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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Polymerization of Styrene Initiated by Acetylenic Peroxides

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Abstract—The initiating activity of acetylenic peroxides in polymerization of styrene was studied. The kinetic parameters of the polymerization and its initiation were calculated. The effect exerted by the structure of radicals on the initiating activity of peroxides was evaluated.

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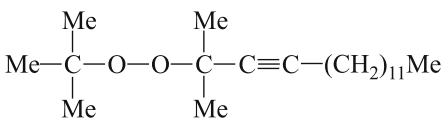
Acetylenic peroxides are stable explosion-proof initiators of radical chain processes [1] and promising high-temperature initiators for polymerization. Also, they are rubber vulcanizing agents [2]. 2,5-Dimethyl-2,5-di(tert-butylperoxy)-3-hexyne (Trigonox 145-E-85 brand) is produced on an industrial scale by the Netherlands Company "AlkzoNobel" and is used as initiator for polymerization of acrylates, styrene, and for cross-linking of polyethylene, especially in cable industry. It was shown [3] that ferrocene-containing acetylenic peroxides are effective initiators for polymerization of styrene, and the whose initiating activity can be varied within wide range depending on the structure of radicals.

In this work we studied polymerization of styrene initiated by acetylenic peroxides, 2-methyl-2-*tert*-butylperoxy-3-hexadecyne (**I**), 4-*trans*-[2-methyl-2-(2-methyl-2-butylperoxybut-3-yn-4-yl)]-*cis*-2,2,6-trimethyl bicyclo[3.1.1.]heptan-4-ol (**II**), 2-methyl-2-(2-methyl-2-butylperoxy)-5-phenyl-5-methoxy-5-(4-methoxyphenyl)-3-pentyne (**III**), 4-*trans*-[2-methyl-2-(2-methyl-2-pentyl peroxybut-3-yn-4-yl)]-*cis*-2,2,6-trimethylbicyclo[3.1.1]-heptan-4-ol (**IV**), 2-methyl-2-(2-methyl-2-pentyl peroxy)-5-phenyl-5-methoxy-5-(4-methoxyphenyl)-3-pentyne (**V**), 1-(1-acetoxy adamantyl)-3-methyl-3-(methyl-2-pentylperoxy)-1-butyne (**VI**). 2-*Tert*-butylperoxy-2-



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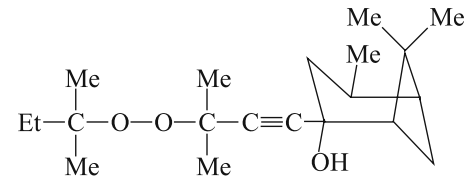

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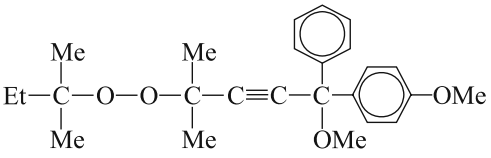

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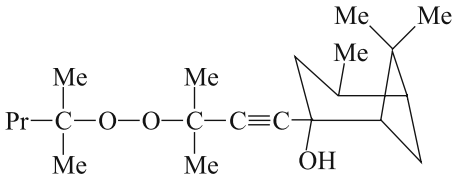

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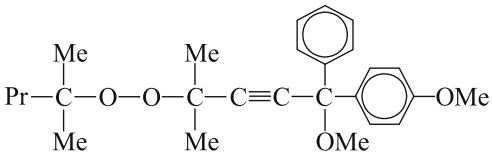

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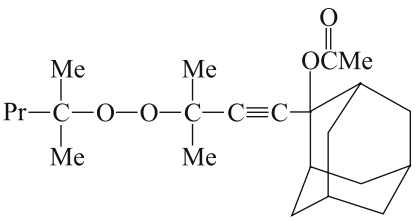
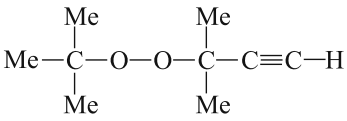


