of the latter, by steric hindrances for crystallizing the second component, which create the formed crystalline regions of PUDEG.

The obtained copolymers are not related to the block copolymers with long units of both of chemical structures, capable of being crystallized it is at the same time and is independent of each other, that confirm the spectra and the thermograms of the physical mixture of PUDEG and PUTEG (Fig. 46). Thermograms and spectra indicate the presence of two crystal structures and after cocrystallization.

In proportion to approach/approximation to eutectic minimum, crystallization ever more hinders, and as a result of the disturbance/breakdown of the regular distribution of intermolecular hydrogen bonds grow/increases the defectiveness of crystal structure of copolymers. the bends which are observed to curve 1 (see Fig. 45) during removal from central section to edges, they appear, obviously, as a result of changes in the character of the crystalline formations, caused by a change in molecular structure of the chain of copolymer. With low content of one of the components of copolymer, it statistically is distributed on chain in the form of the monomeric sections between the units of the component of another chemical structure. Therefore glycol units exert plasticizing effect with respect to the crystalline regions, formed the second, by the predominant in the composition of copolymer constituent. This is reflected in the melting points of copolymers; however, not to this degree as for copolymers with average/mean composition of both of components where must statistically be distributed the already small units of PUDEG and PUTEG.

Thus, the mentioned bends the authors [46] joined with changes in the character of distribution and the lengths of the composing copolymer sections PUDEG and PUTEG.

Special feature/peculiarities of crystallization and melting aliphatic containing fluorine is polyurethane.

In works [44, 84-86] is given the information about synthesis and special feature/peculiarities of the phase transformations of the series/number of the fluorine-bearing aliphatic ones it is polyurethane.

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In particular, were investigated polyurethane of the following chemical structure:

$$[-HNCH_2(CF_2)_4CH_2NHCOO(CH_2)_6OCO-]_n \quad (\text{ПУ-1}),$$
$$[-HN(CH_2)_6NHCOOCH_2(CF_2)_4CH_2OCO-]_n \quad (\text{ПУ-2}),$$
$$[-HNCH_2(CF_2)_4CH_2NHCOOCH_2(CF_2)_4CH_2OCO-]_n \quad (\text{ПУ-3}),$$

and their also nonfluorinated analog

$$[-HN(CH_2)_6NHCOO(CH_2)_6OCO-]_n \; (6{,}6\text{-ПУ}).$$

In PU-1 fluorine it is contained in diisocyanate, in PU-2 - glycol, while in PU-3 - in both composing polyurethane units. Their nonfluorinated analog is synthesized on the basis of 1,6-hexamethylenediisocyanate and 1.6-hexamethylenediol. Since PU-1 and 6.6-PU are obtained by the method of interfacial polycondensation, and remaining two - by mass polymerization, the latter have smaller molecular weight.

Phase transformations were investigated by the method of the differential-thermal analysis. The character of the thermograms of melting and crystallization 6.6-PU is analogous such for 4.6-PU. Heat of fusion 6.6-PU somewhat lower is 2$\overset{0}{\wedge}$.2 cal/g.

Figure 47 shows thermograms PU -1/ reheating they underwent specimen/samples with different previous history. One was heated immediately after the crystallization of fusion/melt, and the second - after five-day aging at room temperature.

¶ Character of the curves of primary heating and coolings is analogous such for 6.6-PU. However, the curves of reheating differ not only from curved primary heating, but also between themselves. The peak of melting during reheating of the uncontrollable specimen/sample has two sharp apex/vertexes, which is explained by emergence under conditions of crystallizing their fusion/melt of two types of crystal structures with different melting points. Exposed/persistent for a while specimen/sample PU-1 develops tendency toward the acquisition of the properties of the initial specimen/sample.

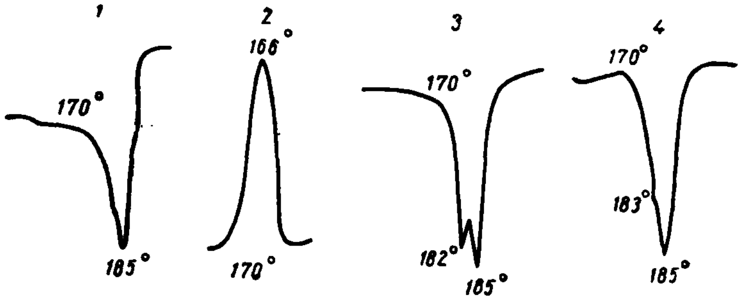

Fig. 47. Thermograms of primary heating (1), of cooling (2) and of reheating (3 - right after crystallization, 4 - after five-day aging at room temperature) of specimen/sample PU-1.

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It is assumed that formed in the course of crystallizing the fusion/melt crystal structure with the melting point of 182°C is metastable at room temperature and changes into stable under these conditions of structures with the melting point of 185°C.

For PU-2 the peak of melting primary heating has two sharp apex/vertexes, and the peak of reheating - only one (Fig. 48). In this case, in the course of reheating, is not reproduced pain low-temperature apex/vertex of peak (112°C). However, the thermogram of heating the exposed/persistent analogously PU-1 specimen/samples has a character of the thermogram of primary heating.

Substantially and that that the peak of melting crystallized made of highly elastic state specimen/sample PU-2 (Fig. 49) also has only one apex/vertex, but in contrast to the specimen/sample, crystallized from fusion/melt, the temperature of its 112°C, i.e., in this case is not reproduced high-temperature apex/vertex (124°C) of the peak of melting initial specimen. A similar phenomenon we observed during the investigation by the method of the differential-thermal analysis of polyurethane on the basis of 1,6-hexamethylenediisocyanate and diethylene glycol [43].

Of the anomalies of the character of melting it is polyurethane, that contain in one of those component fluorine atoms, they testify to the capability of these polymers for the formation of two types of crystal structures. This is confirmed still and by the fact that the specimen/samples of polyurethane, which contain fluorine in both of components (PU-3), as their nonfluorinated analog, they have one melting point.

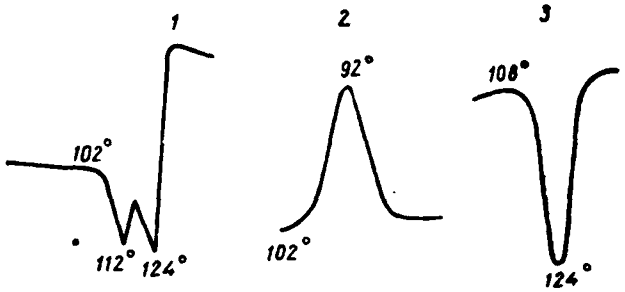

Fig. 48. Thermograms of primary heating (1), of cooling (2) and of reheating (3) of specimen/sample PU-2.

Fig. 49. Thermogram of heating amorphous specimen/sample PU-2.

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It is possible to assume that introduction to macromolecules it is polyurethane fluorine atoms, that is actually the replacement of ethylene links tetrafluoroethylene, conditions the heterogeneity of the geometric structure (transition from zigzag conformation and spiral-shaped) of macro-chains and contributes to the formation of different types of crystal structures. Especially clearly this is developed during the introduction of fluorine to more running glycol block.

LINEAR POLYURETHANE ON THE BASIS OF LOW-MOLECULAR GLYCOLS AND AROMATIC DIISOCYANATES.

In industry widely are used the polyurethane on the basis of toluenediisocyanate (TDI). Usually is used mixture 2.4- and 2,6-isomer TDI in ratio of 80:20 and 65:35. With such ratios of isomers TDI polyurethanes on the basis of low-molecular glycols are not crystallized and are amorphous substances.

The investigation of specimen/samples it is polyurethane on the basis of ethylene glycol and TDI with relationship/ratio 2.4- and 2,6-isomer 100:0; 80:20; 65:35; 40:60; 15:85 [15] showed, then specimen/samples was polyurethane, containing in the mixture of more than 50o/o 2,6-isomer, capable of being crystallized. The degree of crystallinity increases with an increase in the content of 2,6-isomer. This phenomenon is explained by the more symmetrical structure of the diisocyanate link of polyurethane on the basis of 2,6-isomer in comparison with 2,4-isomer. 2.6-TDI can be located in polymer chain only in two, and 2.4-TDI - in eight different configurations.

The study crystallization with the aid of electron microscope shows that polyurethane on the basis of 2.4-TDI and ethylene glycol gives amorphous film. An increase in the content of 2.6-TDI in the mixture of isomers leads to the formation of the more regulated structures. So, polyurethane with relationship/ratio 2.4- and 2,6-isomer TDI 80:20 and 65:35 form globules and piles of amorphous structure. Polyurethane on the basis of 2.6-TDI, having molecules of more regular structure, gives as the primary structures of pile with three-dimensional crystalline order. From piles are form/shaped the spherulites and dendrites. It polyurethane on the basis of the mixture of isomers TDI 15:85 and ethylene glycols during the vaporization of dilute solutions gives spherulites, then for polyurethane on the basis of TDI 5:95 and of ethylene glycol ordering goes further and together with spherulites are formed the dendrites, basis of which are the mono-planes of fibrillar structure.

In contrast to hexamethylene diisocyanate polyurethanes on the basis of 2.6-TDI, diethylene- and triethylene glycol, they are not crystallized due to the lower steric regularity of 2.6-TDI.

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This is explained by the possibility of the emergence of the irregular hydrogen bonds between urethane and simple ether/ester groups of glycol components.

In contrast to TDI for diphenylmethane diisocyanate (DFDI) the crystallizing polyurethane are obtained not only on the basis of ethylene-, but also diethylene- and triethylene glycol. However, capability for crystallization is lowered upon transfer from ethylene glycol to triethylene glycol on the same reasons, as in the case of TDI.

During the study of the crystallization of those indicated, it is polyurethane on the basis of ethylene glycol from solutions and fusion/melt establish/installed, that in both cases is formed crystal structure of identical modification. Close structures are formed also during the crystallization of polyurethane on the basis of diethylene glycol. Polyurethane on the basis of triethylene glycol from solution is crystallized well, and from melt gives product with amorphous structure.

The investigations, carried out with the aid of electron and optical microscopy, they showed, that polyurethane on the basis of DFDI and ethylene glycol forms the large spectrum of the morphological structures: spherulites, dendrites, single crystals.

The polyurethane, obtained on the basis of DEG, gives as supermolecular structure spherulites, while polyurethane on basis TEG does not form any sharp morphological forms.

Data according to synthesis and some physicochemical properties it is polyurethane on the basis of ethylene glycol and diphenylmethane-, diphenyl-, ethane-, diphenyl propane- and diphenylbutandiisocyanates they are given in [263].

Polyurethanes on the basis of enumerated diisocyanates form crystalline products, that by the confirmed data of X-ray analysis. Figure 50 depicts the dependence of the intensity of reflexes on diffraction angle for specimen/samples it is polyurethane on the basis of diphenylmethane diisocyanate, that are crystallized with different speed.

However, transition from diisocyanates with odd number of methylene groups between phenyl groups to even is accompanied by a change in the type of crystal structures it is polyurethane. This phenomenon is explained by a change in the conformations of macromolecules it is polyurethane.

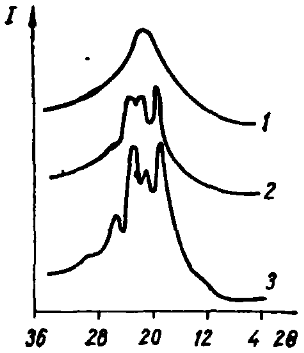

Fig. 50. The dependence of the intensity of reflexes on diffraction angle (2θ) for the specimen/samples of polyurethane on the basis of diphenylethanediisocyanate: 1 - amorphous specimen/sample, obtained by rapid landing; 2 - crystalline specimen/sample, upset from concentrated solution; 3 - crystalline specimen/sample, upset from dilute solution.

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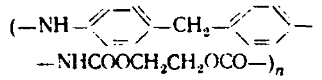
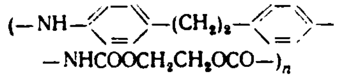
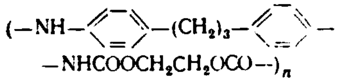
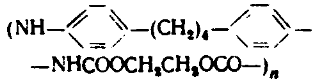
Table 24 gives some properties of those indicated it is polyurethane. Let us note that the value T_c/T_m of ratio/relation does not depend on the chemical structure of macromolecules, but it is determined by the type of crystal structure of polyurethane.

Work [240] given data according to the analysis of crystal structure of polyurethane on the basis of

4,4'-diphenylmethanediisocyanate and tetramethyleneglycol. It is shown, which this polyurethane forms α, β- and γ-crystalline forms. α--form badly/poorly yields to orientation, but with stretching more than to 300o/o it disintegrates. It appears as a result of annealing during removal/taking from the specimen/sample of voltage/stress. Forms β and γ are easily formed, when the molecular chains of polyurethane are oriented. Is assumed that α-type has folding structure, and β-and γ--form - fringed micellar.

Synthesis is polyurethane on the basis of fluorinated and nonfluorinated 1,4-bis-(β-hydroxyethoxy) of -benzene, and also the investigation of some their physicochemical properties they are described in [87]. These polyurethane one should relate to the badly/poorly crystallizing polymers. The melting points and crystallization of those containing fluorine it is polyurethane considerably lower than in their nonfluorinated analogs.

Table 24. Structure and property it is polyurethane on the basis of ethylene glycol and aromatic diisocyanates.

(1) Структура полиуретана	(2) Логарифмическая вязкость ¹	$T_{пл}$, °C	T_c, °C	$T_c/T_{пл}$ ²	Плотность (3) при 30° C, г/см³
 $-NHCOOCH_2CH_2OCO-)_n$	1,01 (4) в ДМФА	239	92,7	0,72	1,3233
 $-NHCOOCH_2CH_2OCO-)_n$	0,70 (4) в H_2SO_4	312	116,9	0,67	1,3055
 $-NHCOOCH_2CH_2OCO-)_n$	0,36 (4) в ДМФА	207	74,1	0,72	—
 $-NHCOOCH_2CH_2OCO-)_n$	0,46 (4) в ДМФА	274	105,7	0,69	—

Key: (1). Structure of polyurethane. (2). Logarithmic viscosity number¹.

FOOTNOTE ¹. Ductility/toughness/viscosity of 0,5o/o solution with 30°C. (3). Density with 30°C of g/cm³. (4). V.

FOOTNOTE ². Value T_c and $T_{пл}$ they are given in °K.

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PROPERTIES OF SOME POLYAMIDE URETHANES.

For explaining the special feature/peculiarities of structure, in comparison with polyamides it was polyurethane to study the structures of polyamide urethanes. Such some polymers on the basis of diethylol amides of the series/number of dibasic acids are described in [155]. Are investigated polyamide urethanes (PAU) of the following structure:

$$[-O(CH_2)_2NHCO(CH_2)_nCONH(CH_2)_2OCONH(CH_2)_6NHCO-]_y,$$

where n - a quantity of methylene groups, which form part initial dibasic acids. In these PAU a quantity of methylene groups between amido groups was predetermined compound/composite of acid on basis of which was synthesized diethylol amide.

PAU, obtained on basis of diethylol amides of oxalic (n=0), succinic (n=2), glutaric (n=3), adipic (n=4), pimelic (n=5), azelaic (n=7), sebacic (n=8) acids, are investigated by the methods of infrared-spectroscopic, X-ray [29] and differential-thermal analyses

[40]. It is establish/installed, that PAU develop the properties, which are inherent in both the polyurethane and in polyamides. In this case, PAU essentially differ in its properties between themselves depending on value of n.

The comparison of the spectra of different PAU shows that the most characteristic changes in them are observed in the region of oscillating the groups, which correspond for the formation of the hydrogen bonds between chains. In the spectra of PAU with odd n, are visible two strips (3260 and 3320 cm^{-1}), but with even n - one (3320 cm^{-1}), in this case, the appearance of an additional strip 3260 cm^{-1} is accompanied by the increase of the intensity of strip 3080 cm^{-1}.

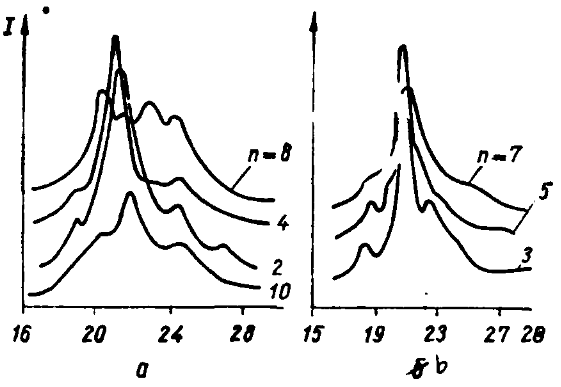

Fig. 51. Intensity curves of scattering X-rays for PAU with even (a) and odd (b) n.

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Based on the example of PAU with n=3 reveal/detected that in specimen/samples (films), obtained by the dissolution of polymer in formic acid with the subsequent removal of the latter, in spectra disappear strips 3260 and 1660 cm^{-1}, and also decreases the intensity of strip 3080 cm^{-1}. However, after prolonged boiling in water and drying, is formed powder PAU whose spectrum takes the initial form. These phenomena gave the foundation for to the authors [29] assuming existence in the series of PAU with odd n of two types of structures and proposing the probable models of unit cells PAU with even and odd n.

Intensity curves of scattering the X-rays of investigated PAU (Fig. 51) testify to the characteristic differences for the structure of separate forms PAU. So, in the X-ray photograph of PAU with n=8 are very clearly visible four maximums. For the present instance it is assumed that in polyurethane section of chain is realized the unit cell of polyurethane, and in the poliamide section of chain, - a structure of polyamides.

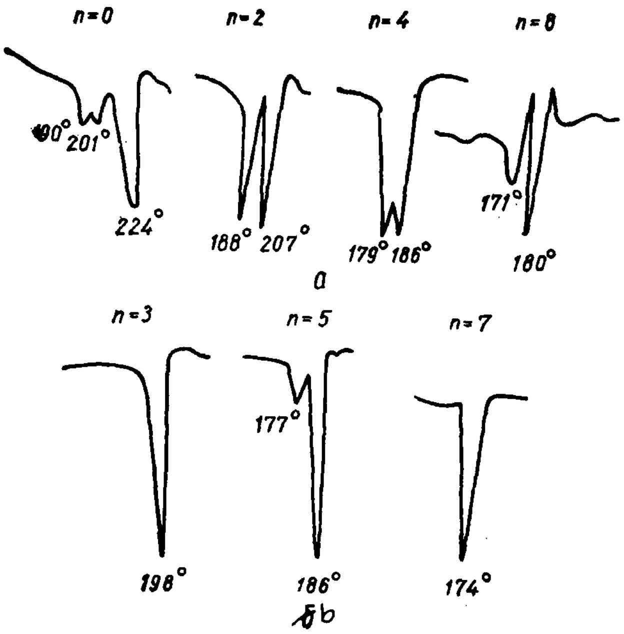

Fig. 52. Thermograms of heating PAU with even (a) and odd (b) n.

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On the basis of the probable model of the unit cell of PAU with odd n, the conclusion is made that the decomposition of strips in the region of the bonded NH- and C=O-oscillation/vibrations is caused by the presence in this form of PAU of the strained hydrogen bond.

In contrast to [29], where actually was studied the structure of initial specimens PAU, in [40] was investigated the effect of thermal effect on structure and structural transformations into PAU (Fig.

52).

In all PAU with even number n, the peaks of melting have complex character and differ for separate PAU. For PAU with odd n only of PAU n=5, has the complex peak of melting. On this basis/base is made the assumption about the capability of PAU for the formation of polymorphic crystal structures, especially for PAU with even n.

PHASE TRANSFORMATIONS AND VITRIFICATION LINEAR AND OF THREE-DIMENSIONAL ONES IS POLYURETHANE WITH OLIGOETHER GLYCOL UNITS.

Capacity it is polyurethane to be crystallized it depends not only on the structure of the composing polyurethane diisocyanate and glycol (ether glycol) units, but also on the length of the latter [4, 15]. So, based on example it is polyurethane with the oligohydroxyethylene units of different molecular weight establish/installed [15], that the capacity to be crystallized passes through the minimum with an increase in the length of oligoether unit.

