Translated from *Uspekhi Khimii*, **57**, 134-148 (1988)

Steric Structuring of Polyolefins by Chemical Methods

U.D.C. 678.74.01:53:541.459

I.V.Konoval, N.G.Konovalenko, and S.S.Ivanchev

The present state of the problem of the steric structuring of polyolefins by chemical cross-linking agents (organic peroxides, azo-compounds, and organo-silanes) is examined. The structure formation mechanisms, the process conditions, the requirements which must be met by cross-linking agents, the factors determining the properties of cross-linked polymers, as well as the prospects for the development of the method are discussed.
The bibliography includes 28 references.

CONTENTS

I. Introduction 72
II. The mechanism and kinetics of the cross-linking of polyolefins by chemical methods 72
III. The requirements which must be met by cross-linking agents 76
IV. The conditions in the structure formation processes 77
V. The constitution and properties of compositions undergoing cross linking 77
VI. Conclusion 80

I. INTRODUCTION

The steric structuring (cross-linking) of polyolefins is one of the principal ways of modifying their structure, which makes it possible to improve their operating characteristics and to extend the temperature range and types of applications of polyolefins.

Steric structuring is achieved by different methods: by radiation or ultraviolet light or with the aid of chemical cross-linking agents. The radiation structuring method does not as a rule require the introduction of special additives into the polymer. However, its application requires cumbersome and expensive apparatus and the maintenance of safety conditions. At the present time chemical structure formation is the commonest and most convenient procedure in practice and is employed in two principal versions: (1) the cross-linking of polyolefins with the aid of radical-forming agents (peroxides and azo-compounds) and (2) the cross-linking of polyolefins by organosilanes. The structuring of polyolefins by peroxides has been known for a long time. Organosilanes began to be used for this purpose more than 10 years ago, while azo-compounds have been applied only in recent years.

Despite the evident advances in the industrial use of chemical structuring, the theoretical aspects of the problem, in particular, the kinetics and mechanism of the process have not as yet been duly developed. The point is that the cross-linking reaction of polyolefins occurs either in the solid polymer or in its melt. It is known[1] that the structural-physical state is the most important factor influencing the chemical process in polymers. Structural microinhomogeneity of polymers is due to the inhomogeneity of the distribution of additives and reactants in the polymer system, the spatial localisation of the physical processes and chemical reactions in certain regions of the polymer, and also the dependence of the kinetic parameters on the kinetics of the molecular motions and molecular-relaxation properties of the polymer.[1] However, the kinetics and mechanisms of chemical structuring have so far been scarcely investigated from these standpoints.

There are extensive literature data concerning the structures and properties of cross-linked polyolefins, their relation with the initial compositions, and the determination of the kinetic parameters for the decomposition of peroxides and for the structure formation process. However, a considerable proportion of the results are unsuitable for the analysis of the state of the problem.

II. THE MECHANISM AND KINETICS OF THE CROSS-LINKING OF POLYOLEFINS BY CHEMICAL METHODS

The mechanism of cross-linking by radical forming agents has been investigated only in relation to organic peroxides. According to existing ideas,[2] it includes radical formation by the homolytic decomposition of the peroxide, the transfer of the radical activity to the polyolefin macromolecule by the abstraction of a hydrogen atom from the latter, and the recombination of the polyolefin macroradicals with formation of carbon–carbon cross-links:

$$I \xrightarrow{k_1} 2\dot{R}\,, \tag{1}$$

$$\dot{R} + PH \xrightarrow{k_2} \dot{P} + RH\,, \tag{2}$$

$$\dot{P} + \dot{P} \xrightarrow{k_3} P{-}P\,, \tag{3}$$

Apart from the three main elementary reactions, there is a possibility of the occurrence of radical side reactions, for example, the radical-induced decomposition of the peroxide, the fragmentation of the macroradicals, their interaction with low-molecular-weight radicals, disproportionation, etc.:

$$\dot{R} + I \xrightarrow{k_4} \dot{R}' + R{\sim}\,, \tag{4}$$

$$\dot{P} + I \xrightarrow{k_4} \dot{R}' + P{\sim}\,, \tag{5}$$

$$\dot{P} \xrightarrow{k_5} P_{=} + \dot{P}'\,, \tag{6}$$

$$\dot{P} + \dot{P} \xrightarrow{k_3'} \text{products of disproportionation of macroradicals,}$$

$$\left.\begin{aligned} \dot{P} + \dot{R} &\xrightarrow{k_7} \\ \dot{R} + \dot{R} &\xrightarrow{k_8} \end{aligned}\right\} \text{products of the recombination and disproportionation of radicals,} \tag{7, 8}$$

where $P_{=}$ is a macromolecule with a double bond.

The rate-limiting stages of the cross-linking process are the consecutive reactions (1) and (2). Part of the peroxide, decomposing via a mechanism other than the unimolecular mechanism, is effectively lost as regards the structuring process.[3] The presence or absence of the induced decomposition is determined by the nature of the cross-linking agent, other conditions being equal.

From the standpoint of the final result, two elementary reactions are decisive: the recombination reaction (3) and the degradation reaction (6) of the polymer radicals. Depending on the structure of the polymer radicals, reaction (3) leads to linear growth, branching, or cross-linking of the macromolecule; reaction (6) entails degradation. The preferential occurrence of each of these reactions depends to a large extent on the efficiency of the steric structuring process, i.e. on the number of cross-links arising in the polymer as a result of the decomposition of one peroxide group. For example, in polyethylene the polymer radicals almost always recombine with formation of cross-links. Polymers containing tertiary carbon atoms tend to undergo degradation.

