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TRANSLATION

NEW WAYS OF SYNTHESIZING RUBBER

By

B. A. Dolgoplosk

FOREIGN TECHNOLOGY DIVISION

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NEW WAYS OF SYNTHESIZING RUBBER

B. A. Dolgoplosk

The first large-scale industrial production of synthetic rubber became possible thanks to the remarkable work of Academician S. V. Lebedev, who selected butadiene as the basic monomer and developed a simple accessible method for its synthesis.

The method of S. V. Lebedev was put into action for the first time on an industrial scale in our country in 1932. The further vigorous development of investigation work in this field led to the creation in many countries of a huge industry producing various kinds of synthetic rubbers for general and special uses. The production of synthetic rubber now considerably exceeds the gathering of natural rubber.

At first the synthetic rubber appears as a substitute for the natural rubber, being considerably inferior to it in its complex of properties. As time went on the efforts of the chemists were devoted mainly to the synthesis of new kinds of rubbers capable of fully replacing the natural highly elastic material given to us by nature. The final result of these efforts was the synthesis of a rubber analogous in structure and properties to the natural product, accomplished in our country and abroad. However, it is now clear that the copying of nature is not the only nor even the most promising way for creating high-quality materials necessary for the rubber industry.

The synthesis of rubbers for special purposes suitable for preparing varieties resistant to high temperature and destructive media, which do not swell in gasoline and oils, preserving elasticity at low temperatures, resistant to radiation, etc.—this is a special field which confronts the investigators with varied and complicated problems. It is developing with special vigor in recent years in connection with its great significance for modern technology. In the case in question nature has not given us a specimen on the model of which the chemists could construct a molecule of rubber.

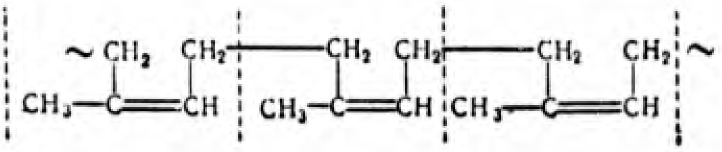
Highly Elastic Rubber for General Use

Because of its very great capacity for very great deformation under the action of a moderate load and quick spontaneous return to its original state when the load is removed rubber as a material for construction has no equal. Some, a very small part of the mechanical energy exerted in deforming rubber, goes for internal friction, which is converted into heat. This mechanical loss is the lesser in proportion as the eleasticity is greater. High elasticity, the greatest essential peculiarity of rubber as construction material, should be attained with sufficient simplicity and with high wearing quality.

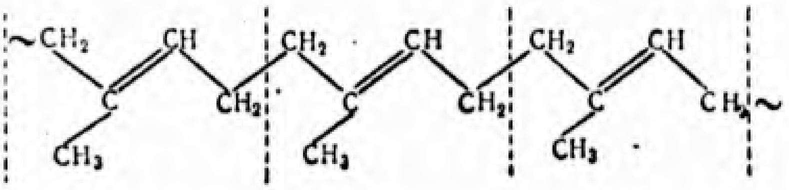
In cooling to a definite temperature characteristic for each given rubber there is a strong limiting of the heat movements of the segments (parts) of the polymer chain, and the elastic rubber becomes hard and brittle like glass. This is the so-called glass point. One of the most important requirements of rubber for general use is the preservation of elasticity and other properties over a broad temperature interval (from —50 to +100°C).

Since the time that the structure of the molecule of natural rubber was determined the chemists by various methods have been trying to synthesize similar materials. The molecules of natural rubber represent a long polymer chain constructed of many thousands of isopreme links. Each such link in turn consists of five atoms of carbon (four of them located in the basic chain) and eight atoms of hydrogen. The molecule of isoprene is a kind of an original brick out of which there are built polymer chains of natural rubber and gutta-percha.

Natural rubber and gutta-percha differ from each other in the spatial arrangement of their atoms in each isoprene link. In the first case the group CH_2 in each link finds itself, as it were, on one side of the double bond (cis-structure of the link) and in the second case these same groups are located on different sides of the double bond (trans-structure of the link):



Natural rubber (cis-polyisoprene)

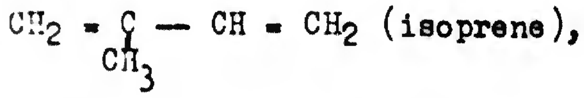


Gutta-percha (trans-polyisoprene)

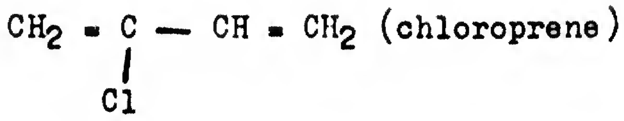
It is just by these peculiarities in the microstructure of the chain that there are determined the differences in the complex of properties of natural rubber and gutta-percha. The one and the other material are characterized by high uniformity of structure of the whole polymer chain (in the natural rubber almost all the links have cis-structure and in the gutta-percha trans-structure).