It is found also, that lattice structure for it is polyurethane with oligoester units in contrast to it is polyurethane with low-molecular glycol units it does not depend on the structure of diisocyanate, but it is determined by structure and nature of oligoether glycol. This is caused by the fact that with an increase in the ether/ester unit grow/increases the probability of the formation of the hydrogen bonds between hydrogen of urethane group and oxygen of the ester group of ether/ester unit, which it is led to defects in crystal structure and increases the share amorphous structure. However, with further increase in the oligoester unit, urethane links begin to play only role of the defective sections which impede crystallization, but they cannot completely interfere it. In this case the crystallization occurs only over oligoether links and the lattice structure of polyurethane becomes sufficient to close to the structure of the lattice oligoether.

In connection with that presented expedient to examine together with the properties of those crystallizing it is polyurethane and the property of components them oligoether glycols.

In practice widely are used the cross-linked polyurethane with such crystallizing oligoether glycol units as oligoethyleneglycoladipate and oligohydroxytetramethyleneglycol (polyfurit). Therefore we primary attention will give to these oligomers, and also to linear and cross-linked polyurethane on their basis.

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Properties of oligoethyleneglycoladipate and synthesized on their basis of linear ones and cross-linked is polyurethane.

Crystallization in oligoethyleneglycoladipate (OEA) with M=2000 is thoroughly studied [134] by the methods of differential-thermal and X-ray diffraction analyses, IR spectroscopy, optical and electron microscopy (Fig. 53, see insert). For the specimen/sample, crystallized at -8°C, is observed fine-crystalline structure (Fig. 53, 1a, b); the spherulitic character of crystalline grains revealed well only during electron-microscope increases (Fig. 53, 1c). In temperature range from 0 to +20°C, are crystallized radial spherulites (Fig. 53, 2a, b), for which electron microscopy reveal/detects lamellar structure (Fig. 53, 2c). Higher than this temperature are formed ring type spherulites (Fig. 53, 4a, b). In turn, before achievement by 40°C spherulites acquire acicular structure (Fig. 53, 3a, b), to which on electron microphotography/microphotograph (Fig. 53, 3c) corresponds the surface with a large number seemingly of projecting from it projections.

According to the data of X-ray diffraction analysis, DTA and IR spectroscopy, it is establish/installed, what OEA can exist in two crystalline modifications - α- and β-types. In the region of temperatures from 0 to +20°C, it is stable β-types, but is higher than 40°C - α-type; in intermediate temperature range coexist both of forms.

Thus, β-type predetermines the formation of radial ones, α-type - acicular, and the mixture of these forms - ring spherulites.

In connection with this is assumed that the peculiar structure of ring spherulites is caused by rhythmic crystallization alternately α- and β-types OEA. However, during heating of the spherulites, molded at low temperatures, in them are observed the polymorphic transformations, fixed/recorded by X-ray and spectrum investigations, but there are no visible changes in the forms of spherulites up to from melting. This testifies to the stability of the supermolecular structures of higher order, what are spherulites, not changing even with the rearrangement of the primary structures, which are determining the character of the arrangement of molecular chains.

Using calorimetric method are studied OEA, and also the linear and cross-linked polyurethane on its basis [109]. The investigations of this systematic series/number made it possible to estimate the effect of such parameters as the flexibility of the chain of oligoether, the denseness of physical and chemical grids, to some bonded with the mobility of macro-chains properties of the cross-linked polyurethane elastomers. Table 25 gives the initial characteristics of the investigated substances. By diisocyanate component with synthesis is polyurethane it served toluene-2,4-diisocyanate.

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Table 25. The characteristics of oligoethyleneadipate it is polyurethane on its basis.

(1) Вещество	(2) Условное обозначение вещества	M	(3) Соотношение сшивателя ДЭГ/Гл
(4) Олигоэтиленгликольадипинат	ОЭА-1000	1000	—
(5) Олигоуретан на ОЭА-1000	ОУ-1000	47 000	—
(5) Олигоуретан на ОЭА-2000	ОУ-2000	44 000	—
(6) Эластомер на ОЭА-1000	ЭЛ-1	3800 *	1:3
(6) Эластомер на ОЭА-1000	ЭЛ-2	54 000 *	1:1
(6) Эластомер на ОЭА-2000	ЭЛ-3	—	1:3
(6) Эластомер на ОЭА-2000	ЭЛ-4	—	1:1

Note. With asterisk corrected value M_c.

Key: (1). Substance. (2). Conventional designations of substance. (3). Relationship/ratio of cross-linking agent DEG/Gl. (4). Oligoethylene glycol adipinate. (5). oligourethane on. (6). Elastomer on.

Table 26. Equation $C_p = f(T)$ for oligoether/ester, oligourethane and cross-linked it is polyurethane.

(1) Полимер	(2) Исходный образец			(3) Закаленный образец		
	(4) Уравнение	(5) Температурный интервал, °C		(4) Уравнение	(5) Температурный интервал, °C	
		(6) от	(7) до		(6) от	(7) до
ЭА-1000	$-0{,}012+1{,}49\cdot10^{-3}T$	—60	20	$-0{,}012+1{,}49\cdot10^{-3}T$	—60	20
	$0{,}462+10^{-4}T$	50	100	$0{,}462+10^{-4}T$	50	100
ЭА-2000	$-0{,}186+2{,}17\cdot10^{-3}T$	—70	20	—	—	—
	$0{,}453+10^{-4}T$	60	100	0,512	60	100
ОУ-1000	$-0.125+1{,}5\cdot10^{-3}T$	—30	20	—	—	
	$0{,}320+10^{-4}T$	45	100	$0.320+10^{-4}T$	—30	100
ОУ-2000	$-0.103+1{,}52\ 10^{-3}T$	—30	20	$0.376+10^{-4}T$	—30	25
	$0.403+10^{4}T$	50	100	$0{,}403+10^{-4}T$	50	100
ЭЛ-3	$0{,}195+10^{-4}T$	—50	—30	$0{,}195+10^{-4}T$	—50	—30
	$-0{,}116+1{,}51\cdot10^{-3}T$	—20	10	—	—	—
	$0{,}325+10^{-4}T$	50	100	$0{,}325+10^{-4}T$	—20	100
ЭЛ-4	$0{,}191+10^{-4}T$	—50	—30	$0{,}191+10^{-4}T$	—50	—35
	$-0{,}117+1{,}5\cdot10^{-3}T$	—20	10	—	—	—
	$0{,}315+10^{-4}T$	50	100	$0{,}315+10^{-4}T$	—20	100
ЭЛ-1	$0{,}190+10^{-4}T$	—50	—20	(8) То же	—20	100
	$0{,}306+10^{-4}T$	0	100	» »	—20	100
ЭЛ-2	$0{,}190+10^{-4}T$	—50	—20	» »	—20	100
	$0{,}310+10^{-4}T$	—5	100	» »	—20	100

Key: (1). Polymer. (2). Initial specimen. (3). Hardened/tempered specimen/sample. (4). Equation. (5). Temperature interval, °C. (6). from. (7). to. (8). The same.

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Relationship/ratio NCO:OH in prepolymers (oligourethane) was equal to 1:1. The cross-linked polyurethane elastomers were obtained through the stage of prepolymer during relationship/ratio NCO:OH=2:1; cross-linking was produced by the mixture of diethylene glycol (DEG) with glycerin (Gl). Common/general/total relationship/ratio

NCO:OH=1:1.

The curves of the temperature dependence of the heat capacity of the specimen/samples of all forms of polymers indicated are given in Fig. 54 and 55. As can be seen from the figures, the curves of heat capacities C_p/T consist of several linear sections, which correspond to the regions of the glassy, highly elastic, crystalline and viscous flow states of polymers, and also sections with anomalous deviations from linearity in the regions of vitrification and phase transitions (Table 26).

The course of the temperature dependence of heat capacity for crystalline (annealed) specimen/samples OEA-1000 and OEA-2000 (Fig. 54) in the wide temperature range, which lies is lower than the temperature of the beginning of phase transformations, it is linear. Beginning with 20°C to curved 1 both oligomers it is observed the lift which for OEA-1000, in passing by through point of inflection with 40°C, changes into the peak of melting with 50°C with $C_p = 1,95$ cal/g•deg. For OEA-2000 this lift is ended by the endothermal peak with 40°C with $C_p = 0,94$ cal/g•deg, after which the value of heat capacity sharply falls to 0.76 with 43°C and again it grow/increases, changing in the second endothermal peak (meltings) at 53°C with $C_p = 1,76$ cal/g•deg. The obtained values of melting point OEA-2000 coincide with value for high-molecular polyethyleneglycoladipinate [221].

At the end melting (60°C) the heat capacity of fusion/melts of both of oligomers barely is changed. The thermal effects of melting the annealed specimen/samples OEA-1000 and OEA-2000 are equal to with respect 18.7 and 17.8 cal/g.

More essential differences in the course of heat capacity are observed for the specimen/samples, subjected to quenching. As can be seen from Fig. 54a, specimen/sample OEA-1000 does not undergo quenching, to which testifies the absence of characteristic curve knee 2 during vitrification and the linear dependence of heat capacity on the temperature in range from -60 to 5°C, which coincides with the same for the annealed specimen/sample. However, at 16°C to curved 2, there is an exothermic peak of crystallization, after which the heat capacity continuously grow/increases, changing into the peak of melting with 45°C with $C_p = 1{,}98$ cal/g·deg, and it decreases to 0.493 with 55°C.

During heating of the hardened/tempered specimen/sample OEA-2000 (Fig. 54b, curve 2) is observed the jump of heat capacity in range from -62 to -54°C, caused by the transition of oligomer of the glassy into viscous flow state, and two exothermic peaks of crystallization at -16 and 20°C, after which the heat capacity continuously grow/increases to 0.46 cal/g•deg with 53°C.

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As in the case of the annealed specimen/samples, heat capacity of the fusion/melts of the hardened/tempered specimen/samples of both oligomers only insignificantly they are increased with temperature. In view of the imposition of the effects indicated it was not the possible to estimate them quantitatively. However, the approximately thermal effect of melting the hardened/tempered specimen/sample OEA-2000 is 1.5 times more than the summary thermal effect of crystallization.

The curves of the temperature dependence of the heat capacity of oligourethane and elastomers are given in Fig. 55. In initial specimens it is polyurethane (curve 1) not reveal/detected vitrification and their heat capacity linearly increases from low temperatures to 20°C.

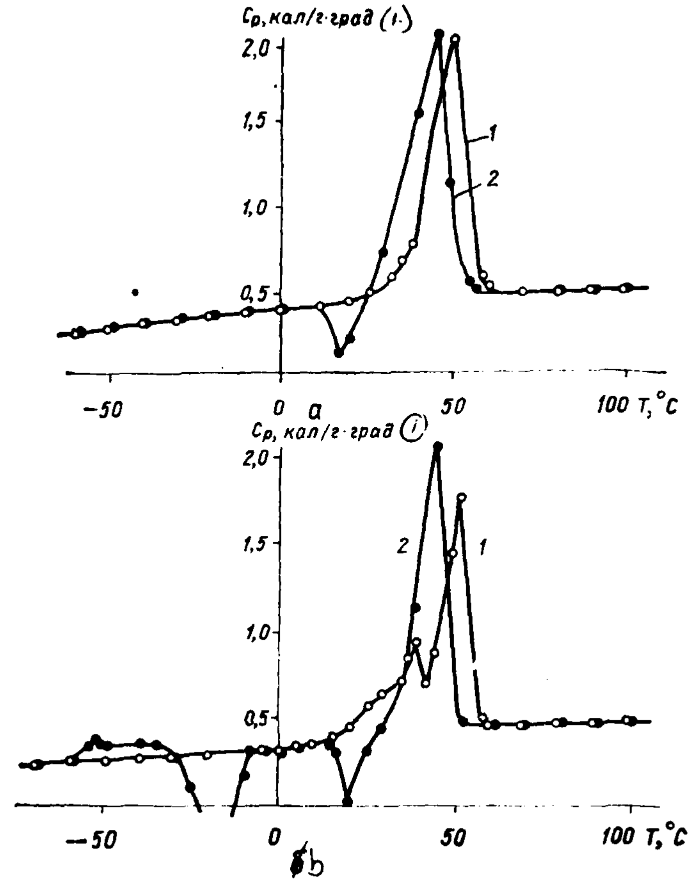

Fig. 54. The heat capacity of oligoethyleneglycoladipinate OEA-1000 (a) and OEA-2000 (b): 1 - annealed specimen/sample; 2 - hardened/tempered specimen/sample.

Key: (1). cal/g•deg.

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Higher than 20°C heat capacities of initial specimens smoothly grow/increase and appear the peaks of melting for OU-1000 with 38°C ($C_p = 1,02$ cal/g•deg) and for OU-2000 at 40°C ($C_p = 1,66$ cal/g•deg). The corresponding thermal effects are 6.9 and 12.8 cal/g. Melting OU-1000 and OU-2000 is ended respectively at 43 and 49°C, after which the heat capacity remains almost constant.

In the hardened/tempered specimen/samples (curve 2) OU-1000 and OU-2000 are observed the jumps of heat capacity at -36 and 46°C respectively, bonded with transition from glassy to highly elastic state. Higher than the temperature of the vitrification of heat capacity of both of hardened/tempered specimen/samples linearly they depend on the temperature (see Table 26) up to 100°C; however, in OU-2000 is observed small maximum with 40°C with $C_p = 0,44$ cal/g•deg. Higher than 50°C the heat capacity of the initial and hardened/tempered specimen/samples coincide.

From Fig. 55c, d it is evident that elastomers EL-3 and EL-4 on basis OEA-2000 are capable of crystallization, to which testify the peaks of melting initial specimens (curves 1). Temperatures and heat of fusion of initial specimens EL-3 and EL-4 are equal to 36°C, 8.95 cal/g and 36°C, 8.20 cal/g respectively. The presence of the small (order 0.02-0.03) jumps of heat capacity in the temperature range of vitrification tells about the incompletness crystallization in these systems.

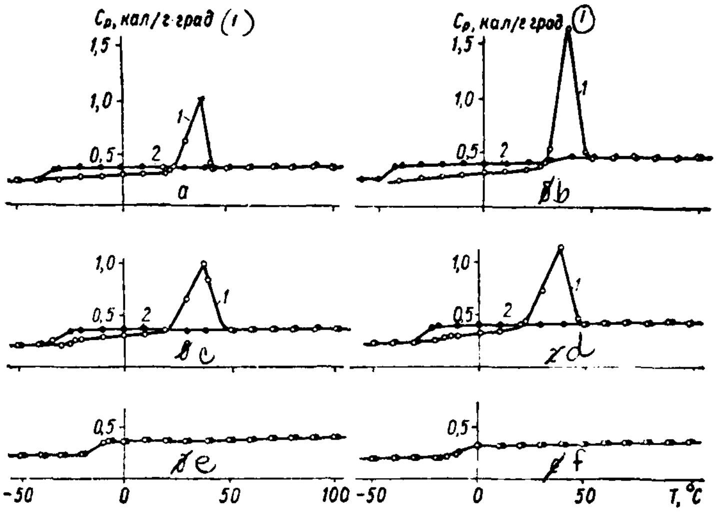

Fig. 55. The heat capacity of oligourethane OU-1000 (a), OU-2000 (b) and cross-linked it is polyurethane EL-4 (c), EL-3 (d), EL-2 (e), EL-1 (f): 1 - initial specimen; 2 - hardened/tempered specimen/sample.

Key: (1). cal/g•deg.

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The curves of the heat capacities of the hardened/tempered specimen/samples consist of linear sections before and after vitrification temperature, which for EL-3 and EL-4 is equal to with respect -27 and -29°C. Elastomers EL-1 and EL-2 are not capable of crystallization (Fig. 55e, f). The curves of the initial and hardened/tempered specimen/samples for these elastomers coincide and consist of the linear sections, divided by intervals of bends, corresponding to the temperatures of vitrification (-7°C for EL-1 and -14°C for EL-2).

All investigated specimen/samples, with exception OEA-1000, underwent quenching, and for them were determined the values of some values, characterizing vitrification (Table 27). In this case as for systems with oligodiethyleneglycol units, upon transfer from oligomer to cross-linked elastomer T_c regularly it is raised.

Since T_c polymers depends on molecular weight, regularity of structure, flexibility of chain, presence and arrangement of functional groups, the network density of chemical cross-linkings etcetera, increase T_c in linear oligourethane it is caused either greater in comparison with initial oligoether by the rigidity of chains determined thermodynamic flexibility or the presence in the last/latter polar urethane groups, which affect the kinetic flexibility (mobility) of chains. For systems with oligodiethyleneglycol units, is already shown the indisputable effect of the second factor.

In this case the comparison of the thermodynamic flexibility of oligoether/ester and oligourethane is carried out on the basis of the equivalency of form and size/dimensions of macromolecules in θ-solvent and disordered state. As the measure of thermodynamic flexibility, is selected parameter K_θ from the equation of Kun-Mark-Khuvink for the ductility/toughness/viscosity of polymers in θ-solvents, since K_θ depends only on structure and conformation of macromolecule.

Table 27. Characteristics the vitrification of systems on the basis of oligoethyleneglycoladipate.

(1) Вещество	(2) ΔC_p, кал/г × град	ΔT_c^*, °C	T_c^{**}, °C	$\overline{M}$	(3) ΔC_p, кал/моль × град
ОЭА-1000	0.108	8	—57	17,2	1,86
ОУ-1000	0.132	8	—36	22,4	2,96
ОУ-2000	0,130	8	—46	22,4	2,91
ЭЛ-4	0.127	9	—29	22,4	2,85
ЭЛ-3	0,135	8	—27	22,4	3.02
ЭЛ-2	0.126	12	—14	22,4	2,82
ЭЛ-1	0.120	15	—7	22,4	2,69

Key: (1). Substance. (2). cal/g•deg. (3). cal/mole•deg.

FOOTNOTE 1. ΔT_c - interval of vitrification.

2. T_c - was defined as temperature by which increment of heat capacity C_p during vitrification reached half its value. ENDFOOTNOTE.

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K_θ they determined according to the equation of Krevelen [252]:

$$K_\theta = (S_* M_*^{1/2})^4, \qquad (IV,6)$$

where M_*- molecular weight, which is necessary to one atom of main circuit; S_*- value, depending on the specific hardness, which is necessary to one atom of main circuit.

The numerical value of parameter K_Θ render/showed $K_\Theta = (51\cdot 10^{-2}/4,14)^3 = 17,8\cdot 10^{-4}$ and $(51.2\bullet 10^{-2}/4.15)^3 = 18.8\bullet 10^{-4}$ for OEA and OU respectively. Calculated value K_Θ for OEA in accuracy coincides with experimental data, that confirms the authenticity of the obtained results.

Since value K_Θ for OEA and OU they are close in value, then count that the thermodynamic flexibility of macromolecules OEA and OU virtually identical. Hence it follows that the presence of diisocyanate unit does not affect the thermodynamic flexibility of the chains of linear oligourethane, and consequently, increase T_c upon transfer from OEA to OU is caused only by decrease of the kinetic flexibility of chains, which depends on the concentration of polar urethane groups. For the present instance is observed linear dependence T_c on the concentration of urethane groups into OU (Fig. 56).

The presence of chemical cross-linking in elastomers also considerably decreases the segmental mobility of macromolecules, leading to further increase T_c. However, the predominant contribution to increase T_c upon transfer from oligomer to elastomer and for this system introduces formed by polar groups physical grid (table 28). Certain increase T_c EL-3 and EL-4 can give the partial crystallization of these elastomers (see Fig. 55c, d). Rigid crystalline sections also limit mobility of chain in the adjacent regions, producing increase T_c.

