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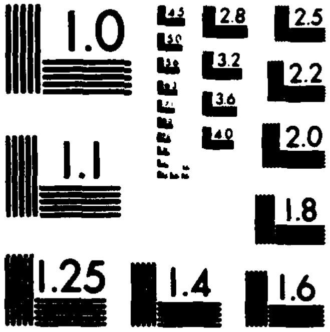

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by

L.B. Peyeva, M.A. Natov

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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
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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 ë in Russian, transliterate as yë or ë.

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

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SPHERULITE SIMILAR STRUCTURES IN AMORPHOUS POLYMERS

L. B. Peyeva, M. A. Natov

On the basis of a number of direct and indirect experimental results, Kargin, Kitaygorodskiy and Slonimskiy examined old concepts ~~[1]~~ were examined and ~~developed~~ a new concept of the structure of a amorphous polymers Was develope ~~[2]~~. According to this concept, amorphous polymers are well ordered systems, which in the glass like, highly elastic and viscous states can be constructed of individual macromolecules in the form of globules or from convoluted macromolecules, which are assembled in fibrillar formations, which are called packets. The existence of a complete unordered state of macromolecules is a rare exception and not the rule. A characteristic feature of the structural formation of amorphous polymers is a tendency to self-spontaneous formation of correct anisotropic with large dimensions and further aggregation to the formation of more complex structures. This tendency to self organization of amorphous polymers has been established for irregular statistical copolymers ~~[3-5]~~, which form geometrically correct

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structure. In the most general case these formations are characterized by optical anisotropic, but they have amorphous defractional aspect of the electron or x-ray rays. An interesting object of study in this direction is polymethylmethacrylate (PMMA). We obtained ~~[8]~~ double ray refracting hexagons in thick films of a mixture of atactic and syndiotactic PMMA, which exhibit amorphous x-rays. In mixtures of PMMA with crystalline polyesters one can observe intermediate structures, which differ in dimensions from spherulites and spherulitic fragments of pure crystallizing polymers ~~[17, 20]~~. They exhibit good macro ordering and optical anisotropic, but the micro ordering of the crystalline lattice is noticeably degraded. The occurrence of these intermediate structures is explained by the simultaneous participation of two kinds of molecules in the structural formation.

Characteristics Viscosities of Fractions of PMMA and NK

(1) Фракция	[η], дл/г	
	(2) ПММА	(3) НК
I	6	4,4
II	4,8	3,6
IV	3,10	2,4
III	1,50	1,5
V	0,25	0,4

Key: (1) Fractions; (2) PMMA; (3) NK.

One could expect that for specific conditions in the presence of a crystallizing polymer as a nucleating agent there is a tendency to aggregation of molecules of the amorphous polymers.

Objects and Method of Study

We studied fractions of PMMA (Diakon brand) and natural rubber (NK).

Characteristic viscosities of fractions of PMMA, which are determined in dichloroethane and 20^{0}, and NK, determined in toluene at 25^{0}, are given in the table.

The structural-optical observations were carried out in a polarization microscope. The temperature, at which the double refraction of crystalline aggregates disappears, is determined in the polarization microscope which is equiped with a heating platform.

The x-ray structural studies were conducted with Cu K_{α}-radiation.

Results of the Discussion

For the formation of super molecular structures in amorphous polymers one requires not only sufficient mobility of macromolecules, but also considerable interaction between them. These conditions are created in polymer solutions. We assumed that correctly formed super molecular structures can be formed with very slow evaporation of the solvent. For this purpose we used vials with polished stoppers, which allow one to carry out valitolazation of dichlorothane and toluene at

30° at a rate on average of 1g/20 days. Into such vials we poured 30 ml each of solutions of different fractions with concentration 0.5, 1 and 1.5%.

