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A. I. Yurzhenko, S. S. Ivanchev, and V. I. Galibei

Thermal Stability and Initiating Activity of Diacyl Peroxides of Paraffinic and Phenylcarboxylic Acids

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Diacyl peroxides have long found broad application as initiators of various chain processes. In particular, benzoyl peroxide has been widely and comprehensively studied as an initiator of styrene polymerization ([1,2]). The literature contains data on certain other diacyl peroxides ([3,4]). However, there has been no systematic study of the initiating activity of such peroxides in relation to the structure of the acyl radical and to the position of the peroxide in the homologous series. In particular, it has not been established how the initiating activity of these peroxides changes, with lengthening of the organic radical of their molecule, in the polymerization even of such widely studied monomers as styrene. In this connection it was of interest to study the dependence of the initiating activity of a series of diacyl peroxides of paraffinic acids on the length of their organic radical, and also of phenylcarboxylic peroxides on the number of methylene groups between the phenyl nucleus and the peroxide grouping. Such a study is important in connection with the recent spread of the suspension method of polymerization, where the use of oil-soluble diacyl peroxides is highly promising.

By a procedure analogous to that described in ([5]), we synthesized the following peroxides of phenylcarboxylic acids: phenylacetic (PFUK), hydrocinnamic (PGKK), phenylbutyric (PFMK), benzoic (PB, for comparison)—and of paraffinic acids: butyric (PMK), valeric (PVK), caproic (PKAK), enanthic (PEK), caprylic (PKLK), pelargonic (PPK), capric (PKNK), lauric (PLK), palmitic (PPaK), and stearic (PSK). The purity of the main product in the peroxides studied was not below 96% (with the exception of PFMK, whose purity was 78%).

The rate of bulk polymerization of styrene and of suspension polymerization of styrene, as well as of methyl methacrylate in bulk, was investigated, and the molecular weights of the polymers formed were determined. The thermal stability of the indicated compounds in ethylbenzene solution was also determined.

The polymerization rate was determined dilatometrically. The molecular weight of the polymers was judged from the intrinsic viscosity of benzene solutions of the polymers. The amount of undecomposed peroxide was determined iodomet-

Fig. 1. Dependence of the polymerization rate of methyl methacrylate on the nature and concentration of initiators: 1—peroxides of hydrocinnamic acid, 2—peroxides of caproic and caprylic acids, 3—peroxide of phenylbutyric acid, 4—benzoyl peroxide. Polymerization temperature 60°

Figure 1: Fig. 1. Dependence of the polymerization rate of methyl methacrylate on the nature and concentration of initiators: 1—peroxides of hydrocinnamic acid, 2—peroxides of caproic and caprylic acids, 3—peroxide of phenylbutyric acid, 4—benzoyl peroxide. Polymerization temperature 60°

rically by the Kokatnur-Jelling method ([6]). The kinetics of bulk polymerization and suspension polymerization in the case of styrene proved to be identical; therefore, below are given the data obtained in bulk polymerization.

On the basis of a study of the rate of thermal decomposition of the indicated peroxides in ethylbenzene at various temperatures, the decomposition rate constants and the values of the activation energy of the decomposition reaction were calculated; these are given in Table 1.

Table 1

Rate constants of decomposition and activation energies of the decomposition reaction
of the peroxides studied

Peroxide	$K \cdot 10^3$ at 73.5°	$K \cdot 10^3$ at 85.0° C	E, kcal/mol	Peroxide	$K \cdot 10^3$ at 73.5°	$K \cdot 10^3$ at 85.0° C	E, kcal/mol
PB	1.19	4.44	31.2	PEK	4.6	17.7	30.7
PFUK	2.8 (0°C)	36.0 (25°C)	22.0	PKLK	4.3	18.7	29.9
PGKK	5.0	20.3	30.1	PPK	4.7	19.3	29.7
PFMK	3.0	14.8	31.0	PKNK	4.6	19.0	30.1
PMK	4.1	16.7	30.1	PL	4.6	19.0	30.1
PVK	4.1	16.5	30.0	PPaK	4.7	19.7	30.0
PKAK	4.1	17.4	30.7	PSK	4.6	18.9	29.9