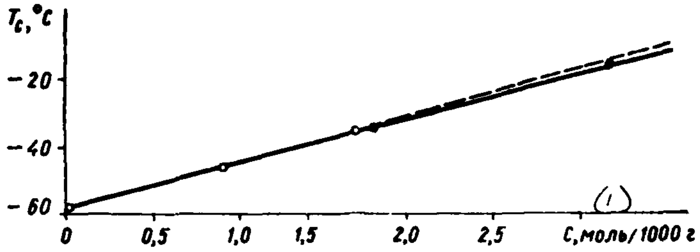

Fig. 56. Dependence T_c of oligourethane on the concentration of the urethane groups: $-T_c$ it is calculated; $--T_c$ is determined experimentally.

Key: (1). mole.

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Let us examine now the characteristic vitrification via the comparison of the jump of heat capacity during the vitrification of the separate objects of the investigated system taking into account Wunderlich's rule [343]. According to this rule the increment of heat capacity during vitrification taking into calculation 1 mole of the structural "beads" of molecule is the constant value, equal to 2.97 cal/mole•deg. Table 27 corrected values ΔC_p for the investigated series/number of polymers, obtained on the formula

$$\Delta C_p' = \overline{M} C_p,$$

where $\overline{M}$ - average molecular weight, which is necessary to one "bead";

ΔC_p - observed in experiment jump of heat capacity during vitrification.

Values $\Delta C_p'$ for all investigated systems (see Table 27), with exception OEA-2000, they are close to theoretical. Somewhat low value $\Delta C_p'$ for OEA-2000 is explained by the partial crystallization of oligomer with quenching. This indicates the fact that the ratio of the theoretical increment of heat capacity during the vitrification to experimental, which can serve as the measure of the depth of crystallization of polymer, for OEA-2000 is close to value (1.5) of the relationship/ratio of its heat of fusion and crystallization.

According to [343], $\Delta C_p'$ is proportional to the specific volume of energy of the formation of new holes and is inversely proportional T_c. It is known [for 343] that the cross-linking of polymers is accompanied by the decrease of specific volume. At the same time upon transfer from OU to cross-linked elastomers $\Delta C_p'$ it remains invariable and T_c grow/increases (see Table 27). Hence, the presence in molecular structure it is polyurethane the grid of physical and chemical bonds raises energy of the formation of new holes the greater, the greater the network density.

Table 28. Contribution of diisocyanate and chemical cross-linking in increase T_c in oligodiethyleneglycoladipate.

(1) Вещество	(2) C, моль/1000 г	(3) T_c ОУ (рассчитанная), °C	T_c, °C	ΔT_c ТДИЦ	(4) ΔT_c сшивателя
ОЭА-2000	—	—	—57	—	—
ЭЛ-1	1,8	—19	—7	38	12
ЭЛ-2	1,8	—19	—14	38	5
ЭЛ-3	3,2	—35	—27	22	8
ЭЛ-4	3,2	—35	—29	22	6

Key: (1). Substance. (2). mole. (3). calculated. (4). cross-linking agent.

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It should be noted that the absolute value, and also the rate of growth in the heat capacity in low-temperature ones region upon transfer from oligoether/ester To the cross-linked rubbers is lowered (see Table 26). This can be explained by a decrease of a number of the vibrational degrees of freedom of system because of the presence of the strong interaction between polar groups in oligourethane, and in the cross-linked elastomers - to the presence of the grid of chemical bonds.

Made of the comparison of the curves of the temperature dependence of the heat capacity of the annealed and hardened/tempered specimen/samples OEA-1000 and OEA-2000 (see Fig. 54a, b) it is evident that the maximums of the peaks of melting hardened/tempered specimen/samples of both of oligomers are misaligned into the region of lower temperatures. Furthermore, for the hardened/tempered specimen/sample OEA-2000 is observed two exothermic peaks of crystallization. The discovered phenomenon is explained by the fact that depending on the conditions/mode of heat treatment in the specimen/samples of OEA are formed different crystalline modifications.

The small area of the peak of the crystallization of high-temperature form (at 16°C) and the absence of the peak of the crystallization of low-temperature form in OEA-1000 indicate its extremely high crystallization rate which it is not possible to completely suppress even quenching in liquid nitrogen. The complex character of the dependence of heat capacity of both of oligoether/ester in interval of 20-40°C (see Fig. 54, curve 1) is explained by rearrangement and decomposition of supermolecular structures.

As can be seen from Fig. 55, transition from OEA to OU is accompanied by the noticeable decrease of the capacity to be crystallized, to which testify the significant decrease of the thermal effects of melting initial specimens and the absence of crystallization in the hardened/tempered specimen/samples OU. OU are crystallized only in time moreover OU-2000 is crystallized considerably faster than an OU-1000.

Crystallizing the polymers can be divided into two stages: the formation of the metastable two-dimensional-regulated state (without a change in intermolecular interaction) and the spontaneous transition into final state with three-dimensional order, which is accompanied by an increase in intermolecular interaction. For the polymers, which do not have polar functional groups, the capability for crystallization is determined in essence by the thermodynamic flexibility of chains, and therefore for them the stages of crystallization indicated it is not possible to experimentally divide. However, the properties of macromolecules OU are determined not only by the thermodynamic, but also kinetic flexibility, which depends on the concentration of urethane groups. In this case the intermolecular hydrogen bonds which are formed during the first stage of crystallization, noticeably stabilize two-dimensional-ordered pseudocrystalline state, as a result of which under the temperature conditions indicated the second stage of crystallization occur/flow/lasts for a long time [276, 266].

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Since the concentration of urethane groups in OU-2000 is less than in OU-1000, capability for crystallization, i.e., the smaller duration of the first stage of crystallization, in OU-2000 it is more. On the other hand, although the energy density of cohesion into OU is above because of the presence of urethane groups, than in existing OEA, temperature and heat of fusion is below. This is explained by considerably greater defectiveness of crystal lattice OU, by caused asymmetry of the molecular structure of the links of the isomer of 2.4-TDI. On this same reason the thermal effect of melting OU-1000 is considerably less than in OU-2000. Since the concentration of units 2.4-TDI in OU-1000 is more than in OU-2000, it is possible to expect that a temperature decrease of melting in OU-1000 will be more. However, a difference in the temperatures of melting of OEA and corresponding OU is approximately identical. It is assumed that the relatively high melting point OU-1000 is caused by small entropy of fusion, as a result of an increase in the entropy in crystalline state because of the disordering action/effect of links 2.4-TDI.

Transition to the cross-linked elastomers is accompanied by further reduction in the capability for crystallization as a result of steric limitations, applied on mobility of chain by the nodes of chemical grid. Capability for crystallization they retain only EL-4 and EL-3 (see Fig. 55), network density in which is considerably less than into EL-1 and EL-2.

According to the theory of melting cellular polymers [88], the cross-linking of statistical chains must lead to the temperature decrease of melting, proportional to network density. An insignificant (order of 2°C) temperature decrease of melting EL-3 and EL-2 is explained so by small network density which the exception/elimination of the cross-linked sections of chains from crystal lattice leads only to an insignificant increase in the entropy of fusion and it barely affects melting point.

The absolute value of the heat capacity of the fusion/melts of studied OEA and OU in the range of temperatures to 100°C barely grow/increases.

In accordance with free-volume concept [231] the heat capacity of liquids is composed of "oscillatory" and "hole" (bonded with the formation of new holes) parts. Assuming that melting is reduced to formation and enrichment of fusion/melt by holes [143], then the observed course of the heat capacity of the fusion/melts of the oligomers being investigated one should, obviously, explain by zero contribution of one of the addend common/general/total heat capacity, namely "hole" part. This tells about the fact that energy of the formation of new holes exceeds energy of the thermal agitation of molecules in the fusion/melts of OEA and OU.

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Properties oligohydroxytetramethyleneglycol and synthesized on their basis of linear ones and cross-linked is polyurethane.

Some properties it is polyurethane on the basis of oligohydroxytetramethyleneglycol (polyfurit) they are investigated by calorimetric method [77] (Table 29). Relationship/ratio OH/NCO for oligourethane and elastomers was the same as for such on basis OEA.

As is evident in Fig. 57a, the heat capacity of the annealed specimen/sample PF-1000 (curve 1) in range from -70 to -50°C has constant value and then smoothly it grow/increases, developing small endothermal peak (thermal effect of 5.84 cal/g) with maximum with 0°C, after which it is lowered at 6°C and then sharply it grow/increases at 13°C. In interval of 13-18°C, increase in the heat capacity somewhat is retarded, and then appears into the basic peak of melting with 23°C. Melting is ended at 33°C, after which the value of heat capacity to 100°C virtually is unchanged. The common/general/total thermal effect of melting is 28.65 cal/g.

During heating of the hardened/tempered specimen/sample PF-1000 (Fig. 57a, curve 2) the heat capacity increases linearly in the range of temperatures from -80 to -20°C, after which the heat capacity rapidly grow/increases, changing into endothermal peak with maximum with 11°C and by thermal effect of 10.6 cal/g. After decrease with 15°C, the heat capacity again rapidly grow/increases at melting point with 22°C and decreases up to 32°C. The summary thermal effect of melting is 27.95 cal/g.

Table 29. The initial characteristic of oligohydroxytetramethyleneglycol it is polyurethane on its basis.

(1) Вещество	(2) Условное обозначение вещества	M	(3) Соотношение сшивателя ДЭГ/ГЛ
(4) Полифурит	ПФ-1000	960	—
(5) Олигоуретан на ПФ-1000	ОУФ-1000	6700	—
(5) Олигоуретан на ПФ-2000	ОУФ-2000	15 600	—
(6) Эластомер на ПФ-1000	ЭЛФ-1	4600 *	1 : 1
(6) Эластомер на ПФ-1000	ЭЛФ-2	2540 *	1 : 3
(6) Эластомер на ПФ-2000	ЭЛФ-3	7950 *	1 : 1
(6) Эластомер на ПФ-2000	ЭЛФ-4	4360 *	1 : 3

Key: (1). Substance. (2). Conventional designations of substance. (3). Relationship/ratio of cross-linking agent. (4). Polyfurit. (5). oligourethane on. (6). Elastomer on.

FOOTNOTE 1. Corrected values M_c ENDFOOTNOTE.

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The heat capacity of the annealed specimen/sample PF-2000 (Fig. 57b, curve 1) linearly grow/increases from -70 to -10°C and then smoothly appears endothermal peak with 19°C (thermal effect of 6.95 cal/g). At 23°C heat capacity is reduced then rapidly grow/increases and becomes maximum at melting point with 32°C. Common/general/total thermal effect of melting is equal to 26.7 cal/g.

In the curve of the heat capacity of the hardened/tempered specimen/sample PF-2000 (Fig. 57b, curve 2) is observed the small endothermal lift in the range of temperatures from -95 to -80°C, characteristic for transition from glassy to highly elastic state. Value T_c for polyoxytetramethylene is equal to -55 on [341], -84 on [338], -86°C on [337].

From results of calorimetric measurements, it follows that T_c the PF-2000 has value on the order of -88°C, which is close to value of -86°C, obtained by dilatometric method [337] for a high-molecular polymer.

From -80°C heat capacity of the quenched specimen/sample PF-2000 linearly grow/increases to -20°C and it passes through the endothermal step with 11-15°C (thermal effect of 5.45 cal/g), changing then into the peak of melting with 26°C; melting is completed at 36°C and heat capacity it decreases.

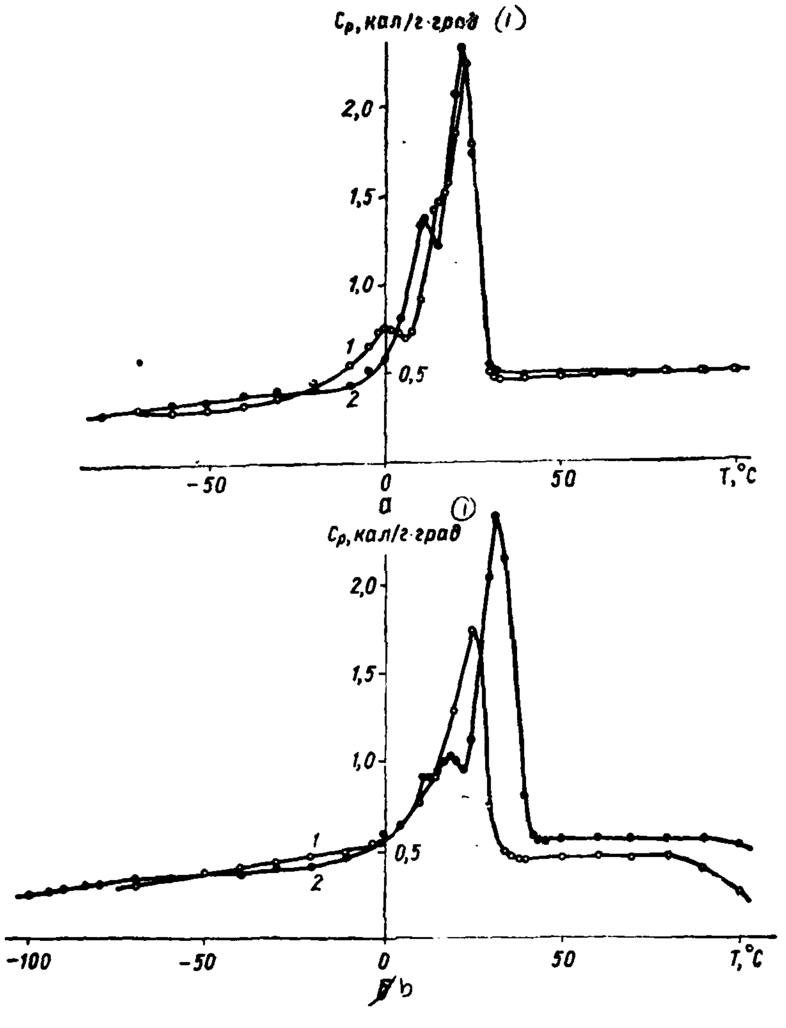
Cp, кал/г·град (1)
2,0
1,5
1,0
0,5
1
2
-50
0
50
T,°C
a
①
Cp, кал/г·град
2,0
1,5
1,0
0,5
1
2
-100
-50
0
50
T,°C
b

Fig. 57.

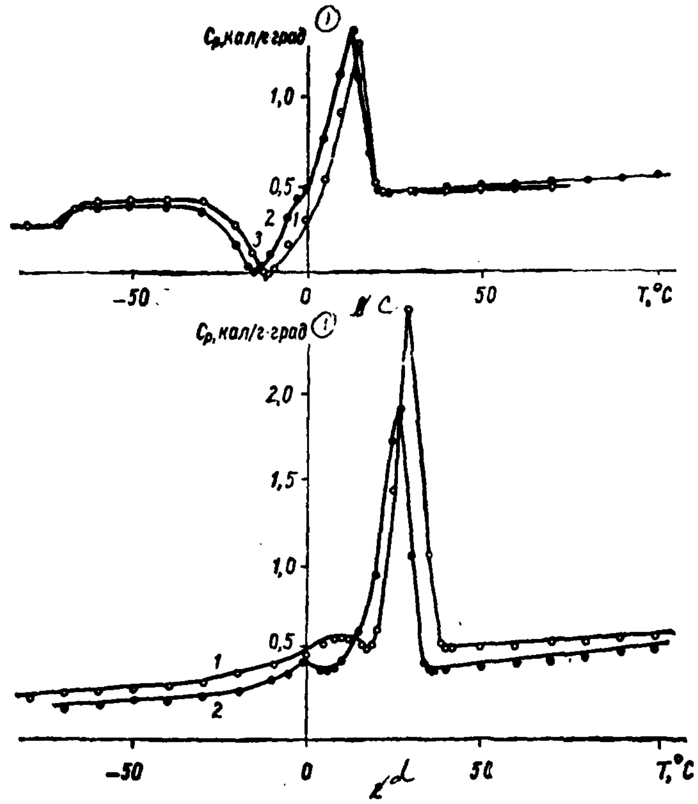

Fig. 57. Heat capacity is polyurethane a PF-1000 (a); the PF 2000 (b); oligourethane OUF-1000 (c); OUF-2000 (d); 1 - annealed specimen/sample; 2 - hardened/tempered specimen/sample.

Key: (1). cal/g•deg.

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The thermal effect of melting is 19.65 cal/g. In interval of 36-80°C, heat capacity barely grow/increases, but beginning with 80°C it decreases, developing exothermic peak with maximum with 135°C. The thermal effect of exothermic process with 145°C is equal to 64.8 cal/g.

In the curve of the heat capacity of the annealed specimen/sample OUP-1000 (Fig. c, d) is observed the jump in range from -75 to -64°C, which corresponds to the devitrification of oligomer, after which the heat capacity retains linear dependence with insignificant lift to -35°C. Further it decreases before the achievement of exothermic peak with -11°C in solidification range from -35 and approximately to 3°C and directly it changes into the peak of melting with 15°C. In view of the imposition of crystallization and melting, accurate determination of the heat of these processes was not impossible. The data of heat are close to each other and are approximately 6.8 cal/g.

Similar pattern is observed also for the hardened/tempered specimen/sample OUF-1000; however, in this case an interval of vitrification somewhat becomes narrow, and solidification range is misaligned into the region of the lower (from -40 to 0°C) temperatures with peak at -15°C. At the same time an interval of melting is expanded (from 0 to 22°C), moreover the peak of melting is misaligned to 13°C. The thermal effects of crystallization and melting are equal to 6.43 and 8.95 cal/g respectively.

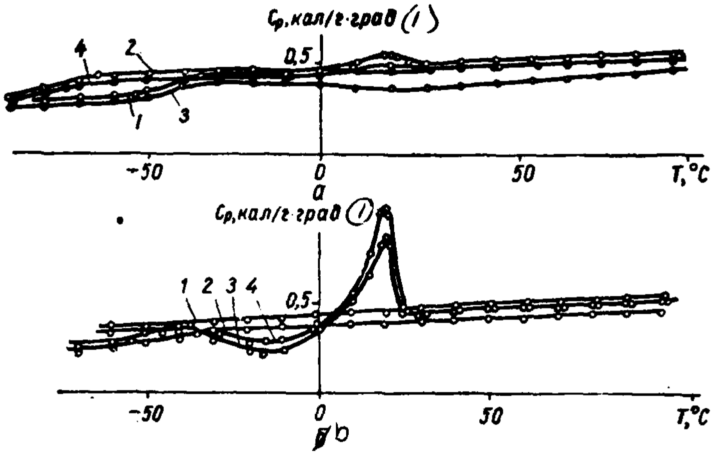

Fig. 58. Heat capacity of the initial (a) and exposed/persistent at temperature of -40°C (b) specimen/samples of those cross-linked it is polyurethane:

1 — ЭЛФ-1; 2 — ЭЛФ-2; 3 — ЭЛФ-3; 4 — ЭЛФ-4.

Key: (1). cal/g•deg.

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The curve of the heat capacity of the annealed specimen/sample OUF-2000 (Fig. 57 c, d, curve 1) in low-temperature ones region consists of two sections of range from -70 to -40 and from -30 to 0°C, then it passes through the small lift with maximum with 10°C, it is lowered at 18°C and sharply it grow/increases at melting point with 29°C. Thermal effect is 17.35 cal/g.

The heat capacity of the hardened/tempered specimen/sample OUP-2000 (Fig. 57d, curve 2) linearly grow/increases from -70 to -20°C, it passes through the lift with -1°C and after insignificant lowering with 6°C, rapidly it grow/increases at melting point of 27°C. Heat of melting 16.9 cal/g.

Figure 58a depicts the curves of the heat capacities of the initial specimens of the cross-linked elastomers. These elastomers are not capable of crystallization at room temperature, to which testifies the absence of the noticeable peaks of melting, and also the presence of sharp bends at vitrification temperatures on the curves of heat capacity in low-temperature ones region. The temperatures of the vitrification of elastomer on basis PF-2000 (curves 1 and 2) lie/rest at the region of lower temperatures, than in elastomers on basis PF-1000 (curves 3, 4).

Figure 58b gives the curves of the heat capacities of the elastomers indicated, exposed/persistent long time at temperature of -4°C.

Table 30. Equations $C_p=f(T)$ for the linear sections of the heat capacities of oligoether/ester, oligourethane and cross-linked it is polyurethane.

