CHEMISTRY

S. S. IVANCHEV, A. I. YURZHENKO, and N. I. SOLOMKO

1961

SovietRxiv

Figure 1. Dependence of the rate of styrene polymerization on the concentration of the investigated initiators at different temperatures: 1 –PTB at 85°; 2 –TBPB at 73.5°; 3 –PTB at 95°; 4 –TBPB at 85°; 5 –PTB at 105° and 6 –PB at 85°

Figure 1: Figure 1. Dependence of the rate of styrene polymerization on the concentration of the investigated initiators at different temperatures: 1 –PTB at 85°; 2 –TBPB at 73.5°; 3 –PTB at 95°; 4 –TBPB at 85°; 5 –PTB at 105° and 6 –PB at 85°

Abstract

Full Text

CHEMISTRY

S. S. IVANCHEV, A. I. YURZHENKO, and N. I. SOLOMKO

FEATURES OF THE KINETICS OF STYRENE POLYMERIZATION INITIATED BY tert-BUTYL PEROXIDE AND tert-BUTYL PERBENZOATE

(Presented by Academician B. A. Kazanskii, May 19, 1961)

As shown in several works ([1]), tert-butyl peroxide and tert-butyl perbenzoate (PTB and TBPB), individually and especially in mixtures with other peroxide compounds, are active initiators of suspension polymerization, combining high polymerization rates with a high molecular weight of the polymers formed.

In connection with this, it was of interest to study in more detail the process of polymerization initiated by the indicated peroxide compounds. For this purpose, in the present work we studied the rate of styrene polymerization at various concentrations of PTB and TBPB and at different temperatures. For comparison, under the same conditions, styrene polymerization was studied in the presence of the initiator benzoyl peroxide (PB). The change in the molecular weight of polystyrenes with the change in the depth of conversion and certain other conditions was also investigated. Polymerization was carried out in the monomer mass and in an emulsion stabilized with a 0.2% solution of sulvar. The polymerization rate was determined dilatometrically. The experiments were performed in the temperature interval from 85 to 115°. The concentration of initiators was varied from 0.01 to 0.12 g-mole/l of monomer. The molecular weight of the polymers was judged from the intrinsic viscosity of benzene solutions of the polymers, determined at 25°.

Fig. 1. Dependence of the rate of styrene polymerization on the concentration of the investigated initiators at different temperatures: **1** –PTB at 85°; **2** –TBPB at 73.5°; **3** –PTB at 95°; **4** –TBPB at 85°; **5** –PTB at 105° and **6** –PB at 85°.

In view of the identity of the kinetic picture of polymerization in bulk and by the suspension polymerization method ([2]), which we verified experimentally, the data given below pertain only to bulk polymerization.

The kinetic curves for the accumulation of polystyrenes at various concentrations of PTB, TBPB, and PB are presented in Fig. 1. It should be noted that a linear dependence of the depth of conversion on the polymerization time in the case of the use of PTB and TBPB occurs only at low depths of conversion (up to 20-30%); subsequently, self-acceleration of the process is observed.

The rate constant for the thermal decomposition of PB in an ethylbenzene solution at the polymerization temperature of 85° is $4.4 \cdot 10^{-3}$, for TBPB $6.1 \cdot 10^{-4}$; for PTB, thermal decomposition under these conditions proceeds extremely slowly. Thus, the observed increase in the polymerization rate, depending on the nature of the initiators used, is parallel to the rate of their thermal decomposition.

The dependence of the characteristic viscosity of the polymers on the concentration and nature of the initiators studied is shown in Fig. 2. As was to be expected, it decreases regularly in the series PB–TBPB–PTB. In the case of PB and TBPB, we observe the characteristic pattern of a decrease in the molecular

Fig. 2. Dependence of the characteristic viscosity of polymers on concentration: 1 –PB, 2 –TBPB, 3 –PTB. Polymerization temperature 85°.

Fig. 3. Change in the characteristic viscosity of polymers with change in the depth of conversion in the presence of initiators: 1 –PB, 2 –PTB at 95°, 3 –PTB at 115°, 4 –TBPB at 85°. Peroxide concentration 0.05 g-mol/l of monomer.

weight of the polymers with increasing initiator concentration. In the presence of PTB, with a change in its concentration in the system, no decrease in molecular weight is observed. Within the range of PTB concentrations studied–from 0.01 to 0.10 mol/l of monomer–the characteristic viscosity of the polymers increases slightly with increasing concentration. This fact is difficult to reconcile with the generally accepted rule according to which an increase in initiator concentration leads to a decrease in the molecular weight of the polymers.

