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Abstract

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ON MECHANOCHEMICAL TRANSFORMATIONS IN MACROMOLECULES AT 80° K

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In polymers, chemical reactions can proceed under the action of mechanical stresses. The primary act, or the mechanochemical process proper, ends with the rupture of a chemical bond in the macromolecule. In many cases, bond rupture leads to the formation of free radicals and to their secondary reactions: migration, interaction with one another, with surrounding molecules, etc. The final result is a decrease in molecular weight and changes in the structure of the macromolecules.

The secondary reactions of free radicals proceed in a mechanically stressed material and therefore may differ from analogous reactions under ordinary conditions. In addition, during mechanical action the structure of the material is destroyed, a new surface is formed, electrification and other processes occur. All this obscures the primary act of conversion of mechanical energy into chemical energy. In order to free ourselves from a considerable part of the accompanying phenomena and secondary processes, we began our investigations not with pure polymers, but with solid dilute solutions, where individual macromolecules are distributed in the crystal lattice of a low-molecular solvent and are isolated from one another. Transformations in macromolecules were monitored by electron paramagnetic resonance (EPR) spectra and by the decrease in molecular weight. The measurement procedure used was the same as in work (^{1}). Solid solutions were dispersed in a laboratory vibrational mill in vacuum or in air. All experiments and recordings of EPR spectra were carried out near the temperature of liquid nitrogen (80–100° K).

For the work, polymers were chosen for which the radical mechanism of destruction had already been proven by the EPR method (^{1}–^{3}): polymethyl methacrylate (PMMA), polystyrene (PS), polyethylene oxide (PEO), polyacrylonitrile, polyvinyl alcohol, carboxymethylcellulose, and gelatin. Low-molecular substances were taken of two types: chemically inert ones, such as ordinary solvents (benzene, toluene, acetone, water, etc.), and substances chemically active in reactions with free radicals—of the monomer type (methyl methacrylate, methacrylic acid, acrylonitrile) and inhibitors (aniline, α-naphthol, hydroquinone, thiourea). The polymer content in the solution was varied from 0.5 to

90%.

In none of the experiments with pure low-molecular substances did an EPR signal appear: the solvents are resistant to mechanical action. When even a small amount of polymer was added, distinct EPR spectra arose, indicating the formation of free radicals in the macromolecules. It could be expected that, in solid dilute solutions at nitrogen temperature, the concentration of free radicals would characterize the number of ruptured chemical bonds. Changes in radical concentration during dispersion of solutions of two polymers—PMMA and PS—in inert (toluene, acetone, and butyl acetate) and active (aniline) solvents are shown in Fig. 1. Both curves are similar in shape: in the first minutes the formation of radicals proceeds at a constant rate, but then the rate decreases. The data of Fig. 1 correspond to systems in which destruction proceeds easily, at a high rate—

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however, there exist solvents in which radicals are formed 10–100 times more slowly (water, benzene, acetic acid, etc.).

In dilute solid solutions of polymethyl methacrylate, polystyrene, and polyethylene oxide in toluene, acetone, aniline, α-naphthol, and certain other systems, radical concentrations of the order of 10^{21} g^{-1} (calculated per polymer) have been achieved. Such a high concentration of radicals corresponds to a state of the macromolecules with one free valence per 5–10 monomer units. At the same time, the molecular weight of the polymers after dispersion (Table 1) decreases only to 10^4–10^5, which corresponds to a chain length of 10^2–10^3 links.

Table 1

Molecular weight of PMMA (M) after dispersion of its solutions at 80°K

Solvent	Duration of dispersion, min	Molecular weight	$X = \frac{6 \cdot 10^{28}}{M}$
Toluene	0	$3 \cdot 10^6$	–
Toluene	1	$9 \cdot 10^5$	$7 \cdot 10^{17}$
Toluene	4	$5 \cdot 10^5$	$1.2 \cdot 10^{18}$
Aniline	2	$1.7 \cdot 10^5$	$3.5 \cdot 10^{18}$
Aniline	4	$9.3 \cdot 10^4$	$6.4 \cdot 10^{18}$
Aniline	8	$4.0 \cdot 10^4$	$1.5 \cdot 10^{19}$

As a rule, upon gradual heating of the solutions all radicals disappear long before the melting temperature is reached, i.e., in the solid solution, where the possibility of their recombination with restoration of the polymer chain is unlikely, especially in solutions of inhibitors. It may therefore be expected that the concentration of radicals does indeed correspond to the total number of broken bonds, while changes in molecular weight reflect only destruction in the

Fig. 1. Formation of radicals during dispersion of solid solutions in liquid nitrogen: a –PMMA solutions in acetone (1), toluene (2), and PS in toluene (3); b –PMMA solutions in aniline

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main chain of the macromolecule. The occurrence of radicals in an amount of 10^{21} g^{-1} cannot in any way be explained by rupture of bonds only in the main chain valences. The reaction of macromolecules to mechanical stresses is considerably more complex, and the damage is deeper than could have been supposed, apparently also involving side groups. The efficiency coefficient in the conversion of mechanical energy into chemical energy, when estimated from the concentration of free radicals, reaches values of the order of 10%.

