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Abstract

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Chemistry

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STUDY OF THE POLYMERIZATION AND COPOLYMERIZATION OF CERTAIN PEROXIDE MONOMERS

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At present there is great interest in obtaining graft and block polymers using peroxide ($-\text{O}-\text{O}-$) groups, which are introduced into the initial polymer by oxidation (¹⁻⁴), ozonation (⁵⁻⁸), and chemical reactions (⁹⁻¹²).

In connection with the synthesis of a new type of unsaturated polymerizable peroxide esters (monomers) (^{13,14}), the present work set the task of studying their polymerization and copolymerization with nonperoxide vinyl monomers for the purpose of their further use in obtaining grafted and modified polymers.

Polymerization of alkyl peresters: tert-butyl peracrylate $\text{H}_2\text{C}=\text{CH}-\text{CO}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$ (I), tert-amyl peracrylate ($-\text{C}(\text{CH}_3)_2\text{C}_2\text{H}_5$) (II); dimethylethynylmethyl peracrylate ($-\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CH}$) (III); *p*-nitrocumyl peracrylate ($-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{NO}_2$) (IV), and tert-butyl permethacrylate $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CO}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$ (V).

The rate of polymerization was studied in dilatometers and ampoules at 0, 40, 50, and 60°. Active oxygen was monitored by the iodometric method (¹⁵), and the molecular weight of the polymers was determined viscometrically (¹⁶) using the corresponding constants for nonperoxide polymers. The results of the studies are presented in Table 1.

As can be seen from the data in Table 1, the polymerization of peroxide acrylates is distinguished by a number of features due to the presence in their molecules

Table 1

Characteristics of the polymerization of peresters and of their polymers

Peresters	Temperature, °C	Polymerization rate, %/h	Degree of polymerization, %	Intrinsic viscosity	Molecular weight	Active [O ₂], % in monomer	Active [O ₂], % in polymer
I	0	0.25	92.3	0.2940	74 500	11.1 (theor. 11.11)	10.5
I	40	2.3	50.0	0.0946	13 700	11.1 (theor. 11.11)	9.63
I	50	5.0	48.0	0.0822	11 100	11.1 (theor. 11.11)	9.95
I	60	10.0	30.4	0.0673	8250	11.1 (theor. 11.11)	9.95
II	0	0.25	88.3	0.3965	116 300	7.0* (theor. 10.12)	6.24
II	40	2.5	25.5	0.1762	34 700	7.0* (theor. 10.12)	5.1
II	50	1.5	9.0	0.1377	24 000	7.0* (theor. 10.12)	5.4
III	0	0.09	31.8	0.0214	1500	10.4 (theor. 10.4)	6.6
III	40	0.8	32.4	0.0247	1850	10.4 (theor. 10.4)	—
III	50	10.8	10.8	0.0210	1450	10.4 (theor. 10.4)	7.2
IV	0	0.02	21.5	0.0747	9600	6.12 (theor. 6.31)	5.94
IV	40	3.3	33.3	0.0535	5900	6.12 (theor. 6.31)	5.23
IV	50	4.4	44.2	0.0151	900	6.12 (theor. 6.31)	5.20

Fig. 1. Rate of copolymerization of peresters I, II, III, IV, V with styrene at 50° and a concentration of 5 mol.%. The curve numbers correspond to the perester numbers.

Figure 1: Fig. 1. Rate of copolymerization of peresters I, II, III, IV, V with styrene at 50° and a concentration of 5 mol.%. The curve numbers correspond to the perester numbers.

