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THERMAL DECOMPOSITION OF THE PEROXIDE BONDS IN POLYMERS

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Peroxide-containing polymers containing diacyl peroxide groups in the main chain and in the side parts of macromolecules were obtained. The thermal decomposition of peroxide groups in macromolecules is well described by the first-order kinetic equation of rate. During the decomposition of O–O groups of polymers containing peroxide groups in the main chain, a decrease in the degree of polymerization of polymers is observed. The solvent in which the process takes place and the nature of the polymer-matrix, which contains peroxide groups, affects the rate of decomposition of peroxide groups and the degree of degradation of polymer macromolecules. Peroxide-containing polymers can be successfully used to obtain block copolymers, crosslinking agents, and macromolecular initiators.

Keywords: Peroxide-containing polymers, Thermal decomposition, Degree of polymerization, Constants of thermal decomposition, Activation energy

Introduction

Polymers that contain peroxide groups in the macromolecule can be used to obtain block copolymers, surface modification of mineral fillers, synthesis of composite materials [1, 2]. One of the methods that allow obtaining peroxide groups in the main chain is to carry out polymerization in the presence of oligomeric peroxide compounds or oxygen [3–5]. Another method of obtaining peroxide-containing polymers is the modification of reactive groups in polymer macromolecules with low molecular weight peroxide compounds [4, 5]. In our work, polymers with reactive peroxide groups were obtained and the thermal decomposition of O–O groups in polymers in the condensed state and various organic solvents was investigated.

Experimental

Polymers containing peroxide groups in the main chain of polystyrene (PS), polyvinyl acetate (PVA) and polymethacrylic acid (PMAA) were obtained by radical polymerization in the presence of oligomeric peroxide of sebacic acid (PSA). Oligomeric peroxide was obtained by the method of interfacial polycondensation according to the method [6]. The degree of polycondensation of PSA (n) was in the range of 12–25. The formula of peroxide $(-O-O-C(O)-(CH_2)_8-C(O)-)_n$. In the first stages of polymerization, up to 5–10% of the conversion, a polymer is formed, which contains peroxide bonds in

the main chain. Monomeric units of the oligomeric peroxide in the main chain of the polymer can exist as one peroxide unit or several. Polystyrene (PS) containing peroxide groups was obtained by polymerization of styrene in the presence of 0.05 mol/l PSA. Upon reaching 5 to 8% conversion of the monomer to the polymer, the mixture was quenched and the peroxide-containing product was isolated. Polyvinyl acetate with peroxide groups was synthesized in a solution of ethyl acetate. Isolated in the initial stages of PVA was characterized by the degree of polymerization of 1710 and contained 1.67% of peroxide groups. The average content of peroxide groups per polymer macromolecule was 6.3. Polymethacrylic acid was obtained by precipitating polymerization from dioxane solutions in the presence of PSA. The obtained PMAA had an intrinsic viscosity determined in ethanol solution of 0.60 g/dl and contained 0.78% active oxygen. Active oxygen in the studied polymers was determined by the method [7]. Acid numbers of polymers based on maleic anhydride were determined by the method [8]. The electrical conductivity of aqueous-organic solutions was measured according to the standard method.

Peroxide groups in the macromolecules of a copolymer of styrene and maleic anhydride (SMA) were introduced by the method of modification of this polymer with peroxydecanoic acid. The SMA copolymer was synthesized by radical polymerization of an equimolecular mixture of styrene and maleic anhydride in the presence of benzoyl peroxide at a concentration of 0.025 mol/l at 75°C. The molecular weight of SMA, determined viscosimetrically was 66000. As it is known under these conditions, a polymer is obtained monomer units in which they alternate [9]. Peroxydecanoic acid was synthesized according to the method [10].

