ACTIVE INTERMEDIATE STATES DURING THE MECHANICAL DESTRUCTION OF POLYMERS*

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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Abstract

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ACTIVE INTERMEDIATE STATES DURING THE MECHANICAL DESTRUCTION OF POLYMERS*

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Intense mechanical action on polymeric substances is accompanied by destruction of the material structure and by degradation of macromolecules (⁀1). In our work, primary attention is devoted to the intermediate states in this process; they were studied in solid polymers, where secondary reactions are strongly hindered, especially at low temperatures.

Polymeric materials were mechanically treated in a laboratory vibrational mill (⁀2), in which the medium, temperature, and intensity of energy input could be varied. The degree of destruction of a solid polymer was evaluated from changes in the specific surface area (S), measured by the BET method,

Fig. 1. Destruction of PMMA at 77°K; **1** –number of broken bonds X; **2** – concentration of radicals $R\cdot$; **3** –specific surface area S.

Fig. 2. Specific surface area: **1** –PMMA, $S_{77^\circ K} = 115$ m^2/g; **2** –PMS, $S_{77^\circ K} = 150$ m^2/g; **3** –polypropylene, $S_{77^\circ K} = 27$ m^2/g.

and macromolecular degradation–from the decrease in molecular weight (viscometric method). The concentration, structure, and transformations of free radicals were studied by the method of electron paramagnetic resonance (EPR) on a radio spectrometer of type (⁀3). The luminescence accompanying destruction was recorded with an FEU-19 electron photomultiplier. The following polymers were investigated: polymethyl methacrylate (PMMA), polystyrene (PS), polyacrylonitrile (PAN), polyvinyl alcohol (PVA), polyethyl acrylate (PEA), linear polyethylene (PE), a copolymer of polystyrene with divinylbenzene (SPDS), poly-α-methylstyrene (PMS), and carboxymethylcellulose (CMC) (see Fig. 3).

During mechanical dispersion of polymers, as in other solids, an increase in specific surface area is observed. As a rule, S increases with time according to a linear law up to a certain limit; under otherwise identical conditions, the

limiting value and the rate of increase depend strongly on temperature.

For PMMA, PS, polypropylene—polymers of the vinyl series with a CH_3-

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* I. V. Kolbanev and A. R. Kuznetsov took part in carrying out the experiments.

by a group in the α-position—after 2-3 min. S reaches 120-150 m^2/g (Fig. 1, curve 3). Such high values were obtained only in those experiments in which dispersion, measurements, and all intermediate operations were carried out at the temperature of liquid nitrogen, 77° K. Upon gradual heating of the samples (see Fig. 2), near 130° K intensive sintering occurs, with the surface area decreasing by tens of times, to 3-8 m^2/g. Under ordinary conditions, i.e., considerably above the sintering temperature, the latter values of S are the natural limit of polymer dispersion.

Sintering indicates the appearance of mobility of stressed macromolecules at 130° K. This effect is possibly associated with a structural transition caused by unfreezing of the freedom of rotation of α-methyl groups, which was detected near this temperature by the nuclear magnetic resonance method ([4,5]). For polymers with an H atom in the α-position, the sintering temperature should lie considerably below 77° K and, possibly for this reason, in none of the experiments with PS, PNAK, PVC, etc. was it possible to attain a surface greater than 10-15 m^2/g.

In observations of luminescence, a characteristic intense luminescence was noted, consisting of flashes following one another, corresponding to the destruction of individual polymer grains; it was observed in quartz, PMMA, PS, PEA, and others at room temperature. For natural rubber and PE, weaker luminescence could be noticed during the relaxation of stresses, upon rapid release of the pressure applied to the sample. Prolonged chemiluminescence of type ([6]) arose upon recombination of peroxide radicals. Measurements of luminescence are a convenient method for stage-by-stage investigation and detection of destruction.

The molecular weight of the linear polymers studied decreased after mechanical treatment by 10-100 times, as a rule to $M \sim 10^4$. Under the experimental conditions the destruction limit was reached in 10-20 min. In three-dimensional systems the solubility of the polymer increased considerably; for quartz an analogous phenomenon had been known previously ([7]).

In experiments in which the molecular weight was measured over a sufficiently wide range (PMMA, PS, PNAK), the exponential ([3]) law of the rate of destruction is satisfactorily obeyed (Fig. 1, 1):

$$M = M_0 \exp(-k\tau), \quad \text{or} \quad X \simeq A \exp(k\tau),$$

where $X = 6 \cdot 10^{23} \left(\frac{1}{M} - \frac{1}{M_0}\right)$ is the number of broken bonds in 1 g, k is the overall rate constant of destruction, and τ is time.

Figure 3. Electron paramagnetic resonance spectra.

Figure 2: Figure 3. Electron paramagnetic resonance spectra.

