Pressure Dependence of Free-Radical Decay in Irradiated Poly(vinyl Acetate)

INTRODUCTION

The free radicals in poly(vinyl acetate) were generated either by γ-irradiation[1,2] or by mechanical destruction of the polymer.[3] In either case, a distinct triplet which was assigned to the radical —$CH_2\dot{C}(OCOCH_3)CH_2$— was observed. It was assumed that among the four α-protons, only two conveniently twisted protons split off. Milinchuk and Pshezhetskii subjected an irradiated poly(vinyl acetate) to the effects of UV radiation. Besides the triplet, they also observed a quartet, and they assigned this quartet to the radical —$CH(OCOCH_3)\dot{C}HCH(OCOCH_3)$—. In addition to these two-component spectra, they also observed a weaker broad doublet which was assumed to correspond to the formyl radical $H\dot{C}O$.

The free-radical decay in poly(vinyl acetate) is relatively little elucidated. In a mechanically destroyed poly(vinyl acetate), the rate constants and the activation energy of decay, 23 kcal/mole,[3] were determined for the temperature interval between 20°C and 61°C.

The aim of this study is to investigate the effect of pressure on the decay of the free radicals generated by γ-irradiation in poly(vinyl acetate).
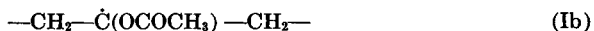
EXPERIMENTAL

Poly(vinyl acetate) was prepared by block polymerization of vinyl acetate in presence of α,α'-azobisisobutyronitrile, 0.1%, functioning as an initiator. The temperature of the polymerization bath was 60°C. Before polymerization, vinyl acetate was twice distilled, and the fraction with the boiling point of 72°C was collected. After irradiation, the samples were kept in liquid nitrogen. The samples were stored in liquid nitrogen prior to insertion into the resonator of an ESR spectrometer where the initial concentration of free radicals was determined. Then the sample was transferred into a pressure device[5] where it was subjected to pressure and heated to the necessary temperature. Afterward, the sample was thermostated for 20 min, and on releasing the pressure it was put again into the resonator of an ESR spectrometer on which the spectrum was recorded. From the difference between the concentration corresponding to the initial and final spectrum, the rate constant of free-radical decay was determined. The concentration was determined by a double integration of the spectrum and subsequent comparison with a strong pitch normal (Varian). The spectra were recorded on an X-band spectrometer ER-9 (Zeiss). The molecular weight of poly(vinyl acetate) $\bar{M}_w = 63250$ was determined by viscosimetric method in benzene at 30°C.[4] The free radicals were generated by a total dose of 6 Mrad of γ-radiation.

RESULTS AND DISCUSSION

After irradiating the sample, the initial spectrum was obtained (Fig. 1a). Further spectra were recorded after thermostating the samples at a high pressure. In the initial spectrum a triplet prevails. This triplet may be assigned to the radical

$$—CH_2—\dot{C}H(OCOCH_3) \tag{Ia}$$

or

$$—CH_2—\dot{C}(OCOCH_3)—CH_2— \tag{Ib}$$

On the basis of the given experimental material, it is not possible to decide which of the above two types of free radicals is responsible for the spectrum, because the spectra of chain-end radicals as well as chain radicals are equal. The situation is probably analogous to the case of a system with polystyrene where it was proved by deuteration
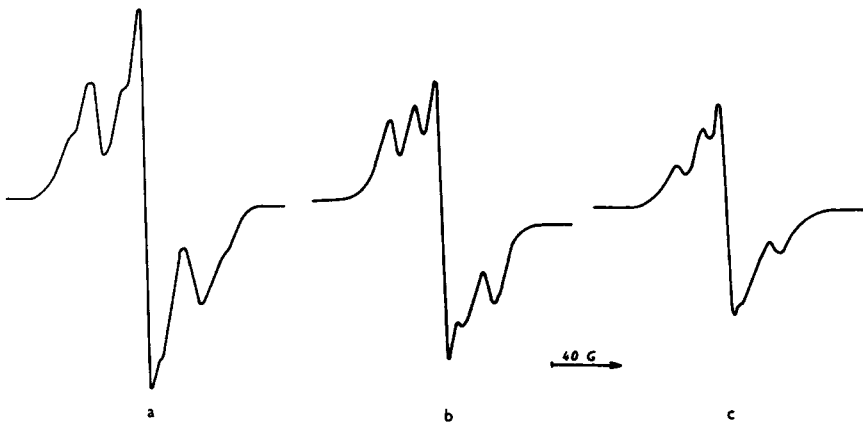
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Fig. 1. ESR spectrum of irradiated poly(vinyl acetate): (a) immediately after irradiation; (b) after 90 min of thermostating at 70°C and 7000 atm; (c) after 20 min of thermostating at 90°C and 7000 atm.
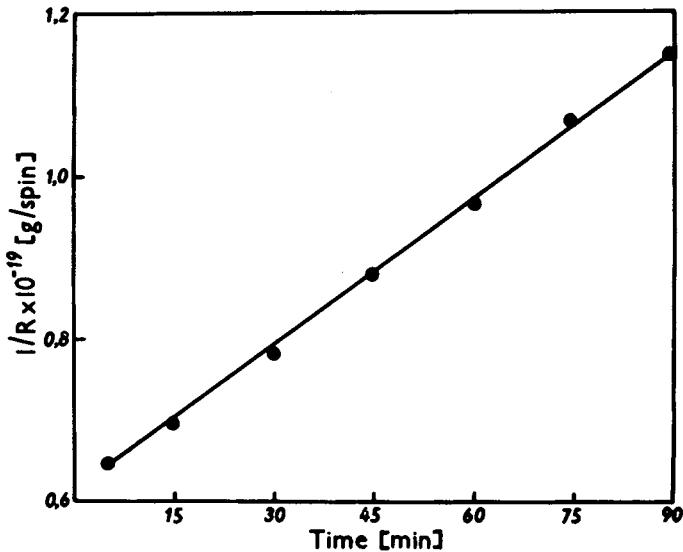