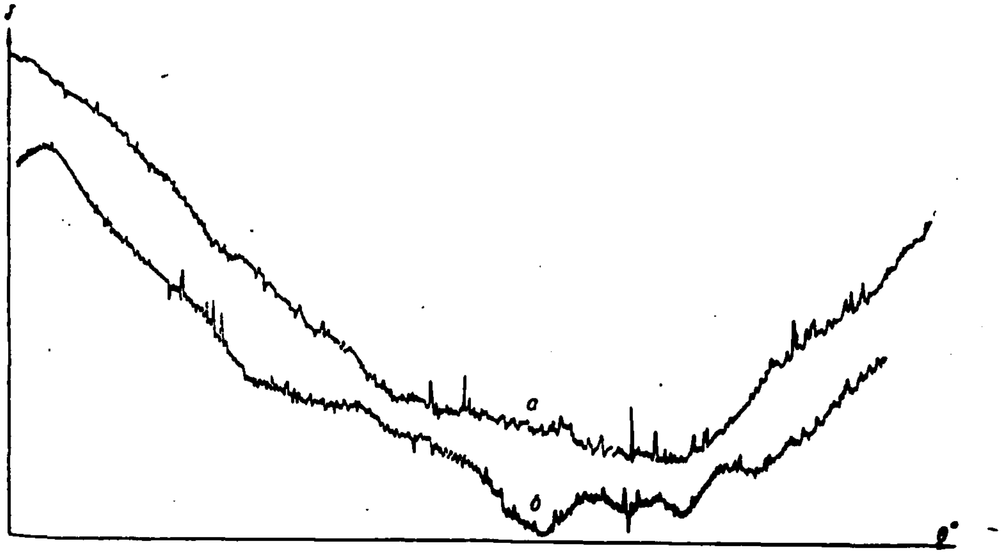

Fig. 3. Scattering curves of x-rays for PMMA (a) and NK (b).

Earlier we added to PMMA solutions as nucleating agents 0.05% polyethyleneadipinate, and to the solution of NK we add 0.05% gutta percha.

Evaporation of the solvent for the described conditions continues from 24-30 months, during which for the major part of the fractions a dense amorphous vitrified mass is formed. However, for low-molecular fractions of PMMA ($[\eta]=1.50$) we obtained large spherulite like structures (Fig. 1, see insert on page 877 [sic]), whose dimensions reached 2 to 3 cm in diameter.

Fig. 4. Infrared spectrum of PMMA.

The Debye gram (Fig. 2, a) and scattering curve (Fig. 3. a) of these structures indicate the absence of crystalline reflexes. The macro ordering disappears at 170-180° and during the action of solvents (acetone, dichloroethane).

Thermal annealing at 100° continued for 4 hours does not change the picture of the macro ordering.

In order to determine which type of PMMA the studied product belongs to, we produced its infrared spectrum (Fig. 4.). The presence of a double line at 1250 cm^{-1} and a weak line at 1060 cm^{-1} indicates that the product contains atactic and syndiotactic polymers, and also their mixture does not contain the isotactic polymer [9].

Similar dendrite like structures were produced for lower molecular fractions of NK ($[\eta]=2.4$) (Fig. 5), for which amorphous picture of the x-rays is characteristic (Fig. 2, b and 3, b) in the presence of intense double refraction in the polarization light. This ordering disappears in the temperature range 80 - 85° and during the action of solvents (toluene, benzene).

The production of these large spherulite like structures confirms the concept that the amorphous polymers represent highly ordered systems.

Obviously, the mutual ordering of long polymer chains in the amorphous state under specific conditions can be done to such a high degree that it can lead to the production of structures, which are similar to crystal structures. It is completely possible that the formation of the observed spherulite like structures was stimulated by the orientating action of molecules of the crystallizing polymer, which was introduced in minimal amounts into the solution, and that the relatively identical length of macro molecules in each of the fractions is favorable to the formation of such super molecular structures.

Conclusions

1. We derived spherulite like amorphous structures, which are characterized by intense double refraction in polarization light.

2. It is shown that amorphous polymers have a tendency to self-spontaneous formation of correct anisotropic structures of large dimensions.

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