VC
PVC Degrad?

Liquid-Phase Degradation of Poly(Vinyl Chloride)

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The main kinetic regularities of the thermal and thermal-oxidative degradation of poly(vinyl chloride) (PVC) in the liquid phase have been analyzed in comparison with the solid-phase degradation of PVC. The thermal (in an N_2 atmosphere) degradation of PVC in the form of dilute solutions is characterized by a number of essential distinctions, the primary peculiarity consisting of a lower dehydrochlorination rate due to the retarded reaction of the formation of $\diagdown C{=}C \diagup$ bond polyconjugated systems. The same is observed for the thermal degradation of PVC plasticized with di- and polyesters. On the contrary, in an oxygen-containing atmosphere the solvents promote PVC decomposition. Accelerated PVC degradation under such conditions is due to the solvent oxidation that causes the appearance, within the system, of products activating the PVC macromolecular decomposition. The intensified degradation processes are accounted for, in the first place, by an increased reaction rate of the statistical (by the random law) detachment of HCl from normal macromolecular units. In general, the kinetics of the thermal-oxidative liquid-phase degradation of PVC is determined by the partial pressure of oxygen in the reaction zone, by the quantity of the solvent introduced into the polymer, as well as by the oxidative stability of the solvent. It has been shown that an effective stabilization of PVC in the liquid phase, particularly in the systems highly plasticized with esters, can be achieved through stabilizing the solvent, first of all, rather than the polymer, against oxidative decomposition. In this case the PVC dehydrochlorination rate decreases sharply and may reach an essentially lower value than under similar conditions of the solid-phase thermal degradation of PVC. PVC stabilization with respect to the reaction of HCl elimination achieved through the solvent stabilization against thermal-oxidative decomposition has been called the effect of "echo-stabilization" of PVC.

INTRODUCTION

Up to the present the most important kinetic data on the degradation and stabilization of poly(vinyl chloride) (PVC) have been obtained through the study of the polymer decomposition in the solid phase (powder, films). The process of PVC degradation in solution has far less been considered, practically no investigations on the problem of the phase influence on the PVC dehydrochlorination process being under way. Meanwhile, this is an interesting problem from the theoretical and practical point of view with reference to the wide application of PVC materials obtained on the basis of strong (plasticates) or relatively dilute (fiber) solutions.

The main reaction in PVC degradation is the hydrogen chloride detachment from the polymeric macromolecules, the PVC dehydrochlorination process being complicated and including: a) statistical (by the random law) HCl elimination from normal sequences of vinyl chloride units proceeding at the rate V_r and accompanied by the formation of single internal $\diagdown C{=}C \diagup$ bonds within the macromolecules; b) propagation of polyconjugated systems of $\diagdown C{=}C \diagup$ bonds (at the rate V_p) due to activation of the reaction of HCl elimination by labile conjugated carbonylallyl groups structured as ~~C(O)—CH=CH—CHCl—CH_2~~ (1). The rate of the PVC brutto-dehydrochlorination V_{HCl} in an inert atmosphere (or under vacuo) is described by the equation:

$$V_{HCl} = V_r + k_p\bar{\gamma}_o \qquad (1)$$

and is determined by the content of carbonylallyl group $\bar{\gamma}_o$ within the PVC macromolecules (2-4).

Introduction of oxygen into the reaction zone accelerates PVC degradation. In an oxidizing atmosphere, the PVC dehydrochlorination process proceeds in accordance with the equation (5, 6):

$$V_{HCl} = (V_{1r} + V_{1p}) + (V_{3r} + V_{3p})$$
$$= \left(k_{1r} + k_{1p}\frac{\overline{\gamma}_n}{a_n}\right) a_n + \left(k_{3r}[pO_2]^{1/2} + k_{3p}\frac{\overline{\gamma}_n}{a_n}[pO_2]\right) a_n \quad (2)$$

where k_{1r} and k_{1p} are the rate constants of a non-catalytic reaction of random HCl elimination and of the formation of polyconjugated systems of $\diagdown C{=}C \diagup$ bonds; k_{3r} and k_{3p} are those for a catalytic (under the influence of O_2) reaction; $[pO_2]$ denotes a partial pressure oxygen in the zone of thermal degradation; a_n stands for the content of HCl in PVC before the polymer dehydrochlorination started.

The degradation kinetics of PVC undergo a substantial change during the transition from the solid phase to the dilute solutions of the polymer in inert solvents (o-dichlorobenzene, decalin, benzyl alcohol, cyclohexanone and others), namely, the brutto-rate of HCl elimination (in an inert atmosphere) shows a considerable drop (*Fig. 1*) which is an essential peculiarity of PVC degradation (7, 8). A decrease in the rate of PVC brutto-dehydrochlorination is clearly observed at various temperatures as well as with a number of solvents and PVC samples (*Table 1*).

The division of the brutto-process of PVC dehydrochlorination V_{HCl} into the reactions V_r and V_p has made it possible to establish that the values of the random detachment of HCl during the polymer decomposition in solution and in the solid phase are close to each other (*Table 1*). A decrease in the rate

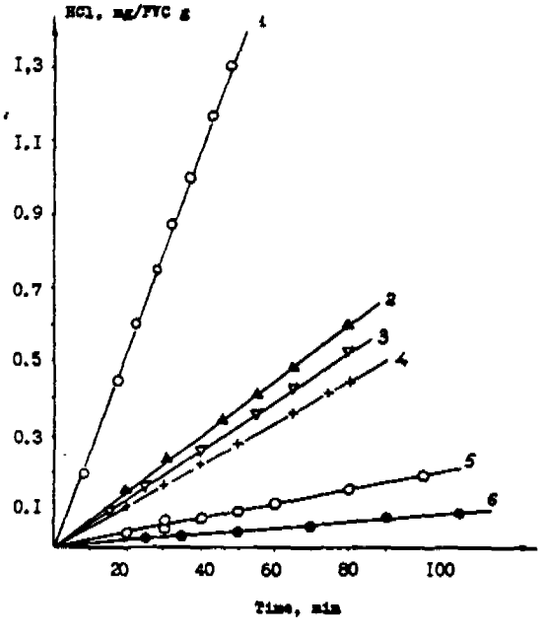


Fig. 1. Kinetics of PVC brutto-dehydrochlorination (175°C, in the atmosphere of N_2): 1—powder; 2—in o-dichlorobenzene; 3—in benzyl alcohol; 4—in decalin; 5—powder (150°C); 6—in cyclohexanone (150°C).