The uniformity of the structure of the whole chain is of exclusively important significance for the obtaining of the optimum mechanical properties of rubber. Thus in the non-impregnated (without lampblack) rubbers from the natural product the transition of about 20% of the cis-links into the trans-links brings about a sharp drop in the strength. An analogous effect is observed where the uniformity of the structure of the chain in gutta-percha is broken down as a result of the formation in it of about 5% of cis-links. In trying to approximate the structure of natural rubber the chemists selected as the starting monomers different dienes[1] of which the most used were three:

$CH_2 = CH - CH = CH_2$ (butadiene),



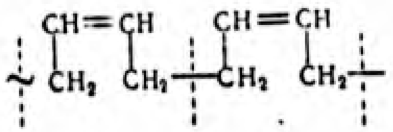
$CH_2 = C(CH_3) - CH = CH_2$ (isoprene),



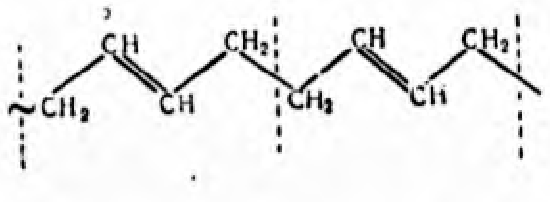
$CH_2 = C(Cl) - CH = CH_2$ (chloroprene)

The industrial methods of the synthesis of butadiene and isoprene are based on the use of products from the processing of petroleum, and chloroprene on the basis of acetylene. The most complicated problems arose in the accomplishment of the process of the synthesis of polymers of molecules from monomers —the process of polymerization. In the accomplishing of it by the ordinary method, for example, in accordance with the chain radical mechanism, the original monomer links are arranged in a chain in different structural modifications. The polymer chain thus formed contains a mixture of chaotically distributed links of different structure.

Let us consider as an example of polymers of butadiene how the properties of the material are changed as depends on the microstructure of the chain. Polybutadiene, in which all the links have cis-structure,



reaches the glass point and becomes brittle at the temperature of —115°C. It, however, with the trans-structure of the links



represents a crystalline material with a melting temperature of about 140°. Polybutadiene in which each link takes part in the structure of the chain by only two atoms of carbon (1,2-polybutadiene),

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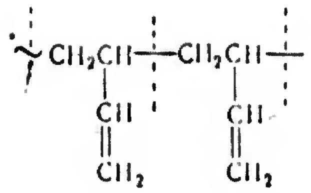
[1] Unsaturated hydrocarbons with two double bonds.

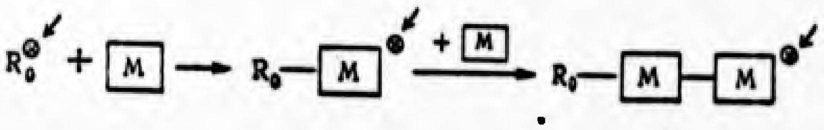


$$\cdots CH_2CH(CH{=}CH_2)-CH_2CH(CH{=}CH_2)\cdots$$

freezes already at 0°.

Rubber SKB, obtained from butadine by the method of Academician S. V. Lebedev, which contains in the chain a mixture of links of different structure, freezes at —53°. The maximum flexibility and elasticity are obtained in the first case. Analogously the structure of the chain and the properties of the rubber change in the polymerization of isopreme and other monomers. From this it follows that for the synthesis of rubbers out of dienes with a given structure of the chain there is necessary the development of such catalystic systems and conditions of polymerization as will make possible for each link the formation of chains only in one definite position. It was necessary to pursue a long and difficult path before there were developed systems of stereo-specific action with the aid of which this problem was solved.

It is known that polymerization proceeds in accordance with a chain mechanism under the influence of active particles whereby each of them brings into the process thousands of original molecules of the polymer (M). If the process goes on under the influence of free radicals or ions the original active center (R^*_0) takes part only in the first step of the joining up of the polymer and it exercises no effect on all of the following steps in the growth of the chain (the arrow indicates the place of the entry of the polymer into the chain).