Peresters	Temperature, °C	Polymerization rate, %/h	Degree of polymerization, %	Intrinsic viscosity	Molecular weight	Active [O ₂], % in monomer	Active [O ₂], % in polymer
V	0			0.0308	2500	9.9 (theor. 10.12)	8.74
V	40	0.3	5.5			9.9 (theor. 10.12)	4.22

* This perester corresponds to the pure product (¹³), in which [O₂] is not fully determined iodometrically.

two unstable bonds—the double bond and the peroxide bond. The data show that polymerization of pure peroxide monomers can take place only at relatively low temperatures and within a narrow temperature range (0–50°). It is characteristic that the upper temperature limit of polymerization is determined by the nature of the peroxide monomer. Thus, tert-butyl peracrylate (I) at 60° can be polymerized up to 30.4%, tert-amyl peracrylate (II) at 50° up to 9%, dimethylethynylmethyl peracrylate (III) at 50° up to 10%, and tert-butyl permethacrylate (V) at 40° only up to 5%. Upon reaching the indicated degree of polymerization, decomposition of the polymerizing mixture is observed with the evolution of gaseous products. The observed dependence of the polymerization of peroxide acrylates on temperature is determined by the thermal stability of the perester monomers and their polymers (¹³).

Fig. 1. Rate of copolymerization of peresters I, II, III, IV, V with styrene at 50° and a concentration of 5 mol.%. The curve numbers correspond to the perester numbers.

Along with this, it has been shown that peroxide acrylates polymerize relatively slowly with the formation of polymers of low molecular weight.

The results of Table 1 also show that only the relatively stable tert-butyl and tert-amyl peracrylates at 0° form high-molecular-weight polymers (74,500 and 116,300, respectively), whereas the others form low-molecular-weight polymers. At 40 and 50° all perester monomers form low-molecular-weight polymers. Con-

sequently, polymerization of peroxide monomers proceeds with a sharply pronounced termination reaction of the growing

Table 2

Characteristics of the copolymerization of peresters and their polymers

Mixture composition	Temperature, °C	Perester content in mixture, mol. %	Polymerization rate, %/h	Degree of polymerization, %	Intrinsic viscosity	Molecular weight
St. + I	40	1	0.4	26.7	0.712	168 000
St. + I	40	2	0.5	38.8	0.428	83 000
St. + I	40	5	0.55	42.5	0.203	29 400
St. + I	40	10	0.55	41.9	0.139	17 400
St. + I	50	1	1.0	41.1	0.610	135 000
St. + I	50	2	1.1	42.2	0.403	76 300
St. + I	50	5	1.5	42.0	0.238	36 700
St. + I	50	10	1.25	42.6	0.143	18 000
St. + I	50	25	1.01	42.7	0.093	9 960
St. + I	60	2	3.1	45.8	0.406	77 000
St. + I	60	5	4.1	41.1	0.183	25 500
St. + I	60	10	3.8	37.7	0.126	15 200
St. + II	50	1	1.0	40.8	0.530	111 000
St. + II	50	2	1.2	42.0	0.405	77 000
St. + II	50	5	1.6	43.7	0.205	29 800
St. + II	50	10	1.4	41.8	0.125	15 000
St. + II	50	2	1.99	40.0	0.1804	24 930
St. + III	50	5	3.3	39.2	0.0888	9300
St. + III	50	10	4.45	39.0	0.0582	5200
St. + III	50	1	0.75	37.1	0.145	18 000
St. + IV	50	2	0.8	39.9	0.101	11 000
St. + IV	50	5	0.9	43.0	0.055	4 800

Mixture composition	Temperature, °C	Perester content in mixture, mol. %	Polymerization rate, %/h	Degree of polymerization, %	Intrinsic viscosity	Molecular weight
St. + V	50	1	3.0	49.0	0.247	39 000
St. + V	50	2	4.4	48.9	0.150	19 000
St. + V	50	5	5.8	46.5	0.0924	9 900
St. + V	50	10	7.4	59.2	0.090	9 500
MMA + I	40	1	6.8	27.3	0.984	762 800
MMA + I	40	2	11.7	23.4	1.250	1 074 000
MMA + I	40	5	18.7	37.4	0.602	376 700
MMA + I	40	10	5.3	26.7	0.287	131 200

chains and the involvement of peroxide groups in this process; moreover, under the indicated temperature conditions, polymerization of I proceeds with only a small loss of active oxygen (5-10%) and with preservation of the remaining part of it in the polymer. Polymerization of the other peroxide monomers is accompanied by a loss of active oxygen within the range of 15-45%, which is associated with their low thermal stability⁽¹³⁾.

