

ESR Study of free radicals generated during polymerization of vinyl monomers in poly(methyl methacrylate) matrix under high pressure

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Received 2 January 1974

The e.s.r. spectra of free radicals generated during the polymerization of vinyl monomers (methyl methacrylate, butyl methacrylate, styrene, ethyl acrylate, acryl amide, vinyl acetate) initiated by thermal decomposition of benzoyl peroxide in the poly(methyl acrylate) matrix under the pressure 6000 atm were observed. The observed e.s.r. spectra and the mechanism of the free-radical generation are discussed.

In our previous works [1, 2] we presented a new method of trapping the polymer radicals in a polymer matrix by thermal decomposition of benzoyl peroxide in poly(methyl methacrylate) (PMMA) and polystyrene (PS) under the effect of high pressures. The principle of this method is a stabilizing effect of the high pressure on the polymer radicals generated in the polymer by thermal decomposition of benzoyl peroxide. The decrease of the polymer viscosity owing to the increased temperature is compensated by the pressure effect upon the polymer. For instance, in PMMA at the pressure 10 000 atm. the free radicals are relatively stable [3] and measurable by e.s.r. even at 150°C.

The study of the mechanism of the free-radical generation revealed that the polymer radicals can be most easily trapped if the used polymer matrix contains, in addition to benzoyl peroxide, a small amount of the vinyl monomer. In such a case, the polymerization of the vinyl monomer occurs and the life-time of the propagating radical is prolonged by the effect of pressure.

In this work we applied the high-pressure method of trapping the free radicals to the study of other monomers than in the previous works, *i.e.* butyl methacrylate, vinyl acetate, ethyl acrylate, and acryl amide, with PMMA used as a polymer matrix for all these monomers.

Experimental

PMMA used as a matrix was obtained by radical polymerization of methyl methacrylate with 0.2% of azobisisobutyronitrile (AIBN) in toluene at 80°C. The polymer was freed at the monomer by double precipitation of the benzene solution with methanol. The average molecular weight of PMMA determined by viscosimetric method [4] was 2.25×10^5 . Benzoyl peroxide in the form of a solution in acetone-methanol was spread on the powdered PMMA (2.1×10^{-4} moles of BP/1 g PMMA). The volatile components were evaporated at room temperature. Benzoyl peroxide was recrystallized from the chloroform solution before use (m.p. 107°C).

Samples with various content of the monomer (Table 1) were prepared from the PMMA matrix with benzoyl peroxide. The polymer matrix was impregnated by methanol solution

Table 1

Composition of the PMMA samples containing benzoyl peroxide and vinyl monomer
Samples were tempered at various temperatures under the pressure 6000 atm

Sample	Monomer	Monomer concentration · 10 ³ (mole/l g of PMMA)	Temperature of annealing [°C]	Time of annealing [min]
A	—	—	130	20
B	Methyl methacrylate	4.7	130	20
C	Butyl methacrylate	3.1	120	20
D	Styrene	2.6	130	20
E	Vinyl acetate	2.6	130	20
F	Ethyl acrylate	4.9	110	20
G	Ethyl acrylate	4.9	120	20
H	Acryl amide	2.8	100	60

of the monomer, in the case of acryl amide by a chloroform—methanol solution. The samples B—H were dried for two days in vacuum at 20°C. The monomers, methyl methacrylate, butyl methacrylate, styrene, vinyl acetate, and ethyl acrylate were purified by usual methods. Acryl amide was recrystallized (m.p. 85°C).

The samples (0.15 g) were put into a pressure equipment described elsewhere [3, 5]. At the pressure 6000 atm the samples were quickly heated to the corresponding temperature given in Table 1. When the annealing was finished, the samples were quickly cooled to room temperature and after releasing the pressure, they were placed in a resonator of the X-band e.s.r. spectrometer (Zeiss ER-9). The e.s.r. spectra were recorded at room temperature and normal pressure. In the course of measurements, no changes in spectral amplitudes were observed under the described conditions.

Results and discussion

Fig. 1A shows the spectrum of the sample A (Table 1) prepared by diffusion of benzoyl peroxide from methanol—acetone mixture into PMMA without monomer. The spectrum differs from the usual nine-line spectrum of the free radicals of PMMA. A similar spectrum was observed in the irradiated PMMA in the course of the free-radical decay under high pressure [6]. A simulated theoretical spectrum revealed that the overall spectrum is composed of four-component spectra. A comparison of the spectrum in Fig. 1A with the corresponding one in [6] shows that the following types of the free radicals are in the observed overall spectrum: the end radical $-\text{CH}_2-\dot{\text{C}}(\text{CH}_3)(\text{COOCH}_3)$ (nine-line spectrum), the chain radical $-\text{C}(\text{CH}_3)(\text{COOCH}_3)-\dot{\text{C}}\text{H}-\text{C}(\text{CH}_3)(\text{COOCH}_3)$ (doublet), the polyene radical (singlet), and the allyl radical (quartet). The concentration ratio is *ca.* 1.8 : 1.4 : 1 : 0.8, respectively.