With such a mechanism of the polymerization there is formed a mixture of different structures with a prevailing content of trans-forms. The possibility of regulating the structure of the link in the chain occurs only when each step of the joining up of the polymer proceeds with immediate participation of the catalyst (K) on the growing end of the chain.

$$\boxed{M}\overset{/}{-}[K] \xrightarrow{+\boxed{M}} -\boxed{M}-\boxed{M}\overset{/}{-}[K] \xrightarrow{+\boxed{M}}$$

The structure of the whole chain is determined by the nature of the catalyst. Now there have been developed catalyst systems that enable one to obtain regularly constructed chains with different structure of the links. Such a stereospecific synthesis requires the use of very pure original monomers, because some admixtures, even in very small quantities, have a great effect on the microstructure of the chain, and thereby on the properties of the rubber. Thus, in the polymerization of isoprene and butadiene under the influence of lithium and lithium-organic compounds admixtures of substances containing oxygen, nitrogen and sulfur lead to a serious breakdown of the uniformity of the chain and to a deterioration of the properties of the rubber.

On the basis of the catalytic systems of stereospecific action there has been accomplished the synthesis of cis-polybutadiene (rubber SKD) and cis-polyisoprene (rubber SKI). The latter is analogous in structure and properties to the natural rubber. In the coming years they will become the basic kinds of highly elastic rubbers for general purposes.

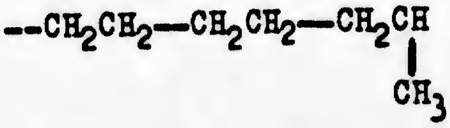
The rubber SKD is inferior to the natural rubber in strength and technological properties. However, it considerably surpasses it in wearing quality and is not inferior to it in elastic properties, which opens up the possibility of wide use of SKD for the making of tires.

The processes of stereospecific polymerization in hydrocarbon solutions, particularly the obtaining of the rubbers SKI and SKD are technologically complicated on account of the high viscosity of the medium and the great thermal effect of the polymerization. Very much to the point is the problem of working up systems which enable one to effect polymerization in aqueous-emulsion media, which will simplify the technology. Indications of the possibility of the principles for the creation of such systems are already to be found in the literature.

On the example of the rubber SKD it is seen that already now there has arisen a real possibility of obtaining highly elastic rubbers which surpass the natural rubber in some important properties. There is no doubt that in the near future there will be synthesized rubbers which will surpass the natural rubber in a broader complex of properties. We are confronted with a real problem of the synthesis of rubbers which will lengthen the service life of tires to that of the automobile itself.

Exclusively high wearing qualities are possessed by polyurethane rubbers. The work in this direction up to the present time has not received sufficient development on account of the great difficulties in the technology of the production of the different rubbers and the high cost of manufacturing.

In recent years progress has been made in the synthesizing of highly elastic rubbers based on the use of cheap raw material, ethylene and propylene, products of the cracking of petroleum. Polyethylene, $CH_2CH_2—CH_2CH_2—CH_2CH_2$, actually a highly elastic rubber with the glass point at about —90°C. However, as a result of the high uniformity of the structure of the chain it finds itself in a crystalline state. In order to convert polyethylene into highly elastic rubber it is necessary to "spoil" its structure, for example, by introducing into the chain in the course of the polymerization some number of "alien" links which hinder the crystallization. It is enough to introduce 25 to 30% of propylene in order to change over completely the material to a rubberlike state.



$$--CH_2CH_2—CH_2CH_2—CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}$$

Rubber from such materials is very resistant to oxygen aging at high temperatures, being superior in this respect to all other known rubbers for general purposes.

The valuable complex of properties along with the accessibility and cheapness of the original raw materials make rubber of this type very promising for a variety of purposes.

In individual cases considerable gain in the properties can be obtained by means of the introduction into the molecule of rubber a small amount of specific groups. If, for instance one introduces one carboxyl group to 400 hydrocarbon atoms of the basic chain, then the rubber will acquire the capacity to be vulcanized by oxides of metals, magnesium, zinc, calcium, and others with the formation with the formation of the peculiar vulcanization lattice. On account of the insolubility of the salts formed on stretching the rubbers there are observed strong orientation effects, which lead to an improvement in the rupture strength and resistance to the expansion of cuts (see table).

Table

Effect of carboxyl groups on the properties of rubber

	Rupture strength of unimpregnated rubbers in kg/cm^2	Resistance to expansion of cuts in lampblack rubbers, Number of cycles
SKS 30	60	130 000
SKS 30-1 (with carboxyl group)	350	> 300 000
SKB	30	25 000
SKB 1 (with carboxyl group)	300	> 360 000
Natural rubber	300	270 000

The gain in the properties in case is attained not on account of the inner structure of the whole molecule of rubber but as a result in the change in the character of the interaction between the molecules of the rubber due to the supermolecular structure. This way also affords definite interest.