Determination of the intrinsic viscosity of poly-tert-butyl peracrylate showed that in the course of polymerization of I up to 75% no structuring of the polymer occurs.

Thus, the intrinsic viscosity of poly-tert-butyl peracrylate obtained at 50° remains within the range 0.1070-0.1057. These observations agree with decomposition data⁽¹³⁾, which show that monomer I decomposes faster than its polymer. The pure polymer of tert-butyl peracrylate undergoes structuring, and an insoluble polymer is formed at 70° after heating for 60 h, at 80° after 12 h, and at 90° after 3 h.

Copolymerization of peresters with styrene and methyl methacrylate at different ratios was carried out in dilatometers, and the results are given in Fig. 1 and Table 2.

It is seen from Fig. 1 that peracrylates I, II, III, and IV copolymerize with styrene approximately according to a zero-order equation, while tert-butyl per-

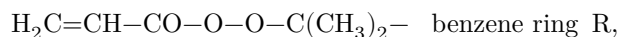
methacrylate (V) does so according to an exponential law, owing to the fact that the polymer of the latter is thermally less stable than the monomer, and as it accumulates the initiation reaction is accelerated. Along with this, as is seen from the data of Table 2, copolymerization of peracrylates I, II, and IV with styrene, when their content in the mixture is within 1-10%, proceeds at almost the same rate, not following proportionality to the square root of the initiator concentration (the peresters). Apparently, this is connected with the fact that at an increased content of perester in the mixture the chain-termination reaction increases sharply. Indeed, the data show that with an increase in the concentration of perester in the mixture, the intrinsic viscosity and molecular weight of the polymers decrease greatly.

Copolymerization of tert-butyl permethacrylate (V) with styrene is accelerated with an increase in its content in the mixture, owing to the aforementioned lower thermal stability of its polymer. Moreover, as is seen from the data of Table 2, copolymers of low molecular weight are obtained with this perester.

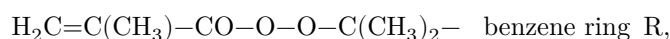
Copolymerization of tert-butyl peracrylate (I) with methyl methacrylate (MMA) (Table 2), compared with styrene, proceeds at a considerably higher rate, and it increases with an increase in the perester content in the mixture. It is characteristic that in this case very high-molecular-weight copolymers are obtained, which is apparently connected with a different mechanism of the chain-termination reaction, namely disproportionation of macroradicals⁽¹⁷⁾, in which the peresters are involved to a lesser extent in the chain-termination process.

It is interesting to note that upon copolymerization of peresters with styrene, no structuring of the copolymers occurs up to 75%. Thus, the intrinsic viscosity of a styrene copolymer with 5% tert-butyl peracrylate (obtained at 70° and a polymerization depth of 74.4%) fluctuates within the range 0.1765-0.2020. When an analogous polymer was heated (80°) in bulk for 24 h, the intrinsic viscosity remained within the range 0.1875-0.1872.

Along with those described, in the polymerization processes cumyl peracrylates were tested under the same conditions,



where $R = H, \text{Cl}, \text{and Br}$; and cumyl permethacrylates,



where $R = H, \text{Cl}, \text{Br}, \text{and } \text{NO}_2$. The indicated peresters polymerize slowly with the formation of low-molecular-weight

colored polymers and the loss of a large amount of active oxygen. Such behavior of these peresters is evidently explained by the presence in them of heterolytic decomposition, as is observed for saturated aryl peresters (18, 19).

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