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Abstract

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SOME LOW-TEMPERATURE REACTIONS OF MACRORADICALS IN THE SOLID PHASE

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Upon mechanical destruction of solid polymer solutions, high concentrations of free radicals arise ([1]). Solvent molecules are, as a rule, inert to mechanical action, and radicals are formed only as a result of destruction of the macromolecules. In cases where free radicals are capable of reacting with the solvent, the reaction can readily be observed from changes in the electron paramagnetic resonance spectra. In work ([1]), this method revealed reactions of peroxide radicals with certain inhibitors at −196°.

We investigated the possibility, in the solid phase at low temperatures, of a number of reactions characteristic of alkyl radicals: addition to a multiple bond (ethylene, various monomers), interaction with polynuclear aromatic compounds (anthracene, acridine), interaction with quinones (benzoquinone, tetrachlorobenzoquinone), and abstraction by a radical of a mobile atom (hydrogen in the case of ethylbenzene, chlorine in the case of triphenylchloromethane). The sources of radicals were polystyrene (PS) with molecular weight $3 \cdot 10^5$, polymethyl methacrylate (PMMA) with molecular weight $3 \cdot 10^6$, and polybutylene glycol dimethacrylate (PMB).

The procedure for mechanical dispersion of solid solutions and measurement of the EPR spectra was the same as in ([1,2]). Crystalline substances were purified by sublimation or recrystallization. Monomers were freed from inhibitors, dried, and distilled in vacuum. The polymer concentration in solution was varied from 0.5 to 10%. Substances with high melting points (quinones, acridine, anthracene, etc.) were dissolved together with the polymer in a common solvent, which was then distilled off. The polymer solution was loaded into a glass ampoule with glass balls and evacuated to 10^{-3}–10^{-4} mm Hg. During evacuation of volatile substances, the solution was periodically frozen and thawed. In the case of monomers capable of polymerizing upon repeated freezing and thawing, they were pumped off separately and distilled into the ampoule with the polymer before the start of the experiment. The ampoule with the solution was sealed off from the vacuum apparatus, fastened in the clamps of a vibratory mill, and, with the vibrator switched on, cooled with liquid nitrogen. Dispersion was carried out at −196° for several hours. Immediately after dispersion, without

thawing or contact of the samples with the atmosphere, the EPR spectra were recorded in the same ampoule. To observe the reaction at higher temperatures, the ampoule with the solution was immersed in a cooling mixture (−130, −116, −95, −78°, etc.) for a definite interval of time (usually several tens of minutes).

The most characteristic spectra are shown in Fig. 1 in the form of the first derivative of the absorption curve. All measurements were carried out at −196°. The results of the experiments are summarized in Table 1. The parameters of the EPR spectra in Table 1 are indicated only for the reaction products. The spectra of the initial radicals are well known: in PS—a poorly resolved triplet, while in PMMA and PMB the spectrum usually consists of 5 main and 4 intermediate lines ([3],[4]),

Table 1

Free-radical reactions in solid solutions

No.	Reacting substance	Polymer	t_1, °C	Parameters of the spectrum arising as a result of the reaction	t_2, °C
1	Acrylic acid	PMMA	−100	Three lines (1 : 2 : 1)	−10 to 0
2	Methacrylate	PS	−196	Three lines (1 : 2 : 1)	−80 to −90
2	Methacrylate	PMMA	From −100 to −130	Same	−80 to −90
3	Acrylonitrile	PMMA	From −100 to −130	Spectrum poorly resolved	−90 to −100
4	Methyl methacrylate	PS	−196	Five lines (1 : 4 : 6 : 4 : 1) + four lines (weakly expressed)	−60 to −70
5	Butylene glycol dimethacrylate	PS	−196	Same	

No.	Reacting substance	Polymer	t_1, °C	Parameters of the spectrum arising as a result of the reaction	t_2, °C
6	Styrene	PMMA	From −100 to −130	Three lines (poorly resolved)	−50 to −60
7	Ethylene	PMMA	From 0 to +20	Five lines (poorly resolved)	+80 to +100
7	Ethylene	PMB	From 0 to +20	Same	
8	Benzoquinone	PMMA	−196	Single line $\Delta H = 9$ Oe	
9	Tetrachlorobenzoquinone	PMMA	−196	Same, $\Delta H = 13$ Oe	+10 to +20
10	Acridine	PMMA	From −20 to −40	Single line $\Delta H = 20$ Oe	From +80 to +100
10	Acridine	PS	−80	Same	
11	Anthracene	PMMA	From −20 to −40	Single line $\Delta H = 13$ Oe	Radicals stable at room temperature
11	Anthracene	PS	−80	Single line $\Delta H = 18$ Oe	Radicals stable at room temperature
12	Triphenylchloromethane	PMMA	From −20 to +20	Single line $\Delta H = 8$ Oe	Radicals stable at room temperature

No.	Reacting substance	Polymer	t_1, °C	Parameters of the spectrum arising as a result of the reaction	t_2, °C
13	Ethylbenzene	PMMA	From −196 to −94 the reaction does not proceed; at −94 PMMA radicals are lost		
13	Ethylbenzene	PS	−196	Five lines, each of which is split into 4 components	From −130 to −115

Conventional notation. t_1 is the temperature interval in which the transformation of the spectrum is completed. t_2 is the temperature at which radicals are lost. ΔH is the line width.

These same signals were detected by us during the destruction of the given polymers in inert solvents.