As is evident from the data in Table 1, the thermal stability of peroxides of the paraffin series changes little with lengthening of their hydrocarbon radical. But in the series of phenylcarboxylic peroxides, a large difference in thermal stability is observed. The most stable of them is PB. The next representative in the series—PFUK—has the lowest thermal—

Fig. 1. Dependence of the polymerization rate of methyl methacrylate on the nature and concentration of initiators: 1—peroxides of hydrocinnamic acid, 2—

Fig. 2. Dependence of the intrinsic viscosity of methyl methacrylate polymers on the concentration and nature of polymerization initiators: 1—benzoyl peroxide, 2—peroxide of phenylbutyric acid, 3—peroxides of caproic and caprylic acids, 4—peroxides of hydrocinnamic acid. Polymerization temperature 60°

Figure 2: Fig. 2. Dependence of the intrinsic viscosity of methyl methacrylate polymers on the concentration and nature of polymerization initiators: 1—benzoyl peroxide, 2—peroxide of phenylbutyric acid, 3—peroxides of caproic and caprylic acids, 4—peroxides of hydrocinnamic acid. Polymerization temperature 60°

peroxides of caproic and caprylic acids, 3—peroxide of phenylbutyric acid, 4—benzoyl peroxide. Polymerization temperature 60°

Fig. 2. Dependence of the intrinsic viscosity of methyl methacrylate polymers on the concentration and nature of polymerization initiators: 1—benzoyl peroxide, 2—peroxide of phenylbutyric acid, 3—peroxides of caproic and caprylic acids, 4 —peroxides of hydrocinnamic acid. Polymerization temperature 60°

stability; PFUK decomposes at a noticeable rate already at low temperatures, which created certain difficulties in studying it. Further along the series an increase in the stability of the peroxides is observed. Thus, PFMK is close in stability to the peroxides of the paraffin series, which fully agrees with its structure: the influence of the phenyl radical on the peroxide grouping is already considerably weakened because of its remoteness.

Of great interest is a comparison of the data obtained on the thermal stability of the peroxides studied with the kinetics of the polymerization initiated by them. The rate of polymerization of methyl methacrylate, initiated by some of the indicated peroxides, as a function of their concentration is presented in Fig. 1. The highest polymerization rates are observed with PGKK, which has the lowest thermal stability. Further, the polymerization rate decreases in the same order as the rate of decomposition of the peroxides decreases.

The change in the molecular weight of the polymers formed as a function of the peroxide concentration in methyl methacrylate is presented in Fig. 2. As was to be expected, with an increase in the rate of generation of free radicals, which is determined by the rate of thermal decomposition of the peroxides, the polymerization rate increases and the molecular weights of the polymers formed decrease. In view of the analogous structure of the radicals, their activity is, in all probability, the same.

Fig. 3. Dependence of the polymerization rate of styrene, initiated by various diacyl peroxides, on their concentration in the system: **1** —enanthic acid peroxide, **2** —valeric and caproic acid peroxides, **3** —caprylic acid peroxide, **4** —pelargonic acid peroxide, **5** —stearic acid peroxide, **6** —palmitic acid peroxide, **7** —lauric acid peroxide, **8** —hydrocinnamic acid peroxide, **9** —phenylacetic acid

peroxide, **10** –benzoyl peroxide. Polymerization temperature 73.5°.

Fig. 4. Dependence of the intrinsic viscosity $[\eta]$ of polystyrenes obtained in the presence of various concentrations of diacyl peroxides: **1** –peroxide of paraffin acids, **2** –hydrocinnamic acid peroxide, **3** –phenylacetic acid peroxide, **4** –benzoyl peroxide. Polymerization temperature 73.5°.