The generation of free radicals with the nine-line and doublet spectrum was first of all expected from the reaction of free radicals from benzoyl peroxide with PMMA. However, the polyene radical corresponding to the singlet spectrum results from consecutive reactions of the primary radicals in the polymer. The allyl radical is probably generated by a reaction of the free radicals from benzoyl peroxide with doublet bonds at the ends of PMMA chains, arising already in the disproportionating reaction of the polymerization

during the sample preparation. When the thermal decomposition of benzoyl peroxide in PMMA under the high pressure occurred in the presence of methyl methacrylate, the characteristic nine-line spectrum, corresponding to the propagating PMMA radical, was obtained (Fig. 1B), with only a slight contribution of other component spectra.

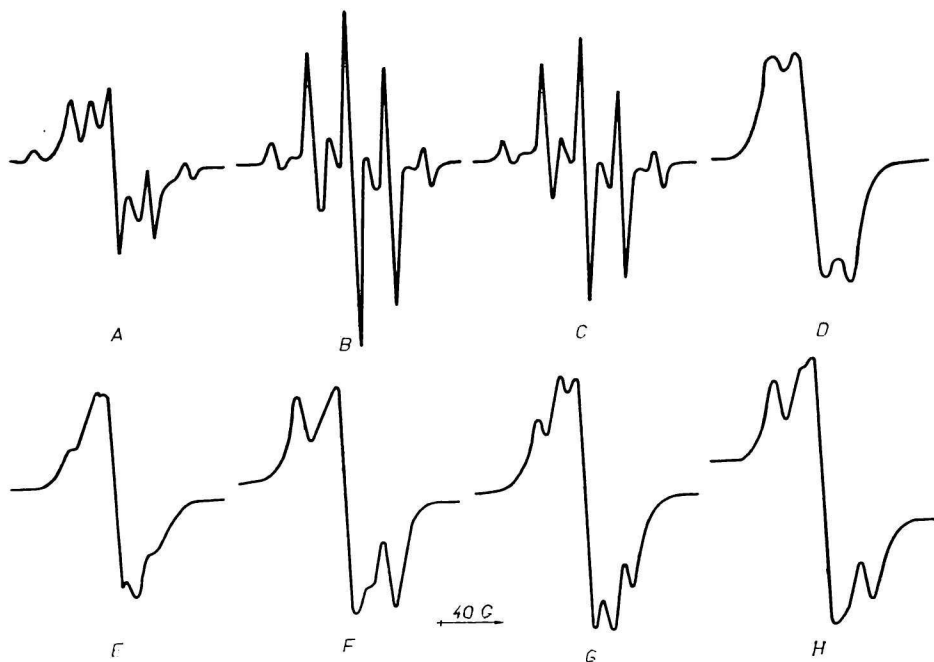
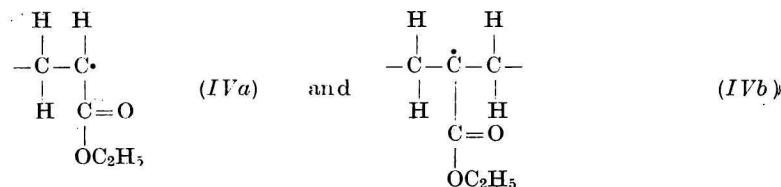


Fig. 1. The e.s.r. spectra of free radicals generated during polymerization of vinyl monomers in the poly(methyl methacrylate) matrix under the pressure 6000 atm. A-H stand for the corresponding samples in Table 1. The gain for A = 2.5, B = 1.0, C = 1.0, D = 1.6, E = 2.5, F = 5.0, G = 1.3, H = 2.8. Concentration of the sample B = 7×10^{17} spin/g.

Another nine-line spectrum (Fig. 1C) corresponding to propagating radicals during the butyl methacrylate polymerization (sample C), was obtained when both benzoyl peroxide and butyl methacrylate were diffused into PMMA. The propagating radicals of PBMA exhibit the nine-line spectrum as well. The nine-line spectrum is known to be a result of the interaction of the unpaired electron with protons of methyl and methylene groups. Protons of the carboxyl group do not affect the spectrum. Since the spectra of the propagating radicals of PBMA and PMMA are the same, it may be objected that the nine-line spectrum belongs to the radicals of the PMMA matrix. However, the reaction of benzoyl peroxide with PMMA shows a more component spectrum (Fig. 1A) in which the propagating radical does not prevail as much as in the spectra, in Figs. 1C and 1B.