Special Rubbers

The development of modern machine construction and reactive technology has required the production of rubber articles which work under conditions of high (from 120 to 400--500°C) and low (to --60°C) temperature. Many of such articles should possess considerable resistance to chemicals, inasmuch as they are used under conditions of corrosive media (in concentrated acids, reactive fuels, strong oxidants, etc.), and they should not noticeably swell in gasolines, oils, and other liquids. The question arises also of the synthesis of radiation-resistant rubbers, capable of standing up against the action of radiation of great intensity, fire-resistant elastometers, etc. For the time being there no ways of synthesizing rubber like polymers which satisfy all these requirements. The efforts of the chemists are directed towards the obtaining of materials in which there would at least be a partial realization of a definite combination of the required properties, in the creation of a great assortment of rubbers of which each proves to be the carrier of some group of properties.

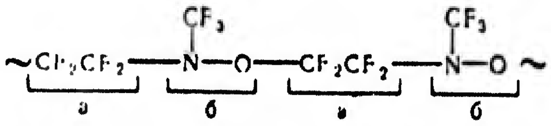
As has already been noted at a determined temperature of the various kinds of rubber they lose elasticity and become brittle. The problem of the synthesis of rubbers resistant to cold, suitable for operation under sever climatic conditions, in the scientific and practical respect has been practically solved. Now the conformities to law are well known that determine the connection between the streucture of the chain and the resistance to cold.

The rubber most resistant to cold is polybutadiene, constructed of a mixture of cis- and trans-links. The presence of some number of trans-links eliminates the crystallization at low temperatures, and makes it possible to bring the temperature of brittleness of rubber down closer to the glass point (--115°). The rubbers synthesized up to the present time can be used, i.e., different ones of them, can be used at temperatures of --50, --70°, and below,

The synthesis of rubbers which do not swell in gasolines and hydrocarbon oils is attained by means of introduction into the polymer chain of some number of polar groups and atoms, for example atoms of fluorine, chlorine, disulfides, nitryls, pyridine groups, etc. Now many rubbers are known which satisfy in this regard the necessary requirements.

A much more complicated and still not satisfactorily solved problem is the synthesis of rubbers which have at the same time high resistance to cold and to gasoline, since the introduction into the chain of polar groups leads to a reduction in the flexibility of the chain because of the increase in the interaction among the molecules and to a lessening of the cold resistance of the rubber. The greatest interest in this regard is afforded by some fluorine rubbers, inasmuch as the gain in the resistance to gasoline in them is connected with a smaller loss in flexibility of the chain.

Of all the problems in the field of the synthesis of special rubbers the most complex turns out to be the obtaining of materials resistant to heat which at the same time are resistant to different corrosive media and maintain their elasticity at low temperatures. All the ordinary rubbers for general purposes in the interval of temperatures 200-250° undergo great irreversible changes connected with the disintegration of the carbon-carbon-bond chain and other structural conversions. The rubber from such materials can work practically only up to the temperature of 150°. Some of the synthesized materials, among them fluoracrylate and fluorized complex polyesters which arecharacterized by little swelling in hydrocarbon solutions can be used at temperatures of 170 to 210°. To this group there is referred also the fluornitrose rubber



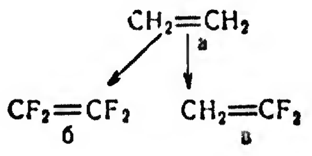
$$\sim \underbrace{CF_2CF_2}_{a} - \underbrace{\overset{CF_3}{\overset{|}{N}} - O}_{\text{б}} - \underbrace{CF_2CF_2}_{a} - \underbrace{\overset{CF_3}{\overset{|}{N}} - O}_{\text{б}} \sim$$

which does not contain atoms of hydrogen and is characterized therefore by very high resistance to corrosive media. Such a rubber consists of consecutively arranged links of tetrafluorethylene (a) and trifluornitrozomethane (b).

The problem of the synthesis of highly heat-resistant rubber for temperatures above 250° in one respect is distinguished in principle from the requirements for the obtaining of high-temperature-resisting plastics. The disintegration of the polymer molecule at high temperatures to a great runs like the process of depolymerization. This signifies that following on the primary step of disintegration of the carbon-carbon-bond chain one observes a gradual process of the breakdown of the molecule with the freeing of a monomer or a more complicated fragment of the chain.