Fig. 1. Formation of radicals during dispersion of solid solutions in liquid nitrogen: **a** –PMMA solutions in acetone (1), toluene (2), and PS in toluene (3); **b** –PMMA solutions in aniline.

The principal EPR spectra of the dispersion products are shown in Fig. 2. Spectrum 1 was obtained after dispersion in vacuum of a benzene solution of PMMA. The same spectrum was recently published in work (4), where it is explained by overlap of the doublet with the well-known spectrum of radicals in PMMA. Similar spectra were measured in PMMA solutions in aniline, α-naphthol, methacrylic acid, and toluene. In an acrylonitrile solution the hyperfine structure is distorted because of the reaction of radicals with the monomer. After dispersion in air of the systems polymer–an inert solvent and polymer–monomer, the characteristic anisotropic spectrum of the peroxide radical was always observed (5), while in the systems polymer–inhibitor, spectra 3-6 were observed. In solutions of PMMA, PS, and PEO in aniline, spectrum 3 was recorded; the spectrum parameters do not depend on the nature of the polymer. In the spectrum one can distinguish a weak anisotropic line, a signal of 13 components with splitting of 6–7 oersteds, and a singlet about 40 oersteds wide. For solutions of polymers in α-naphthol, spectrum 4 is characteristic. As in the preceding case, the spectrum resembles neither the spectrum of the peroxide radical nor the spectra of PMMA and PS radicals;

its form is determined by the nature of the inhibitor. An analogous regularity was also obtained in the study of polymer solutions in thiourea (spectrum 5) and in hydroquinone (spectrum 6).

The appearance of radicals with spectra 3-6 is possible by transfer of excitation from macromolecules to the inhibitor or by interaction of inhibitor molecules with polymer radicals. The first path–transfer of excitation–should have been accompanied by phenomena of the type of protection of the polymer from mechanical effects, with a decrease in the rate of destruction. However, in the

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presence of inhibitors, destruction proceeds faster and, it may be thought, the mechanism of transfer of free valence is more probable. Macroradicals react with the inhibitor only in air, when oxygen is present in the system. The reaction probably proceeds through an intermediate stage of formation of a peroxide radical, i.e., first the alkyl radical adds an oxygen molecule to itself, and then abstracts a hydrogen atom from the inhibitor or forms with it an intermediate complex compound.

Fig. 2. E.p.r. spectra of polymers in solid solutions. **1, 2**—dispersion in vacuum at 80-100° K: **1**—solutions of PMMA in benzene, toluene, methacrylic acid, aniline, α-naphthol; **2**—solution of PMMA in acrylonitrile. **3-6**—dispersion in air: **3**—solutions of PMMA, PS, and PEO in aniline; **4**—solutions of PMMA and PS in α-naphthol; **5**—solution of polyacrylonitrile in aniline; **6**—solutions of PMMA and PS in hydroquinone. Scale: the small division corresponds to 10 oersted.

Free radicals formed under mechanical action on macromolecules evidently possess excess energy—they interact at nitrogen temperature with monomers, oxygen, and inhibitors. It is quite possible that in inert systems the radicals are also prone to rearrangement or migration; therefore, under our conditions, in specifying the site of bond rupture, the e.p.r. method cannot give unambiguous results: it is unknown whether the observed e.p.r. spectra correspond to primary radicals or to the site of localization of the free valence after migration.

Deep mechanochemical changes, when the number of damages in each macromolecule reaches tens and hundreds, were detected in solid dilute polymer solutions near 80° K, where radical-termination reactions are maximally inhibited. An analogous destruction mechanism also plays the main role in the low-temperature dispersion of pure polymers, since here too the rate of radical formation in the initial period considerably exceeds the rate of bond rupture in the main chain of valences (^{3}). At ordinary temperatures the lifetime of radicals is short, and the e.p.r. method records their stationary concentration, which does not reflect the true number of broken bonds. Here, more detailed studies are necessary for analysis of the mechanism of the process.

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