(1) Полимер	(2) Отожженный образец			(3) Закаленный образец		
	(4) Уравнение	(5) Температурный интервал, °C		(4) Уравнение	(5) Температурный интервал, °C	
		(6) от	(7) до		(6) от	(7) до
ПФ-1000	$0{,}247+1{,}97\cdot 10^{-4}T$	-80	-20	$0{,}298$	-70	-50
	$0{,}162+9{,}8\cdot 10^{-4}T$	33	100	$0{,}503$	32	100
ПФ-2000	$-0{,}293+3{,}06\cdot 10^{-3}T$	-70	-10	$0{,}036+1{,}49\cdot 10^{-3}T$	-80	-20
	$0{,}550$	43	90	$0{,}450$	36	80
ОУ-1000	$0{,}182+9{,}8\cdot 10^{-4}T$	-60	-35	$0{,}166+9.8\cdot 10^{-4}T$	-60	-40
	$0{,}300+4{,}95\cdot 10^{-4}T$	23	100	$0{,}148+1{,}03\cdot 10^{-3}T$	23	100
ОУ-2000	$0{,}102+9{,}6\cdot 10^{-4}T$	-70	-40	$-0{,}083+1{,}51\cdot 10^{-3}T$	-70	-20
	$0{,}227+1{,}03\cdot 10^{-3}T$	40	100	$-0.198+2.02\cdot 10^{-3}T$	35	100
ЭЛФ-1	$0{,}113+9.8\cdot 10^{-4}T$	-70	-54	$0{,}113+9{,}8\cdot 10^{-4}T$	-80	-54
	$0{,}190+9{,}8\cdot 10^{-4}T$	-35	100	$0{,}198+9{,}8\cdot 10^{-4}T$	-36	100
ЭЛФ-2	$0{,}094+9{,}8\cdot 10^{-4}T$	-90	-50	$0{,}094+9{,}8\cdot 10^{-4}T$	-70	-50
	$0{,}137+9.8\cdot 10^{-4}T$	-30	100	$0{,}088+9{,}8\cdot 10^{-4}T$	30	100
ЭЛФ-3	$0{,}172+9{,}8\cdot 10^{-4}T$	-60	-40	$0{,}232+9.8\cdot 10^{-4}T$	-65	-20
	$0{,}186+9{,}8\cdot 10^{-4}T$	35	100	$0{,}232+9{,}8\cdot 10^{-4}T$	30	100
ЭЛФ-4	$0{,}148+9{,}8\cdot 10^{-4}T$	-60	-40	$0.202+9{,}8\cdot 10^{-4}T$	-60	0
	$0{,}186+9{,}8\cdot 10^{-4}T$	30	100	$0{,}175+1{,}05\cdot 10^{-3}T$	30	100

Key: (1). Polymer. (2). Annealed specimen/sample. (3). Hardened/tempered specimen/sample. (4). Equation. (5). Temperature interval, °C. (6). from. (7). to.

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From curves it is evident that under these conditions are crystallized only the elastomers on basis PF-2000 (curves 1 and 2) in sufficiently wide temperature interval from -40 to 5°C. Melting these specimen/samples is accompanied by the appearance of sharp maximums of heat capacity with 20°C. Heat of crystallization and melting comprise with respect to 5.06 and 5.83 cal/g for ELF-3 and 2.93 and 3.66 cal/g for ELF-4.

Table 30 gives the parameters of equation $C_p=f(T)$ for the linear sections of the given curves, calculated by the method of least squares. Table 31 contains the values of the values, which characterize the transition of the investigated objects from glassy to highly elastic state. Constant K_θ, calculated by formula (IV, 6), upon transfer from oligoether to oligourethane in this case is not virtually changed. Its values for PF and OUF are equal to $19.1\cdot10^{-4}$ and $19.4\cdot10^{-4}$ respectively. Consequently, the thermodynamic flexibility of macromolecules and these oligomers is approximately identical, i.e., the presence of the units of toluene-2,4-diisocyanate is not reflected in the flexibility of chain and T_c for these systems is predetermined mainly by a change in the kinetic flexibility of macro-chain. This corresponds to the data given in chapter II.

The presence of the grid of chemical bonds also leads to certain increase T_c. However, basic effect cross connections are exerted to the value of an interval of vitrification, moreover is observed tendency toward the expansion of an interval of vitrification during an increase in the degree cross-linking and the decrease of molecular weight of initial oligoether. Since vitrification is relaxation process, an increase in the interval of vitrification can be explained by the expansion of the spectrum of relaxation times as a result of localization of the free space of system in the places of cross-linking [246], and also by the partial dissociation of relatively weak hydrogen bonds in polyurethane on the basis of simple oligoether/ester.

The values of the increment of heat capacity during vitrification $\Delta C_p'$ for studied series/number of polymers (Table 31) are close to the values, calculated for organic glasses [343]. Exception is the PF-2000, which is explained by its partial crystallization with quenching.

Table 31. Characteristics the vitrification of polyfurit and polyurethane on its basis.

(1) Образец	(2) ΔC_p, кал/г× ×град	ΔT_c, °C	T_c, °C	M	(3) $\Delta C'_p$ кал/моль× ×град
ПФ-2000	—	—88	0,062	14,4	0,89
ОУФ-1000	6	—67	0,116	23,3	2,71
ЭЛФ-1	23	—43	0,104	23,3	2,42
ЭЛФ-2	21	—39	0,098	23,3	2,28
ЭЛФ-3	20	—77	0,113	23,3	2,63
ЭЛФ-4	20	—80	0,106	23,3	2,47

Key: (1). Specimen/sample. (2). cal/g•deg. (3). cal/mole•deg.

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The value of the increment of heat capacity during vitrification is proportional to energy of the formation of new holes and it is inversely proportional to vitrification temperature. Hence it is possible to draw the conclusion that and for this series/number of polymers energy of the formation of new holes grow/increases upon transfer from initial oligoether to the cross-linked elastomer.

In bond with aforesaid, it is interesting to compare the parameters the vitrification of polymers of both of investigated series/numbers. Since T_c is polyurethane on the basis polyethers (polyfurit) considerably lower than in it is polyurethane on the basis of polyesters (oligoethyleneadipate), then energy of the formation of holes in the latter accordingly higher. Since polyurethane on the basis polyethers differ from it is polyurethane on the basis of complex polyethers only by character of intermolecular hydrogen bonds, it is logical to assume that the hydrogen bonds between oxygen of complex ester groups and hydrogen of the terminal hydroxyl groups or NH-groups of urethane link more strong/durable, than bonds with the collaboration of oxygen of simple ester groups. This is confirmed by literature data [13, 327, 332].

For the hardened/tempered and annealed specimen/samples PF-1000 and PF-2000, is observed the in stages character of the melting (see Fig. 57). Formally this character of the decomposition of crystal structure resembles the picture of melting the annealed specimen/sample OEA-2000 (see Fig. 54), which in crystalline state can exist in two modifications. However, the results of the X-ray diffraction analysis of polyoxytetramethylene [183, 236] make it possible to consider that for it is characteristic only one crystal structure and that the observed shape of the curve of melting is caused by the kinetic conditions of crystallizing polyfurit. In this case, are noted two special feature/peculiarities. First, melting the hardened/tempered and annealed specimen/samples has the analogous character, which attests to the fact that the mechanism of nuclei forming during the crystallization of these oligomers does not depend on the degree of supercooling and rate of cooling of fusion/melts.

Hence, the nucleation of crystalline phase has the athermic character, caused by the existence of micro-heterogeneity in fusion/melts PF-1000 and PF-2000, heated to temperature of 100°C. Such micro-heterogeneity, apparently, are associates from macromolecules, generatrices because of the hydrogen bonds between ether/ester oxygen and terminal hydroxyl groups.

In the second place, in accordance with Flory's thermodynamic theory [210] the melting point of polymer crystalls is determined by their size/dimensions. In the case of the even distribution of crystals according to size/dimensions, fusion curve of polymer must be smooth and have one maximum at the temperature, which corresponds to melting bulk of crystals.

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On obtained curves of heat capacity PF-1000 and PF-2000 there is several maximums in an interval of the melting (see Fig. 57a, b). Therefore it is assumed that during the crystallization of these oligomers occurs the formation of crystals of several discrete size/dimensions which are melted at the temperatures, which correspond to maximums in the curves of heat capacity. This will agree with the results of the roentgenographic and dilatometric investigations of similar in structure low-molecular polyoxyethylenes [161], for which is reveal/detected the phenomenon of fractionation in the unit of flat/plane crystals depending on their height.

In turn, the height of crystallite in low-molecular polyether/polyesters is determined by the length of macromolecule [161]. Thus, the observed character of melting can testify simultaneously to polydispersion low-molecular PF-1000 and the PF-2000, which depending on synthesis condition can achieve significant magnitude [83, 334].

Low melting points PF-1000 and PF-2000 (Table 32) are explained by the high values of entropy of fusion. Since the entropy of fusion strongly depends on the conformation of macromolecules in the molten state, is given below the estimation of the contribution of the conformational entropy of these oligomers upon transfer from crystalline to liquid state.

The entropy of fusion of polymers can be presented in the form of following expression [88]:

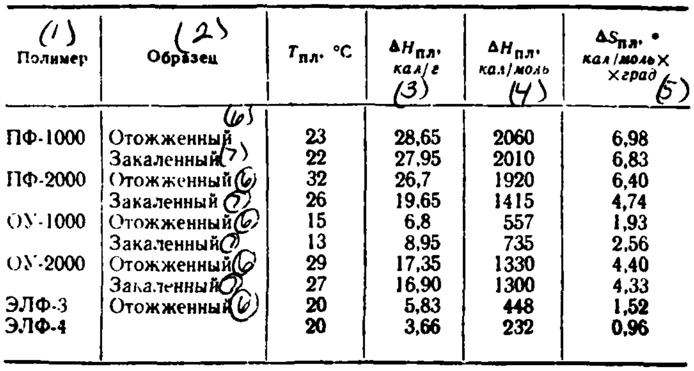
$$\Delta S_{пл} = \Delta S_V + (\Delta S_{пл})_V,$$

where ΔS_V - the contribution to entropy, caused by volume variation during melting $\Delta V_{пл}$; $\Delta S_{пл}$ - the contribution, caused by a change in the chain conformation during melting at a constant volume. Value ΔS_V was determined from the formula

$$\Delta S_V = -\frac{\alpha}{\beta}\Delta V_{пл},$$

where α - a coefficient of volumetric thermal expansion; β - isothermal compressibility.

Table 32. Thermodynamic parameters of melting.



(1) Полимер	(2) Образец	$T_{пл}$, °C	$\Delta H_{пл}$, кал/г (3)	$\Delta H_{пл}$, кал/моль (4)	$\Delta S_{пл}$, * кал/моль×град (5)
ПФ-1000	Отожженный (6)	23	28,65	2060	6,98
	Закаленный (7)	22	27,95	2010	6,83
ПФ-2000	Отожженный (6)	32	26,7	1920	6,40
	Закаленный (7)	26	19,65	1415	4,74
ОУ-1000	Отожженный (6)	15	6,8	557	1,93
	Закаленный (7)	13	8,95	735	2,56
ОУ-2000	Отожженный (6)	29	17,35	1330	4,40
	Закаленный (7)	27	16,90	1300	4,33
ЭЛФ-3	Отожженный (6)	20	5,83	448	1,52
ЭЛФ-4		20	3,66	232	0,96

Key: (1). Polymer. (2). Specimen/sample. (3). cal/g. (4). cal/mole. (5). cal/mole•deg.

FOOTNOTE [1]. Entropy of fusion was calculated from formula $\Delta S_{пл} = \Delta H_{пл}/T_{пл}$. END FOOTNOTE

(6). Annealed. (7). Harden/tempered.

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Values α and β are undertaken from [313]. Since PF-1000 and PF-2000 with 20°C are in the partially molten state, then for calculation $\Delta V_{пл}$ it is not possible to use the experimental values of density with 20°C (ρ_{20}). Therefore were used values ρ_{16} and ρ_{71} for the PF-3000 from [313], extrapolating them to the appropriate melting points. The obtained values of an increase in the volume during melting are identical for PF-1000 and PF-2000 and are 0.08 cm^3/=5.76 cm^3/mole, and $\Delta S_V = -(7{,}29\cdot 10^{-4}/6{,}85\times 10^{-5})\cdot 5{,}76 = -61{,}4$ cm^{3}atm/deg•mole=-1.48 cal/deg•mole.

Since the contribution of volume variation into entropy of fusion is not more than 21-23o/o, the high value of entropy of fusion PF-1000 and PF-2000 is caused mainly by an increase in the number of conformations of macromolecules during melting. Thus, macromolecules PF in fusion/melt must have more or less coiled conformations in comparison with the conformation of flat/plane zigzag in crystalline state [236, 183].

For linear oligourethane, especially for OUF-1000, are observed the decrease of heat of fusion and the shift of the melting points in the region of lower temperatures in comparison with initial oligoethers. This is explained by the fact that in OUF-1000 the concentration of links 2.4-TDI whose presence in chain leads to the defects of crystal lattice [15], higher than in OUF-2000. On the same reason the entropy of fusion OUF-1000 is less than the entropy of fusion OUF-2000 (Table 32).

It is substantial, that the presence of diisocyanate units does not virtually affect the capacity of oligourethanes on the basis of polyfurit (OUF) to be crystallized, while OU on the basis of complex oligoether/ester Are capable of being crystallized only in time. This phenomenon is bonded with greater regularity of the molecular structure of polyfurit and presence in fusion/melts OU on the basis of complex oligoether/ester of the more strong/durable intermolecular hydrogen bonds, which impede the formation of three-dimensional crystal structure. As confirmation serves the fact that the heat capacity of fusion/melts OUF grow/increases faster than in OU, probably, as a result of high energy of the formation of holes in the latter.

As for elastomers on the basis of oligoethyleneglycoladipate, capability for crystallization develop only elastomers with polyfurit units with a molecular weight of 2000 (ELF-3 and LF-4), although, as can be seen from Table 29, the network density of chemical cross-linkings ELF-1 and ELF-4 (elastomer on basis PF-1000) is approximately identical. Hence it follows that basic effect on the capability of polyurethane elastomers for crystallization has the network density not of the chemical, but physical (hydrogen) bonds whose number into ELF-3 and ELF-4 is less than into ELF-1 and ELF-2 due to the concentration of urethane groups.

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The low value of entropy of fusion ELF-3 and ELF-4 is explained by the small contribution of configurational entropy during melting.

Comparative characteristic the vitrification of those cross-linked is polyurethane on the basis of oligoethyleneglycoladipate and oligohydroxytetramethyleneglycol.

For cross-linked elastomers of both of series/numbers, is made a semiquantitative evaluation of the contribution of inter- and intramolecular reaction to their kinetic properties [110].

In accordance with [231], transition from glassy state to liquid is accompanied by the formation of the new holes, which are characterized by molar volume V_h and molar excess energy (in comparison with initial "holeless" state) ε_h. Energy ε_h is bonded with an increase in the heat capacity by approximate relationship/ratio [88, 231]

$$\Delta C_p = \frac{E_c}{T_c} \cdot \frac{\varepsilon_h}{RT_c} \exp\left(-\frac{\varepsilon_h}{RT_c}\right),$$

E_c - molar internal residual steam-generating heat (energy of cohesion) at the temperature of vitrification T_c. Value E_c can be determined from empirical dependence [182]

$$\frac{E_c - E}{E} = 1{,}73 \cdot \frac{V - V_c}{V_c},$$

where E - molar energy of cohesion; V - molar specific volume at boiling point; V_c - molar specific volume when T_c. E and V were calculated from the values of the corresponding increases for functional groups [182].

Values V_c determined by extrapolation V_{20} to T_c, for which were used the values of the coefficient of the volumetric thermal expansion of liquid state $\alpha_ж$, determined according to empirical relationship/ratio $T_c \cdot \alpha_ж = 0{,}164$ [313]. Since the macromolecules of the investigated polymers are alternating very long oligoester and short diisocyanate sections, in further calculations M, $\bar{M}$ and corresponding molar values for the repeated structural cell/elements of those investigated it is polyurethane they determined, considering polyurethane the block copolymers (for example, that was being repeated network element of macromolecule EL-1 they accepted that consisting of 86o/o of link OEA-1000 and 14o/o of link of 2.4-TDI). Value V_h was calculated from formula [343]

$$V_h = \frac{\varepsilon_h V_c}{E_c}.$$

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It is known that the theoretical bases vitrification in the free space based on assumption about the fact that the transition from glassy state occurs at the temperature by which the value of free space becomes greater certain critical value. It is obvious, this critical free space depends on the value of the structural elements, which accept collaboration in transition [64]. In turn, forming the free space (holes) in low-molecular glass is accompanied by an increase of average distance between separate molecules that has statistical character. In this case, the size/dimension of the generating holes is commensurable with molecular dimensions. During the devitrification of organic glasses besides an increase in the medium intermolecular distance, will be changed also the chain conformation as a result of acquisition by the macromolecules of segmental mobility. In this case the size/dimension of holes is determined already by the value of the segment of chain. Since the value of segment characterizes the flexibility of chain, that, therefore, the smaller values of hole volume (i.e. V_h) possess the more flexible chains. Thus, forming the holes in polymers is bonded with the value of both inter- and intramolecular reaction. Since the value of heat capacity is determined by the summary contribution of all forms of the molecular mobility, calculated by ΔC_L values e_h (see Table 33) they will also depend on the amount of inter- and intramolecular forces. From Table 33 it is evident that the value of molar hole volumes for it is polyurethane on the basis of complex oligoether/ester (EL-1-EL-4) less than for it is polyurethane on the basis of simple oligoether/ester (ELP-1-ELP-4). Consequently, the thermodynamic flexibility of the macromolecules of polyurethane with ester units is higher than in the macromolecules of polyurethane with simple ether/ester units.

Table 33. Thermodynamic parameters of vitrification.

① Эластомер	$\overline{M}$	V, ② см³/моль	$V_{в}$, ② см³/моль	V_c, ② см³/моль	E, ③ кал/моль	E_c, ③ кал/моль	ΔC_p, ④ кал/моль×град	e_h, ③ кал/моль	V_h, ② см³/моль	e_h/V_h, ⑤ кал/см³	T_c, °C
ЭЛ-1	173	190,0	141,0	138,0	19900	17980	21.40	885	6,80	130,0	— 7
ЭЛ-2	178	190,0	141,0	137.0	10900	18200	22.40	845	6.35	151.5	—14
ЭЛ-3	175	189,5	140.5	136.0	10450	17600	23.60	770	5,95	129,5	—27
ЭЛ-4	175	189.5	140.5	135,5	10450	17800	22.20	845	6,40	132.0	—29
ЭЛФ-1	81	101,0	73,0	70,0	4800	8480	8.17	1080	8,90	121.5	—43
ЭЛФ-2	81	101,0	73,0	70,0	4800	8480	7.95	1100	9.06	121.3	—39
ЭЛФ-3	77	99,0	73,0	66.5	4363	8055	8,70	945	7.80	121,0	—77
ЭЛФ-4	77	99,0	73,0	66.5	4365	8065	8.15	975	8,05	121,0	—80

Key: (1). Elastomer. (2). cm³/mole. (3). cal/mole. (4). cal/mole•deg. (5). cal/cm³.

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Analogous conclusion is made as a result of investigations of the dilute solutions of linear ones it is polyurethane identical nature [98]. Value e_h for EL-1 -EL-4 is also higher than for ELF-1 - ELF-4. Consequently, the basic contribution to energy of the "hole" state of those investigated is polyurethane it introduces intramolecular reaction.