The study of the transformations occurring on decomposition of benzoyl peroxide in polyethylene, polypropylene, and polyisobutylene made it possible to derive general kinetic equations, which take into account the possibility of the simultaneous occurrence of the structuring and degradation reactions in polyolefins.[4]

1. For the unimolecular decomposition of the peroxide [reaction (1)]:

$$\Delta n = K_s[I]_0(1 - e^{-k_1 t})/k_1 - K_d\{[I]_0(1 - e^{-k_1 t})/k_1\}^{1/2} .$$

2. For the chain composition of the peroxide [reaction (4)]:

$$\Delta n = K_s \frac{2.303 \lg \{e^{k_1 t}(k_c[I]_0/k_1 + 1) - k_c[I]_0/k_1\} - k_1 t}{k_c} - K_d\left\{\frac{2.303 \lg \{e^{k_1 t}(k_c[I]_0/k_1 + 1) - k_c[I]_0/k_1\} - k_1 t}{k_c}\right\}^{1/2} .$$

3. For the chain decomposition of the peroxide [reaction (5)]:

$$\Delta n = K_s \frac{2k_1}{k_c^2}\left[(a+1) - \frac{A(a+1)}{A(a+1) - a} - 2.303 \lg \frac{A(a+1) - a}{A}\right] - K_d\left\{\frac{2k_1}{k_c^2}\left[(a+1) - \frac{A(a+1)}{A(a+1) - a} - 2.303 \lg \frac{A(a+1) - a}{A}\right]\right\}^{1/2} ,$$

where Δn is the change in the concentration of bonds in the polymer, $K_S = k_1 k_3/(k_3 + k'_3)$ the structuring constant,

$$K_c = k_1^{1/2} k_6/(k_3 + k'_3)^{1/2}$$

the degradation constant, k_c the rate constant for the chain decomposition of the peroxide, $[I]_0$ the initial peroxide concentration, t the time, $a = k_c[I]_0^{1/2}/k_1$, and $A = e^{k_1 t/2}$.

The equations take into account, on the one hand, the possibility of both the unimolecular and chain decomposition of the peroxide and, on the other, various types of radical termination. However, these equations are nevertheless specific in character and, like the mechanism presented above [reactions (1)–(8)], did not take into account the structural-physical characteristics of the polymer, its molecular weight distribution, and the role of the cage effect in the system and of the delay transfer in the transport of the reacting species—radicals and molecules. The necessity to take these factors into account is indicated by experimental data. For example, the rate of radical reactions in low density polyethylene (LDPE) is higher by two orders of magnitude than in high density polyethylene (HDPE).[5] The introduction of identical amounts of the cross-linking agent, other conditions being equal, leads to the formation of a larger number of cross-links in HDPE than in LDPE (Fig. 1).[6]

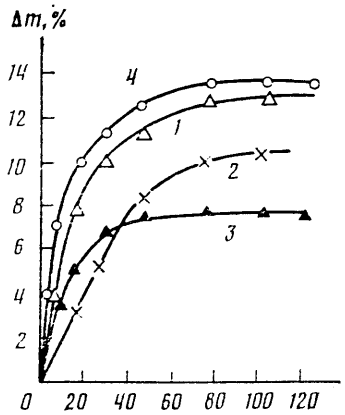


Figure 1. Kinetic curves for the swelling (at 140 °C) in *p*-xylene of HDPE (curves *1*–*3*) and LDPE (curve *4*) specimens cross-linked by di-t-butylperoxyisopropylbenzene. The content of peroxide (%): 1) 1.5; 2) and 4) 2.0; 3) 3.0.

Table 1. The efficiency of the cross linking of linear polyethylene (d = 0.960 g cm^{-3}) by dicumenyl peroxide at the initial gel formation point (at 150 °C).[7]

Polymer	$10^{-3}M_w$	M_w/M_n	c^{**}, mmol kg^{-1}		Efficiency of cross linking***, %
			experiment	calculation	
1	79.0	9.0	42	12.6	30
2	70.0	10.0	50	14.3	29
3	81.0	12.5	55	12.3	22
4	61.0	5.0	63	16.4	26
5	60.0	4.0	66	16.7	25
6	40.0	5.0	77	25.0	32
7	58.0	8.0	68	17.3	25
8	60.0	6.0	70	16.7	24
9	95.0	3.0	33	10.5	32
10	49.5	2.7	70	20.0	29
C	60.0	3.5	22	16.7	76
H	52.0	6.0	81	19.3	24

*Polymers 1–10 contain less than 0.07 of a vinyl group per 1000 carbon atoms. The mixture of polymer 10 with dicumenyl peroxide was freed from oxygen in an atmosphere of nitrogen before the reaction. Polymer C contains 0.5 of a vinyl group per 1000 carbon atoms and H represents the hydrogenated polymer.

**Here c is the concentration of dicumenyloxy-radicals.

***The ratio of the calculated and real peroxide concentrations at the beginning of gel formation.

The study of the characteristic features of the cross linking of linear polyethylene[7] in the presence of dicumenyl peroxide showed that the efficiency of cross linking, the yield of the product of the thermolysis of the peroxide, and the preferential occurrence of one of the competing reactions are

significantly influenced by the presence of a vinyl group in the system, whose carriers may be both the peroxide decomposition products and the polyolefin. This is expressed, in particular, by the considerable discrepancy between the theoretical amount of cumenyloxy-radicals, calculated from the Flory–Stockmayer relation, and its experimental amount ensuring the same efficiency of cross linking[7] (Table 1). The kinetic parameters of the cross linking by peroxides depend on the concentration of active oxygen in the system, the nature and concentrations of the components, and the process temperature (Fig.2).[6] Furthermore, the rate of cross linking and the yield of the cross-linked polymer are influenced by the pressure;[8] it may be that the observed effect is caused by the decrease in the activation volume of the reaction.[9]

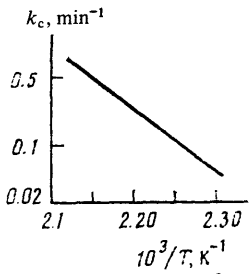


Figure 2. Temperature dependence of the rate constant for the cross linking of polyethylene with the density $d = 0.960$ g cm^{-3}.[6]

The examples considered clearly indicate the imperfection of the existing ideas about the mechanism of the cross linking of polyolefins by organic peroxides, as they fail to take into account a whole series of significant factors.