V_{HCl} in the liquid phase is due to inhibition of the reaction of polyconjugated systems propagation (the rate constant of the process k_p decreases during the transition to the polymeric solutions), although no chemical interaction with carbonylallyl groups or polyconjugated systems of $\diagdown C{=}C \diagup$ bonds is observed.

As a result, the value of V_{HCl} for the "PVC + solvent" system approximates that of the rate V_r. This is another peculiarity of the liquid-phase thermal degradation of PVC.

The third distinction consists in a decreased activation energy of the PVC dehydrochlorination process in solution as compared with the polymer decomposition in the solid phase (*Table 2*). The activation energy of the brutto-dehydrochlorination process of powdered PVC samples depends on the contribution from the activation energies of the random HCl detachment and of the formation reactions of polyconjugated systems of $\diagdown C{=}C \diagup$ bonds. It is to be noted that the polyene formation rate is connected with the content of carbonylallyl groups in the polymeric macromolecules. The higher is the magnitude of $\overline{\gamma}_n$, the greater is the value of the ratio V_p/V_r. During degradation of PVC dissolved in an inert solvent, th contribution from the reaction of the random HCl elimination, which proceeds at a lower activation energy (E_{act} = 23 kcal/mol) than the polyene formation (E_{act} = 35 kcal/mol) (4, 9, 10), to the brutto-process of PVC dehydrochlorination increases, i.e., the ratio V_p/V_r becomes about one order less (*Table 1*). The latter results in a decrease in the observed activation energy of the brutto-process of HCl elimination (*Table 3*). The above facts suggest that with PVC decomposing in inert solvents the correlation between $\overline{\gamma}_n$ and E_{act} (2-4) is apparently retained.

Noticeable is the fact that the introduction of some solvents, such as benzyl alcohol, o-dichlorobenzene and the like (*Fig. 2*), into PVC in concentrations up to 1 g of the solvent per 1 g of th polymer does not change the rate of HCl brutto-elimination, i.e., the introduction of the above type of solvents into PVC in relatively small quantities does not affect the degradation kinetics of PVC. The inhibition effect of the PVC dehydrochlorination reaction is only observed in dilute solutions of the above agents.

Another matter is the use of a different class of solvents which are well compatible with PVC unlike the above compounds. Such solvents readily form solutions with PVC even at the "solvent-polymer" ratios below one. In contrast to the solvents that are non-compatible with PVC, this seems to be the case of a plasticizer dissolved in PVC rather than the polymer solution in the solvent medium. The introduction of low-molecular plas-

Table 1. Kinetic Parameters of Thermal (in the Atmosphere of N_2) Degradation of PVC in Various Solvents

$\overline{M}_n$	$\gamma_0 \cdot 10^4$, mol PVC mol	Solvent	Concentration, wt. percent	T, °C	$V_{HCl} \cdot 10^7$	V'_{HCl}	V_r	V'_r	V_p	V'_p	$k_r \cdot 10^7$	$k'_r \cdot 10^7$	$k_p \cdot 10^3$	$k'_p \cdot 10^7$	$\frac{V_{HCl}}{V'_{HCl}}$	$\frac{V_p}{V_r}$	$\frac{V'_p}{V'_r}$
					10^7, HCl mol/PVC mol · s						s^{-1}						
57,000	1.54	o-Dichlorobenzene	1.5	175	11.5	2.1	0.80	0.75	10.7	1.35	0.80	0.75	6.95	0.88	5.5	13.4	1.80
70,000	1.53	o-Dichlorobenzene	1.5	175	11.5	2.1	0.80	0.75	10.7	1.35	0.80	0.75	6.99	0.88	5.5	13.4	1.80
102,500	1.52	o-Dichlorobenzene	1.5	175	12.0	2.2	0.80	0.75	11.2	1.45	0.80	0.75	7.37	0.95	5.5	14.4	1.93
157,000	1.04	o-Dichlorobenzene	1.5	175	8.0	1.4	0.80	0.75	7.20	0.60	0.80	0.75	6.92	0.58	5.6	9.0	0.80
157,000	1.04	o-Dichlorobenzene	1.5	165	3.0	0.60	0.46	0.40	2.54	0.20	0.46	0.40	6.49	0.19	5.0	5.5	0.5
157,000	1.04	o-Dichlorobenzene	1.5	155	0.8	0.31	0.26	0.21	0.34	0.10	0.26	0.21	0.33	0.096	2.6	1.3	0.5
157,000	1.04	Decalin	2.0	175	8.0	1.8	0.80	—	7.20	—	0.80	—	4.92	—	4.4	9.0	—
157,000	1.04	Benzyl alcohol	1.9	175	8.0	2.0	0.80	—	7.20	—	0.80	—	6.92	—	4.0	9.0	—
157,000	1.04	Cyclohexanone	2.1	150	0.8	0.25	0.20	—	0.40	—	0.20	—	0.38	—	2.4	9.0	—

V_{HCl}, V_r, V_p are the reaction rates for PVC degradation in the solid phase.
V'_{HCl}, V'_r, V'_p are the reaction rates for PVC degradation in the liquid phase.

Table 2. Activation Energy Values for Brutto-Dehydrochlorination of PVC Dissolved in o-Dichlorobenzene (175°C; in the Atmosphere of N_2)

$\overline{M}_n$	$\gamma_0 \cdot 10^4$, mol/PVC mol	E_{act}, kcal/mol	E'_{act}, kcal/mol
57,000	1.54	33 ± 1	28 ± 1
70,000	1.53	33 ± 1	28 ± 1
102,500	1.52	33 ± 1	28 ± 1
157,000	1.04	31 ± 1	25 ± 1

* Degradation in solution.