It is somewhat unexpectedly, that the temperature of the vitrification of ester ones it is polyurethane above than in appropriate it is polyurethane on the basis of simple oligoether/ester (Table 33). This absence of the correlation between the thermodynamic flexibility of chain and the temperature of vitrification once again tells about the fact that the latter depends mainly not on thermodynamic, but on the kinetic flexibility of chains, which is determined by the concentration of the polar groups, capable of the formation of secondary bonds, or by relative strength (intensity) the latter. Since the concentration of urethane groups in the appropriate polyurethane is virtually identical, then the higher temperatures of the vitrification of ester ones it is polyurethane bears out the greater intensity of intermolecular interaction. This is evident also from the comparison of values ε_h/V_h (Table 33). Ratio/relation ε_h/V_h, which can be call/named the "hole" energy density of cohesion, is the characteristic of the bulk properties of polymer, i.e., it is sensitive to molecular bonds. The comparison of the values of the "hole" energy densities of cohesion it is polyurethane it confirms assumption about the fact that the intensity of intermolecular interaction is more in ester polyurethane.

Polyurethane on the basis of other oligoether glycol units.

Investigation of the effect of the chemical structure of polyether/polyesterurethane for their capability for crystallization [94] showed that the polymers, synthesized on the basis of ether glycols (di-, tri- and hexaethyleneadipateurethane), and also polymers with lateral groups (methoxymethyl- and propyleneethyleneadipateurethane) are amorphous. At the same time polymers on the basis of glycols of polymethylene series/number (ethylene-, trimethylene-, tetramethylene- and pentmethyleneadipateurethane) are the crystallizing polymers.

From the comparison of the heights of the maximums of the curves of the temperature dependence of the dynamic modulus of the crystallizing polymers indicated it is evident that higher maximum in polytetramethyleneadipateurethane (Fig. 59). On the basis of this, is made the conclusion that polyurethane indicated possesses the maximum speed of crystallization, which is confirmed by dilatometric data [94].

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Is studied dependence T_c of the block copolymers both on the nature, molecular weight, molar content of the units and the presence in the block copolymers of the crystalline phase, formed by crystallizing units [25, 26, 160]. As object are selected the urethane block copolymers of the following general formula:

$$(-A-OCONHRNHCOO-)_{1-n}(-B-$$
$$-OCONHRNCOO-)_n,$$

where A - a unit of the aliphatic polyester: polyethyleneglycoladipate (PEA) or polydiethyleneglycoladipate

(PDEA); C - unit of ester on basis o-, m-, and n-bis (β-hydroxyethoxy) phenyleneadipinic acid

$$[-OC_2H_4OC_6H_4OC_2H_4OCOC_4H_8CO-]_n,$$

designated subsequently o-, m- and n-PFA.

Were investigated the series of the block copolymers on the basis of the following pairs of polyether/polyesters: PEA - n - PFA, PEA - m-PFA, PEA - o-PFA, PDEA - m-PFA, PDEA - o-PFA. For each series of copolymers n, it was changed from 0 to 1. Value T_c was determined by thermomechanical method.

It is establish/installed, that the character of dependence T_c of the block copolymers on molar ratio of units is not changed upon transfer from one isomer of PFA to another and only transition from PEA to PDEA produces change for the specimen/samples, exposed/persistent in the course of six months at room temperature.

To dependence T_c for copolymers PDEA - m-PFA on molar ratio of units it shows that T_c for all copolymers they lie down well on the straight line, which unites values T_c for homopolyurethane on the basis of PDEA and m-PFA (Fig. 60a).

On the basis of observed linear reduction T_c in the copolymers from an increase in the content of units PDEA, obtains satisfaction the conclusion about the plasticizing effect of the latter on the units of m-PFA. In this case, it is considered that the units of PDEA are not capable of crystallization, but the units of m-PFA easily form crystalline phase.

In connection with this is examined the series of copolymers PEA - m-PFA in which to both units is specific the formation of crystalline phase (Fig. 60b), and in this case only for the amorphized specimen/samples characteristically linear magnification T_c with an increase in the content of PFA. However, for the exposed/persistent in time specimen/samples picture is changed.

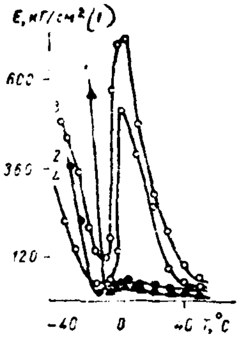

Fig. 59. The temperature course of the dynamic modulus: 1 - polyethylene glycol-adipinateurethane, 2 - polytrimethylene glycol adipinate urethane, 3 - polytetramethylene glycol adipinate urethane, 4 - polypentamethyleneglycol adipinate urethane.

Key: (1). kgf/cm².

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So T_c copolymers with the predominant quantity of PEA (not less than 60o/o) becomes equal to T_c of polyurethane on the basis of PEA, whereas for the copolymers where the content PEA is lower than 60o/o, T_c remains equal to T_c of the amorphized specimen/samples or somewhat below.

To the observed phenomenon is given following explanation. For the copolymers where the unit A is in amorphous state, characteristically uninterrupted decrease T_c from B- to an A-urethane, since the units of the latter are the plasticizing agent with respect to the aryl-containing units B. Since the plastification must occur/flow/last at molecular energy levels, also T_c must vary linearly with a change in the percentage of aliphatic unit.

In the case when an A-block is crystallized, prolonged storage of the specimen/samples of copolymers at room temperature conditions the emergence in them of crystalline formations of both of assembly views, which, in turn, leads to appearance in the specimen/samples of microheterogeneities.

The microregions where are grouped the units of one nature, must develop the properties, which are inherent in this component in the form of homopolymer and, in particular, to have it T_c. Therefore in the copolymers where the aliphatic unit PEA (on less than 60 mol. ones o/o), T_c copolymer after prolonged storage becomes equal to T_c of polyurethane on the basis of PEA. Increase T_c in the copolymers with the content of PEA-blocks of more than 40 mol. ones o/o is explained by the absence in them the crystalline formations of units PEA.

Thus when in the specimen/samples of copolymers does not occur the liberation/isolation of aliphatic units A in the form of independent crystalline phase, then T_g is determined T_c B-blocks, plasticized by units A.

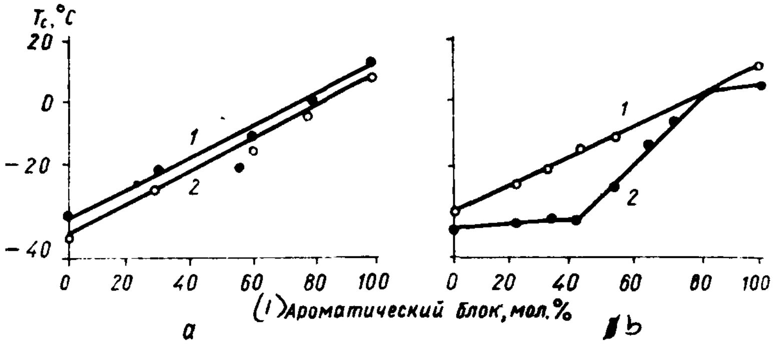

Fig. 60. Dependence T_c on the composition of the copolymer of the series of PDEA - m-PFA (a) and PEA - m-PFA (b): 1 - amorphized specimen/samples; 2 - exposed/persistent six months at room temperature.

Key: (1). Aromatic unit, mol. o/o.

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This explanation of special feature/peculiarities T_c of the exposed/persistent specimen/samples of the copolymers of the series of PEA - m-PFA explains the fact that the prolonged holding of the specimen/samples of the copolymers of the series of PDEA - m-PFA does not give and to their change T_c in comparison with initial ones.

Dependence T_c of n-PFA and homopolyether/polyesterurethane on their basis on molecular weight of n-PFA shows adiabatic nature of change T_c in the series/number of polyether/polyesters and homopolyether/polyesterurethane will agree well with the given above data and once again testifies to the which is determining roles concentration of urethane groups in change T_c in polyether urethanes (Fig. 61).

It is substantial, that even with molecular weight of polyether/polyester units, equal to 2000, the block copolymer not of one of the investigated series reveal/detected two T_c. This, obviously, it is explained higher by the values of molecular weights of the mechanical segments of polyether/polyesters. As can be seen from Fig. 62, experimental values T_c will agree well with T_c, calculated in Fox's formula [218] for the copolymers

$$T_c = T_cAT_cB/(\omega_A T_cB + \omega_Б T_cA),$$

where T_cA and T_cB - temperatures of the vitrification of homopolymers A and B: ω_A and $\omega_Б$ - their weight fractions in the appropriate copolymers.

Thus, T_c polyether/polyesterurethane is characterized, on one hand, by nature and concentration of diisocyanate component, but on the other hand - nature and molecular weight of the glycol units, which are determining tendency toward crystallization and concentration of the polar groups, which condition emergence between the macro-chains of polyurethane of the physical bonds of different degree of intensity.

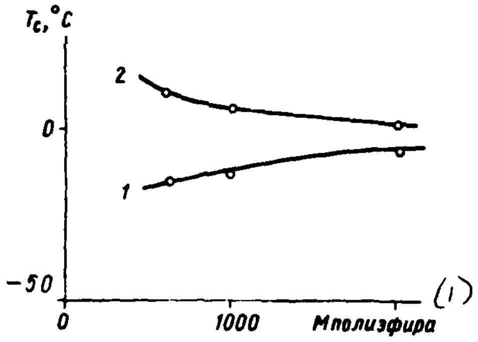

Fig. 61. Dependence T_c for n-PFA (1) of different molecular weight and polyether/polyesterurethane (2) on their basis.

Key: (1). M-polyether.

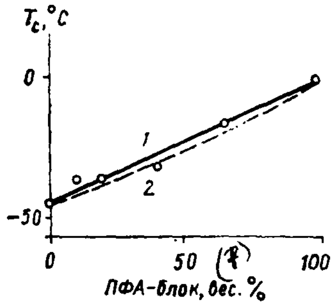

Fig. 62. Dependence T_c on composition of copolymers of series of PEA - N-PFA with molecular weight of units 2000: 1 - experimental data for amorphized specimen/samples; 2 - data, calculated by formula of Fox.

Key: (1). PFA-block, weight o/o.

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It is shown [to 26], what separate units of the copolymer of PEA-n-PFA are capable of forming independent crystalline phases, and that this capacity falls in the series/number of the copolymers of series 2000, 1000 and 600. For the copolymers of series 2000, constancy $T_{пл}$ of PFA-blocks is retained up to the content of latter on the order of 50 weight o/o. In the region of average/mean compositions, is observed melting the two types of the crystalline formations, which correspond to crystallization of each of the assembly views. In the copolymers of series 1000 and 600, occurs change $T_{пл}$, which reminds eutectic type diagrams, and only copolymers with the predominant content of PEA have $T_{пл}$, equal to $T_{пл}$ of homopolymer. The decrease of the value of a PFA-block is accompanied by the emergence of less modern crystal structures and by narrowing the region of independence T_c from the composition of copolymer. Thus, the decrease of the length of the component block copolymers of polyether/polyester units produces the appearance of properties of the random copolymer.

Were investigated some monomeric and oligomeric glycols, which can be used for synthesis it is polyurethane [41]. In particular, on the basis of the thermogram of heating the copolymers of tetrahydrofuran and oxide of propylene with different content of the latter it was established that the capability for crystallization is lowered with an increase in the content of propylene oxide. However, even with the 25o/o content of propylene oxide copolymer is still capable to be crystallized.

For those cross-linked it is polyurethane at the same time on the basis of mixture 2.4- and 2.6-TDI and copolymer of tetrahydrofuran with different content of propylene oxide, but with the one and the same degree of chemical cross-linking, it is establish/installed, that polyurethane loses the capacity to be crystallized with the lower contents of oxide of propylene, i.e., with 12o/o [15]. This tells about that which diisocyanate component impedes the course of the process of crystallization in polyurethane elastomers.

The investigation of polyurethane elastomers on the basis of toluenediisocyanate with different relationship/ratio 2.4- and 2.6-TDI copolymer with 10o/o of propylene oxide showed that the transition from 2.4- to 2.6-TDI does not change the lattice structure of polyurethane, but increases the crystallization rate and the final degree of the crystallinity of polyurethane elastomer.

From that presented it follows that capability for crystallization they develop only also they are crystallized. In this case, molecular the weight of oligomeric units must exceed certain critical value. Crystal structure of polyurethane elastomers is formed as a result of the crystallization of oligoester units, and diisocyanate links play only the role of defective sections in structure.

If lattice structure depends only on nature and structure of oligomeric unit, then tendency toward crystallization and degree of crystallinity are defined by the structure of both diisocyanate and oligomeric unit. The last/latter parameters are bonded also with the degree of the chemical cross-linking of elastomer.

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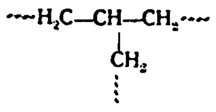
Chapter V. The structure of the grid of amorphouss it is polyurethane.

CHARACTERISTIC OF THE GRIDS OF THREE-DIMENSIONAL POLYURETHANES.

Obtaining polyurethanes with the utilization polyfunctional connections leads to formation of polymers with three-dimensional/space structure, or the so-called three-dimensional polymers. Simplest criterion of formation of polymers with three-dimensional grid - its insolubility in the series/number of solvents. The junctions of the segments of chains are called nodes or branch points.

The special feature/peculiarities of the chemical structure of polyurethanes determine the possibility of the existence in them themselves of different in structure chemical cross connections. Together with biuret and allophanate cross connections can be formed the cross-linking nodes, which present the residue/remainder of polyol, (I, II), or branched isocyanate (III, IV)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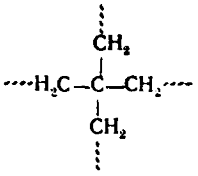
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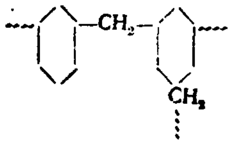
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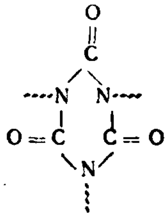
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Thus, in polyurethanes is formed the whole collection of different types of the chemical bonds, which possess different strength.

Tobol'skiy and coworkers [188, 330] conducted the investigations of stress relaxation in the cross-linked polyurethane elastomers, which made it possible to obtain some information about the strength of bonds in grid. They established that at the elevated temperatures in the cross-linked polyurethane is observed the so-called chemical flow, which testifies to the break of chemical bonds.

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Is studied the chemical relaxation polyurethane and polyether/polyester rubbers, which contain the bonds of different types, and are calculated the values of relaxation times (Table 34, Fig. 63).

As can be seen from given data, weakest weak bonds in polyurethane are uric and biuret.

Further investigations in this direction showed that stress relaxation in the cross-linked polyurethane it is possible to represent in sum two processes [335] the energies of activation of which were equal to with respect 37+-3 and 42+-2 kcal/mole. However, the results, obtained during the study of stress relaxation, did not allow Tobol'skiy to give chemical treatment to the discovered processes.

Table 34. Times of the chemical relaxation of polyurethane and polyether/polyester rubbers with 120°C.

Резина (1)	Тип связи (2)	Время релаксации, ч (3)
1	Эфирная, уретановая, мочевинная, биуретовая (4)	2,1
2	Сложноэфирная, уретановая, мочевинная, биуретовая (5)	3,0
• 3	Сложноэфирная (6)	500
4	Сложноэфирная, уретановая (7)	14,0
5	» »	9,7
6	Сложноэфирная, уретановая, мочевинная, биуретовая (8)	1,6

Key: (1). Rubber. (2). Type of bond. (3). Relaxation time, h. (4). Ether/ester, urethane, uric, biuret. (5). Ester, urethane, uric, biuret. (6). Ester. (7). Ester, urethane. (8). Ester, urethane, uric, biuret.

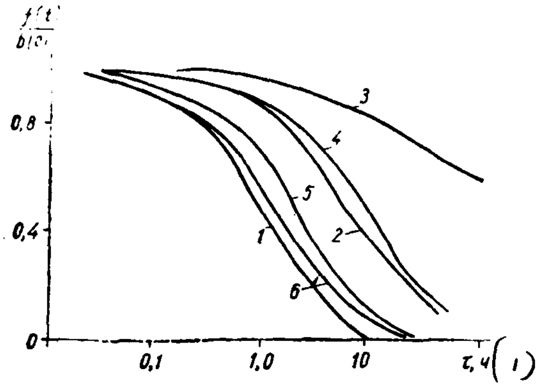

Fig. 63. Chemical relaxation of stress with 120°C of different polyurethane rubbers and polyester rubber. (numeral they correspond to ordinal number of rubbers in Table 34).

Key: (1). τ,h.

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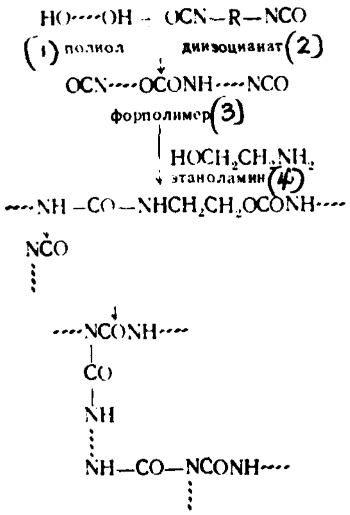
It is possible to speak only about different strength of the chemical bonds, which compose the grid of polyurethane elastomers.

The presence in polyurethane of different chemical bonds and large number of polar groups leads to formation in them together with the chemical ones of strong/durable physical bonds (hydrogen and van der Waals), of caused by reaction polar groups with each other.

The investigation of the structure of grid it is polyurethane the extremely complex problem, necessary for explaining the numerical ratio between the structure and physical properties.

Most in detail studied the structures of cross-linked ones was polyurethane Tanaka and Yokoyama [325, 326, 347, 348] on system polyol - diisocyanate - ethanolamine. Diagram of the formation of cross-linked product in this case following:



Key: (1). polyol. (2). diisocyanate. (3). prepolymer. (4). ethanolamine.

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The molar relationship/ratio of components is represented thus:

$$K = \frac{\text{мольное содержание NCO-групп в диизоцианате}\,(1)}{\text{мольное содержание OH-групп в полиоле}\,(2)},$$

$$M = \frac{\text{число молей этаноламина}\,(3)}{\text{мольное содержание NCO-групп в аддукте}\,(4)}$$

Key: (1). the molar content of NCO--group in diisocyanate. (2). molar content of OH-groups in polyol. (3). number of moles of ethanolamine. (4). molar content of NCO--group in adduct.

Before fit/approaching the description of three-dimensional grid, the authors [348] examine obtaining prepolymer, taking into account of the equations, which describe the reactions of polycondensation. The average/mean degree of polymerization

$$x_n = \frac{K+1}{2(1-p)+(K-1)},$$

where p - degree of the perfection of reaction. With p=1

$$x_n = \frac{K+1}{K-1}.$$

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Average/mean degree of polymerization x_n shows how many molecules of polyol and diisocyanate they form one molecule of prepolymer. Distribution according to degrees of polymerization is described by the equation

$$P_x = \left(\frac{1}{K}\right)^{\frac{x-1}{2}}\left(1-\frac{1}{K}\right).$$

where X - a degree of polymerization. The share of the molecules of diisocyanate, which remains in adduct after the completion of reaction P_1, while the portion/fraction of the molecules, which contain polyol, $1-p_1=1/K$. A number of molecules of prepolymer with $p=1$

$$v = v_0(K-1),$$

where v_0 — number of molecules of polyol. Then a number of molecules of prepolymer, which contain polyol,

$$v = \frac{v_0(K-1)}{M}.$$

It is assumed that the brought out equations are valid with the distribution of molecules according to lengths, since is taken into attention a number of molecules.

After introduction to the prepolymer of ethanolamine of the molecule of prepolymer, they increase because of the addition to them of the amino- and hydroxyl groups which form uric ones and urethane ones during reaction with the excess of isocyanate groups. Consequently, ethanolamine can be considered as trifunctional agent.

At the first moment of reaction, is correct the relationship/ratio $[\mathrm{OH}]_0 = [U] \doteq$ the initial concentration of ethanolamine where [U] - the concentration of uric groups. The reaction rate constants of the formation of the urethane and uric groups, which take place simultaneously, let us designate K_1 and K_2:

$$\sim\mathrm{NCO} + \sim\mathrm{OH} \xrightarrow{k_1} \text{мочевинная},^{(1)}$$

$$\sim\mathrm{NCO} + \sim\mathrm{NHCONH}\sim \xrightarrow{k_2} \text{биуретовая}.^{(2)}$$

Key: (1). uric. (2). biuret.