VI

Kinetic parameters of styrene polymerization initiated by acetylenic peroxides

Initiator	T, °C	$\omega_p \times 10^5$, M	$K_p \times 10^5$, M	A_p, M s^{-1}	E_p, kJ mol^{-1}	$k_{in} \times 10^6$, s^{-1}	A_{in}, s^{-1}	E_{in}, kJ mol^{-1}
(I)	90	3.82	3.9	3.06×10^{10}	103.5 ± 5.4	0.7	4.90×10^{15}	151.7 ± 10.8
	110	2.43	26.7			12.9		
	120	7.9	50.5			29.8		
(II)	90	6.1	7.7	1.60×10^{9}	92.5 ± 1.9	2.8	1.79×10^{13}	130.7 ± 3.4
	100	14.1	18.2			9.5		
	110	29.2	38.3			26.4		
(III)	100	1.62	20.7	4.56×10^{9}	95.5 ± 8.8	12.2	1.38×10^{13}	136.4 ± 17.3
	110	9.27	38.8			27.2		
	120	4.6	99.4			115.0		
(IV)	100	8.34	10.8	1.73×10^{9}	94.2 ± 6.0	3.3	2.10×10^{13}	134.1 ± 11.9
	110	20.5	26.8			13.0		
	120	37.9	50.5			30.0		
(V)	90	5.4	6.3	8.63×10^{9}	98.1 ± 7.8	1.8	4.67×10^{14}	141.6 ± 15.9
	100	13.6	17.6			8.9		
	110	25.6	34.0			20.8		
(VI)	90	6.01	7.6	2.28×10^{10}	100.7 ± 1.2	2.7	3.60×10^{15}	147.0 ± 2.5
	100	4.03	18.1			9.33		
	110	2.9	43.2			3.7		
(VII)	110	16.8	18.3	2.15×10^{10}	103.2 ± 1.6	6.1	2.90×10^{15}	151.8 ± 3.3
	120	40.5	40.5			19.2		
	130	75.9	91.4			64.7		



VII

methyl-3-butyne (**VII**) possessing a nonsubstituted triple bond was chosen for comparison.

Polymerization of styrene under the influence of acetylenic peroxides (**I**)-(**VII**) was performed at 90-110°C in the bulk and monitored dilatometrically. The concentration of peroxides at room temperature was 0.01 M. The kinetic curves of styrene polymerization initiated by peroxides (**I**)-(**VII**) are described by a linear dependence. The polymerization rate of styrene in the presence of peroxides (**I**)–(**VII**) is proportional to the square root of their concentration and therefore the rate constants of polymerization (k_p) and initiation (k_{in}) may be calculated by the following equations:

$$k_p = \left(\frac{\theta_p^2 - \theta_T^2}{[\mathrm{ROOR}][\mathrm{M}]^2} \right)^{0.5},$$

$$k_{in} = \left(\frac{k_p}{k_g / k_0^{0.5}} \right)^2,$$

where θ_p is the polymerization rate in the presence of the initiator; θ_T is the rate of thermal polymerization of styrene; [ROOR] is the peroxide concentration (M); [M] is the styrene concentration (M); and k_g and k_0 are the rate constants of the chain growth and termination, respectively.

The ratio of the constants $k_p/k_0^{0.5}$ ($l^{0.5}$ mol$^{-0.5}$ s$^{-0.5}$) for styrene was calculated by the formula [4] (with the activation energy given in cal/mol^{-1}).

$$k_p/k_0^{0.5} = 380\exp(-6500/RT) .$$

The kinetic parameters of the polymerization are given in the table.

The comparison of the rate constants of the elementary stages of chain initiation presented in Table 1 shows that acetylenic peroxides are arranged in the following order with respect to the increasing initiating activity: (**VII**) < (**I**) ≈ (**IV**) < (**V**) < (**II**) ≈ (**III**) < (**VI**). Replacement of the hydrogen atom in peroxide (**VII**) for the dodecyl radical increases approximately twice the initiating activity of peroxide (**I**). Replacement of the ethyl radical in peroxides (**II**) and (**III**) for the propyl radical decreases the initiating activity of peroxides (**IV**) and (**V**). Data obtained by the

study of the thermal stability of peroxides (**III**) and (**V**) by the derivatographic method in [5] show that replacement of the ethyl group for the propyl group increases the decomposition temperature of peroxides, i.e., makes their thermal stability higher. Similar features were found in studying the initiating activity of ferrocene-containing peroxides in polymerization of styrene [3].