The thermal decomposition of peroxidized polymers was investigated by ampoule method. The polymer solution of a certain concentration was placed in an ampoule, purged with argon and sealed. At certain intervals, the ampoules were removed from the thermostat, cooled sharply, opened and analyzed for the content of peroxide groups remaining by the iodometric method [7]. The ampoules were placed in a thermostat, the temperature of which was maintained with an accuracy of ± 0.1 °C. Kinetic experiments were performed in the temperature range 333–358 K. All solvents used in the work were purified and distilled in an argon atmosphere according to the methods [11, 12]. The molecular weights of the polymers were determined viscosimetrically. The intrinsic viscosity of polystyrene was determined in benzene solution, and the molecular weight (M) was determined by the formula:

$$M = 1606 \cdot [\eta] \cdot 1.3 \cdot 10^4, \quad (1)$$

where $[\eta]$ is the intrinsic viscosity. The intrinsic viscosity of PVA was determined from a solution of acetone at 30 °C. To calculate M we used the formula:

$$[\eta] = K \cdot M^\alpha, \quad (2)$$

where K and α are respectively $1.02 \cdot 10^{-4}$ and 0.72. The molecular weight of PMAA was determined from a solution of 0.002 N HCl solution at a temperature of 25°C. To calculate the molecular weight of PMAA used the formula:

$$[\eta] = 6.6 \cdot 10^{-4} M \quad (3)$$

The characteristic viscosity of the copolymer SMA was determined from a solution of acetone at 30°C. The values K and α are respectively $8.69 \cdot 10^{-5}$ and 0.74. Constants for calculating molecular weights are taken from the reference book [13].

Results and discussion

The kinetics of thermodestruction of peroxide groups in polymer macromolecules is well described by the kinetic equation of the reaction rate of the first order. In Fig. 1 shows the kinetic curves of the thermolysis of peroxide groups in the PVA macromolecule in dioxane solution. In the coordinates $\ln C_0/C_t$ from t the kinetic curves are linear. By the tangent of angles of inclination of the dependences (Fig. 1) were calculated the effective constants (k) of the thermal decomposition. Numerical values of the effective constants of the rate of thermolysis are given in Table 1. According to the temperature dependences k , the total activation energies (E_a) of the process of thermal decomposition of peroxide groups in polymers, the numerical values of which are in the range of 109.2–144.3 kJ/mol (Table 1), were calculated. The nature of the polymer matrix in which the peroxide groups are introduced affects the rate of thermolysis and the numerical value of E_a . In the PMAA matrix at 348 K the peroxide groups decompose at a high rate, and in PVA and PS the rate constant is more than twice smaller decomposition of peroxide groups in the main chain of the studied polymers.

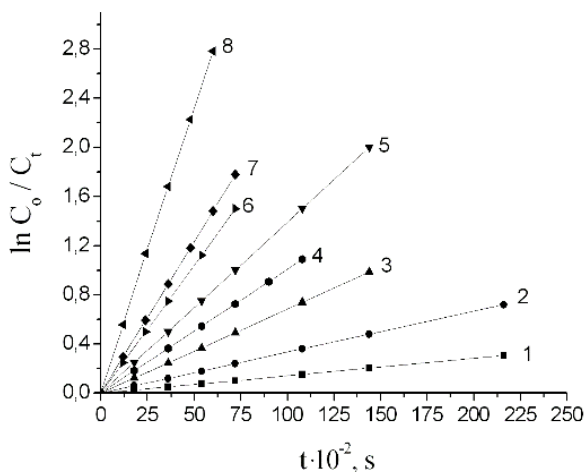


Fig. 1. The kinetic curves of the thermal decomposition of peroxide groups in PVA macromolecules (1, 2, 3, 5, 7) PMAA (8,) and PS (4). Solvent: dioxane (1, 2, 3, 5, 7), toluene (4), ethanol (6) solid polymer (8). Temperature, K: 1 – 333; 2 – 338; 3 – 343; 4, 5 – 348; 6, 7, 8 – 353.

Numerical values of E_a for the decomposition process in the PVA matrix is 144.3 kJ/mol, and in PMAA the value of E_a is the smallest and is 109.2 kJ/mol. Therefore, the nature of the polymer in the main chain of which the introduced peroxide groups has a significant effect on the thermal stability of the O–O groups. The constants of thermal destruction of diacyl peroxide groups in polymers and the corresponding values of E_a are close to the corresponding values of diperoxides in different solvents [14].

During the thermal decomposition of peroxide groups in the investigated polymers, one should expect a change in the degree of polymerization (P) of the original polymer. The study of the molecular weights of PVA, PMAA and PS after heat treatment confirms this conclusion. Heating solid polymers in an argon atmosphere does not change the degree of polymerization. This fact indicates that after the initial decomposition of the O–O group

there is a high probability of recombination of the radicals formed. Thermal decomposition of polymers containing peroxide groups in the main chain in solutions in the presence of ionol leads to a decrease in the degree of polymerization (Fig. 2). The change in the degree of polymerization of PVA during heat treatment in the solid state and in solutions of dioxane, chloroform, ethyl acetate and benzene are shown in Fig. 2.