Then

$$\frac{[\mathrm{OH}]}{[\mathrm{OH}]_0} = \frac{[U]}{[U]_0}.$$

Since branch point, or network point, is the molecule of ethanolamine whose all reaction groups react, the number of nodes

$$N = (\text{число молекул этаноламина})^{(1)}\, p_{\mathrm{OH}}\, p_{U},$$

Key: (1). (number of molecules of ethanolamine).

where p_{OH} and p_{U} — probability of reactions OH- or of uric groups respectively.

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They can be calculated, if are known values [OH] and K_1/K_2. A number of chains whose ends are converged into node, $v_i = 3N/2$. In this examination the formation of grid, is difficult to determine K_1 and K_2. Therefore for simplicity they accept, that the addition of uric groups begins after the full/total/complete exhaustion of hydroxyl ones.

Let us dismantle/select the formation of grid for three different relationship/ratios of components with the degree of the perfection of reaction, equal to one.

1. $M=1/3$. All uric groups react with NCO- group. In system it does not remain free isocyanate groups.

2. $M<1/3$. All uric groups react with isocyanate ones, but the latter remain in excess.

3. $M>1/3$. The part of the uric groups reacts with NCO- group, free NCO- group it does not remain.

The structure of grid for the examined cases is schematically represented in Fig. 64.

The chains, forming polyurethane grid, branch from the molecules of adduct. With $M=1/3$ a number of internal circuits both of ends of which are bonded with branch points, is equal to a number of molecules of the adduct

$$\nu_i = \nu = \nu_0 (K - 1).$$

Last/latter equation considers a quantity of remaining molecules of diisocyanate. A number of chains into which enter the molecules of polyol as component unity, is expressed by the equation

$$\nu_i' = \nu' = \frac{\nu_0 (K - 1)}{K}.$$

Here chains do not have free ends and grid can be considered modern.

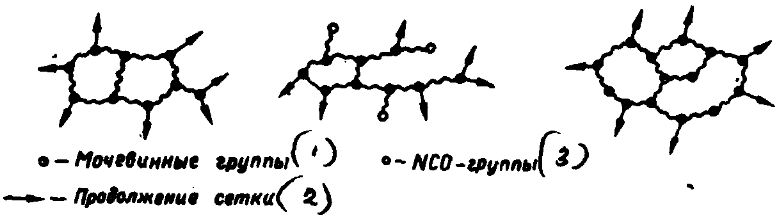

Fig. 64. Structure of grid for three different relationship/ratios of components with the degree of the perfection of reaction, equal to one.

Key: (1). Uric groups. (2). continuation of grid. (3). group.

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With M<1/3 there is an excess of NCO--group; therefore is formed a smaller number of internal circuits in comparison with the preceding case. There are chains with the free ends whose number is equal to excess quantity of NCO--group: then

$$\nu_l = 2\nu - 2\nu 3M,$$
$$\nu_i = \nu - \nu_l = \nu_0 (K-1)(6M-1),$$
$$\nu_i = \frac{\nu_0 (K-1)(6M-1)}{K}.$$

If M>1/3, a number of molecule ends which are formed during the reaction of elongation by adduct,

$$2\nu - 2 \cdot 2\nu M = 2\nu(1-2M),$$

and number of molecules $-\nu$ $(1-2M)$. At this point a number of uric groups is equal to a number of molecules of ethanolamine, i.e., $2\nu M$.

When the free ends of the chains (NCO--group) are added to uric groups, circuital, an increase in the number of circuits is equal to a number of additions. Then a number of internal circuits

$$\nu_i = \nu(1-2M) + 2\nu(1-2M) = 3\nu_0(K-1)(1-2M).$$

Grid in this case will be modern.

Value ν_i is calculated somewhat otherwise. The portion/fraction of the molecules which are not added to ethanolamine, $p_1=1-2M$. Quantity of molecules of diisocyanate, which are located in adduct,

$$\nu - \nu' = \nu_0(K-1)\left(1-\frac{1}{K}\right)\cdot$$

A number of molecules of diisocyanate in prepolymer, which do not interact with ethanolamine, is equal

$$\nu_0(K-1)\left(1-\frac{1}{K}\right)(1-2M),$$

whence

$$\nu_i = 3\nu_0(K-1)(1-2M) - \nu_0(K-1)\left(1-\frac{1}{K}\right)(1-2M) =$$
$$= \nu_0(K-1)\left(2+\frac{1}{K}\right)(1-2M).$$

The authors consider that value ν_i', i.e. a number of internal circuits or cuts of the chains between the points of branching, insufficiently accurately characterizes the actual picture of the formation of grid, since not all branch points are the nodes of three-dimensional grid. Sometimes on the end of the chain, exiting/waste from the point of branching, is located free NCO--group, but branch point is not network point. Therefore the authors introduce concept "number of elastic cell/elements" (ν_e) or the number of effectively linked chains according to Flory [211], which most completely characterizes three-dimensional three-dimensional/space grid.

Value ν_e for case $M \geqslant 1/3$ is expressed by the equation

$$\nu_e = 2[2\nu - (\nu + 2\nu M - 1)] = 2\nu(1 - 2M) = 2\nu_0(K - 1)(1 - 2M).$$

With $M<1/3$

$$\nu_e = 2[6\nu M - (\nu + 2\nu M - 1)] = 2\nu(4M - 1) = 2\nu_0(K - 1)(4M - 1).$$

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Thus, Tanaka and Yokoyama they formed an equation according to which it is possible to calculate the concentrations of the cross-linked chains in three-dimensional polyurethane for different molar relationship/ratios of the crosslinking agent and isocyanate groups in adduct. They consider that the proposed method of calculation is simplified and does not consider some factors, for example entagling of chains.

For the check of the given equations experimental determination of the concentration of effectively linked chains conducted in polyurethane on the basis of polyol, toluenediisocyanate and ethanolamine. As polyol are used polyethylene glycol, polypropylene glycol, polyethyleneadipate, polyethylenesebacyanate, etc. Experimental determination ν_e was conducted according to the equation of the kinetic theory of high elasticity

$$\tau = RT\left(\frac{\nu_e}{v}\right)\left(\alpha - \frac{1}{\alpha^2}\right),$$

where τ - a voltage/stress, d/cm²; $\frac{\nu_e}{v}$ - a concentration of the effectively linked chains per unit of volume; α - degree of the stretching of specimen/sample. This equation it is possible to rewrite in the form

$$E = 3RT\frac{\nu_e}{v} = 3RT\frac{\rho}{M}, \qquad (V,1)$$

where E - a module/modulus of high elasticity.

Equation (V, 1) is derived only for equilibrium systems with following assumptions [254, 331]: 1) the chains, which generate grid, have identical overall length; 2) spacing distribution between the ends of chains in the undeformed state is represented by the formula of Gauss; 3) volume during deformation remains constant; 4) changes in the projections of the distance between the ends of each chain during deformation are similar to changes in the size/dimensions of the deformed specimen/sample of rubber.

Although these conditions in essence are observed only for the natural rubber, for the comparative characteristic of the degree of the cross-linking of the three-dimensional grids of equation (V, 1) they use to many other systems, including to polyurethane [326]. It is known that if dependence αS on $\gamma\ (\alpha = \frac{l}{l_0},\ \gamma = \frac{\Delta l}{l_0}$, where S - voltage/stress on unit of area during deformation) gives straight line, then this is the confirmation of equilibrium of state. The slope/inclination of straight line must be equal to unity.

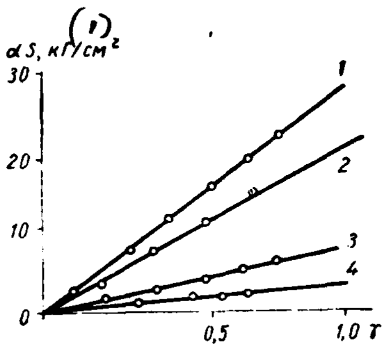

Fig. 65. Dependence αS on γ for polyuretnane on the basis of polyethylene glycol (M=1540): 1 - K=2.45; 2 - K=1.98; 3 - K=1.51 4 - K=1.21.

Key: (1). kgf/cm².

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The dependence α S on γ for polyurethane on the basis of polyethylene glycol molecular at the different values of K [96] is represented in Fig. 65. Slope/inclination log γ from log γS composes approximately unity (Fig. 66). Consequently, the condition of equilibrium is observed in this case which gives the possibility to use results of determining the module/modulus for the experimental finding of the effective density of cross-linking.

Figure 67 depicts the relationship/ratio between $\frac{v_e}{v}$, calculated according to equations Tanaka and Yokoyama, and $\frac{v_e}{v}$, observed for is polyurethane on the basis polyethers. Almost in all cases $\frac{v_e}{v}$ calculated more than observed, moreover disagreement great for it is polyurethane on the basis of polypropylene glycol. For polyurethane on the basis of polyethylene glycol with a molecular weight of 4000 with M-1/3 value $\frac{v_e}{v}$, that observed and calculated, is almost identical. Somewhat more disagreement in the case it is polyurethane on the basis of polyether/polyesters of smaller molecular weight.

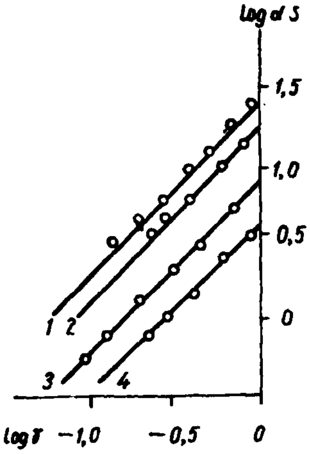

Fig. 66. Dependence log αS on log γ polyurethane on the basis of polyethylene glycol (designation the same as in Fig. 65).

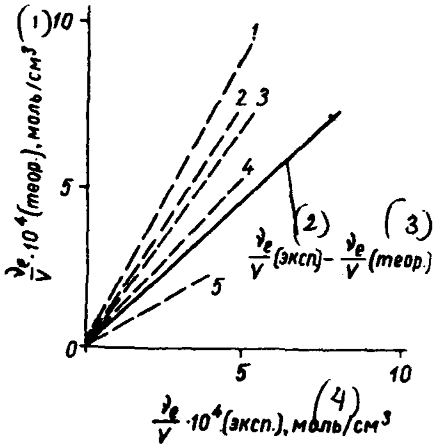

Fig. 67. Comparison of theoretical and experimental values $\frac{v_e}{v}$ it is polyurethane on basis of 2.2-TDI and different glycols with M=1/3; 1 - POPG-545; 2 - POPG-1950; 3 - PEG-1540; 4 - PEG-4000; 5 - PEG-4000 (M=0.3) (designation see in Table 36).

Key: (1). (theor.) mole/cm³. (2). exp. (3). (Theor.) (4). (exp.), mole/cm³.

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The convergence of experimental direct/straight in the beginning coordinates the authors consider the proof of the correctness of the proposed method of calculation $\frac{v_e}{v}$. With M<13

$$M = \frac{\text{концентрация этаноламина (1)}}{\text{число NCO-групп в аддукте (2)}}$$

Key: (1). ethanolamine concentration. (2). number of NCO--group in adduct.

that observed $\frac{v_e}{v}$ becomes more than calculated Tanaka it joins this with the fact that the free terminal isocyanate groups, are added to uric and urethane ones and increase experimental $\frac{v_e}{v}$ in comparison with that calculated.

RELATIONSHIP BETWEEN CHEMICAL AND PHYSICAL NODES IN GRID OF POLYURETHANES.

If when deriving the equations for the calculation of the effective network density of polyurethanes is not considered the possibility of the formation of physical bonds; which exist in this specific grid, it is not possible to search for the coincidence of calculated and calculating value $\frac{\nu_c}{v}$. Their coincidence can be only accidental. as a rule, $\frac{\nu_c}{v}$ experimental will be more than theoretical to the force of the given above reasons. The experimental results, obtained by some researchers, confirm this [317, 198]. Theoretical calculation $\frac{\nu_c}{v}$ most frequently is conducted on the basis of assumption about the fact that during the utilization of the trifunctional crosslinking agent each mole of the latter gives 1.5 moles of the cross-linked chains, i.e.,

$$\frac{\nu_c}{v} = 3/2C_T, \qquad (V.2)$$

where C_T — concentration of the trifunctional cross-linking agent, mole [133, 198]. They in parallel experimentally determine that $\frac{\nu_c}{v}$ according to the module/modulus of high elasticity or according to the method of Flory-Rener [211].

The comparison of values $\frac{\nu_c}{v}$, conducted specific according to module/modulus of high elasticity and calculated by equation (V, 1) for it is polyurethane on the basis of polyoxypropyleneglycol and toluenediisocyanate, it showed, that $(\frac{\nu_c}{v})$, can be closely in value to theoretical, but it can considerably exceed the latter. All this depends on the effectiveness of the solidification of those investigated it is polyurethane, which depends on the nature of the catalysts used and conditions for obtaining.

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In other words, the less the effectiveness of solidification polyurethane, i.e., the more defective grid, the more $\frac{\nu_e}{v}$ experimental differed from that calculated ($\frac{\nu_e}{v}$ experimental $< \frac{\nu_e}{v}$ theoretical). With an increase in the effectiveness of solidification because of a change in the conditions of obtaining the polymers (introduction of catalyst, etc.) experimental value $\frac{\nu_e}{v}$ approached theoretical or exceeded it five-six times. Thus, the comparison of the effective density of cross-linking, found experimentally and by computed, shows that $\frac{\nu_e}{v}$ experimental, as a rule, is more than theoretical. Disagreement it is possible to explain only fact that in polyurethane grid together with chemical cross connections is a large number of cross physical bonds, which lead to an increase in the value of the effective density of cross-linking, determined experimentally.

Frequently network density they calculate according to the method of Flory-Rener [211], which is convenient and simple in experimental sense. In this case is used the equation of form [198]

$$-[\ln(1-v_2)+v_2+\Psi_1 v_2^2]=v_1\left(\frac{\nu_e}{v_0}\right)\left(v_2^{\frac{1}{3}}-\frac{2v_2}{f}\right),$$

where v_2 - the volume fraction of polymer in the swollen gel; Ψ_1 — parameter of reaction polymer - solvent; v_1 - the molar volume of solvent and f - a functionality of the crosslinking agent. Equation is derived on the basis of the thermodynamic examination of the swelling of the weakly-vulcanized natural rubber in thermodynamically good solvents. The boundary/interfaces of the application/use of this equation for the polymers of the different degree of chemical cross-linking during the utilization of different solvents are not establish/installed. Flory experimentally showed that being relative, this method is more convenient for determining the network density by studying swelling of one and the same polymer in one and the same solvent. Other researchers use it for determining the degree of the cross-linking of the polymers of different nature [191, 258] and even for strongly linked epoxies [258]. To estimate the conformity of the experimentally obtained values of the real density of cross-linking is difficult, since there is no at present yet method of obtaining the cellular polymers with the accurately assigned structure.

Flory's method is based on the investigation of the swelling of polymers; therefore it is interesting to trace, as affects the quality of solvent the determination of effective network density.

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In such polymers as the natural rubber where besides the introduced during vulcanization chemical cross connections there are couplings of chains, the degree of cross-linking must not strongly differ during a change in the thermodynamic quality of solvent, especially as into the equation of Flory-Rener is introduced the parameter :ps, which considers the reaction of polymer with the studied solvent. Unfortunately, the investigations in this direction were not conducted. The effective density of cross-linking usually is determined in one solvent which is selected purely empirically. Sometimes the density of cross-linking, determined with swelling in two different solvents, proved to be close [19].

The effect of solvent on the results of determining the density of cross-linking is investigated only in one work [312] for the filled natural rubber. As solvents served the alcohols, ketones, aromatic hydrocarbons. It turned out that within the solvents of one class the density of cross-linking was increased with the decrease of the polarity of solvent. Were not observed at the same time the correlations between the densities of links by the physical characteristics of the solvents of different classes.

In this case obviously, it is necessary to consider the presence of a large number of physical bonds between rubber and filler. The dissociation of bonds under the action/effect of solvents occurs differently depending on the nature of solvents. Therefore the density of cross-linking, determined in different solvents, proves to be dissimilar.

For determining the density of cross-linking in polyurethane from the method of Flory-Rener, it is necessary to take into consideration the specific character of the latter. The presence in chains it is polyurethane the sections of different polarity and the capacity it is polyurethane to formation of hydrogen bonds leads to emergence in polyurethane together with chemical strong/durable physical grid, to which the solvents depending on nature will act differently. Some solvents are capable of giving complexes during reaction with urethane group [3, 5]. The strength of such complexes is different. Most strong/durable complexes are formed with swelling it is polyurethane in dioxane and tetrahydrofuran. It is possible, in this case with swelling, is obtained new reticular structure, different from initial. In solvents of the type of dioxane with an increase in the temperature, occurs the irreversible swelling, i.e., it is obvious, occurs the break of some comparatively weak chemical bonds.

Thus, the determination of the density of cross-linking it is polyurethane on Flory-Rener with the aid of the solvents, which enter into specific interaction with functional by groups it is polyurethane, there is not a sense. The impossibility of the utilization of such solvents is bonded also with the fact that it is not possible to determine by the existing methods the actual value of reaction polymer-solvent (Ψ) due to inapplicability of theory to the irreversible processes.

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However, it is possible to obtain certain presentation/concept of network density it is polyurethane according to the method of Flory-Rener with the aid of the solvents, which do not interact with functional groups it is polyurethane. Spectrum investigations showed, [5] that for such solvent will be polyurethane benzene; probably, and toluene is suitable for this purpose.

During the investigation of the swelling of polyurethane on the basis of oligodi-ethyleneglycoladipate in toluene at different temperatures, we reveal/detected that the swelling in this case is reversible (Fig. 68). The same picture was observed also for benzene [5]. In acetone and cyclohexane, which are capable of entering into specific reaction with polyurethane, swelling is irreversible.

Consequently, the indirect criterion of the absence of reaction is the reversibility of swelling during a change in the temperature.

But even during the utilization of such solvents it is difficult to assume that they do not act on molecular bonds in polyurethane. Therefore the method of Flory-Rener gives only relative information about network density, but nevertheless it is very convenient for determining the change in the network density of polyurethane under the influence of such factors as temperature, moisture of air, medium.

Thus, the existing methods of evaluating the network density give only approximate results during their application/use to the calculation of the degree of cross-linking it is polyurethane. Degree of approximation to the actual value of network density can be estimated is only in the presence of specimen/samples polyurethane with the accurately known chemical degree of cross-linking, which presents difficult problem, taking into account the complexity of processes, taking place with synthesis it is polyurethane. However, the calculation of network density on the basis of stoichiometric composition and the comparison of the obtained results with experimental can give useful information about the nature of three-dimensional grid it is polyurethane.

We conducted [115] the comparison of the results of determining the density of the cross-linking of polyurethane elastomers with the aid of equations (V, 1 and V, 2), and also for the method of

Klaff-Gleding [185] (Table 35), at basis of which lie/rests the equation

$$\frac{\nu_e}{v} = \frac{h_0 S}{3A_0 RT} = \frac{\rho}{M_c},$$

where A_0 - area of the transverse section of specimen/sample; R - gas constant; h_0 - height of the undeformed ne-swollen specimen/sample; S - slope/inclination by direct/straight, presenting by themselves the dependence of the amount of strain from load.

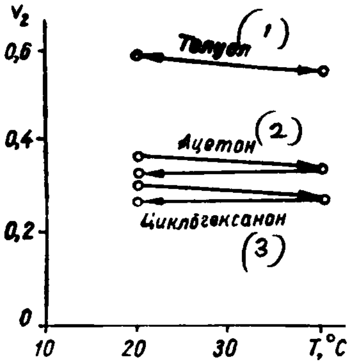

Fig. 68. Dependence V_2 on temperature for polyurethane on the basis of the oligodiethylene glycol adipinate.

Key: (1). Toluene. (2). Acetone. (3). Cyclohexanone.

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Elastomers are obtained on the basis of oligodiethyleneglycoladipinate (mol. weight 2000) and of TDTs. As the crosslinking agent served the mixture of di- and triethanolamine in molar ratio 1 : 1,5.