Table 3. Kinetic Parameters of PVC Thermal Degradation (175°C; in the Atmosphere of N_2) in the Presence of Ester Plasticizers

Plasticizer	Concentration of plasticizer, g/PVC g	$V_r \cdot 10^7$ HCl mol / PVC mol · s	$V_p \cdot 10^7$ HCl mol / PVC mol · s
—	—	0.80	7.30
DOP	0.03	0.80	4.40
	0.06	0.75	3.85
	0.10	0.74	3.66
	0.20	0.74	3.46
	0.60	0.75	3.25
DOA	0.01	0.78	5.42
	0.03	0.76	5.04
	0.10	0.77	4.43
	0.30	0.79	3.81
	0.50	0.77	4.13
DOS	0.03	0.79	5.61
	0.10	0.80	4.90
	0.30	0.78	4.22
	0.50	0.78	4.12
PAS-22	0.07	0.80	5.20
	0.18	0.77	4.23
	0.37	0.77	4.23
	0.45	0.76	4.64
	0.60	0.77	4.73
PDEA-4	0.03	0.80	7.10
	0.05	0.78	6.22
	0.10	0.76	6.04
	0.20	0.77	5.78
	0.30	0.78	6.02
	0.40	0.76	5.94
	0.50	0.78	6.02

ticizers, such as di(2-ethylhexyl)phtalate (DOP), di(2-ethylhexyl)adipate (DOA), di(2-ethylhexyl)-sebacate (DOS), into PVC even in the quantities ranging from 0.05 to 1.0 g/PVC g results in a noticeable decrease in the HCl elimination rate (*Fig. 2*) though to a less extent than in the case of the polymer decomposition in dilute solution (11, 12). The same is observed for PVC degradation in the medium of oligomer polyesters, namely: PDEA-4 (the product of dibutyladipate reesterification with diethylene glycol), PAS-22 (the reesterification product of a blend of dibutyladipate and dibutylsebacate).

The presence of a plasticizing agent in the system has hardly any effect of the formation rate of random single $\diagdown\!\!\diagup C{=}C\diagdown\!\!\diagup$ bonds (*Table 3*).

Thus the thermal degradation of PVC in the form of dilute and strong (in plasticizers) solutions re-

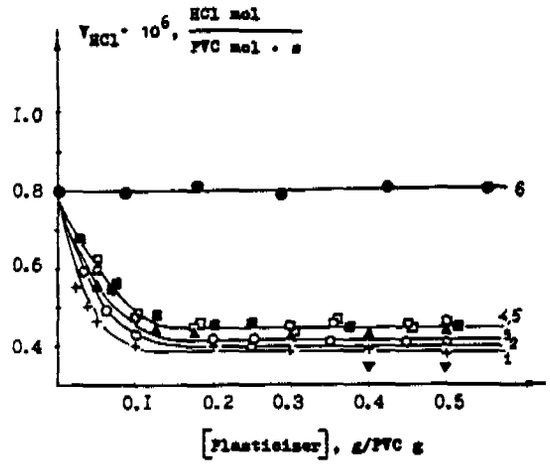


Fig. 2. Effect of di- and polyester plasticizers on the rate of the thermal (175°C, in the atmosphere of N_2) brutto-dehydrochlorination of PVC: 1—DOP; 2—DOA; 3—DOS; 4—PAS-22 (■); 5—PDEA-4 (□); 6—benzyl alcohol.

veals a number of basic distinctions as compared with the polymer decomposition in the solid phase. First of all, a considerably reduced dehydrochlorination rate is observed, the decrease in the rate of HCl detachment from the polymer macromolecules during the transition to the liquid phase occurring mainly due to the reaction of polyene sequences formation.

The observed effect may be accounted for by two factors: 1) a difference between the PVC structure on the supermolecular (powder) and molecular (solution) levels; 2) a catalytic influence of hydrogen chloride on the polyene formation during PVC degradation in the solid phase. At the moment of the detachment of another HCl molecule, the [polymer · HCl] complex forms in situ to activate dehydrochlorination of the neighbouring vinyl chloride unit in the PVC macromolecule. It is known (13) that hydrogen chloride does not affect the rate V_r, while it accelerates the reaction V_p. Apparently, in the case of the polymer degradation in solution, such a catalytic action is eliminated due to the solvation of macromolecules by the solvent.

As can be seen in *Fig.* 2, the PVC dehydrochlorination rate is falling if the plasticizing additive concentration increases only to a certain critical value *ca.* 15 wt percent. The existence of a critical concentration for a plasticizer is evidently connected with the creation of such conditions under which the groups that initiate the reaction of the polyene system formation find themselves "blocked" due to their solvation by the plasticizer's molecules, thus making difficult in a certain way the growth of polyene sequences. The introduction of plasticizers in concentrations above the critical value no longer affects the degree of "shieldedness" of the polyene growth labile sites. Therefore the exceeding of the critical concentration is not accompanied by any further reduction in the PVC degradation rate. As a result, a certain correlation between the critical concentration and the content of labile structures (carbonyl allyl groups) within the macromolecules in expected to exist. Indeed, it can be seen from *Fig.* 3 that the greater value of $\bar{\gamma}_0$ calls for the higher content of the ester plasticizer to cause the brutto-dehydrochlorination rate V_{HCl} to reach a constant value. As a result, there exists a linear relation between the parameters $\bar{\gamma}_0$ and $[DOP]_{cr}$ (*Fig.* 4).

The kinetic mechanism of PVC degradation in the liquid phase changes considerably if an inert atmosphere is replaced by one containing oxygen (14). No retardation of PVC dehydrochlorination

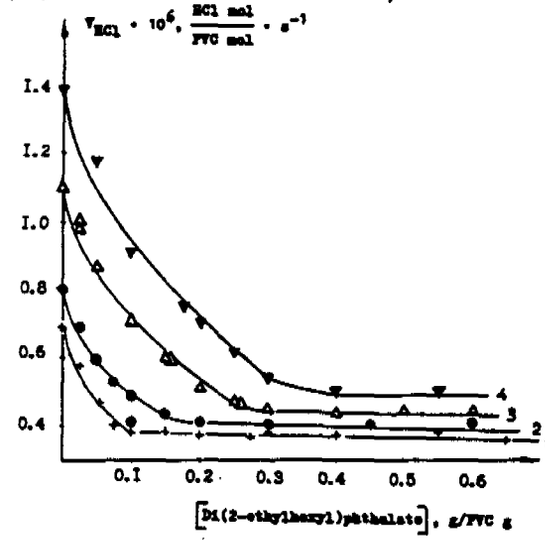


Fig. 3. Dependence of the rate of PVC brutto-dehydrochlorination on the content of di(2-ethylhexyl)phthalate for polymer samples with various content of labile carbonylallyl groups $\bar{\gamma}_0$ (mol/PVC mol): 1—0.82 · 10^{-4}; 2—1.02 · 10^{-4}; 3—1.55 · 10^{-4}; 4—1.80 · 10^{-4}.