The cross linking of polyolefins by azo-compounds has been studied still less. It has been assumed for a long time[10] that azo-compounds cannot serve as initiators of the cross linking of polyolefins, because the radicals formed on decomposition of the majority of them [via reaction (1)] are incapable of abstracting hydrogen from the polyolefin macromolecule. However, when the polymer system contains double bonds (ethylene–propene–diene copolymers, their mixtures with saturated polyolefins, etc.), structuring can occur as a result of the addition of primary radicals with dissociation of double bonds according to the mechanism[10]

$$R + CH_2{=}CH{-}R'{-}CH{=}CH_2 \rightarrow R{-}CH_2{-}\dot{C}H{-}R'{-}CH{=}CH_2 ,$$

$$R{-}CH_2{-}\dot{C}H{-}R'{-}CH{=}CH_2 + PH \rightarrow R{-}CH_2{-}CH_2{-}R'{-}CH{=}CH_2 + \dot{P} ,$$

$$R{-}CH_2{-}\underset{\dot{P}}{CH}{-}R'{-}CH{=}CH_2 + P \rightarrow R{-}CH_2{-}\underset{P}{CH}{-}R'{-}CH{=}CH_2 ,$$

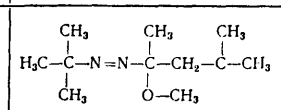
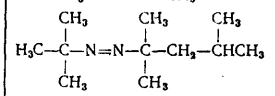
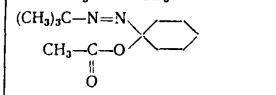
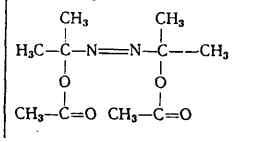
$$R{-}CH_2{-}\underset{P}{CH}{-}R'{-}CH{=}CH_2 + \dot{R} \rightarrow R{-}CH_2{-}\underset{P}{CH}{-}R'{-}\underset{\dot{R}}{CH}{-}CH_2{-}R ,$$

$$R{-}CH_2{-}\underset{P}{CH}{-}R'{-}\underset{\dot{P}}{CH}{-}CH_2{-}R + P \rightarrow R{-}CH_2{-}\underset{P}{CH}{-}R'{-}\underset{P}{C}{-}CH_2R .$$

Thorough investigation of the mechanism is still to come, but it is already clear that the use of azo-compounds makes it possible to avoid degradation [reaction (6)] in the structuring of polyolefins containing tertiary carbon atoms. Furthermore, additional possibilities arise for increasing the efficiency of the action of the cross-linking agent as a result of the use of mixtures of azo-compounds, or regulating the duration and extent of the structuring process, etc.[10] Table 2 presents certain azo-compounds recommended for the cross-linking of polyolefins.

Whilst having a series of undoubted advantages, which include high strength of the finished article, resistance to cracking and the action of organic solvents and mechanical stresses at high temperatures, the possibility of varying its properties over a wide range, the uniformity of its structuring throughout its volume, etc., cross linking by radical forming compounds also suffers from significant disadvantages. In the first place, one should note the possibility of the premature cross linking of the material already in the stage where the cross-linking agent is introduced into the polymer. Another disadvantage is the limited choice of methods suitable for the preparation of the finished articles and the compositions undergoing cross linking. The use of organosilanes as cross-linking agents makes it possible to eliminate some of these disadvantages and provides a fundamentally new solution to the problem.

Table 2. Azo-compound cross-linking agents.[10]

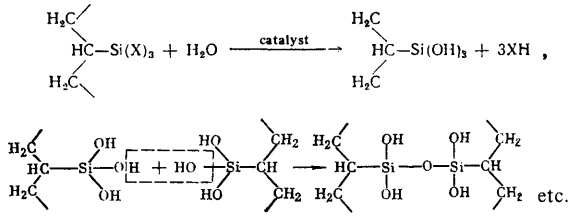
Name		Formula	Temperature, °C	
chemical	commercial		τ = 10 h	τ = 12 h
2-t-Butylazo-2-methoxy-4-methylpentane	Luazo-135		135	155
2-t-Butylazo-2,4-dimethylpentane	Luazo-148		148	168
1-t-Butylazo-1-acetoxycyclohexane	Luazo-165		165	187
2,2-Azobis-2-acetoxypropane	Luazo AP		189	215

Notation: τ is the decomposition half-life of the azo-compound.

The mechanism of the cross linking pf polyolefins by organosilanes has been described in the literature in the most general form and we are unaware of any far reaching studies on the process kinetics. According to the available data, the cross linking of the polyolefins includes two main reactions: the grafting of the organosilane of the type $R_nSIX_{(4-n)}$ to the polyolefin and subsequent structuring of the modified polymer in the presence of water and a hydrolysis catalyst[11] [X = hydrogen, a halogen, or a radical (alkyl, aryl, arylalkyl, cycloalkyl, alkylamine, arylamine, etc.); R = radicals with olefinic double bonds containing 2–12 carbon atoms; n = 1, 2]. It has been suggested[12] that the grafting of the silane to the polyolefin can be represented as follows in a general form:

$$\sim CH_2{-}CH_2{-}CH_2 \sim + RSi(X)_3 \rightarrow \sim CH_2{-}\underset{Si(X)_3}{\overset{H}{C}}{-}CH_2 \sim ,$$

and the second stage can be represented schematically by



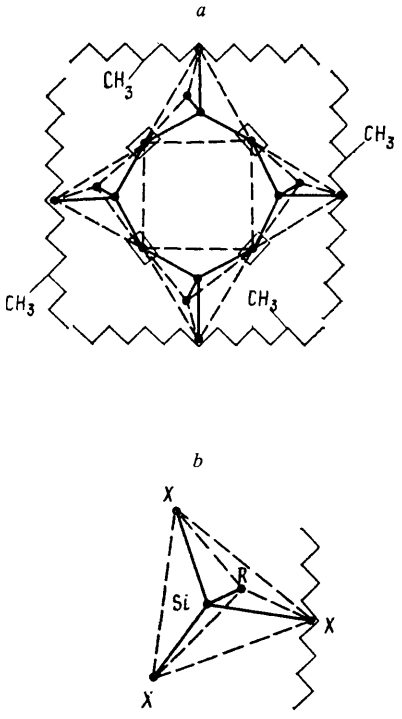


Figure 3. The configuration of the cross-linking nodes: *a*) the node linking four macromolecules, the centres of the intermolecular interaction of the silane substituent being indicated by rectangles; *b*) schematic illustration of the position of substituents capable of participating in the cross-linking process.

A polyolefine modified by silane is a polyfunctional compound which constitutes a kind of cross-linking centre capable of binding several macromolecules at once. Under these conditions, the four substituents in the silane molecule capable of being joined to macromolecules and to one another form a tetrahedron with the silicon atom at the centre (Fig.3*b*).[13] In the polymer there are usually three reactive substituents. However, as can be seen from Fig.3*a*, on average only two substituents are involved in the structuring process. Structuring by silanes results in the formation of polymers whose properties differ from those of polyolefins cross-linked by organic peroxides, which is caused to a large extent by the difference in the nature of the cross-link (–Si–O–Si–C instead of –C–C–) and in the functionality of the nodes of the network.[13]

The silane is usually grafted to the polyolefin by the mechanochemical degradation method using one of the familiar procedures for the processing of polymers. The best results have been obtained in a Banbury blender and on a rolling machine.[12] The conditions in the mechanical treatment depend on the type of polymer, its molecular weight, the required degree of grafting, and the type of equipment.[11] The efficiency of the grafting process can be increased by introducing into the polymer substances capable of generating free radicals (peroxides and azo-compounds). The content of the radical forming compound is determined by the type of polyolefin and the required degree of grafting, but it should not be so large that the polymer is cross-linked.