A triplet was observed in the presence of styrene in the system (sample D, Fig. 1D). The triplet spectrum of polystyrene was already reported and attributed either to the propagating radical

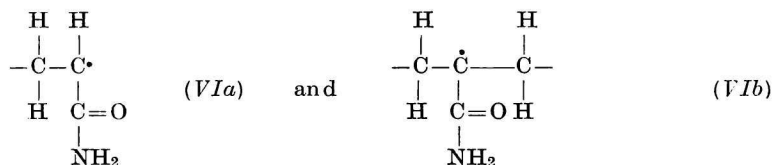


On the basic triplet, a spectrum of another radical is superimposed, it is probably the free radical

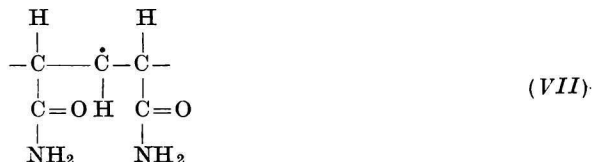


The contribution of the free radicals (*V*) to the overall spectrum is more marked in the spectrum of the sample *G* also with the ethyl acrylate monomer (Fig. 1*G*). This sample was tempered at 120°C. Other conditions, pressure and time of the annealing, were the same as in the previous case. The increase of temperature by 10°C brought about a three-fold increase of the free-radical concentration. The generation of free radicals at higher temperature increases owing to the more rapid decomposition of benzoyl peroxide, but simultaneously the free-radical decay is increased too. In the course of this decay, the presence of the less reactive radicals is more marked in the overall spectrum (Fig. 1*G*).

Also the sample *H* with the acryl amide monomer exhibits the triplet spectrum which we ascribe, like in the two previous cases, to the free radical



Another component spectrum, superimposed on the basic triplet, is ascribed to the chain radical of the following type



As for the radicals (*II*), (*IV*), and (*VI*) we assume a gradual transition of the propagating radicals, types *a*, into types *b*, analogously as in the case of polystyrene (radical *I*).

Most of the discussed e.s.r. spectra in Figs. 1*B*–*H* correspond to the polymer radicals formed during the polymerization of vinyl monomers in the polymer matrix under the effect of high pressure. In this connection we have to explain the mechanism of the initiation of this polymerization. The general conception of the initiating reaction of such polymerization is the addition of the primary radicals generated by thermal decomposition of the initiator into the monomer. If this were our case, the e.s.r. spectra of the propagating radicals should be observed even when AIBN was used as the initiator instead of benzoyl peroxide. However, our attempt to obtain the e.s.r. spectrum in the case of the initiation

by thermal decomposition of AIBN in the PMMA matrix was unsuccessful, either in the absence or in the presence of the vinyl monomer in the matrix.

Such results prove that the initiating reaction of the polymerization is not a direct reaction of the primary radicals of the initiator with the monomer or that these radicals are not directly responsible for the propagating reaction of the polymerization. As the initiating centre of the polymerization we may then consider the radicals formed by transition on the polymer matrix during the thermal decomposition of benzoyl peroxide by the effect of high pressure. Thus the inefficiency of AIBN to generate free radicals in the absence or in the presence of the monomer in the PMMA matrix can be understood. The free radicals generated by thermal decomposition of AIBN have less than one tenth of the efficiency of the radicals from benzoyl peroxide in the transfer on polypropylene [9]. A similar, very small efficiency in the transfer on polystyrene is assumed at the polymerization of styrene [10]. The low reactivity of the radicals of AIBN is assumed to be the cause of their low accumulation on the polymer matrix by the transfer, so that their concentration is not sufficient for the e.s.r. detection. Consequently, it was not possible to observe the radicals arising during the polymerization even in the presence of the monomer.

The achieved results as well as the results of the previous works, demonstrated feasibility provided by the new method of generating the free radicals and their stabilizing by the effect of pressure in the solid polymer matrix. It was pointed out that the increased viscosity of the polymer, brought about by the effect of pressure up to 10 000 atm, is sufficient to stabilize the polymer radicals in polymers prepared by the radical polymerization of usual vinyl monomers. It is one of the methods enabling to investigate the course of polymerization reactions by the e.s.r. method. However, a proper choice of the matrix is important with regard to the used monomer, namely its solubility in the matrix and the matrix reactivity. In our experiments with vinyl monomers, the PMMA matrix has proved to be the best choice. It exhibits relatively good dissolving power towards the used monomers and the best stability towards the free radicals arising during the polymerization of the used series of monomers.

The observation of the polymerization reactions in the foreign matrix provides a possibility to investigate such radicals which could not be investigated in their own matrix because of the low T_g and experimental difficulties. Butyl methacrylate is an example. We did not succeed in generating the free radicals in PBMA matrix containing benzoyl peroxide and butyl methacrylate but in the PMMA matrix we observed the e.s.r. spectrum of the propagating radical of poly(butyl methacrylate).

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Translated by F. Kopecký