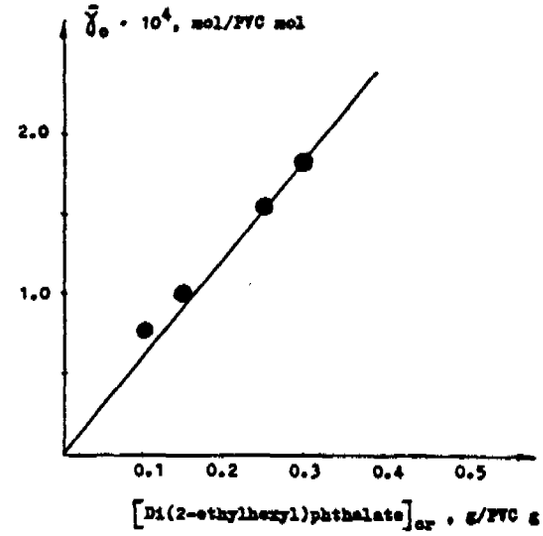


Fig. 4. Dependence of the critical concentration of di(2-ethylhexyl)phthalate $[DOP]_{cr}$ on the content of carbonylallyl groups $\bar{\gamma}_0$ in PVC responsible for initiating the formation of $\diagdown C{=}C \diagup$ *bonds polyconjugated systems.*

occurs in this case. The HCl elimination rate increases rapidly. Moreover, the greater concentration of the plasticizing agent introduced into the polymeric composition causes a higher rate of the PVC thermal decomposition at a permanent partial pressure of O_2, i.e., in an oxidizing medium, ester plasticizers accelerate significantly the decomposition of the polymeric macromolecules rather than inhibit it (*Fig. 5*), the kinetic dependence of PVC dehydrochlorination acquires an autocatalytic character (*Fig. 6*). It should be pointed out that the accelerating HCl evolution under the influence of a plasticizer is only observed with the concentrations of the latter above some critical value [Plasticizer]$_{cr}$.

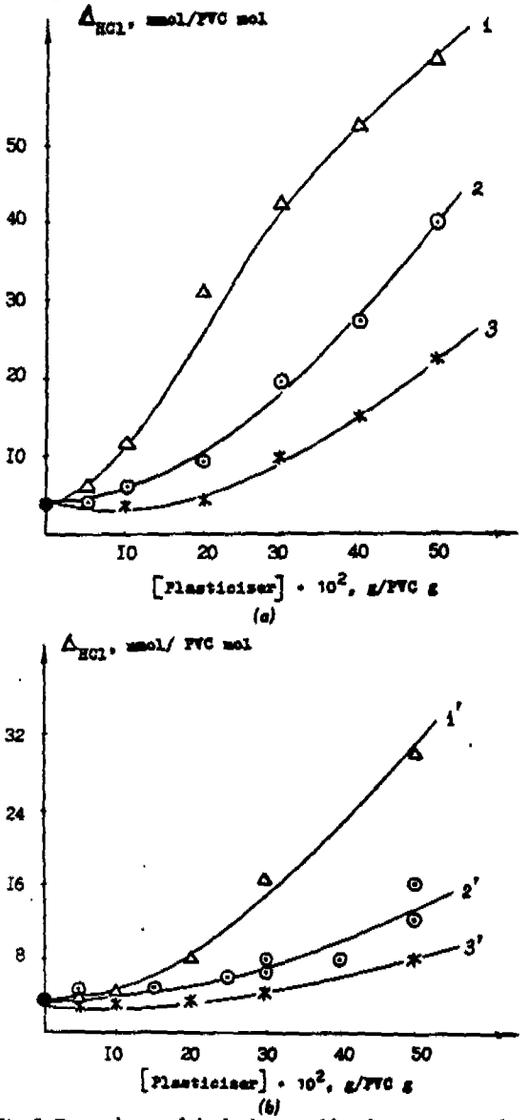


Fig. 5. Dependence of the hydrogen chloride quantity evolved within 60 min Δ_{HCl} on the concentration of the ester plasticizer during thermal degradation of plasticized PVC (175°C) in the atmosphere of oxygen (a) and air (b): 1,1'—DOS; 2,2'—DOA; 3,3'—DOP.

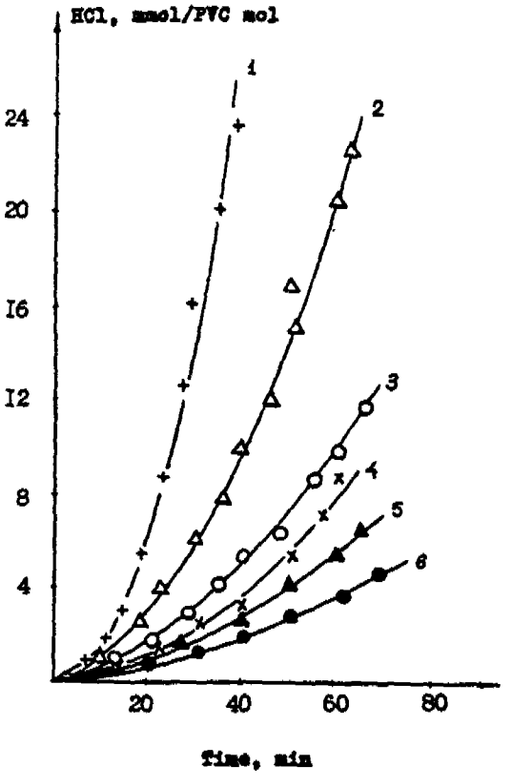


Fig. 6. Kinetics of HCl brutto-elimination during thermal-oxidative degradation (175°C, in the atmosphere of O_2) of PVC containing DOS (1, 4), DOA (2, 5), DOP (3, 6): 1-3—0.3; 4-6—0.1 g/PVC g.

Another special feature of the PVC thermal-oxidation degradation, as compared with the thermal one, consists of the fact that the plasticizers produce an unequal effect on the polymer dehydrochlorination kinetics. Specifically this manifests itself in the values of the critical concentration of the plasticizer which differ for the investigated esters, the value [Plasticizer]$_{cr}$ being dependent on the partial pressure of oxygen in the reaction zone (see *Table 4*).

The above peculiarities of the influence of ester plasticizers on the PVC thermal-oxidative decomposition can obviously be explained in the following way: first, the replacement of an inert medium by the oxygen-containing atmosphere gives rise to various oxidation reactions involving the plasticizer molecules, where the plasticizer decompo-

Table 4. Values of Critical Concentrations of Ester Plasticizers Obtained during Thermal-Oxidative Dehydrochlorination of Plasticized PVC at 175°C

Ester	Atmosphere	[Plasticizer]$_{cr}$, g/PVC g
DOP	air	0.20
DOA	air	0.10
DOS	air	0.05 – 0.06
DOP	oxygen	0.15
DOA	oxygen	0.06 – 0.07
DOS	oxygen	0.01 – 0.02

sition is accompanied by the formation of products accelerating the degradation of the polymeric macromolecules. This is also substantiated by the fact that the value V_{HCl} grows with the increasing content of the plasticizing agent in the composition (*Fig. 5*). Secondly, judging by the degradation kinetics of plasticates, the investigated plasticizing ester additives to thermal oxidation possess different stability.