The EPR spectra of radicals arising during mechanical destruction are shown in Fig. 3. Radicals with a free valence at a carbon atom are characterized by EPR spectra with superhyperfine structure. The spectrum of PMMA (1a) corresponds to two stereoisomeric radicals ([9]); upon mild heating, the spectrum of the less stable radical gradually disappears (1b), and in the end one quadruplet remains (1e). The spectra of PS, SPS, and PMS are similar to one another; probably they should be regarded not as a triplet but as a superposition of single lines of different widths, but with the same g-factor.

Radicals of this type are stable in an inert atmosphere up to temperatures close to the glass-transition temperature. The activation energy (E) of the decay reaction for PMMA is 37 ± 4 kcal/mol. The radicals are active and capable of entering into various reactions: with one another, with monomers, with oxygen, etc. Changes in the EPR spectra during the reaction of PMMA radicals with acrylonitrile are shown in Fig. 3, spectra 2a, , , . Upon interaction with oxygen, peroxide radicals (15a,) are formed, with a characteristic anisotropic EPR spectrum ([10]). This reaction proceeds at 120° K and above with $E = 3.8$ kcal/mol. The decay of peroxide radicals at room temperature is completed within minutes (for PMMA $E = 16$ kcal/mol), and the rate of decay in the stressed polymer is many times greater than in the previously annealed material.

Fig. 3. Electron paramagnetic resonance spectra. **1** –PMMA, **2** –copolymers of PMMA with acrylonitrile, **3** –PEA, **4** –PNAA, **5** –PVC, **6** –PS, **7** and **8** –SPS, **9** –PMS, **10** –gelatin, **11** –CMC, **12** –PE, **13** –cellulose, **14** –quartz, **15** –spectra of peroxide radicals in PMMA and PE. Spectra **5b**, **8**, and **13b** were obtained after radiation destruction; the others, after mechanical destruction. Scale: one division equals 20 oersteds.

In quartz, the primary radicals (**14b**) react with oxygen only during mechanical action; otherwise this reaction does not occur even upon heating to 200°C.

For gelatin, a specific EPR spectrum can be observed only after destruction at 77°K (**10a**); upon heating, this complex spectrum, corresponding to at least two different radicals, is transformed into doublet and singlet lines superposed on one another (**10b**). A similar, but simpler, picture is also observed for CMC (**11a, b**). The spectra stable at 77°K probably correspond to primary radicals, while the doublet appears after migration of the free valence to an oxygen atom (**11**).

The EPR spectra of radicals obtained by the mechanical method are in many cases similar to the spectra of radicals formed under the action of ionizing radiation on polymers. For PMMA, PS, PEA, SPS, PVC, CMC, and gelatin, both types of spectra are identical (see, for example, spectra **5a, b**, **7**, and **8**). The difference consists only in the stability of the radicals: after irradiation they are

more stable. For cellulose and quartz, the two types of spectra differ from one another.

The concentrations of radicals in the destruction products were measured by the EPR method and by the consumption of oxygen for their oxidation. Experimental data for PMMA are shown in Fig. 1. The radical accumulation curve has

an S-shaped character, and after 2–3 min the concentration of radicals reaches a limiting value, although degradation continues. The existence of limiting concentrations was found for most of the polymers studied; the limiting concentrations range from 10^{18} g^{-1} (PE, PS, PAN, PVC) to 10^{20} g^{-1} (PEA, SPS).

In Fig. 1 the scales for curves 1 and 2 differ by a factor of 40, i.e., the concentration of radicals recorded by the ESR method is many times greater than the number of broken bonds calculated from changes in molecular weight.

In polymer solutions frozen to 77°K, where the macromolecules are distributed in the crystal lattice of the solvent, degradation proceeds more intensively, and the highest attainable radical concentrations increase by a factor of 10–100, up to $5 \cdot 10^{20}$ g^{-1} for PMMA and $3 \cdot 10^{20}$ g^{-1} for PS dissolved in toluene, butyl acetate, acetone, etc. These are probably indeed limiting concentrations, since there are now 20–100 paramagnetic centers per macromolecule. The nature of the solvent strongly affects the course of degradation, and one may speak of a distinctive protective action of benzene, dioxane, and certain other substances against mechanical action in solutions at low temperatures. The ESR spectra of polymers in frozen solutions remained unchanged, except in special cases when solutions of a polymer in monomers were studied.

The processes of growth of new surface, decrease in molecular weight, and formation of radicals in solid polymers proved to be dissimilar to one another: the number of radicals is many times greater than the number of ruptures in the main chain, the laws of dispersion and of degradation are different, etc. These discrepancies cast doubt on the idea that the principal process in mechanical degradation is rupture of the main chain of the macromolecule. It may be supposed that the primary act under mechanical action is the appearance of intermediate nonequilibrium states of macromolecules; the subsequent chain of secondary processes, including bond rupture (probably also side-bond rupture), radical formation, and their transformations is already determined in many respects not by the primary action, but by the structure of the polymer, more precisely, by the structure of the polymer in a stressed state. From this point of view, the anomalously high radical concentrations and the similarity between radiation and mechanical degradation of polymers become understandable.

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