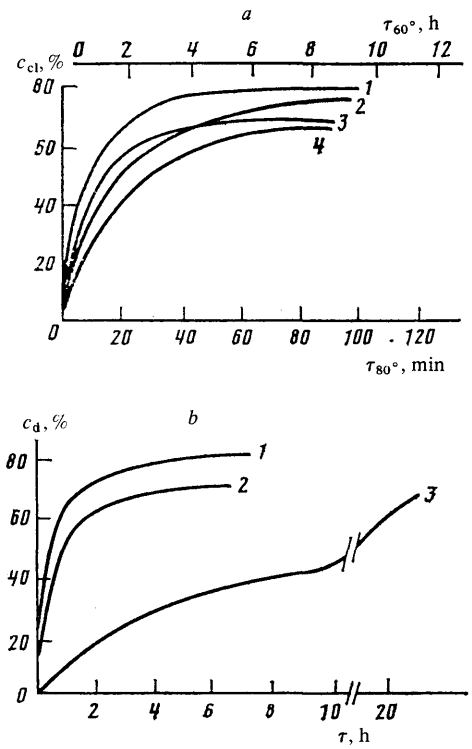
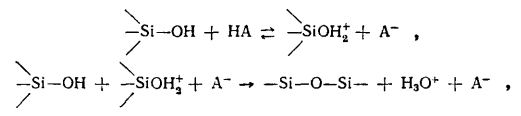


Figure 4. Dependence of the content of the cross linked-fraction c_{cl} in the composition on the structuring process conditions: *a*) Moldex S-181 in water: 1) at 80 °C; 2) at 60 °C; 3) and 4) Moldex S-161 under analogous conditions [$\tau_{60°}$ (h) and $\tau_{80°}$ (min) are the times during which the compositions are kept in water at 60° and 80 °C]; *b*: 1) Moldex S-181 at 40 °C and 90% humidity; 2) Moldex S-161 under the same conditions; 3) Moldex S-161 at 25 °C [τ is the exposure time (h)].[12]

The polymer modified with a silane is hydrolysed by atmospheric moisture even at room temperature. Nevertheless, in order to accelerate the reaction, the cross linking is frequently carried out in an aqueous medium at 40–90 °C in the presence of a catalyst or by treatment with water vapour at a temperature ≥100 °C. The limiting cross-linking density achieved under these conditions does not then change (Fig.4). The hydrolysis catalysts can be inorganic

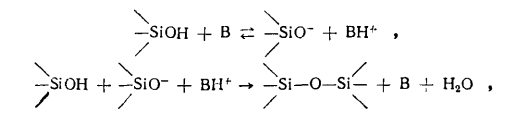
and aliphatic acids, organic bases (ethylamine, dibutylamine, and piperidine), orthotitanate esters, chelates, and metal carboxylates. Depending on the nature of the catalyst, the following mechanisms have been proposed for the formation of the siloxane linkage:[12]

(a) in the presence of acids:



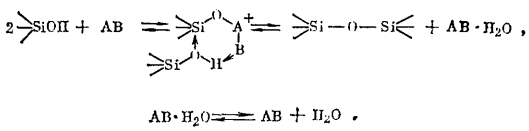
where A is the acid anion;

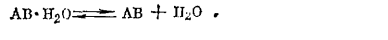
(b) in the presence of alkali:



where B is the base;

(c) in the presence of neutral salts:





Among the multiplicity of catalysts for cross linking by organosilanes, preference is given to organotin compounds such as dibutyltin dilaurate, dibutyltin diacetate, and dibutyltin dioctanate. These compounds are neutral salts, exhibit a high catalytic activity, and do not generate a corrosive medium.[11,12]

The grafting and structuring stages can be combined by introducing into the system additives forming water in the course of their chemical interaction with the components of the system.[12] Polyolefins with any density and any parameters of the fluidity of the melt can be subjected to structuring by organosilanes.

III. THE REQUIRMENTS WHICH MUST BE MET BY CROSS-LINKING AGENTS

The essential requirements which must be satisfied by the agents for the cross linking of polyolefins are determined primarily by the mechanism of the cross-linking process, its kinetic features, and the way in which it is achieved. Furthermore, there exist a series of technical and economic requirements, common to all types of chemical cross-linking agents: stability and low volatility under the conditions where they are combined with the polymer, volatility and lack of toxicity of the thermolysis products or the products of the interaction with the components of the composition, and ready availability of the raw material; for radical forming agents, a high rate of decomposition (decomposition half-life 4–6 min) at a temperature exceeding by 40–60 °C the temperature at which they are introduced into the polymer is sufficient.

Reactions (1) and (2) determine the principal requirement which must be met by peroxides as cross-linking agents: the ability to generate radicals which are sufficiently active in reactions involving the abstraction of hydrogen from the polymer chain. It is known that the activity of radicals in hydrogen abstraction reactions depends both on their intrinsic structure and on the structure of the elements of the macrochain.[7,8] In the cross-linking reactions of polyolefins, it is preferable to use peroxides generating alkoxy-radicals on decomposition. The study of the behaviour of a series of asymmetric peroxides of the type R–O–O–R′ in a cross-linking process showed that t-butyl cumenyl peroxide exhibits the maximum efficiency. Its decomposition results in the formation of t-butoxy- and cumenyloxy-radicals, which decompose in their turn to methyl radicals and correspondingly to acetone and acetophenone.