This means that the PVC decomposition rate in the presence of plasticizers presubjected to thermal-oxidative exposure should be higher than with the use of the parent esters due to a higher content of their decomposition products which are active towards PVC degradation. Indeed, one can see from *Table 5* that the rate V_{HCl} increases with the prolongated thermal pretreatment of the plasticizer. A comparison of these results with the data on the thermal oxidative degradation kinetics of plasticates shows, however, that the introduction of a preoxidized plasticizer into PVC does not accelerate the decomposition of the polymeric molecules as significantly as one could expect. These results make it possible to suggest that the accumulating products of the plasticizer oxidative decomposition, such as acids, ketones, etc., within the system are not the basic and only reason for the intensification of HCl elimination during the PVC thermal-oxidative decomposition in the medium of esters. Another reason lies apparently in the appearance of free radicals in the plasticate in the course of its oxidative degradation due to an interaction between ester molecules and oxygen. The forming radicals attack the polymeric macromolecules, thus increasing the rate V_{HCl}.

A kinetic study of the initiated (by di-tertiary butyl peroxide) oxidation of DOP, DOA, DOS has shown (15) that the process rate is directly proportional to the ester concentration and the square root of the initiator concentration (*Fig. 7*). These experimental results indicate that a thermal-oxidative attack on the plasticate causes an intense oxidation of esters, the reaction proceeding according to the radical-chain mechanism with a quadratic termination at the peroxide radicals. The oxidation rate is described by the equation:

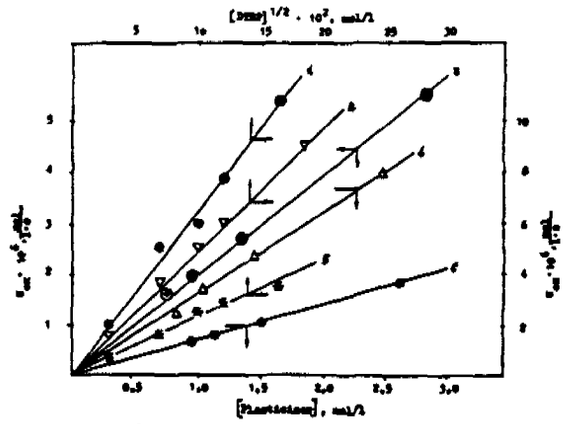


Fig. 7. Dependence of the oxidation rate W_{ox} (135°C) of DOS (1, 4), DOA (2, 5), DOP (3, 6) on the concentration of the ester plasticizer (1-3; [ditertiary butyl peroxide]$_0$ = $5 \cdot 10^{-3}$ mol/l) and ditertiary butyl peroxide (4-6; [plasticizer]$_0$, mol/l: 4—2.35; 5—2.70; 6—2.56).

$$W_{ox} = k_2[RH][ROO\cdot] = k_2 \cdot k_6^{-1/2}[RH]\sqrt{W_i} \quad (3)$$

where $[RH]$ denotes the ester concentration; k_2 and k_6 are the rate constants for the propagation and termination of the reaction chain, W_i stands for the initiation rate.

The dependence of W_{ox} on the square root of the initiator concentration (*Fig. 7*) has made it possibl to determine the parameter $k_2 \cdot k_6^{-1/2}$ (*Table 6*) characterizing the plasticizer oxidizability. As one can see from *Table 6*, the investigated ester plasticizers of PVC form the following sequence according to their tendency to oxidation: DOS > DOA > DOP.

The above results are in good agreement with the data on the kinetics of the plasticized PVC thermal-oxidative dehydrochlorination. The highest value of the polymer brutto-decomposition rate is observed for the thermal-oxidative degradation of PVC plasticized with DOS, while the lowest one has been obtained with DOP used as the plasticizer. An essentially lower rate of PVC dehydrochlorination in the presence of DOP, as compared with that in the presence of DOS or DOA, is apparently the result of the fact that it is the alcohol group of the ester molecule only that is subject to oxidation in DOP.

Table 5. Effect of Preoxidation of Ester Plasticizers (175°C, Air) on Kinetic Parameters of PVC Thermal Degradation

Plasticizer, 0.3 g/PVC g	Duration of thermal treatment, h	$V_{HCl} \cdot 10^6$	$V_i \cdot 10^7$	$V_p \cdot 10^7$
		HCl mol/PVC mol · s		
DOA	0	0.62	0.80	7.22
	1	1.10	0.80	5.41
	2	1.21	0.81	10.19
	4	1.40	0.79	11.31
	6	1.70	0.78	16.20
DOS	0	0.65	0.80	5.70
	2	0.86	0.79	7.81
	4	0.98	0.77	9.03
	6	1.30	0.78	12.22

Table 6. Values of the Parameter $k_2/k_6^{1/2}$ for some Ester Plasticizers of PVC

Temperature, °C	Plasticizer	$k_2/k_6^{1/2} \cdot 10^3$, 1/mol · s
115	DOP	0.58
115	DOA	1.03
115	DOS	2.00
125	DOP	1.31
125	DOA	2.68
125	DOS	3.38
135	DOP	1.61
135	DOA	3.70
135	DOS	4.90
145	DOP	1.99
145	DOA	4.74
145	DOS	7.66

A study on the autooxidation of ester plasticizers at 140-210°C, i.e., under the conditions similar to those of the thermal-oxidative degradation of plasticized PVC, has indicated that the interaction of esters with oxygen is accompanied by the accumulation of hydroperoxide groups within the plasticizer, the process autoaccelerating (*Fig. 8*, curves 1-7) due to the reaction of a degenerated chain branching:

$$\mathrm{ROOH} \xrightarrow{k_3} \mathrm{RO}\cdot + \mathrm{HO}\cdot \qquad (4)$$

while chains originate (at the rate W_{i_0}) according to the reaction:

$$\mathrm{RH} + \mathrm{O}_2 \rightarrow \mathrm{R}\cdot + \mathrm{HOO}\cdot \qquad (5)$$

The rate of ROOH accumulation is determined through the expression:

$$d[\mathrm{ROOH}]/dt = k_2[\mathrm{ROO}\cdot][\mathrm{RH}] = k_2 \cdot k_6^{-1/2}[\mathrm{RH}](W_{i_0} + k_3[\mathrm{ROOH}])^{1/2} \qquad (6)$$

