# STUDY OF THE POLYMERIZATION AND COPOLYMERIZATION OF CERTAIN PEROXIDE MONOMERS

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## Abstract

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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 (—O—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 $H_2C{=}CH{-}CO{-}O{-}O{-}C(CH_3)_3$ (I), tert-amyl peracrylate ($-C(CH_3)_2C_2H_5$) (II); dimethylethynylmethyl peracrylate ($-C(CH_3)_2C{\equiv}CH$) (III); *p*-nitrocumyl peracrylate ($-C(CH_3)_2C_6H_4NO_2$) (IV), and tert-butyl permethacrylate $CH_2{=}C(CH_3){-}CO{-}O{-}O{-}C(CH_3)_3$ (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 $[O_2]$ 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. Consequently, 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. + III | 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. + IV | 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 permethacrylate (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,

$$\mathrm{H_2C{=}CH{-}CO{-}O{-}O{-}C(CH_3)_2{-}}\ \text{ benzene ring } \mathrm{R},$$

where $R = H$, Cl, and Br; and cumyl permethacrylates,

$$\mathrm{H_2C{=}C(CH_3){-}CO{-}O{-}O{-}C(CH_3)_2{-}}\ \text{ benzene ring } \mathrm{R},$$

where $R = H$, Cl, Br, and $NO_2$. 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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## REFERENCES

1. H. Mark, Angew. Chem., **67**, 53 (1955).
2. B. J. Metz, R. B. Mesrobian, J. Polym. Sci., **16**, 345 (1955).
3. W. Hahn, H. Lechtenböhmer, Makromol. Chem., **16**, 50 (1955).
4. G. Natta, E. Beati, F. Severini, J. Polym. Sci., **34**, 685 (1958).
5. V. V. Korshak, K. K. Mozgova, Izv. AN SSSR, OKhN, 1958, 651.
6. V. V. Korshak, K. K. Mozgova, M. A. Shkolina, Vysokomol. soed., **1**, 1364 (1959); **3**, 1462 (1961).
7. P. V. Kozlov, M. M. Iovleva et al., Vysokomol. soed., **2**, 1575 (1960).
8. N. A. Plate, V. P. Shibaev, T. I. Patrikeeva, V. A. Kargin, Vysokomol. soed., **3**, 292 (1961).
9. G. Smets, A. Poot et al., J. Polym. Sci., **34**, 287 (1959).
10. G. Smets, A. Poot, J. Polym. Sci., **54**, 159 (1961).
11. W. Hahn, U. Fischer, Makromol. Chem., **16**, 1 (1950).
12. A. A. Berlin, L. V. Stupen, B. I. Fedoseeva, D. M. Yanovskii, DAN, **121**, 644 (1958).
13. T. I. Yurzhenko, V. A. Puchin, M. R. Vilenskaya, O. E. Boisan, Abstracts of the 21st Jubilee Scientific-Technical Conference, Lviv Polytechnic Institute, 1964, p. 394.
14. T. I. Yurzhenko, M. R. Vilenskaya, S. I. Kozak, V. N. Nosan, ibid., p. 390.
15. L. S. Silbert, D. Swern, Anal. Chem., **30**, 385 (1958).
16. A. I. Shatenshtein, Yu. P. Vyrskii et al., *Instructions on methods for determining the molecular weight of polymers, fractionation, and determination of the molecular-weight distribution*, Moscow, 1964.

17. Tsuruta Teiji, *Reactions for the Preparation of Synthetic Polymers*, Moscow, 1963.

18. V. A. Yablokov, V. A. Shushunov, A. V. Kolyaskina, ZhOKh, **33**, 2714 (1962).

19. H. Hock, H. Kropf, Ber., **88**, 1554 (1955).

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