Table 1

The kinetic and activation parameters of thermal decomposition of peroxide groups in Polyvinyl acetate (PVA), Poly(methacrylic acid) (PMAA) and polystyrene (PS)

Polymer	Environment	The rate constant of thermolysis, $k \cdot 10^5, s^{-1}$					Energy of activation (E_a), kJ/mol
		333 K	338 K	343 K	348 K	353K	
PVA	Polymer	1.31	2.89	6.06	13.6	26.5	144.3
PVA	Dioxane	1.41	3.33	6,84	13.9	24.7	137.2
PVA	Chloroforme	1.56	3.63	6.76	13.9	23.4	133.5
PVA	Benzene	1.23	2.40	5.65	9.60	23.0	141.8
PVA	Ethyl acetate	1.12	2.57	6.01	9.64	21.7	143.5
PMAA	Polymer	5.09	8.70	14.4	27.6	46.4	109.2
PMAA	Methanole	1.67	3.37	6.40	15.3	23.4	129.7
PMAA	Ethanole	1.39	2.55	4.81	10.3	20.8	133.9
PS	Toluene	1.38	2.77	5,00	10.1	–	127.7

The error in determining of the energy of activation ± 4.0 kJ/mol.

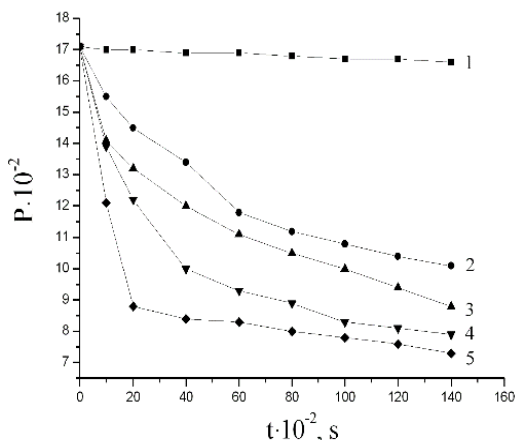


Fig. 2. Changing the degree of polymerization of PVA macromolecules during heat treatment. Temperature 353 K. Solvent: 1 – solid polymer; 2 – ethyl acetate; 3 – dioxane; 4 – chloroform; 5 – benzene. The concentration of PVA 1 g/100 ml.

When heating the peroxidized polymers in solution, there is a change in the degree of polymerization of the original PVA. The least peroxidized PVA decomposes in ethyl acetate (Fig. 2 curve 2). In dioxane, the polymer degrades to a greater extent. Conducting

thermal decomposition in chloroform leads to a significant change in the degree of polymerization, and in the gasoline solution the degree of polymerization of PVA changes the most (Fig. 2). The study of the intrinsic viscosity of the original PVA in these solvents increases in a number of benzene > chloroform > dioxane > ethyl acetate. It is known that the intrinsic viscosity is related to the size of the polymer ball in solution.

The larger the polymer ball is, the more the degree of polymerization of the original PVA decreases. After heat treatment for two hours, the change in the degree of polymerization of all investigated peroxide-containing polymers does not change.

To characterize the change in the degree of polymerization (P) from the time of heat treatment, we used the ratio of the initial degree of polymerization (P_0) to the degree of polymerization of the polymer after heat treatment (P_1). These values are shown in Table 2. The degree of degradation of PVA macromolecules depends on the nature of the solvent in which the heat treatment was performed (Table 2). To the greatest extent the degradation of peroxide-containing PVA takes place in benzene. In ethyl acetate, the change in the degree of polymerization of PVA is the smallest.