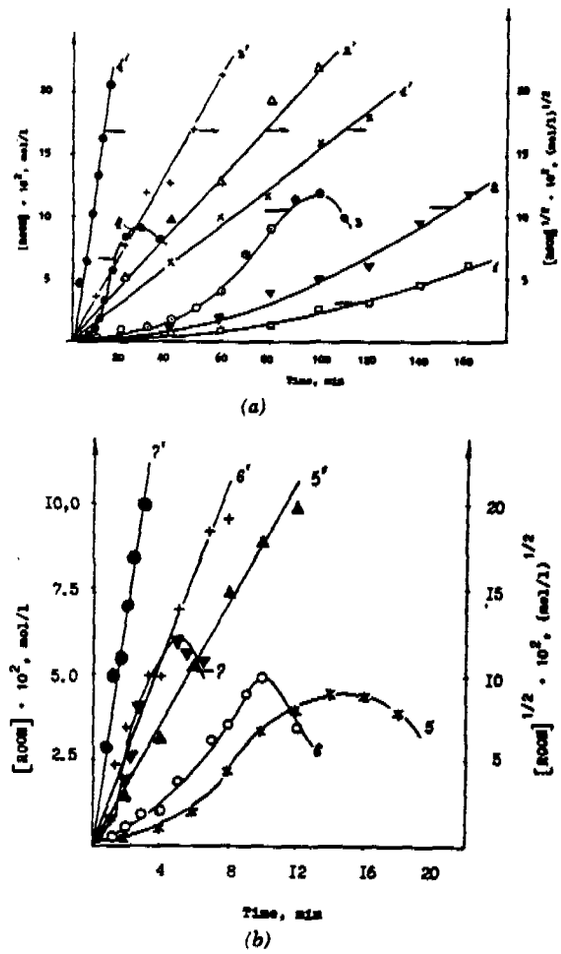


Fig. 8. Kinetic curves for the accumulation of di(2-ethylhexyl)adipate hydroperoxide in the autooxidation duty (1-7) and the relative straight lines (1'-7'): a) 1,1'—140°C; 2,2'—150°C; 3,3'—162°C; 4,4'—175°C; b) 5,5'—186°C; 6,6'—198°C; 7,7'—210°C.

with $W_{i_0} \ll k_3$ ROOH the integration of *Eq 6* yields:

$$\mathrm{ROOH}^{1/2} = \frac{1}{2} k_2 k_6^{-1/2} k_3^{1/2}[\mathrm{RH}]t \qquad (7)$$

In accordance with *Eq 7* the kinetic dependences of the hydroperoxide group formation straighten out in the coordinates "$\mathrm{ROOH}^{1/2}$ – time" (*Fig. 8*, lines 1-7), which is evidence of the first order for the hydroperoxide concentration in the reaction of degenerated chain branching. On the basis of these dependences we have determined the value $k_2 k_6^{-1/2} k_3^{1/2}$ and extrapolated the values $k_2 k_6^{-1/2}$ found from the results of an initiated oxidation of esters onto the temperature range used for the study of autooxidation. Further the decomposition rate constant for hydroperoxides k_3 has been calculated (*Table 7*).

The maximum point of the kinetic curves for the accumulation of hydroperoxides (*Fig. 8*) can be expressed as:

$$W^{\max}_{form} = W^{\max}_{deg} = k_2 \cdot k_6^{-1/2}[RH]\sqrt{W_i^{\max}} = k_2 \cdot k_6^{-1/2}[RH]\sqrt{k_3[ROOH]} \qquad (8)$$

where $W^{\max}_{form}$ and $W^{\max}_{deg}$ are the rates of the hydroperoxide formation and degradation respectively.

The values of the maximum hydroperoxide concentrations, the respective initiation rates $W_i^{\max}$ and the maximum rates of the hydroperoxide decomposition are summarized in *Table 8*. The comparison of the rates $W_i^{\max}$ and $W^{\max}_{deg}$ indicat s that the brutto-decomposition of hydroperoxides proceeds much more rapidly than their decomposition via the monomolecular mechanism. This is apparently associated with the growing rate of the radical-initiated decomposition of the hydroperoxide as its concentration grows. The reactions of hydroperoxides with the molecular products of their decomposition might also contribute to a certain extent.

It should be pointed out that the maximum concentrations of the hydroperoxides accumulated

Table 7. Values of Decomposition Rate Constants for Hydroperoxides of Ester Plasticizers, k_3

Temperature, °C	Plasticizer	$k_3 \cdot 10^4$, s^{-1}
150	DOP	0.20
150	DOA	0.29
150	DOS	0.48
162	DOP	1.21
162	DOA	2.46
162	DOS	2.69
175	DOP	1.44
175	DOA	2.59
175	DOS	9.60
186	DOP	8.41
186	DOA	8.50
186	DOS	13.65
210	DOP	11.36
210	DOA	12.50
210	DOS	26.80

Table 8. Rates of Initiation and Brutto-Decomposition of Ester Hydroperoxides at their Maximum Concentrations ([DOP]$_0$ = 2.56; [DOA]$_0$ = 2.70; [DOS]$_0$ = 2.35 mol/l)