When polymers were dispersed in chemically active solvents, we observed three cases: a) at −196° only the spectrum of the reaction products was recorded (solutions of PS in methacrylate, methyl methacrylate, butylene glycol dimethacrylate, ethylbenzene; solutions of PMMA in benzoquinone and tetrachlorobenzoquinone); b) at −196° a mixed spectrum was observed, consisting of the lines of the initial radicals and of the reaction products; after heating, this complex spectrum was converted into the spectrum of the reaction products (solutions of PMMA in methacrylate, acrylonitrile, styrene; solutions of PMMA and PS in anthracene and acridine); c) at −196° the spectrum corresponded to the initial radicals, and after the temperature was raised it was converted into the spectrum of the reaction products (solution of PMMA in triphenylchloromethane).

In most systems, during heating, simultaneously with the change in the form of the spectrum, the total signal intensity decreased noticeably. The temperature interval in which changes in the form of the spectrum ceased

Fig. 1. E.p.r. spectra arising after dispersion and subsequent thawing of solid polymer solutions.

Figure 1: Fig. 1. E.p.r. spectra arising after dispersion and subsequent thawing of solid polymer solutions.

e.p.r., and the temperature of radical destruction, are given in Table 1. Radical destruction, as a rule, was observed near the melting temperature of the solvent.

The reaction of the initial radicals with monomers proceeds at temperatures below −100°. The e.p.r. spectra of the reaction products (spectra I–III in Fig. 1) are similar to the spectra observed during polymerization of these monomers or during destruction of the corresponding polymers ([3],[4]), and therefore it must be concluded that at −100 to −196° addition of the monomer to the radical actually takes place.

The nature of the initial radicals affects the rate of monomer addition: the change in the e.p.r. signal in PS solutions occurs at −196°, whereas in PMMA solutions it occurs from −100 to −130°, i.e., PMMA radicals proved less active in reactions with these monomers than PS radicals.

Fig. 1. E.p.r. spectra arising after dispersion and subsequent thawing of solid polymer solutions. Ia–3% PS in methyl methacrylate, butylene glycol dimethacrylate at −196°. Ib–3% PS in methyl acrylate at −196°. II–2% PMMA in styrene; a–at −196°, b–20 min at −130°. III–2% PMMA in acrylic acid; a–at −196°, b–1 h at −95°. IV–PMB with ethylene; a–at −196°, b–20 min at −20°, c–1 h at +20°. V–3% PMMA in acridine; a–at −196°, b–50 min at −60°, c–30 min at −45°, d–30 min at −30°. VI–10% PMMA in triphenylchloromethane; a–at −196°, b–10 min at 0°, c–20 min at +20°, d–7 h at +20°. VII–3% PS in ethylbenzene.

In experiments with ethylene (spectra IVa, b, c in Fig. 1), the gas pressure in the ampoule at room temperature was about 600 mm Hg, i.e., the ethylene content relative to the polymer was negligibly small (less than 1:100). This circumstance must be taken into account when comparing the results with data for the other systems. At −196°, only part of the radicals reacted with ethylene. During thawing, the spectrum retains its shape down to −30°. At room temperature the reaction was completed in 1 h. The resulting spectrum consists of 5 poorly resolved components (see atlas ([5])), corresponding to interaction of the unpaired electron with 4 protons. The radicals are stable in vacuum and are destroyed on heating to 80–100° without a change in the shape of the spectrum.

In the case of polynuclear aromatic compounds (anthracene, acridine), the reaction of PS and PMMA radicals proceeds partially at −196° and is completed after thawing the system to −20 to −80°. The resulting spectrum does not depend on the nature of the initial radicals (PS or PMMA) and is a single line 15–20 Oe wide. In Fig. 1 one can follow the reaction of PMMA radicals with acridine.

When polymer solutions in quinones (benzoquinone, chloroanil) are dispersed, already at −196° a singlet spectrum with a line width of

9–13 Oe. Attempts to resolve the hyperfine structure and to identify the reaction products in the case of anthracene, acridine, and quinones have so far yielded no positive results.

Polymer radicals are capable of interacting with triphenylchloromethane. Figure 1 shows the characteristic changes in the EPR spectra in this case.

The spectrum of the radicals (Fig. 1, spectra VII) obtained by dispersing a solid solution of PS in ethylbenzene at −196° consists of five components (the width of each component is somewhat greater than the distance between them[5]). When the amplitude of the low-frequency modulation is decreased, an additional splitting of each component into 4 constituents, due to the protons of the benzene ring, becomes distinguishable. The spectrum corresponds to radicals:

$$C_6H_5{-}\dot{C}H{-}CH_3,$$

which were formed as a result of abstraction of an H atom from the secondary carbon atom.

The high reactivity of free radicals under our conditions may be connected with the method of radical initiation—mechanical treatment of solid polymer solutions (excess energy of the free radicals at the moment of formation, mechanical activation of the system, etc.). However, many reactions proceed upon heating the system to a certain temperature after dispersion. Evidently, the method of action is not the decisive factor, and the nature of the chemical interactions of radicals is determined by the special features of reactions in the solid phase at low temperatures.

The method of mechanical dispersion of solid polymer solutions considerably broadens the possibilities for studying elementary reactions of free radicals in the solid phase. In many cases it is more convenient than radiation and photochemical methods, since the mechanical energy is localized only on the high-molecular-weight component of the system.

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CITED LITERATURE

1. P. Yu. Butyagin, DAN, **148**, 129 (1963).

2. G. V. Abagyan, P. Yu. Butyagin, *Biophysics*, **9**, No. 3 (1964).

3. P. Yu. Butyagin, DAN, **140**, 145 (1961).

4. S. E. Bresler, E. N. Kazbekov, E. M. Saminskii, *High-Molecular Compounds*, **1**, 1374 (1959).

5. *Atlas of Electron Paramagnetic Resonance Spectra*, Publishing House of the Academy of Sciences of the USSR, 1962.

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