It is interesting to note that, in polymerization initiated by PTB, increasing the process temperature does not lead to a significant decrease in the characteristic viscosity of the polymers. Thus, for example, when the temperature is raised from 85 to 105°, the polymerization rate increases by almost an entire order of magnitude, while the characteristic viscosity of the polymers decreases by only 50% (Fig. 1 and Table 1).

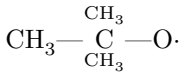
Table 1

Dependence of the characteristic viscosity of polymers on the time of heating at the polymerization temperature

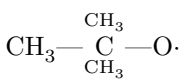
Initiator	Conc.	Temp., °C	Heating duration, h	$[\eta]$	Initiator	Conc.	Temp., °C	Heating duration, h	$[\eta]$
PB	0.05	85	–	0.27	PTB	0.05	95	–	1.30
PB	0.05	85	1	0.27	PTB	0.05	95	1	1.48
PB	0.05	85	3	0.26	PTB	0.05	95	3	1.60
TBPB	0.05	85	–	1.40	PTB	0.057	105	–	1.20
TBPB	0.05	85	1	1.51	PTB	0.057	105	1	1.34
TBPB	0.05	85	3	1.59	PTB	0.057	105	3	1.40
PTB	0.05	85	–	2.30					

We investigated the change in the intrinsic viscosity of polymers during the conversion of styrene into polystyrene. The data obtained are presented in Fig. 3. It turned out that, when polymerization was initiated by PB, up to 50% conversion there was a slight increase in the intrinsic viscosity of the polymers. Above this conversion it remained constant. If, however, polymerization was initiated by TBPB, and especially by PTB, the intrinsic viscosity of the polymers increased strongly even at considerable degrees of conversion, when the concentration of monomer in the system was already insignificant. Moreover, if the polymer was kept for some time at the polymerization temperature after the end of the process, then, despite the practical exhaustion of the monomer (its content could not exceed 2-3%), an increase in the intrinsic viscosity of the polymers was observed. The data obtained are given in Table 1. When polymerization was initiated by PB, this was not observed; the intrinsic viscosity of the polymers did not change on heating.

Such results are associated with the high activity of the radicals formed during the decomposition of PTB and TBPB,



The literature ([3]) contains information on the extremely high reactivity of radicals



which are capable of abstracting hydrogen from various solvents. Moreover, hydrogen is most readily abstracted from tertiary carbon atoms, especially from

those bonded to a phenyl group ([4]). The free radicals formed during the decomposition of PTB and TBPB in the polymerization system can interact with tertiary carbon atoms in the polymer chain according to the scheme:

$$—\overset{H}{C}—CH_2— + CH_3—\overset{CH_3}{\underset{CH_3}{C}}—O\cdot \rightarrow —\dot{C}—CH_2— + CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OH,$$

giving polymer free radicals which, in the presence of monomer, continue to grow, and in its absence can combine with one another, giving a polymer of higher molecular weight. Owing to the high thermal stability of these peroxides, even after the completion of polymerization the system will contain the amount of initiator necessary for this (provided the polymerization temperature is not too high). In those cases where polymerization is carried out at high temperatures, because of the high rates of initiator decomposition it may be exhausted by the end of the process. In this case heating does not change the molecular weight, and the change in intrinsic viscosity with the course of the process (Fig. 3) is weak.

Thus, the high initiating "activity" of tert-butyl-based initiators is associated with the interaction of the tert-butyl radicals formed with tertiary carbon atoms of polystyrene, i.e., with chain transfer through the polymer. In this case, as it were, grafted homopolymerization occurs. The role of the less stable peroxide, if these initiators

are used in mixtures with others, consists in converting the monomer partially into polymer in order to create conditions for the gel effect ([5]).

Odessa State University
named after I. I. Mechnikov

Received
11 V 1961

CITED LITERATURE

[1] A. V. Golubeva, G. A. Nosaev, N. F. Usmanova, E. I. Eremina, K. A. Sivograkova, *Plastmassy*, **1**, 3 (1961); R. P. Perry, K. P. Seltzer, *Modern Plastics*, **25**, No. 3, 216 (1947). [2] W. P. Hohenstein, H. Mark, *Polymer Sci.*, **1**, 127 (1946). [3] J. H. Reley, F. F. Rust, W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 88 (1948); N. A. Milas, D. M. Surgenor, *J. Am. Chem. Soc.*, **68**, 205, 643 (1946). [4] A. L. Williams, E. A. Oberright, J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956). [5] A. A. Berlin, I. M. Gilman, *Khim. prom.*, **8**, 1 (1957); E. Tromsdorf, E. E. Schildknecht, *High Polymer*, **10**, 69 (1956).

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