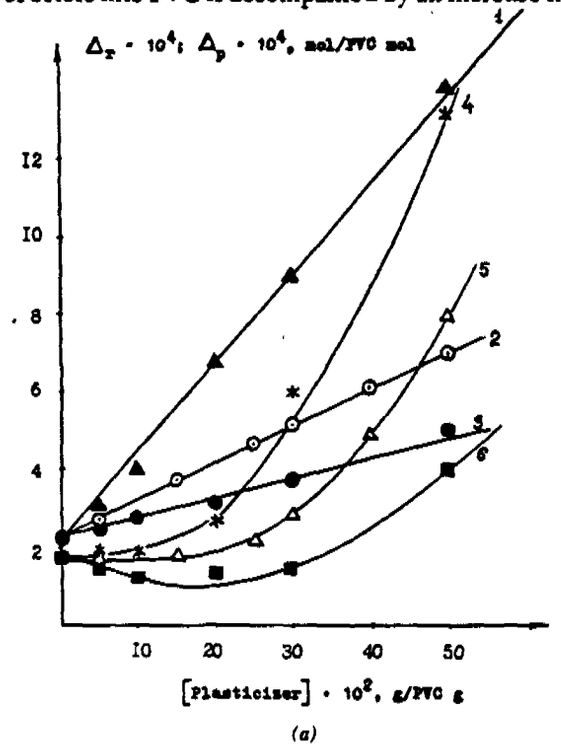
	DOP			DOA			DOS		
t, °C	$[ROOH]_{max} \cdot 10^2$, mol/l	$W_i^s \cdot 10^5$ mol/l · s	$W_{dec}^s \cdot 10^5$ mol/l · s	$[ROOH]_{max} \cdot 10^2$, mol/l	$W_i^s \cdot 10^5$ mol/l · s	$W_{dec} \cdot 10^5$ mol/l · s	$[ROOH]_{max} \cdot 10^2$, mol/l	$W_i^s \cdot 10^5$ mol/l · s	$W_{dec} \cdot 10^5$ mol/l · s
140	—	—	—	—	—	—	—	—	—
150	17.0	0.34	1.10	—	—	—	12.3	0.59	5.58
162	15.4	1.86	3.49	12.0	2.95	11.19	20.8	5.60	25.41
175	—	—	—	9.4	2.44	12.48	9.1	8.74	42.65
186	14.0	11.78	14.55	4.5	3.82	22.50	7.0	9.55	49.10
198	10.0	9.35	15.96	5.0	5.31	31.41	6.2	14.52	83.50
210	9.4	10.68	20.14	6.0	7.50	44.40	8.3	22.27	13.35

reach fairly high values (*Table 8*) which ensures high initiation rates. This means that ester plasticizers of PVC are active generators of free radicals due to the reaction of degenerated chain branching proceeding at 180-210°C, i.e., under the conditions that correspond to the treatment temperature of plasticized PVC compositions.

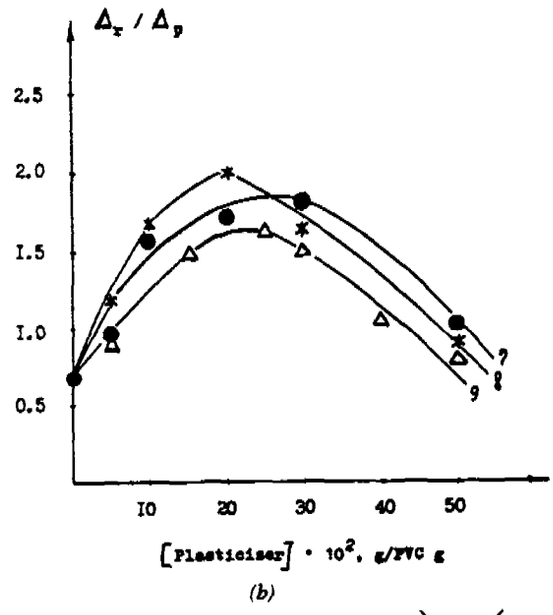
The free radicals that form during the hydroperoxide decomposition are able to propagate the oxidation chains of the plasticizer as well as to attack the PVC macromolecules, thus sharply accelerating the polymer degradation. One could expect the radicals to intensify, first of all, the random elimination of HCl from the polymer macromolecules V_r, since the initiators of free-radical processes are known to accelerate the reaction (16). With reference to the thermal-oxidative degradation of ester-plasticized PVC this means that the higher formation rate of hydroperoxides and the numerical value of the constant k_3 for the plasticizer under investigation, should bring about a higher formation rate of random single $\diagdown C{=}C \diagup$ bonds. Indeed, the steady of ester plasticizers' effect on the reaction rate of HCl random elimination has shown that an essential increase in the rate V_r (*Fig. 9a*, lines 1-3) is observed in the sequence: DOP < DOA < DOS, i.e., in a strict accordance with the decreasing constant k_3.

The end products of the plasticizer oxidation include various oxygen-containing compounds, such as acids, ketones, etc., which are known (1) to be able to accelerate the formation reaction of polyconjugated systems of $\diagdown C{=}C \diagup$ bonds (this is also evidenced by the fact that, as stated above, the introduction of a preoxidized plasticizer into PVC accelerates the polymer degradation due to an increase in the rate V_p only). On the other hand, plasticizers themselves inhibit the polyene formation (during the plasticized PVC degradation in an inert medium). In the range of low concentrations of a plasticizer (0.05-0.20 g/PVC g depending on the nature of the ester plasticizer), the inhibition of the process prevails; while for high concentrations, when the rate of accumulation of the oxidation products grows high enough, the catalytic effect of these compounds on the rate V_p comes to play a decisive role. As a result, during the PVC thermal-oxidative degradation in the medium of an ester plasticizer, the dependence of the formation rate of $\diagdown C{=}C \diagup$ bond polyconjugated systems on the plasticizing agent content essentially differs from that for V_r (*Fig. 9a*, curves 4-6), and the dependence of the rate ratio V_r/V_p on the plasticizer concentration has an extreme character (*Fig. 9b*).

A study of the liquid-phase degradation of PVC in ester plasticizers with regard to the reactions V_r and V_p makes it possible to explain why, in a number of cases, the process of PVC brutto-dehydrochlorination does not depend on the presence of ester plasticizers in the polymer if their content in the polymer is below the critical value (*Fig. 5*). The reason for it lies in the fact that, although the introduction of esters into PVC is accompanied by an increase in



(a)



(b)

Fig. 9. *Dependence of the quantity of internal* $\diagdown C{=}C \diagup$ *bonds formed within 60 min (175°C; in air)* Δ_r *(1-3) and HCl evolved from PVC due to the formation reaction of polyconjugated sequences of double bonds within macromolecules* Δp *(4-6) (a), as well as the dependence of the ratio of these parameters (b) on the content of DOS (1, 4, 8), DOA (2, 5, 9), DOP (3, 6, 7) in the polymer.*

the rate of HCl random detachment, in some cases (depending on the partial pressure of O_2 and the nature of the ester) the increase is compensated for by a decrease in the growth rate of polyene systems. As a result, V_{HCl} might be independent of the plasticizer concentration in the system, since the process of PVC brutto-dehydrochlorination includes both reactions. However, exceeding the critical concentration gives rise to the violation of the compensation due to a rapid accumulation, within the polymer composition, of the ester oxidation products that catalyze the reaction of the polyene formation. Therefore, in the case of a reduced concentration, an increase in the rate of PVC brutto-dehydrochlorination is observed. Other evidence for the above results is the fact that the rate ratio V_r/V_p varies continuously over the whole range of the plasticizer concentrations investigated, including those below the critical one (*Fig. 9b*).