Table 2

The ratio of the initial degree of polymerization (P_0) of the studied polymers to the degree of polymerization after heat treatment in different solvents (P_1)

Polymer	Solvent	The initial degree of polymerization $P_0 \cdot 10^{-2}$	P_0/P_1			
			The heat treatment time, s			
			2400	3600	4800	7200
PVA	-	17.1	1.005	1.012	1.018	1.018
PVA	Ethylacetate	17.1	1.179	1.221	1.425	1.425
PVA	Dioxane	17.1	1.295	1.425	1.693	1.693
PVA	Chloroforme	17.1	1.402	1.555	1.839	1.839
PVA	Benzene	17.1	1.693	1.943	2.111	2.111
PMAA	-	5.23	1.007	1.015	1.020	1.020
PMAA	Methanole	5.23	1,080	1,120	1.200	1,200
PMAA	Ethanole	5.23	1,095	1,180	1.256	1,254
PS	-	6.0	1.000	1.017	1.026	1.026
PS	Toluene	6.0	1.154	2.100	2.321	2.321

During heat treatment of peroxide-containing PMAA in solution, the change in the degree of polymerization is the smallest. Carrying out heat treatment of peroxide-containing PS in toluene leads to a decrease in the degree of polymerization by more than two times (Table 2).

Modification of PSMA (Poly(styrene-co-maleic anhydride)) with peroxydecanoic acid was performed in dioxane and acetone, and during the process the ratio between the amount of PDA (Peroxydecanoic acid) and maleic anhydride units was changed. The experimental conditions and the characteristic viscosities of the obtained products are given in Table 3.

According to the obtained results, by changing the ratio between the amount of PDA modifier and the anhydride units of the SMA (A), you can adjust the number of peroxide groups in the macromolecule. It should be noted that at small values of A, almost all PDA molecules react with the anhydride units of the SMA. The increase in the PDA content in the reaction mixture leads to an increase in the active oxygen content in the final product; however, judging by the obtained data, not all anhydride units in the

macromolecule of the original SMA are available for the PDA. Thus, at a molar ratio (A) of the PDA/anhydride units of the SMA, equal to 1.0, only 87.2% of the anhydride groups react. Even with a 1.5-fold excess of the PDA, the conversion of anhydride groups is approximately 90% (Table 3). An increase in the number of peroxide groups in the PSMA macromolecule leads to a decrease in the intrinsic viscosity of the polymer. The intrinsic viscosity determined at 303 K in dioxane for PSMA decreases with increasing peroxide content by more than 1.6 times (Table 3). As expected, as the number of anhydride groups reacting, the acid numbers (Kn) decrease. The obtained modified PDA peroxide-containing polymers are well soluble in aqueous-organic mixtures. The study of the electrical conductivity of aqueous-organic (1:1) solutions of PSMA confirms the conclusion that the number of carboxyl groups in the copolymer macromolecule decreases. (Fig. 3). Reducing the acid number of the peroxidized copolymer leads to a decrease in the electrical conductivity of its aqueous-dioxane solutions.

Table 3

Synthesis conditions and characteristics of peroxide-containing copolymers (solvent - dioxane)

№	A (molar ratio of PDA/anhydride units SMA)	The content of active oxygen, %	The number of unreacted anhydride units	Characteristic viscosity, (η), dl/g	Acid number (An)
1	0	0	0	0.45	540
2	0.25	0.039	24.6	0.43	450
3	0.50	0.078	49.3	0.42	410
4	0.75	0.093	58.7	0.38	375
5	1.0	0.138	87.2	0.34	310
6	1.5	0.143	90.3	0.27	295

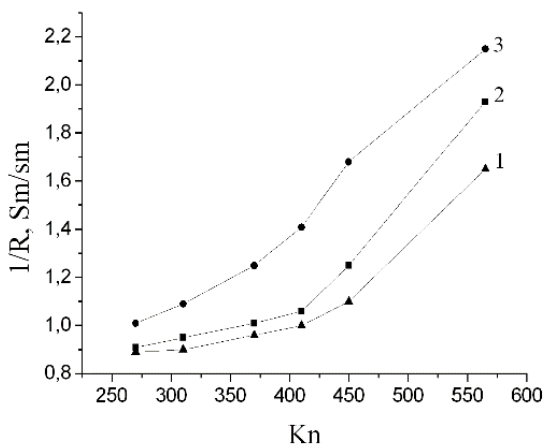


Fig. 3. Dependence of electrical conductivity of water-organic (1:1) PSMA solutions on acid number (K_{ch}). Solvent: 1 – acetone; 2 – dioxane; 3 – DMF (Dimethylformamide). The polymer concentration is 1 g/dl.

Viscosimetric studies of the original polymer (SMA) and peroxidized samples obtained by modification in dioxane (PSMA-1) and acetone (PSMA-2) are given in

Table 4. The intrinsic viscosities of the starting and modified copolymers were determined at 303 K from solutions of acetone, dioxane and DMF.