As can be seen from Table 35, value M_c the calculated on the basis of stoichiometric relationship/ratios, largest, and of equilibrium module/modulus - smallest. The prevalence of the values of the effective density of cross-linking, determined experimentally, above the density, found theoretically, is explained by existence besides the chemical secondary physical bonds, determined by the interaction of chains with each other.

Seems at first glance surprising nonconformity to the effective density of cross-linking, determined from these according to stretching ne-swollen specimen/samples and to compression of those swelled. Both these of method are based on the determination of the value of the equilibrium modulus of high elasticity and usually give identical results [185]. However, most frequently this is related to the case when physical bonds are formed by wrappings and couplings of chains, but not molecular bonds. According to [312] the disagreement in the values of the effective density of cross-linking, determined by different methods, is explained by the presence of the solvent which is capable to break secondary physical bonds. It is possible to assume that in our case during test work for compression of the swollen specimen/samples the solvent weakening physical bonds what is prerequisite/premise for their decomosition during strain. In this case, it is necessary to consider the specific character of the structure of the polyurethane chain, in which are alternated the sections of different polarity. The solvents used differently interact with different sections of polymer chains, acting on different physical bonds.

On the basis of data on the effective density of cross-linking, determined theoretically it is experimental, it is possible to approximately estimate the contribution of each bonds to common/general/total network density (Table 36).

Table 35. Comparison of values $\frac{\nu_e}{v}$ and M_c determined by different methods.

ТДЦ, моль (1)	Сшивающий агент, моль (2)	Стехиометрический метод (3)		Сжатие набухших образцов (4)		Растяжение ненабухших образцов (5)	
		$\frac{\nu_e}{v}\cdot10^4$	M_c	$\frac{\nu_e}{v}\cdot10^4$	M_c	$\frac{\nu_e}{v}\cdot10^4$	M_c
1,10	0,035	0,35	33800	0,30	33000	3,2	3700
1,15	0,070	0,50	24000	0,49	25000	3,4	3300
2,20	0,100	0,70	20000	0,51	24000	4,7	2600

Key: (1). mole. (2). Crosslinking agent, mole. (3). Stoichiometric method. (4). Compression of swollen samples. (5). Stretching of non-swollen specimen/samples.

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The value of the effective density of cross-linking in polyurethane of the datum of nature is determined mainly by the physical secondary bonds, which are generated during the reaction of chains with each other.

It is known that the criterion of this reaction is the energy density of cohesion, which we determined by the method of GEE [28], based on the investigation of the swelling of polymers in the series/number of solvents, that were being distinguished by the parameter of solubility in a wide interval. Figure 69 depicts the dependence $\sqrt{\frac{1}{v_1}\ln\frac{Q_{\text{макс}}}{Q}}$ on δ, where $Q_{\text{макс}}$ — a value of swelling (g/g) in the best of the investigated solvents; Q - value the value of swelling for remaining solvents; δ - parameter of the solubility of solvent. Parameter value of solubility for it is polyurethane on the basis of diethyleneglycoladipinate it composes approximately 9.8. To this value corresponds the energy density of cohesion of approximately 96 cal/cm³. This high density tells about the strong interaction of the cuts of polymer chains in grid, bonded with the presence of different physical bonds.

For the approximate estimation of the portion/fraction of physical bonds in common/general/total network density [335] are used the results of the dependence of module/modulus on temperature. It was assumed that with an increase in the temperature the physical bonds dissociate, chemical remain invariable in certain temperature range. The modulus of elasticity they calculated according to the equation

$$g = \left(\frac{\nu_s}{v} + \frac{\nu_e}{v}\right)RT \approx ARTe^{-E_{\text{акт}}/RT} + \left(\frac{\nu_e}{v}\right)RT,$$

where g - modulus of elasticity; $\frac{\nu_s}{v}$ — concentration of secondary bonds; $\frac{\nu_e}{v}$ — concentration of primary ones, or chemical, bonds; $E_{\text{акт}}$ — energy of the activation of bond.

Table 36. Structural components of the effective density of cross-linking for diethyleneglycoladipinateurethane.

Образец (1)	Величина $\frac{\nu_e}{V} \cdot 10^4$ (2)			Сшивка, % (3)	
	химическая (4)	физическая (5)	общая (6)	химическая (4)	физическая (5)
1	0,35	2,85	3,2	11	89
2	0,50	2,90	3,4	15	85
3	0,70	4,00	4,7	16	84

Key: (1). Specimen/sample. (2). Value. (3). Cross-linking, o/o. (4). chemical. (5). physical. (6). common/general/total.

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It is establish/installed, which in polyurethane on the basis of simple and polyesters is contained in dependence on the degree of the chemical cross-linking of elastomers from 20 to 57o/o of secondary bonds. The decrease of chemical cross-linking leads to an increase in the contribution of secondary bonds to common/general/total network density. This logically, since the greater the distance of the chains between nodes, the more flexibility they they possess, as a result of which the larger possible number of contacts of the cuts of chains with each other, of the leading to the formation strong/durable physical bonds.

One should expect change in the contribution of physical bonds to common/general/total network density and during a change in the nature of polyurethane chain, for example oligoester unit. We this showed during the determination of the network density of polyurethane elastomers on the basis of oligoisoprene and oligobutadiene [127] (Table 37).

The values of the effective density of cross-linking, defined experimentally, also, as in the preceding case, exceeded theoretical values, although not to this degree as for diethyleneglycoladipinateurethane. In specimen/samples 4 and 5, it is possible to trace the effect of the nature of oligodiene on the effective density of the cross-linking of the obtained elastomers.

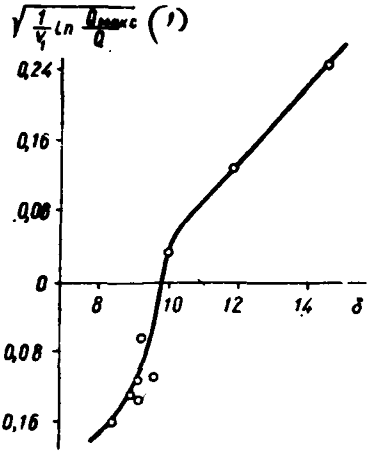

Fig. 69. The dependence $\sqrt{\frac{1}{v_1}\ln\frac{Q_{макс}}{Q}}$ on the parameter of solubility (δ) for specimen/sample 1 (designation see in Table 39).

Table 37. Comparison M_c and $\frac{\eta_e}{v}$ for it is polyurethane on the basis of oligodiene.

Образец (1)	Олигомер (2)	Олигомер : ТДЦ : ТЭА (3)	Теоретически (4)		Экспериментально (5)	
			M_c	$\frac{\nu_e}{v}\cdot 10^4$	M_c	$\frac{\nu_e}{v}\cdot 10^4$
1	Олигоизопрен (6)	1 : 1,2 : 0,100	14800	0,65	10300	0,94
2	То же (7)	1 : 1,3 : 0,133	10250	0,95	5400	1,79
3	» »	1 : 1,45 : 0,234	6000	1,65	3600	2.71
4	» »	1 : 1,68 : 0,400	3600	2,71	3200	3.05
5	Олигобутадиен (8)	1 : 1,68 : 0,400	3600	2,77	2400	4,03

Key: (1). Specimen/sample. (2). Oligomer. (3). Oligomer. (4). Theoretically. (5). It is experimental. (6). oligoisoprene. (7). The same. (8). oligobutadiene.

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The analysis of the data of table 37 shows that polyurethane on the basis of oligobutadiene has the high effective density of cross-linking, than on the basis of oligoisoprene with one and the same quantity of introduced crosslinking agent. It is obvious, the presence in the chain of oligoisoprene of methyl group purely geometrically prevents the formation of the same quantity of secondary bonds as in polyurethane on the basis of oligobutadiene.

Physical secondary bonds make a significant contribution to common network density, but the dominant role in this case belongs to chemical bonds (Table 38). This differs these elastomers from elastomers on the basis of complex oligoether/ester in which the basic contribution to common network density introduce secondary bonds. It is obvious, the presence in the ester unit of carbonyl group leads to emergence in polyurethane on the basis of complex oligoether/ester of a large number of physical bonds as a result of the reaction polar of C=O--group with other functional groups of polymer chains.

From Fig. 70 it is evident that the amount of deflection $\frac{\nu_e}{v}$ experimental from theoretical ones depends on a quantity of introduced crosslinking agent. With the smallest and greatest contents of triethanolamine, experimental value $\frac{\nu_e}{v}$ approaches theoretical.

Table 38. Structural components of the effective density of cross-linking for it is polyuretaane from to the basis of oligodiene.

Образец (1)	Величина $\frac{\nu_e}{v}\cdot 10^4$ (2)			Сшивка, % (3)	
	химическая (4)	физическая (5)	общая (6)	химическая (4)	физическая (5)
1	0,65	0,29	0,94	69	31
2	0,95	0,84	1,79	53	47
3	1,65	1,06	2,71	61	39
4	2,71	0,34	3,05	89	11
5	2,77	1,26	4,03	67	31

Key: (1). Specimen/sample. (2). Value. (3). cross-linking. (4). chemical. (5). physical. (6). common/general/total.

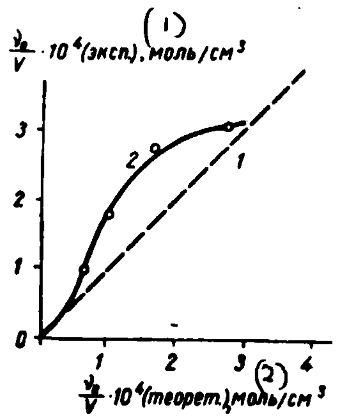

Fig. 70. Comparison of theoretical (1) and experimental (2) values $\frac{\nu_e}{v}$ for polyurethane on basis of oligoisoprene.

Key: (1). (exp.), mole/cm^3. (2). (theoretical), mole/cm^3.

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With the content of triethanolamine from 0.133 to 0.234 mole are observed the greatest deviations. It is obvious, with this content of the crosslinking agent, are created the most favorable conditions for the formation of physical bonds in a three-dimensional grid of such type. But all the same in polyurethane elastomers on the basis of complex oligoether/ester the role of physical bonds is much more than in polyurethane on the basis of oligodiene. It is possible, by this are caused the values of other parameters, for example for it is polyurethane on the basis of oligodiene the energy density of cohesion it is 81 cal/cm^3. The value of the energy density of cohesion for these specimen/samples less than for it is polyurethane on the basis of polyesters, but it is more than, for example, for polybutadiene and natural rubber (66 cal/cm^3). Tensile strengths oscillated in the limits of 10-20 kg/cm^2, ultimate elongation - about 30o/o, while for polyurethane on complex oligoethers it by an order higher (to 700o/o). It is possible, deterioration in the characteristics it is polyurethane on the basis of oligodiene bonded with a smaller quantity of physical bonds in these elastomers in comparison with polydiethyleneglycoladipinateurethane. The sufficiently rapid redistribution of physical bonds in strain contributes, on one hand, greater strength, and on the other hand - to an increase in the maximum length with break it is polyurethane on complex oligoethers.

91 In work [128] is investigated the structure of a grid of the new type of polyurethane-polyurethaneacrylate, obtained on the basis of oligoether/ester, diisocyanates and mono-methacrylic ether/ester of ethylene glycol. The results of the calculations of the contribution of chemical and physical bonds to common/general/total network density it is polyurethane on the basis of polyoxypropyleneglycol of different molecular weight they are represented in Table 39.

Table 39. Structural components of the effective network density of polyurethaneacrylate.

$M_{попг}$	(1) Величина $\frac{\nu_e}{v} \cdot 10^4$			Сшивка, % (2)	
	химическая (3)	физическая (4)	общая (5)	химическая (4)	физическая (5)
400	20,4	234,8	255,2	8	92
400	23,1	331	354	7	93
400	41,5	419,5	461	9	91
1000	14,6	37,3	51,9	28	72
1000	20,7	42,2	62,9	33	67
1000	25,7	54,8	80,5	32	68
2000	11,1	5,8	16,9	65	35
2000	16,1	7,0	23,1	70	30
2000	20	15	35	57	43

Note. $M_{попг}$ - molecular weight of polyoxypropyleneglycol.

Key: (1). Value. (2). Cross-linking. (3). chemical. (4). physical. (5). common/general/total.

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With an increase in molecular weight of initial oligoether, the contribution of physical bonds to common/general/total network density decreases. This is bonded, obviously, with the decrease of the concentration of polar urethane groups per unit of volume and, therefore, with the decrease of a quantity of physical bonds.

Some researchers, noting the large role of secondary physical bonds in polyurethane, consider that the primary meaning in these polymers belongs hydrogen bonds [330, 335]. The last/latter works of Tobol'skiy and of the coworkers [189, 190] according to viscoelastic properties it is polyurethane different nature and copolymers of butadiene with styrene they showed that the role of hydrogen bonds in polyurethane is strongly exaggerated, in any case, during the explanation of temperature transitions. Polyurethane, in the opinion of the authors, one should consider as the block copolymers, moreover with improvement of structural transitions in low-temperature ones region it is necessary to consider the reaction of pliable oligomeric units, and in high-temperature range - rigid. It is obvious, the authors give preference to van der Waals bonds. In the direction of the identification of physical bonds, are necessary further investigations, although the problem this extremely is difficult.

Thus, the special feature/peculiarity of three-dimensional grid it is polyurethane it consists in the fact that it contains a large number of physical bonds together with chemical cross, introduced with synthesis. Sometimes the effective density of the cross-linking of polyurethane elastomers is determined in essence by physical bonds. This specific character of the structure of grid predetermines basic both physico-chemical and mechanical properties is polyurethane.

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Chapter VI.

About the connection between the reaction kinetics of formation, structure and some properties of polyurethanes.

Now no longer are produced doubts, that there is a close connection between the character of supermolecular structures and the physicomechanical properties of polymers. Hence, naturally, appears the problem of learning to rule obtaining one or the other type of structures for purpose of effect on the combination of the physicomechanical properties of polymeric materials.

Before being stopped on questions concerning the formation of supermolecular structures in cross-linked polyurethane, it is necessary to dismantle/select the mechanism of the formation of quite polyurethane grid. There are no works, dedicated to the solution of this problem, virtually. Therefore we is presented the results of investigations in this direction, carried out under the management/manual of T. E. Lipatova.

The special feature/peculiarity the formation of polyurethane grids is the fact that they are form/shaped from the oligomeric molecules which are characterized by the large forces of intermolecular reactions (the hydrogen bond and other means of physical reactions). The formation of supermolecular structures, if it occurs, must occur under conditions for strong intermolecular interactions simultaneously with the course of chemical reaction, which leads as the final result to the formation of the cellular polymer. Berlinyy with coworkers [70] during the study of the three-dimensional polymerization of oligoester acrylates is establish/installed the series/number of the kinetic effects, produced by the preliminary ordering of the chains of crystallizing oligoether/ester and is described the type of the supermolecular structures of polymeric product. In the literature almost there is no information about the interrelation between the kinetic conditions for formation of polymers during the reactions of polycondensation or of step polymerization and the character of supermolecular structures.

First of all, arises the question concerning engendering of supermolecular structures during formation of polymers. In the works of Plate, Kargin and others [35, 108, 159] was placed a question, is the formation of the regulated aggregates of macromolecules in polymerization general regularity and are such the conditions, which facilitate the structurization of polymers. For this purpose, was carried out the electron-microscopic examination of the products of the radiation polymerization of crystalline monomers.

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It is shown, that simultaneously with polymerization occurs the formation of the supermolecular structure of polymeric substance. Usually this of fibrillar type structure with preferred direction with respect to any geometric parameter of initial crystal. Already from the first seconds of reaction, is observed the formation of the fibrillar supermolecular structures of polymers. This, and also establish/installed the authors the dependence of the formation of the specific types of structures on the condition of the course of process it made it possible to make the conclusion that the chemical polymerization reaction and the structurization of polymers are single process and that during the polymerization in solid phase of the studied monomers more preferably occurs an increase not in the separate macromolecules, but immediately the bundles of chains.

In these works is made one additional interesting observation. Supramolecular structures of the polymers, which are generated directly in the course of polymerization, are very close (occur the multistage aggregates of the same morphological forms) to the structures of the same polymers, obtained from solutions. This shows that formation conditions for structures at the torque/moment when macromolecules themselves are built in chemical reaction, are very favorable for the formation of the regulated supermolecular structures.

Researchers' attention was, first of all, directed to kinetics of the formation of polymers and supermolecular structures in them for the crystallizing initial objects both monomeric and oligomeric. However, greatest interest are of amorphous cellular polymers, but for them the bond of kinetics and of supermolecular structures it is not yet investigated.

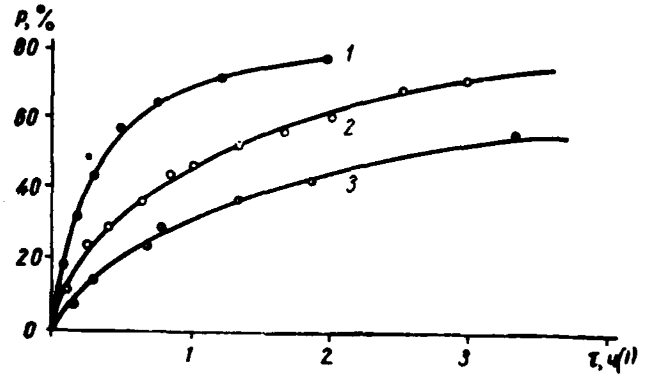

Fig. 71. Kinetic curves of reactions of macro-diisocyanates on basis of PPG-2000 and 4,4'-diphenylmethanediisocyanate with trimethylol propane at different temperatures: 1 — 100; 2 — 80; 3 — 60° C.

Key: (1). h.

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We will examine this based on the example of the mechanism of the formation of the polyurethane grids, obtained on the basis of macro-diisocyanates into which entered glycols of two forms - polyoxypropyleneglycol (PPG) and polytetramethyleneglycol (PTMG) of different molecular weights (500, 1000 and 2000). In all cases for the synthesis of macro-diisocyanates, was used 4,4'-diphenylmethanediisocyanate; trimethylol propane served as the crosslinking agent.

Briefly let us pause at results of the investigation of kinetics the formation of cross-linked polyurethane to the degrees of transformation, close to the point of gel [59].

From Fig. 71 and 72 it is evident that the kinetic curves take the form, characteristic for reaction of second order. As a result of processing kinetic data under the assumption of bimolecular reaction mechanism, it is establish/installed that the reaction rate constant insignificantly or virtually is changed in no way depending on length and chemical nature of ether/esterdiol to degree of conversion of approximately 70o/o (Fig. 73).

In some works [12, 57] it is shown, that in the process of the course of reaction of formation it is polyurethane it occurs the redistribution of hydrogen bonds.

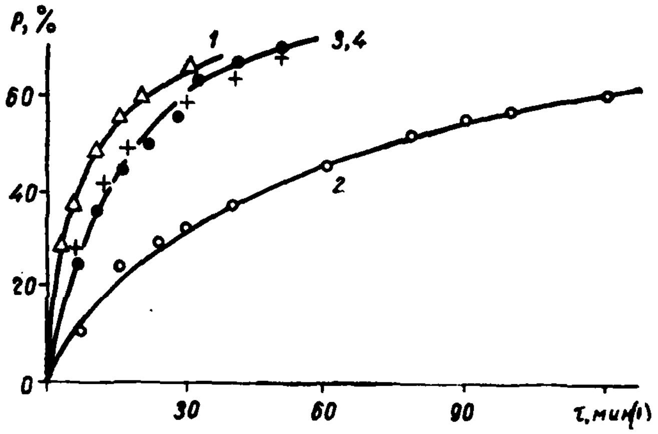

Fig. 72. The kinetic curved reactions of macro-diisocyanates with trimethylol propane at temperature of 80°C on the different bases: 1 - PPG-500; 2 - PPG-2000; 3, 4 - PPG-1000 and PTMG-1000.

Key: (1). min.