The kinetic picture of the polymerization of methyl methacrylate initiated by the peroxide compounds studied is fully consistent with the basic laws of polymerization kinetics:

$$V = \frac{k_p}{k_{\text{ob}}^{1/2}} k_{\text{in}}^{1/2} [M][P]^{1/2}; \qquad \bar{P} = \frac{k_p}{k_{\text{ob}}^{1/2} k_{\text{in}}^{1/2}} \frac{[M]}{[P]^{1/2}},$$

where V is the polymerization rate, $[M]$ is the monomer concentration, $[P]$ is the initiator concentration, and $k_p, k_{\text{ob}}, k_{\text{in}}$ are the constants, respectively, of the propagation, termination, and initiation reactions; $\bar{P}$ is the average length of the polymer chains (for termination by radical recombination).

A somewhat more complex picture is observed in the initiation of styrene polymerization. As can be seen from Fig. 3, the polymerization rate does not change analogously to the change in the thermal stability of the peroxides. Thus, for example, despite the greater thermal stability of the paraffin peroxides in comparison with PGKK, the polymerization rate for the latter is lower. Secondly, despite the practical constancy of the decomposition rate constants of the peroxides of the paraffin series, the polymerization rate initiated by them is not the same. The discrepancy is manifested still more strongly when considering the molecular weights of the polymers obtained, shown in Fig. 4. Despite the lowest polymerization rates observed when initiation is carried out with PB, the molecular weights of the polymers are also the lowest. Along with an increase in the rate of the process upon transition to PGKK, an increa-

molecular weights of the polymers. Finally, the highest rates of polymerization are observed for paraffin peroxides, and with these the molecular weights of the polymers also have a maximum value. Thus, in the present case we do not observe a correspondence between the rate of polymerization and the rate of thermal decomposition of the peroxides.

The data obtained do not fit the general equations for polymerization kinetics given above. To explain this we assume that, despite the identical general character of the free radicals formed during decomposition of the peroxides, the rate of termination of polymer chains during polymerization may vary. The change in the concentration of free radicals in a stationary process is determined by the following relation:

$$\frac{d\mathrm{R}}{dt} = k_0[\Pi] - k_2[\mathrm{R}_0]^2 - k_3[\Sigma \mathrm{M}_n\mathrm{R}]\mathrm{R}_0 - k_4[\mathrm{M}_n\mathrm{R}]^2,$$

where R_0 are primary radicals, [Π] is the peroxide concentration, M_nR are polymer radicals, and k_0, k_2, k_3, k_4 are the constants of the corresponding reactions. Chain termination, therefore, may occur through interaction of primary radicals with polymer radicals, which will affect the molecular weight of the polymers, and of polymer radicals with one another. In the case of PB we allow termination of primary radicals with polymer radicals, which is accompanied by low polymerization rates and a lower molecular weight of the polymers. In the case of paraffin peroxides, termination may proceed through interaction of polymer radicals with one another, which is accompanied by higher rates and greater molecular weights of the polymers.

Despite the high decomposition rates of PFUK, in the polymerization of styrene it proved to be only slightly active; this indicates, along with the low activation energy of decomposition, a different mechanism of thermal decomposition of the peroxide.

Thus, the thermal stability of homologous series of peroxides of paraffin and phenylcarboxylic acids has been investigated. It has been shown that, in the series of peroxides of phenylcarboxylic acids, the introduction of a CH_2 group between the peroxide grouping and the phenyl radical sharply changes the thermal stability, whereas in the paraffin series it remains practically unchanged. The polymerization of methyl methacrylate initiated by the indicated peroxides has been studied. It has been shown that the kinetic picture of the process changes in correspondence with the rate of thermal decomposition of the peroxides. The polymerization of styrene initiated by the peroxides studied has been investigated. In this case there is no correspondence between the kinetics of the process and the rate of thermal decomposition of the initiators. Peroxides of the paraffin series possess considerably better initiating properties in the polymerization of styrene than the widely used PB.

Odessa State University
named after I. I. Mechnikov

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Note: Figure translations are in progress. See original paper for figures.