Table 4

Characteristic viscosities of the starting polymer (SMA) and peroxidized copolymers in different solvents (temperature 303 K)

Copolymer	Solvent during modification	The content of active oxygen, %	Characteristic viscosity (η), dl/g		
			Acetone	Dioxane	DMF
SMA	–	0	0.27	0.45	0.56
PSMA-1	Dioxane	0.143	0.11	0.27	0.30
PSMA-2	Acetone	0.148	0.10	0.25	0.32

The highest intrinsic viscosity is observed for SMA in DMF solution, as this solvent has the highest solvating ability. The size of the macromolecular tangle of peroxide-containing copolymers in the studied solutions is less than the original SMA. The intrinsic viscosities of peroxide-containing copolymers in acetone are the lowest and differ from the corresponding values for DMF more than twice.

The results of the study of the thermal stability of peroxide-containing polymer PSMA-1 in different solvents are given in Table 5.

Table 5

Effective constants of thermodestruction of peroxide bonds in the macromolecule of peroxide-containing copolymers PSMA-1

Solvent	$k \cdot 10^5 \text{ s}^{-1}, \Delta k = \pm 0,03k$						Energy of activation (E_a), kJ/mol
	333	338	343	348	353	358	
Polymer*	1.67	–	4.69	7.75	12.8	21.5	98.9
Dioxane	2.14	4.20	8.08	15.4	26.9	–	127.2
Acetone	2.20	3.61	5.48	8.37	13.7	–	91.1
DMF	6.26	9.39	15.1	22.6	38.2	–	105.3

* Decomposition was performed without solvent. The activation energy is determined with an error of ± 5.0 kJ/mol

As in the case of peroxide-containing polymers PVA, PMAA and PS, the thermolysis process is well described by the kinetic equation of the reaction rate of the first order. The effective rate constants of thermal decomposition are given in table. 5. At 353 K the total rate constants of thermolysis increase from $13.7 \cdot 10^{-5} \text{ s}^{-1}$ in acetone to $38.2 \cdot 10^{-5} \text{ s}^{-1}$ in DMF. It should be noted that in the same sequence increases the size of the macromolecular ball in solution. The rate of thermolysis of diacyl peroxides in the molecule of lauryl peroxide-initiator, which is often used in radical polymerization reactions, is significantly influenced by the solvent in which the process is carried out [15]. Heat treatment of the synthesized peroxide-containing polymers for 8 hours, both in solid form and in solution, does not lead to significant changes in the intrinsic viscosity, despite the fact that during the thermal decomposition of diacyl groups slightly changes the composition of macromolecules.

Conclusions

The obtained peroxide-containing polymers that contain O–O groups in the main chain can be used for the synthesis of block copolymers. Polymers that contain peroxide

groups in the side parts of the molecules can be successfully used as crosslinking agents, the synthesis of highly branched polymers and modifications of both polymers and mineral surfaces.

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РЕЗЮМЕ

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ТЕРМІЧНИЙ РОЗКЛАД ПЕРОКСИДНИХ ЗВ'ЯЗКІВ У ПОЛІМЕРАХ

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Отримано пероксидовмісні полімери, що містять діацилпероксидні групи в головному ланцюзі та в бічних частинах макромолекул. Термічний розпад пероксидних груп у макромолекулах добре описується кінетичним рівнянням швидкості першого порядку. Знадено сумарні константи швидкості розкладу та енергії активації досліджуваного процесу. Числові значення констант швидкості розкладу та активаційні параметри близькі до відповідних величин для дипероксидних чи монопероксидних аналогів. При розкладанні O—O груп полімерів, що містять пероксидні групи в основному ланцюзі, спостерігається зниження ступеня полімеризації полімерів. Розчинник, в якому відбувається процес, і природа полімеру-матриці, яка містить пероксидні групи, впливає на швидкість розкладання пероксидних груп і ступінь деградації полімерних макромолекул. Кількість пероксидних груп при модифікації макромолекул, можна регулювати змінюючи кількість пероксикутислоти в ході проведення реакції з кополімером стирену з малейновим ангідридом. Пероксидвмісні полімери можна успішно використовувати для отримання блок-сополімерів, зшиваючих агентів, макромолекулярних ініціаторів.

Ключові слова: пероксидовмісні полімери, термічний розклад, ступінь полімеризації, константи термічного розкладання, енергія активації.

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