Fig. 2. Reciprocal value of free-radical concentration as a function of time at 80°C and 7000 atm.

that the chain-end radicals successively change into the chain radicals.[5] The second component spectrum becomes more significant during the decay of free radicals. In the spectra (Figs. 1b and 1c) recorded after thermostating the sample exposed to pressure, a relative intensification of the lines corresponding to the radical

$$—CH(OCOCH_3)—\dot{C}H—CH(OCOCH_3)— \qquad (II)$$

is to be observed. This type of radical is more sensitive to the stabilizing effect of pressure than the terminal radical. In the course of the decay of the free radicals subjected to high pressures, the contribution of the more stable radicals to the overall spectrum

increases. A similar effect was also observed during the decay of free radicals in ir-
radiated poly(methyl methacrylate) at high pressure.[7]

The decay of free radicals under high pressures may be described in a wide period of
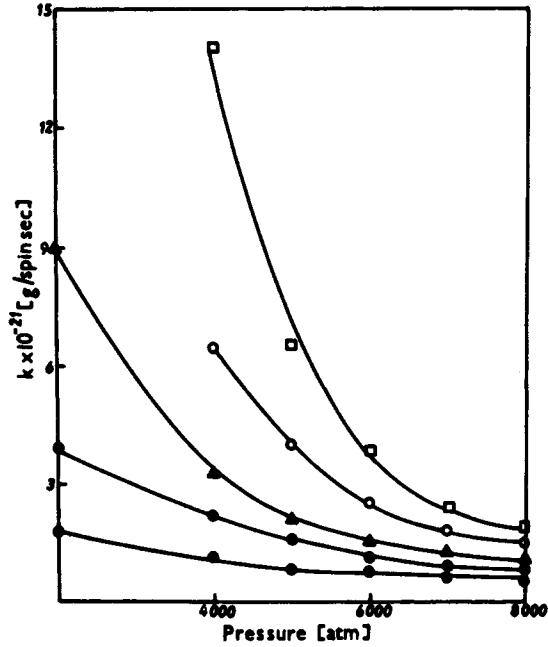time by the law of second-order reactions (Fig. 2). The decay of free radicals in a

Fig. 3. Rate constants of free radicals as a function of pressure at different temperatures:
(●) 60°C; (◐) 70°C; (▲) 80°C; (○) 90°C; (□) 100°C.
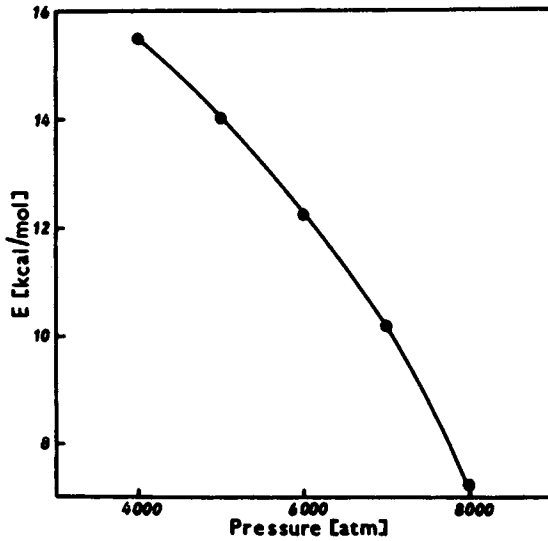

Fig. 4. Activation energy of free-radical decay at different pressures.

mechanically destroyed poly(vinyl acetate) also obeys the temporal law of second-order reactions.[3]

The rate constant of free-radical decay exhibits an expressive dependence on pressure (Fig. 3). At low temperatures, the rate constant varies only insensibly with pressure. The stabilizing effect of pressure manifests itself at higher temperatures; and the closer to the glass transition point T_g as the temperature of free-radical decay is approached, the more this stabilizing effect is operative. By the effect of pressure, the molecular motion controlling the decay of free radicals in the vicinity of T_g is suppressed.

The activation energy defined by the Arrhenius equation also shows a dependence on pressure (Fig. 4). At a pressure of 8000 atm, the activation energy is equal to 7 kcal/mole while at 4000 atm, it amounts to 16 kcal/mole. The determination of activation energy in the temperature interval between 60°C and 100°C at low pressures meets with experimental difficulties. By extrapolating the relationship presented in Figure 4 to low pressures, we obtain the value of about 20 kcal/mole. This value is not far from the value of 23 kcal/mole observed in a mechanically destroyed poly(vinyl acetate) over the temperature range of 20°C to 50°C.

References

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