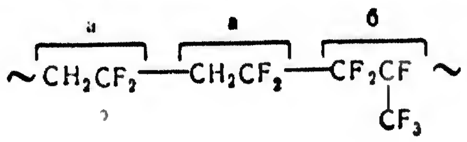
The chain process of disintegration of the molecule at high temperatures easily occurs in rubber like materials and is very difficult in rigid systems (in the glass or crystalline state). Therefore for plastics one often succeeds in getting materials with high resistance to heat on the basis of an ordinary carbon chain if one raises the temperature of the softening of the material. The synthesis of rubbers with high resistance to heat can be accomplished only by means of raising the strength of the chemical bonds in the polymer chain.

Important significance has been attained by fluorine rubbers with a carbon chain in which the heat resistance is combined with chemical inertia.



In ethylene (a) the atoms of hydrogen can be fully or partially displaced by atoms of fluorine (b and c). In the polymerization of these monomers there are formed crystalline materials which fuse at high temperature—$CF_2CF_2CF_2CF_2$—CF_2—CF_2CF_2—(temperature of fusing above 300°), —CH_2CF_2—CH_2CF_2—CH_2CF_2—(temperature of fusing above 100°).

However, these polymers are essentially rubbers since their glass point is below 0°. Their transition into the rubber state is attained by means of breakdown of the uniformity of the structure of the chain through the introduction into the chain of "alien" links. As an example one may cite rubber which has the structure:

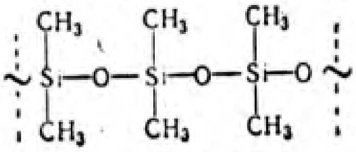


$$\sim\overbrace{CH_2CF_2}^{a}-\overbrace{CH_2CF_2}^{a}-\overbrace{CF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}}^{б}\sim$$

Into the basic chain consisting of the links a there is introduced by means of copolymerization some quantity of "alien" links b which prevents crystallization. The strength of the bond C—F is higher than the strength of the bond C—H.

A great number of atoms of fluorine also heightens the strength of the bond carbon—carbon and imparts to the rubbers high resistance to solvents and corrosive media, but substantially lowers the flexibility of the chain as a result of which they cannot be used for low temperatures but withstand high temperature (150—300°).

For the attaining of rubbers which preserve their elasticity at low temperatures and which are capable of holding out for a long time at a temperature above 250° the most promising way is the synthesis of element-organic polymers. Very important representatives of this group are the silicon-organic rubbers in which the basic polymer chain consists of alternate atoms of silicon and oxygen.



$$\sim\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O\sim$$

The high flexibility of the molecule (temperature of glass point is 123°) is brought about by the peculiarities of the structure of the basic chain.

The tendency of silicon-organic rubbers to crystallization is eliminated by the introduction into the chain of siloxane links with new, for example, phenyl substitutes. In this case rubbers may be obtained which preserve their elasticity up to 90—100°.

Silicon-organic rubbers with a great number of phenyl groups are distinguished by high resistance to radiation. In view of the low temperature of the glass point of rubber it becomes possible to introduce in the hydrocarbon radical a considerable number of atoms of fluorine having preserved a sufficiently high resistance to cold in the material. The fluorosiloxane rubbers can be used at high and low temperatures and swell very little in hydrocarbons.

The rubbers from the silicon-organic products can operate a long time at temperature of 150--300° and for a short time at 350°C. Those rubbers are most resistant to heat which are obtained on the basis of radiation vulcanization. The strength of the rubbers from silicon-organic materials is relatively low, and this apparently is brought about by the convolute form of the chain due to its great flexibility and little intermolecular action.

All the silicon-organic rubbers disintegrate easily under the influence of acids and bases. The heat resistance of this kind of polimers therefore to a great extent depends on the degree of their purification from acids and bases used as catalysts of the process of polymerization.

The problem of the synthesis of rubbers capable under various conditions of for a long time withstanding temperatures above 300° as yet has not been solved. Its solution can be attained not only through the synthesis of new element-organic and inorganic polymers, but also as a result of the use of stabilizers which prevent oxidation and chain disintegration of polymers at high temperatures. The methods of statilization are specific for the polymers of a different nature. It is known, for example, that there is stabilizing action at high temperatures of oxides of iron, lead, and some other metals on rubbers of silicon-organic materials.

The study of the characteristics of the processes of aging of rubbers and the mechanism of the action of stabilizers at high temperatures appears to be very important in the complex of problems connected with the matter of the synthesis of heat-resistant rubbers. For further successful developing of this area, which is vitally bound up with the requirements of the people's economy there is needed a broadening of the searches and the theoretical investigations in various directions.