Among peroxides with different structures—peracids, peracetals, perketals, peresters, hydroperoxides, and dialkyl and diacyl peroxides—tertiary dialkyl peroxides satisfy most fully the requirement specified. The optimum conditions for the technological cross-linking process and the optimum characteristics of the cross-linked polyolefins are ensured by dicumenyl peroxide, which is widely used on an industrial scale. The mechanism and kinetics of its thermal decomposition have been studied in fair detail.[14] The formation of the highly toxic actophenone in the thermolysis of dicumenyl peroxide has led to the search for other peroxides combining all the positive qualities of dicumenyl peroxide with the absence of toxic decomposition products. Such cross-linking agents proved to be certain bifunctional peroxides. The recommended temperatures of their mixing with the polymer (T_{mix}) and the cross linking temperatures (T_{cl}) as well as the efficiencies (f) of the cross linking of LDPE are indicated below:[15]

	T_{mix}, °C	T_{cl}, °C	f
Di-t-butyl peroxide	up to 100	150	–
Dicumenyl peroxide	up to 120	160	0.61
1,3-Di-t-butylperoxyisopropylbenzene	up to 130	170	–
1,4-Di-t-butylperoxyisopropylbenzene	up to 130	170	–
n-Butyl-4,4′-di-t-butylperoxyvalerate	up to 110	150	–
1,1-Di-t-butylperoxy-3,3,5-trimethylcyclo hexane	up to 100	140	–
2,5-Di-t-butylperoxy-2,5-dimethylhexane	up to 130	170	0.29
2,5-Di-t-butylperoxy-2,5-dimethylhex-3-yne	up to 130	170	0.74

The possibility of the cross linking of polyolefins by two-component cross-linking systems generating radicals in the course of the oxidation-reduction reaction is of definite interest. The cross-linking system consisting of a hydroperoxide and a variable valence metal ion may serve as an example.[16] The low activation energy for the interaction of the hydroperoxide with a variable valence metal ion makes it possible to carry out the structuring process at lower temperatures and to avoid the premature cross linking of the polymer. The rate of the process can be regulated by varying not only the temperature but also the content of the metal. The advantage of such systems, consisting in lowering the temperature of the cross linking process, proved at the same time to be their disadvantage, since they can initiate structuring only during the preparation and formation of the mixtures. However, this principle of the formation of macroradicals ensures contact between the components via diffusion at the required stages of the process. When it is applied to the preparation of thin-layer materials, the cross-linking temperature is appreciably reduced, which makes it possible to cross-link polyethylene films at temperatures which do not induce their deformation.

The *meta*- and *para*-isomers of di-t-butylperoxyisopropylbenzene or their mixture (peroxymon) have come to be most widely used. The diperoxy-derivatives of ketones and tri- and tetra-peroxides of different structure can be used as cross-linking agents.[17] However, the methods of their synthesis are as a rule complex, the raw materials are difficult to obtain, and the polyolefins cross-linked by them do not manifest any significant advantages in their properties. For this reason, the above group of peroxides can be of interest only for the investigation of the influence of the

structure and functionality of the peroxide on the mechanism and kinetics of the cross-linking process. The hypothesis that the bifunctional di-t-butylperoxyisopropylbenzene can be more efficient in the cross linking of polyolefins than dicumenyl peroxide has not been confirmed experimentally.[18]

Subsequently it was shown[19] that there is a possibility of the stepwise decomposition of peroxy-groups in diperoxides. The activation energy for the decomposition of the second peroxy-group is greater (E_1 = 152 kJ mol^{-1}, E_2 = 161 kJ mol^{-1}) and the rate of decomposition is lower—$k^1_{\text{decomp}} = 58 \times 10^{-5}$ s^{-1} and $k^2_{\text{decomp}} = 30 \times 10^{-5}$ s^{-1} at 150 °C (for comparison, we may recall that the values determined under analogous conditions for dicumenyl peroxide are E = 153 kJ mol^{-1} and $k_{\text{decomp}} = 53 \times 10^{-5}$ s^{-1}).[19] The observed features are due to the differences in the structures of the peroxide complexes and in the stability of the radicals formed on decomposition of the first and second peroxy-groups.[19] These differences cause the reduced efficiency of the cross linking of polyolefines in the presence of di-t-butylperoxyisopropylbenzene compared with dicumenyl peroxide in the temperature range 140–160 °C. An increase in temperature reduces the difference.

It had been postulated earlier that the mechanism of the thermal decomposition of peroxides remains unchanged on passing from model systems to the polymer.[20] However, in the light of the existing ideas about the mechanisms of solid-phase reactions,[1] this hypothesis must be regarded as erroneous and as associated with the low accuracy of the experiment.

Specific requirements which must be met by cross-linking agents are closely related to the problem of the introduction and decomposition of radical-forming compounds in polyolefins.

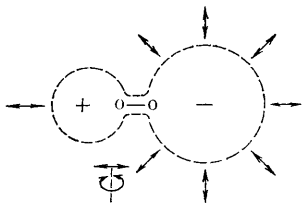
IV. THE CONDITIONS IN THE STRUCTURE FORMATION PROCESSES

Radical-forming cross-linking agents can be introduced into polyolefins by different methods: (1) by stirring into a polymer melt, (2) by the diffusion method, (3) by dry mixing, and (4) by the internal synthesis of the cross-linking agent.[21] As an example of the use of the last method, one may quote the synthesis of di-t-butyl peroxalate from tetraalkyl hydroperoxide and oxalyl chloride directly in the bulk of the polymer.[23]

Silanes can be introduced into the polymer melt or can be dispersed on the surface of the polyolefin. Hydrolysis catalysts are introduced into the composition in different ways: before the start of the reaction involving the grafting of the silane to the polyolefin, during this reaction, or after it has been completed; by mixing the components; by diffusion; by treating the grafted copolymer with an aqueous suspension, emulsion, or solution of the catalyst.[11]

Until recently, only thermolysis has been used to decompose the peroxide into the free radicals. The application for this purpose of an ultrahigh frequency electromagnetic field (microwave mixing or, what amounts to the same thing, UHF mixing, UHF cross linking) has opened up new possibilities.[22] Cross linking by exposure to a UHF field can be achieved in three ways.

1. Decomposition in the UHF field of peroxides, for example, t-butyl peroxybenzoate or di-t-butyl peroxyterephthalate. The peroxide decomposes as a consequence of the instantaneous absorption of energy from the UHF field, usually at a frequency of 2450 MHz, in accordance with the scheme



2. The use of weakly polar peroxides and auxiliary substances highly active in a UHF field, such as halogenohydrocarbons, carbon black, triallyloxy-*s*-triazine, etc. The molecules of the auxiliary substances absorb the energy of the UHF field and transmit it to the peroxide molecules. The polymer composition being cross linked in the UHF field is heated uniformly to the temperature at which the thermal composition of the peroxide begins.[21]

3. The use of auxiliary substances highly active in a UHF field and of weakly polar products forming complexes with them. As a result, the peroxide molecules are always in the immediate vicinity of the molecules of the auxiliary substances which transmit to them the absorbed energy from the UHF field, so that the thermolysis of the peroxide is possible at a lower temperature of the polymer.