Thus ester plasticizers promote the thermal-oxidative decomposition of PVC, while in an inert atmosphere the decomposition of PVC in the medium of plasticizers is inhibited. The acceleration of PVC degradation in an oxygen-containing atmosphere is accounted for by the plasticizing agent oxidation leading to the appearance of intermediate and end products that activate PVC decomposition in the system. The intensity of the process depends on the nature of the plasticizer used and, first of all, is determined by the rate constants $k_2k_6^{-1/2}$ and k_3 characterizing the oxidizability of the plasticizing agent.

The principal way to PVC stabilization is nowadays associated with the chemical modification of carbonylallyl groups that are to be found in the polymeric macromolecules and are responsible for a high rate of PVC decomposition. Howev r the above approach proves ineffective for PVC solutions, specifically for highly plasticized compositions. One can see from *Fig. 10* that the rate of the thermal-oxidative dehydrochlorination of the initial PVC and the PVC with pre-deactivated carbonylallyl groups (for instance, through the interaction of labile structures with triphenyl phosphite (17)) in the medium of DOS is practically the same, though the modified PVC exhibits much higher stability in an inert atmosphere and in the absence of the solvent (*Fig. 10*, cf. lines 2 and 3).

It follows, from the above stated, that effective stabilization of PVC in solution, particularly in ester-plasticized systems, can be achieved through the solvent stabilization against oxidative decomposition in the first place, and not by way of stabilizing the polymer. In this case, the PVC dehydrochlorination rate decreases sharply and can ultimately reach the value V_{HCl} observed during the PVC thermal degradation in solution, i.e., an essentially lower value than the one obtained under similar conditions of PVC decomposition in the solid phase. Thus in this particular case, an effect takes place that we have called the effect of " chostabilization" of the PVC dehydrochlorinati n process. It means that an effective stabilization of PVC with respect to the reaction of HCl elimination achieved through the plasticizer stabilization against the thermal-oxidative decomposition. The

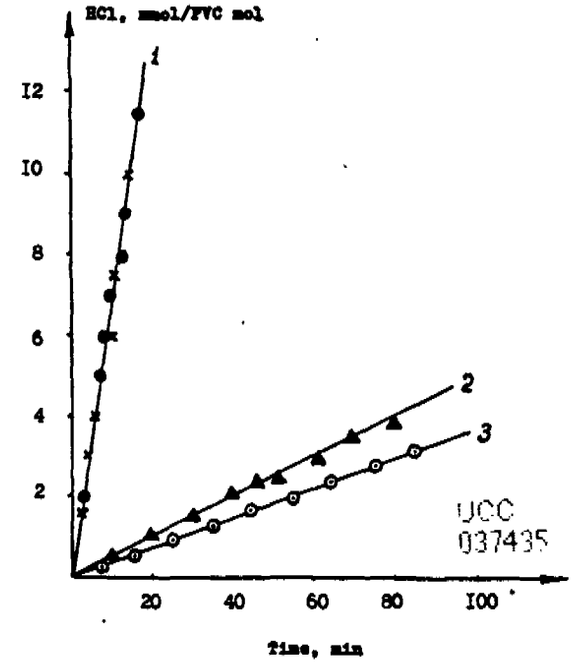


Fig. 10. Kinetic dependences of thermal-oxidative and thermal (2, 3) dehydrochlorination of initial PVC (1 (●) and 2) and PVC with predeactivated carbonylallyl groups (1 (X) and 3).

stabilization of a plasticizing agent causes automatically the PVC stabilization due to the specific feature of the solvent to retard the thermal degradation of the polymer.

REFERENCES

1. K. S. Minsker and G. T. Fedoseeva, "Destruktsiya i stabilizatsiya polivinilkhlorida," p. 14, "Khimiya," Moscow (1979).
2. K. S. Minsker, Al. Al. Berlin, and V. V. Lisitsky, *Vysokomolek. Soed.*, **B18**, 54 (1976).
3. K. S. Minsker, Al. Al. Berlin, V. V. Lisitsky, and S. V. Kolesov, *Vysokomolek. Soed.*, **A19**, 32 (1977).
4. K. S. Minsker, *Plaste Kautschuk*, **24**, 375 (1977).
5. K. S. Minsker, Al. Al. Berlin, and M. I. Abdullin, *Vysokomolek Soed.*, **B16**, 439 (1974).
6. K. S. Minsker and M. I. Abdullin, in: "Degradation and Stabilization of Polymers," Akzo Research Laboratories and Institute of Chemical Physical Acad. of Sci. USSR.
7. K. S. Minsker, M. I. Abdullin, V. I. Manushin, L. I. Malyshev, and S. A. Arzhakov, *Doklady AN SSSR*, **242**, 366 (1978).
8. K. S. Minsker, M. I. Abdullin, S. A. Arzhakov, V. I. Manushin, A. V. Matykin, and V. A. Kraikin, *Vysokomolek. Soed.*, **B21**, 194 (1979).
9. K. S. Minsker, Al. Al. Berlin, V. V. Lisitsky, and S. V. Kolesov, *Plast. Massy*, No. 10, 69 (1976).
10. K. S. Minsker, Al. Al. Berlin, V. V. Lisitsky, S. V. Kolesov, and R. S. Korneva, *Doklady AN SSSR*, **232**, 93 (1977).
11. M. I. Abdullin, V. I. Manushin, L. B. Zhikharevich, and K. S. Minsker, *Vysokomolek. Soed.*, **B22**, 229 (1980).
12. K. S. Minsker, M. I. Abdullin, and V. A. Kraikin, *Plast. Massy*, No. 3, 31 (1980).
13. K. S. Minsker, V. P. Malinskay, M. I. Arsis, S. D. Razumovski, and G. E. Zaikov, *Doklady AN SSSR*, **223**, 138 (1975).
14. K. S. Minsker, M. I. Abdullin, V. G. Kalashnikov, V. P. Birukov, G. M. Trosman, and A. V. Salnikov, *Vysokomolek. Soed.*, **A22**, 2131 (1980).
15. V. S. Martemyanov, M. I. Abdullin, T. E. Orlova, and K. S. Minsker, *Neftekhimiya*, **21**, 123 (1981).
16. K. S. Minsker, M. I. Abdullin, and G. A. Garipova, *Doklady AN SSSR*, **218**, 851 (1974).
17. K. S. Minsker, N. A. Mukmeneva, Al. Al. Berlin, D. V. Kazachenko, S. I. Agadzhanyan, and P. A. Kirpichnikov, *Doklady AN SSSR*, **226** 1088 (1976).