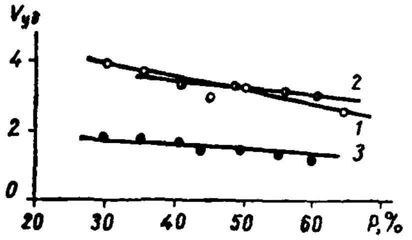

Fig. 73. Dependence of specific rate (equ. NCO/1000 g•min.) of reaction of reaction of macro-diisocyanates on basis of different ether/esterdiol with trimethylol propane on degree of conversion (t=80°C); 1 - PPG-500; 2 - PPG-1000; 3 - PPG-2000.

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This tells about change in the course of reacting intermolecular interactions, which in turn, must affect some physical characteristics of system [60]. The investigation of a change of viscosity of system in the course of reaction showed (Fig. 74)that beginning with degrees of conversion 50-60o/o is observed its sharp increase. In connection with this it was interesting to trace a change of molecular weights in polymerization.

Weight-average molecular weight M_w and z- average/mean molecular weight M_z [145] are determined by the method of approach/approximation to equilibrium of sedimentation on ultracentrifuge G-120 in methylethylketone. By the measured coefficients of forward/progressive diffusion and intrinsic viscosity $[\eta]$ are also calculated the root-mean-square radii of inertia (R^2) and of ratio/relation $(\bar{R}^2)^{1/2}/M_w$ depending on degree of conversion (Fig. 75). In the region of transformation, close to the point of gel, occurs a sharp increase of molecular weights (curves 4 and 5). Increase M_z/M_w indicates the sharp widening of the curve of MVR near to the point of gel. With these results will agree well the viscometric data of the reaction system (see Fig. 74).

On the basis of Fig. 75, it is possible to make following conclusions. Approximately with 60o/o of transformation, begins the intensive process of chain branching. To this, testifies significant decrease $\overline{R^2}/M_w$ (curve 1) with the increase of molecular weight of chains (curves 4 and 5).

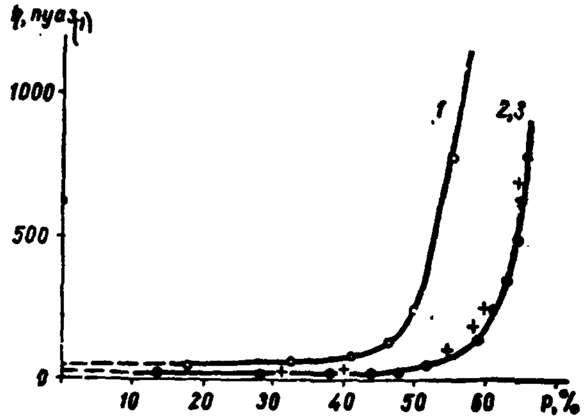

Fig. 74. A change of the ductility/toughness/viscosity of reaction mixture in the course of the process the polymerization: 1 - macro-diisocyanate on basis PPG-500; 2 - macro-diisocyanate on basis PPG-1000; 3 - macro-diisocyanate on basis PPG-2000.

Key: (1). poise.

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About the formation of the strongly branched macromolecules, tells the value of index b in the equation

$$D = KM^b,$$

where D - a diffusion coefficient; M - molecular weight. For all named previously systems b=0.384, which is characteristic for strongly branched polyfunctional chains [145].

Near to the point of gel (beginning approximately with 60o/o of transformation) growth it occurs with the preservation/retention/maintaining of the similarity of particle shape, which is close to spherical. This is confirmed by small decrease of intrinsic viscosity near the point of gel (curve 3) and by decrease of ratio/relation $\bar{R}^2/M_w$ (curve 1).

Near the point of gel, the curve MVR is widened (increase in ratio/relation M_z/M_w, curve 2). The formation of the branched molecules, which is accompanied by a sharp increase of molecular weight, is observed in the comparatively small interval of the variation of degree of conversion. In this case, the growth of molecular weight for percent conversion considerably exceeds designed by theory Flory for the processes of the equilibrium polycondensation of monomers. This it was to be expected, since each event/report of reaction in the case of reactions with oligomers considerably increases molecular weight of the growing chain (to 500-2000 and more) in comparison with the reactions of monomer systems.

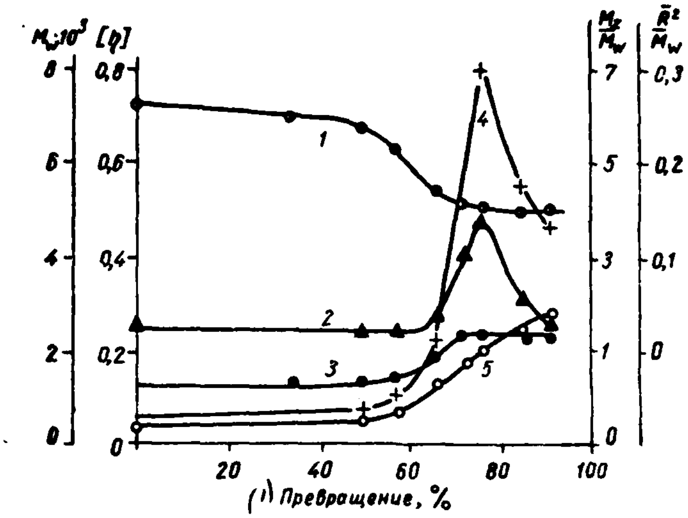

Fig. 75. Some parameters of system depending on degree of conversion:

Key: (1). Transformation.

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A sharply irregular chain growth near the point of gel, apparently, is bonded with the very intensive increase of the ductility/toughness/viscosity of system because of strong intermolecular interactions which are characteristic for it is polyurethane. Hence the grid, which appears immediately after the point of gel, must be characterized by the large nonuniformity of the distances between nodes. In order to check these assumptions, it is necessary to investigate specimen/samples after the point of gel.

For the given systems the point of gel lie/rests at the region 71-73o/o degree of conversion and satisfactorily will agree with the value, calculated according to Flory. The points of maximum in of some curves of Fig. 75 correspond to the point of gel. During the extraction of specimen/samples after the point of gel even with 93o/o of transformation the weight fraction of sol-fraction composes 58o/o. In this case, the gel fraction presents not monolithic system, but microblocks. The completely cross-linked product (during the complete cure the weight fraction of sol-fraction is approximately 4.5o/o) is formed in essence at the quite last/latter stages of reaction as a result of rare chemical cross-linkings between microblocks. The results of the investigation of system after the point of helium (see Fig. 75) indicate the narrowing by the curve of MVR after gel formation. Ratio/relation M_z/M_w virtually becomes equal to initial (curves 2 and 4). Consequently, into gel fraction are drawn in the predominantly strongly branched large molecules. In this case, is continued an increase in the molecules of sol-fraction (increase M_w, curve 5) with the preservation/retention/maintaining of the similarity of form. To this, they testify the invariability of values $[\eta]$ (curve 3) and $\overline{R^2}/M$ (curve 1).

It is logical to expect that a change of the molecular structure of reaction system in the course of polymerization and the appearance in it of cell/elements of grid must affect its relaxation characteristics.

Really/actually, upon transfer from the linear polymer to that cross-linked, is observed increase in vitrification temperature, and also characteristic expansion of an interval of vitrification [160]. In connection with this are measured the parameters of the vitrification of reaction mixture in its solidification which made it possible to reveal/detect/expose some changes in the relaxation properties of system. It is establish/installed, which in the curves of heat capacity in an interval of transition from glassy to liquid state is observed the appearance of a break. Furthermore, occurs the expansion of the temperature interval of vitrification within the limits of the specific degrees of conversion, and then it is not virtually changed to deeper stages (Fig. 76).

In the region of transformations 50-60o/o, is observed the significant expansion of the temperature interval of vitrification, which then is not virtually changed, although the region of vitrification is misaligned to the side of higher temperatures. This shift for macro-diisocyanate on basis PPG-1000 occurs in the limits of transformation 85-95o/o.

The obtained results will agree well with the system characteristics in molecular weights and viscosity. The region of transformations 50-60o/o is characterized by a sharp increase in molecular weight and by the expansion of the curve of MVR, which is developed in the expansion of the temperature interval of vitrification.

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Further, after the point of gel system is exfoliated and appears gel fraction. In this case, the temperature interval of vitrification and the temperature of vitrification are not changed, although occurs the implication in the grid of the large branched molecules and the curve of MVR becomes narrow. Only in the region of transformations 85-95o/o for our example occurs the shift of an interval of vitrification to the higher temperatures as a result of the formation of monolithic grid.

Arises the question concerning that, such as mechanism of the formation of grid after the point of gel and that they are the microblocks, from which is form/shaped the cellular polymer. All given experimental data make it possible to speak about the transition of reaction from homogeneous conditions to micro-heterogenic ones, and then into macro-heterogenic ones. In this case the factor, which are determining the rate the formation of grid, can render/show the interface, and as the final result the reaction rate can be determined the value of this surface. Really/actually, beginning with the specific degrees of conversion reaction it ceases to be subordinated to equation of second order. The application/use of this equation leads to absurd results, although itself process consists only in the reaction of NCO--group with OH-groups.

For explaining laws governing the reaction after the point of gel, is applied calorimetric method [61]. During calculation thermogram they divided in two independent sections: before and after the point of gel. The section of curve after 70o/o of transformation they treated as independent thermokinetic curve, assuming according to Flory [119] that in the point of gel its content is equal to zero, but the part of the product is found in the form of the formations of large complexity with a large number of branchings. These formations can be considered as the centers, around which after the point of gel instantly appear the embryos of three-dimensional structure (microgel). On the basis of these presentation/concepts, for describing kinetics of the formation of cross-linked polyurethane it is possible to apply equation of Avrami - Yerofeyev [30, 165]

$$\alpha = 1 - \exp(-K_0 t^n),$$

where α - share of the substance, which was subjected to transformation; K_0 - specific rate of process; t - time; n - index, depending on geometrically the form of embryo.

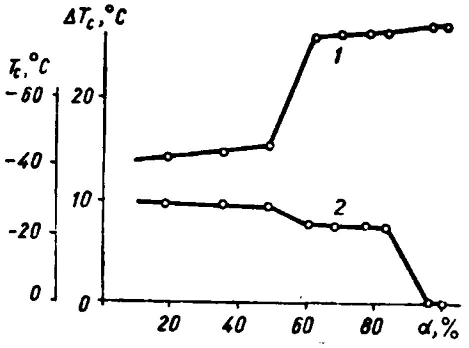

Fig. 76. Dependence of the range of vitrification (1) and of temperature of vitrification (2) from degree of conversion for macrodiisocyanate on base PPG-1000.

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If we for the case of the formation of polyurethane grid by value α imply the share of the substance, which passed over into gel, then, as can be seen from Fig. 77, equation of Avrami - Yerofeyev describes kinetics of the formation of grid after the point of gel. Value n (table 40) in all cases is close to unity, but the specific rate of process at one temperature does not virtually depend on the chemical structure of ether/esterdiol with their identical molecular weights and insignificantly it is changed with the value of molecular weight.

The application/use of equation Avrami - Yerofeyev to the reaction of the formation of polyurethane grids after the point of gel was the attempt to decipher the mechanism of this reaction. The obtained results tell about the fact that the reaction really/actually changes under heterogenic conditions in the specific stage of the formation of polyurethane grids. In connection with this logically arises the question about the fact that they are the particles of microgel, which generate the interface, which, apparently, determines reaction rate after the point of gel.

The electron-microscopic examinations of polyurethane grids showed that they in the majority of the cases (for was polyurethane, obtained through macro-diisocyanates) they are characterized by globular structures [56]. Specimen/samples were remove/taken in the form of replicas with after splitting off after their etching by active oxygen [9].

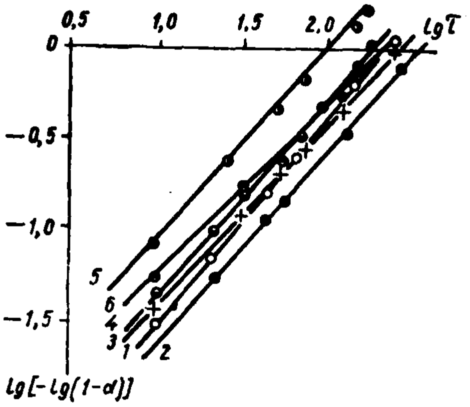

Fig. 77. Results on kinetics of the formation of polyurethane grids in coordinates of Avrami for macro-diisocyanates on the basis of different ether/esterdiol: 1 - PPG-2000, t=70°; 2 - PPG-2000, t=70°; 3 - PTMG-1000, t=70°; 4 - PPPG-2000, t=80°; 5 - PPG-2000, t=90°C; 6 - PP-500, t=70°C.

Table 40. Specific rate (K_0) the formation of cross-linked polyurethane and index n for macro-diisocyanates, obtained on the basis of different ether/esterdiol.

Эфирдиол (1)	(2) Температура процесса, °C	n	$K_0 \cdot 10^{[illegible]}$
ППГ-2000	70	1,00	5,79
	80	1,13	7,29
	90	1,01	15,90
ППГ-500	70	0,95	13,60
ПТМГ-2000	70	1,00	5,40
ПТМГ-1000	70	1,05	7,98

Key: (1). ether/esterdiol. (2). temperature of process.

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Globular formations on photograph (Fig. 78, see insert) have a value approximately by an order more than the value of particles, designed by diffustion method in the course of reaction. This can be bonded with the aggregation of progenitors in more appreciable globular formations [37].

Of all given data it follows that the polyurethane grids, obtained on the basis of macro-diisocyanates, are the globular formations, cross-linked with rare chemical bonds.

Now let us pause at results of electron-microscopic examinations of the polyurethane grids, obtained with different molecular weights of initial diols and their different chemical nature. Figure 79a, b (see insert) depicts the electron-microscope photographs of polyurethane on the basis of macro-diisocyanate, obtained from PPG-2000 both 4,4'-diphenylmethanediisocyanate and trimethylol propane at 60 and 125°C. On them are clearly visible randomly arranged/located globular formations and their rarely arranged/located aggregates. In Fig. 79b concentration of aggregates and their size/dimensions more than in Fig. 79a.

Apparently, an increase in the temperature contributes to the aggregation of globules and, possibly, also to their chemical binding, which must lead to an improvement in the mechanical indices. This really/actually occurs, as can be seen from the results of strength for break (Table 41). With an increase in the temperature of solidification, the strength of specimen/samples increases, remaining, however, sufficient low, which is explained by their globular structure. The relaxation properties of those cross-linked it is polyurethane also they are explained well from the point of view of the formation of globular structures.

During the electron-microscopic examination of the polyurethane specimen/samples, obtained under identical conditions, but on the basis of ether/esterdiol of different chemical structure and identical molecular weight, it is evident (Fig. 80, see insert), that their structures are similar and close the size/dimensions of globular formations.

Table 41. Some mechanical characteristics of specimen/samples it is polyurethane.

Олигоэфирдиол (1)	M_c (2) задаваемое соотношением компонентов	$\sigma_{разр}$, кг/см² (3)	Удлинение % (4)	Температура отверждения, °C (5)
ППГ-500	1000	484	29	80
ППГ-1000	1500	54,3	186,0	80
ППГ-2000	2500	9,6	85	60
	2500	14,0	139	80
	2500	17,0	183,7	125
ППГ-3000	3500	8.2	109	80
ПТМГ-1000	1500	48.3	214,0	80
ПТМГ-1000+1,4-бутандиол (6)	40 000	60,3	984,0	80

Key: (1). oligoether/esterdiol. (2). given by relationship/ratio of components. (3). kg/cm². (4). elongation. (5). temperature of solidification. (6). butanediol.

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The kinetic curves of the reactions, which lead to their obtaining, also are very similar (see Fig. 71). Apparently, with one and the same molecular weights of ether/esterdiol, but with their different chemical nature cross-linked polyurethane have very close structure.

During the comparison of the structures of specimen/samples, it is polyurethane (electron-microscope photographs) on the basis of ether/esterdiol of different molecular weights (Fig. 81, see insert) focuses attention that that the specimen/sample on the basis of diol with large molecular weight (Fig. 81a) virtually has no structure. In specimen/sample on basis PPG-2000, are pronounced the structures in the form of the deformed spherical bodies which consist of the aggregated globules (Fig. 81b). According to mechanical indices "unstructured" specimen/sample is considerably better than the specimen/sample with the clearly expressed structure (see Table 41).

The method of obtaining of cross-linked ones is polyurethane it also affects their supermolecular structure. Polyurethane are obtained using the two-stage method which consists in the fact that they first synthesize macro-diisocyanate on the basis of diisocyanate and ether/esterdiol. Macro-diisocyanate - addition product of two molecules of diisocyanate of two hydroxyl groups of ether/esterdiol. Then macro-diisocyanate by triatomic alcohol is joined into three-dimensional/space grid. In this manner we obtained all specimen/samples. With single-stage method mix in the appropriate relationship/ratios simultaneously all three components.

There is no fundamental difference between kinetics of the course of reaction with mono- and two-stage methods [17]; however, in the structures of such specimen/samples, is noticeable certain difference (Fig. 82, see insert). Polyurethane in both cases are synthesized at one temperature of 80°C on basis PPG-2000. As diisocyanate are taken 4,4'-diphenylmethanediisocyanate, crosslinking agent - trimethylol propane. In the specimen/sample, obtained by single-stage method, virtually lack the signs of structure, whereas the specimen/sample, obtained using two-stage method, has pronounced globular structure. Figure 81b well shows the aggregates of globules, tightly arrange/located relative to each other. According to mechanical indices "single-stage" specimen/sample is better than "two-stage" (see Table 41).

Thus, the data of electron-microscopic examinations will agree with the results, obtained during the study of molecular weights and forms of macromolecules in the course of polymerization. With the formation of cross-linked ones, it is polyurethane directly in the course of step polymerization, probably near the point of gel appear the globular formations which are aggregated depending on conditions of polymerization into more appreciable structural forms. During aggregation can occur the rare chemical cross-linking of formations.

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This is determined the low mechanical strength of the specimen/samples, obtained using two-stage method, and, possibly, also the dependence of mechanical indices on the temperature of reaction and the distance between the nodes of cross-linking M_c.

With the course of reaction using mono- and two-stage methods, the formation of supramolecular structures occurs simultaneously with increase in the molecular chains and formation of microgel. Both of processes are interconnected as for crystallizing monomers [35, 108]. In two-stage process in the beginning of the formation of grid the system, it is probable, more ordered than in single-stage.

The formation of structures in polyurethane systems is caused by strong intermolecular interactions which are characteristic for these systems. With the two-stage method of obtaining, it is polyurethane condition for the realization of intermolecular interactions more favorable than with single-stage. This is connected with the fact that with two-stage method the formation begins in the system, more uniform in molecular weights than with single-stage. Therefore with two-stage method, probably, there is large ordering in system, than with single-stage, which determines differences in ultimate structures.

The given results are proposed to show that in polyurethane, as in other polymeric systems, the kinetic conditions for the formation of polymeric molecules to a certain extent determine the formation of supermolecular structures. The formation of polyurethane grid occurs from oligomeric molecules, which introduces certain specific character into this process.

On the basis entire presented earlier it is possible to formulate series of problems whose solution very is substantial both from the point of view of the development of the theory of the connection of the mechanism of the formation of macromolecules and superstructures and for the administration of the supermolecular structure of polymeric material.

We here note three of them.

1. Study of process of interglobular cross-linking which occurs, apparently, at deep stages of reaction. The solution of this problem is important in connection with the fact that interglobular cross-linking must give to an increase in the mechanical strength of polymeric material. Until now, this process is not virtually studied.

2. Establishment of possibility of cross-linking within globular structures which, according to our opinion, must compulsory occur, and also study of this process. The structure of globular formations and their strength must play large role with deformation of material.

3. Search of conditions, under which oligomeric molecules before

cross-linking would be spread out, and then were fix/recorded by chemical bonds in the form of cross-linked structure. Reaction kinetics in "oriented" state and formation of superstructures under these conditions, until now, is not virtually investigated, although this is important for polymeric chemistry as a whole.