There is as yet little information in the literature about the mechanism of the microwave cross linking, the decomposition of peroxides in a UHF field, and the effect of auxiliary additives, the kinetic process parameters, etc. Only the influence of the nature of the peroxide and of the auxiliary additives on their activity in the UHF field and on the degree of structuring of the polyethylene has been noted and the dependence of the rate of cross linking on the concentration of the peroxide, the initial temperature of the polymer composition, and the duration of the action of the UHF field has also been observed.[22,23] Nevertheless, the advantages of the method of the microwave cross linking of polyolefins are already evident: the decreased energy requirement for the process, the decrease in the length of the industrial production line and of the cooling zone, and the possibility of cross linking a thick-walled article. Furthermore, the decomposition of polar peroxides to weakly polar products has a favourable effect on the dielectric characteristics of the structured polymers (when di-t-butyl peroxyterephthalate is used for polyethylene, the tangent of the dielectric loss angle tan $\delta = 1.5 \times 10^{-4}$ at 20 °C and a frequency of 100 Hz, while the dielectric constant is $\varepsilon = 2.34$).[22] The possibility of cross linking articles regardless of their thickness is the main advantage of the method and is responsible for its vigorous development and industrial application.[22]

V. THE CONSTITUTION AND PROPERTIES OF COMPOSITIONS UNDERGOING CROSS LINKING

The influence of the constitution of the compositions undergoing cross linking on their properties can be examined fully enough only in relation to polyolefins structured by organic peroxides, since these have been most thoroughly investigated.

A real composition undergoing cross linking is a complex polymer system, which contains as a rule stabilisers, accelerators, fillers, and modifying agents which are not always inert towards the cross-linking agents or free radicals. The antioxidant preventing degradation is an obligatory component of cross-linking compositions based on polyolefins. The structuring and inhibited thermal oxidation reactions

proceed via a radical mechanism, so that, when the polymer contains simultaneously a peroxide and an antioxidant, the latter interacts with the radicals formed on decomposition of the cross-linking agent. The reaction products inhibit the cross-linking reaction and reduce the efficiency of the structuring process. Apart from reactions (1)–(8), there is then a possibility of the occurrence of the following elementary reactions:[20]

$$\dot{R} + YH \xrightarrow{k_9} \dot{X} + RH \quad (9)$$

$$\left.\begin{aligned} \dot{Y} + \dot{Y} &\xrightarrow{k_{10}} \\ \dot{P} + \dot{Y} &\xrightarrow{k_{11}} \end{aligned}\right\} \text{reaction products.} \quad (10), (11)$$

For the steric structuring by peroxides, the relative reactivity of the antioxidant can be estimated with the aid of the relation (Fig.5):[20]

$$\left(\frac{[i]}{[i']}\right)^{1/2} = rk\frac{[YH]}{[PH]} + k$$

where [YH] and [PH] are the amounts of the antioxidant in the polymer (moles), k is the ratio of the rate constants characterising the cross-linking reactions of the stabilised and unstabilised polyolefins, r is the relative reactivity of the antioxidant, and [i] is the amount of peroxide which induces the formation of the same number of cross-links in the unstabilised polyolefins as the amount [i'] in the stabilised polyolefin.

Thus the relative reactivity of the antioxidant can be estimated from the ratio of [i] and [i']. The reactivity of antioxidants of the phenolic type is higher than that of antioxidants of the amine type. The values of r and k for the polyethylene–dicumenyl peroxide system are presented below; the data obtained using 1,3-di-t-butylperoxyisopropylbenzene are indicated in brackets:[23]

	r	k
N-Cyclohexyl-*N*-phenyl-*p*-phenylenediamine	60	1.02
NN'-Diphenyl-*p*-phenylenediamine	90	0.97
NN'-Dinaphthyl-*p*-phenylenediamine	160(280)	0.99(0.90)
2,2'-Methylenebis(6-t-butyl-4-methylphenol)	540(600)	0.91(0.86)
4,4'-Thiobis(6-t-butyl-3-methylphenol)	1500	0.83

In order to intensify the peroxide cross-linking process, one may introduce into the composition cross-linking coagents, whose role is usually fulfilled by sulphur or polyfunctional monomers [divinylbenzene, trialkyl cyanurate, tri(hydroxymethyl)propane trimethacrylate, pentaerythrityl tetramethacrylate].[2]

The introduction of a filler also influences the kinetic structuring parameters, since the rates of the elmentary reactions occurring on the filler surface and in the bulk of the polymer are different.[21] This difference is caused by the selective adsorption of the reactant at the interface and by the involvement in the reactions of the functional groups of the filler. The adsorption interaction of peroxides with the filler surface may be abolished by introducing additives (for example, poly-1,2-dihydro-2,2,4-trimethylquinoline) which are adsorbed first on the filler surface.

Fillers containing on their surfaces acid centres (carbon black, kaolin, etc.) induce an ineffective (non-radical) decomposition of the peroxide. This reduces the efficiency and density of the cross linking and the physicomechanical characteristics of the structured polymer are altered (Table 3).

Table 3. The physicomechanical characteristics of cross-linked filled LDPE (d = 0.917 g cm^{-3}, dimethyl peroxide content 2.5 wt.%).[17]

Filler	c_f, %	σ_b, MPa	l, %	$\Delta\Sigma$*, %
—	—	14.5	500	45.0
Chalk	10.0	12.0	350	30.0
Chalk	20.0	13.5	300	23.0
Talc	10.0	11.0	360	23.0
Kaolin	20.0	8.0	120	83.0
Kaolin	30.0	9.0	100	60.0

Notation: c_f is the content of the filler, σ_b the breaking stress on extension, l the relative elongation at rupture, and $\Delta\Sigma$ the deformation under a load of 5 N at 200 °C.

*The cross-linking density was estimated from the degree of deformation.