Introduction of acetoxy adamantyl group into the molecule of acetylenic peroxide (**VI**) increases the initiating activity by a factor of 2.5 and 1.5 in comparison with peroxides (**IV**) and (**V**), respectively. The comparison of the initiating activities of peroxides (**I**)-(**VII**) with that of ferrocene-containing peroxides of the similar structure [3] shows that the introduction of ferrocene fragment increases the initiating activity by a factor of 2.5–3. The comparison of the initiating activities of peroxides (I)–(VII) with those of industrial high-temperature initiators, dicumyl peroxide and di-*tert*-butylperoxide [6] shows that they are promising high-temperature initiators and cross-linking agents. The thermal stability of peroxides (I)–(VII) is by a factor of 3–5 larger than that of dicumyl peroxide and di-*tert*-butylperoxide.

EXPERIMENTAL

The initiating activity of peroxides (**I**)–(**VII**) in polymerization of styrene in the bulk was evaluated dilatometrically at 90–130°C in UTU-2/77 ultrathermostats. The polymerization was performed to conversions not exceeding 10%. Water was a thermostaing liquid at 90°C and silicone oil, at 100–130°C. The fluctuations of temperature did not exceed ±0.05°C in the range 90–100°C and ±0.01°C in the range 110–120°C.

The volume of the working cell of the dilatometers was 4-6 ml. The scale division of the measuring capillary was 0.001 ml. The cell volume was calibrated with purified mercury [7]. Styrene was purified by fourfold washing with 10% NaOH and distilled water to neutral reaction, dried over anhydrous calcium chloride, and vacuum-distilled; bp 46–47°C at 20 mm Hg.

The density of styrene at the polymerization temperature was determined dilatometrically, as in [7], in the presence of Agidol-2 polymerization inhibitor. The concentration of styrene at the polymerization temperature was calculated by the formula

$$[M_t]=\rho_t\,1000/[M_{20}]\,,$$

where $[M_t]$ is the concentration of styrene at the polymerization temperature (M) and $[M_{20}]$ its concentration at 20°C (M); ρt is the density of styrene at the polymerization temperature (g l^{-1}).

We used the thermal expansion coefficient of styrene and introduced a correction for the true concentration of the peroxides at the polymerization temperature, which was calculated by the formula:

$$[ROOR_t] = [ROOR_{20}]\rho_t/\rho_{20},$$

where $[ROOR_t]$ is the concentration of peroxide at the polymerization temperature (M), $[ROOR_{20}]$ is its concentration at 20°C (M), ρ_t is the density of styrene at the polymerization temperature (g l^{-1}) and ρ_{20}, is its density at 20°C (g l^{-1}).

The contraction coefficients were taken from [8]. The rate of thermal polymerization of styrene θth (M s^{-1}) was determined by the method [3] described by the formula

$$\theta_r = 1.746 \times 10^7 \exp\,(-82620 \pm 440/RT).$$

Peroxide (**I**) was synthesized by the procedure [9]. To do this, 2-*tert*-butylperoxy-2-methyl-3-butyne (**VII**) was reacted with *n*-butyllithium in an argon flow in *n*-hexane to obtain the corresponding lithium peroxy acetylenide, which was alkylated with decyl bromide in the presence of hexamethyl phosphoric acid triamide to yield peroxide (**I**). Acetylenic peroxides (**III**), (**V**) were obtained by the following manner [5]. *n*-Butyllithium was brought into reaction with 3-methyl-3-*tert*-alkyl peroxy butynes in a tetrahydrofuran solution to obtain the corresponding lithium peroxy acetylenides which reacted with 4-methoxy benzophenone to yield lithium peroxyalcoholates. Peroxides (**III**), (**V**) were obtained upon the reaction of peroxyalcoholates with methyl iodide in dimethyl sulfoxide. Peroxides (**II**), (**IV**) were obtained in the same way using camphor [10]. Peroxide (**VI**) was synthesized by reaction of *n*-butyllithium with adamantanone with following acylation of the obtained alcohol with acetic anhydride in the presence of perchloric acid [11]. Peroxide (**VII**) was synthesized by the procedure [12].

The results of kinetic runs were processed and plotted using the methods of mathematical statistics.

CONCLUSIONS

The initiating activity of acetylenic peroxides changes in the order (**VII**) < (**I**) ≈ (**IV**) < (**V**) < (**II**) ≈ (**III**) < (**VI**).

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