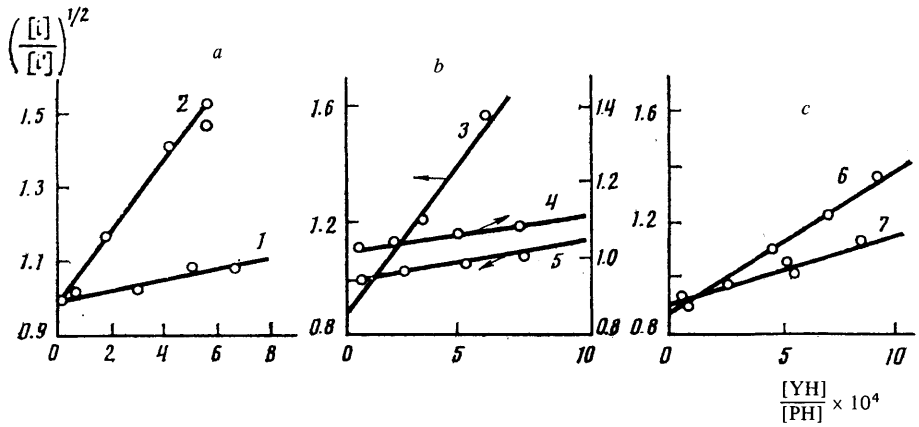


Figure 5. Dependence of $\{[i]/[i']\}^{1/2}$ on the antioxidant/polyethylene concentration ratio;[20] cross-linking agents: *a*) and *b*) dicumenyl peroxide; *c*) 1,3-di-t-butylperoxyisopropylbenzene; antioxidants: 1) and 7) *NN'*-dinaphthyl-*p*-phenylenediamine; 2) nickel dibutyldithiocarbamate; 3) 4,4'-thiobis(6-t-butyl-3-methylphenol); 4) *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine; 5) *NN'*-diphenyl-*p*-phenylenediamine; 6) 2,2'methylenebis(6-t-butyl-4-methylphenol).

The properties of cross-linked polyolefins are determined by a multiplicity of factors, the most important of which is the cross-linking parameter. In a number of studies, use has been made of the concept of the cross-linking density, which is either identical with the concept of the cross-linking parameter or is expressed as (a) the concentration of the effective chains, (b) the number of cross-linking sites referred to 1000 carbon atoms, and (c) the molecular weight of the section of the chain included between two nodes (M_C).[6,13]

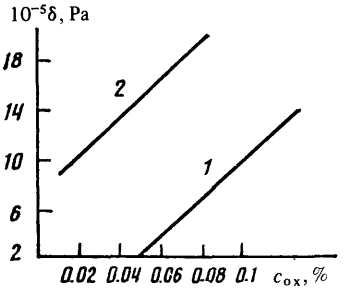


Figure 6. Dependence of the cross-linking density (estimated from the modulus of shear δ) of polyethylene with different densities on the content of active oxygen c_{ox} in the system: 1) d = 0.924 g cm^{-3}; 2) d = 0.960 g cm^{-3}.

The cross-linking parameter of polyolefins is determined by the process temperature, the concentration of active oxygen (Fig.6), the structural-morphological characteristics of the polymer, and the nature and concentration of other ingredients of the composition.[24] With increase in the cross-linking parameter, the relative elongation[24] and density of the polyolefins decrease (Fig.7) (according to Voight,[13] the relative elongation does not change) and their deformability by mechanical loads also diminishes (Fig.8). The content of the gel fraction changes little as the cross-linking density is varied (Fig.9). The point is that, even for low values of the latter, the extractable part of the polymer is small. Theoretically two cross-linking nodes per mass-average macromolecule are sufficient for the formation of an insoluble gel, but, depending on the molecular weight distribution (MWD) of the polyolefin, the content of the gel fraction may be different for the same cross-linking parameter.[25]

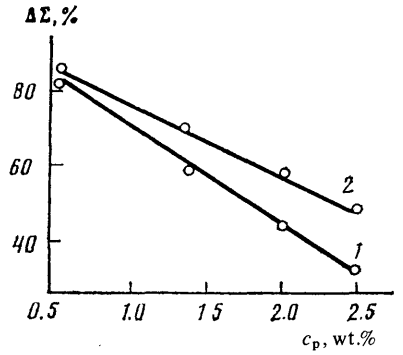


Figure 8. Dependence of the degree of deformation ΔΣ of cross-linked LDPE under a load of 5 N at 200 °C on the peroxide concentration c_p: 1) 2,5-di-t-butylperoxy-2,5-dimethylhexane; 2) 2,5-di-t-butylperoxy-2,5-dimethylhex-3-yne.

Since the main field where cross-linked compositions are used is the electrotechnical industry, it is necessary to know the factors determining their dielectric characteristics. These include the content, volatility, and polarity of the components of the polymer composition. An increase in polarity and a decrease in volatility impair the dielectric parameters.

The degree of crystallinity and the size of the unit cell of the cross-linked polyolefin are independent of the type and content of the peroxide.[26,27] Thus, whereas the degree of crystallinity is about 65% for LDPE (d = 0.917 g cm^{-3}), the value for the same polymer cross-linked in the melt by 2,5-di-t-butylperoxy-2,5-dimethylhexane or 2,5-di-t-butylperoxy-2,5-dimethylhex-3-yne is 33–37% for a peroxide concentration in the composition of 0.5–4.5%. The average size of the crystallites is 70 Å.[27] It is of interest to elucidate whether the structuring process occurs preferentially in the amorphous or crystalline phases of the polymer. So

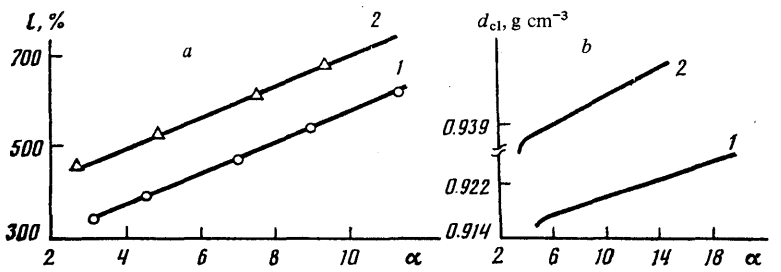


Figure 7. Dependence of the relative elongation l (a) and the cross-linking density d_{cl} (b) of cross-linked polyethylene with different densities [1) d = 0.924 g cm^{-3}; 2) d = 0.960 g cm^{-3}] on the swelling coefficient α determined at 140 °C.[6]

far there is no unanimous view concerning the character of the distribution of the cross-links between the phases of polyolefins. However, there is hardly any point in considering the probability of the occurrence of the structuring process in a particular phase[28] in those cases where it takes place in the polymer melt and the phase structure is established after the completion of the structuring process on cooling the specimen.

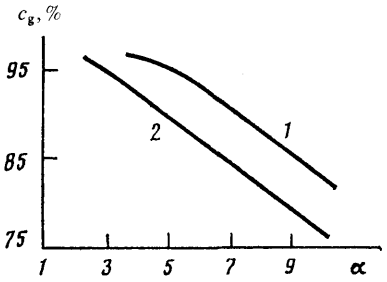


Figure 9. Dependence of the content of the gel fraction c_g in polyethylene with different densities on the swelling coefficient α:[6] 1) d = 0.960 g cm^{-3}; 2) d = 0.924 g cm^{-3}.

VI. CONCLUSION

We examined above the current state of the problem of the steric structuring of polyolefins by chemical methods. The questions of the technology, the specificity and importance of which require special consideration, were not considered.

At the present time, it is evident that the method of cross linking polyolefins or organic peroxides in the thermal decomposition of the latter occupies a leading position as regards its industrial application and practical value. It is also the method which is the most thoroughly investigated. The successive development and improvement of this method requires, firstly, the study of the mechanism of the thermal decomposition of organic peroxides in polyolefins and model hydrocarbons for the critical analysis of the mechanism adopted for the structuring process; secondly, the development and organisation of the industrial manufacture of effective new-generation structuring agents are needed. It is also useful to investigate the structuring effect of mixtures of organic peroxides as one method for increasing the efficiency of the process and for improving the technology.

From the standpoint of industrial application, the structuring of polyolefins by organic peroxides in the course of their decomposition by a UHF field is the most advanced application. The development of this application requires the study of the kinetics and mechanism of the microwave cross linking and the development and industrial application of polar peroxides.

The method of structuring polyolefins by organosilanes has a series of undoubted advantages, which has led to its vigorous industrial application (approximately 25 companies are engaged in this problem in Western Europe alone), despite the fact that it has been comparatively little studied. However, the method has limited applicability, mainly for the cross-linking of thin-walled articles, for example, in the manufacture of tubes, oriented films, packing materials with an increased resistance to moisture and corrosive media and with a reduced gas permeability, and for the insulation of wires and cables. The mechanism of structuring by organosilanes and the composition–structure–properties relation have been little investigated.

Overall, the compositions undergoing cross linking should be the subject of vigorous studies on the basis of modern theoretical approaches and using modern methods for the investigation of the kinetics, structures, and properties of polymers, which will ensure the successful development of this field and the preparation of materials with valuable properties.

REFERENCES

1. N.M.Emanuel' and A.L.Buchachenko, "Khimicheskaya Fizika Stareniya i Stabilizatsii Polimerov" (The Chemical Physics of the Ageing and Stabilisation of Polymers), Izd.Nauka, Moscow, 1982, 356 pp.
2. A.G.Sirota, "Modifikatsiya Struktury i Svoistv Polimerov" (Modification of the Structures and Properties of Polymers), Izd.Khimiya, Leningrad, 1985, pp.138, 139.
3. R.Rado and M.Lazar, "Macromolecular Compounds" (Translated into Russian), 1961, Vol.2, p.310.
4. R.Rado, "Macromolecular Compounds" (Translated into Russian), 1962, Vol.4, p.1746.
5. A.Charlesby, D.Libby, and M.Ormerod, Proc.Roy. Soc., 1961, **A262**, 207.
6. E.Köhulen, Kunstoffe, 1970, **60**, 883.
7. G.E.Hulse, R.J.Kersting, and D.R.Wurfel, J.Polym.Sci.Polym.Chem.Ed., 1981, **19**, 655.
8. J.Boer and A.J.Penning, J.Polymer, 1982, **23**, 1944.
9. S.G.Entelis and R.P.Tiger, "Kinetika Reaktsii v Zhidkoi Faze" (Kinetics of Reactions in the Liquid Phase), Izd.Khimiya, Moscow, 1974, p.242.
10. C.J.Runiec, V.R.Kamath, and C.S.Sheppard, Polymer.Prepr., 1981, **22**, 116.
11. N.G.Konovalenko, L.B.Klimanova, E.D.Safronenko, and E.I.Evdokimov, Plast.Massy, 1878(11), 9.
12. T.P.Khvatova, E.D.Safronenko, L.B.Klimanova, and Yu.I.Firsov, "Sshivanie Poliolefinov Organosilanami" (The Cross-Linking of Polyolefins by Organosilanes), Izd.NIITEKhIM, Moscow, 1980, 17 pp.
13. H.U.Voight, Kaut.und Gummi, Kunst., 1976, **29**, 17.
14. H.Market and R.Wiedenman, Siemens Forsch.-Entwicklungsber., 1973, 2, 85.
15. V.L.Antonovskii, "Organicheskie Perekisnye Initsiatory" (Organic Peroxide Initiators), Izd. Khimiya, Moscow, 1972, p.395.
16. J.Chodak and R.Rado, J.Polym.Sci.Polym.Symp., 1975,
17. S.S.Ivanchev, N.G.Ivanova, and E.I.Evdokimov, Plast.Massy, 1978(7), 16.
18. G.Ballini and A.Portolany, Atti Congr.Intern.Mat. Plast., 1963, **15**, 247.
19. V.I.Myshkovskii, Z.N.Nudel'man, and V.L.Antonovskii, Kauchuk i Rezina, 1980(10), 20.
20. D.Simunkova, Plast.Hmoty and Kauc., 1970, 7, 207.
21. S.S.Ivanchev, "Radikal'naya Polimerizatsiya" (Radical Polymerisation), Izd.Khimiya, Leningrad, 1985, p.198.

22. G.Menges, K.Kircher, B.Franzhoch, and W.Hoffacker, Kunststoffe,, 1979, **69**, 430.
23. D.Simunkova, Plaste und Kaut., 1971, **18**(2), 92.
24. R.Hummel, Kaut. und Gummi., 1968, 21(2), 240.
25. V.P.Zamotaev, Plast Massy, 1986(11), 10.
26. P.Komitov, P.Kartalov, B.Mikhnev, and Kh.Polizov, Nauch.Trudy Plovdiv.Univ., Fiz., 1978/1979, **16**(2), 77.
27. N.G.Ivanova, A.S.Glebko, E.I.Evdokimov, et al., Plast.Massy, 1976(8), 49.
28. R.S.Kashaev, V.P.Prokop'ev, V.Ya.Deverdeev, et al., Vysokomol.Soed., 1984, **B26**, 115.

The Okhtinsk "Plastpolimer"
Scientific-Industrial
Association, Leningrad