ESR Study of Pressure Dependence of the Peroxy Radical Decay in Irradiated Isotactic Polypropylene

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Synopsis

By the use of gamma radiation the free radicals were generated in isotactic polypropylene. The polymer was exposed to the action of atmospheric oxygen and the peroxy radicals were formed. Then the decay of peroxy radicals was investigated at varying temperatures as a function of pressure. The rate constants of the free radical decay were determined, and the corresponding activation volumes were calculated. The kinetic characteristics imply that the peroxy radicals predominantly occured in amorphous region the polymer. The results suggest that useful information on molecular mechanism of radical reactions in the solid phase may be obtained from the determination of activation volumes.

INTRODUCTION

The influence of pressure on the free radical decay in irradiated isotactic polypropylene was studied earlier.[1] It has been found that the rate constant slowly decreases (almost linearly) with pressure in the pressure region 1–800 MPa. On the basis of the kinetic characteristics and parameters obtained, it has been concluded that the observed free radicals occur mainly in the crystalline regions of the polymer or in the interface of the amorphous and crystalline phase.

Further information is expected to be obtained from the study of the peroxy radical decay in similar polymer. The diffusion of oxygen into γ-irradiated isotactic polypropylene gives rise to peroxy radicals which are suited to such investigation.

EXPERIMENTAL

The isotactic polypropylene used (IPP) was a commercial product. The density of samples was 0.896 g/cm³. Cylinders of 6 mm diameter and 6 mm length were prepared by casting powdered polymer at the pressure of 50 MPa and 150°C. The free radicals were generated by gamma radiation at room temperature for 17 h with a total dose of about 3 Mrad. Then the irradiated samples were exposed to the action of atmospheric oxygen for 24 h at room temperature. The EPR spectra were recorded at room temperature with an X-band spectrometer before and after thermostatting the sample under pressure. The high-pressure equipment where the samples were thermostatted was described earlier.[2] In principle, it was a steal cylinder with piston that could be rapidly heated and cooled. During compressing, the temperature and pressure

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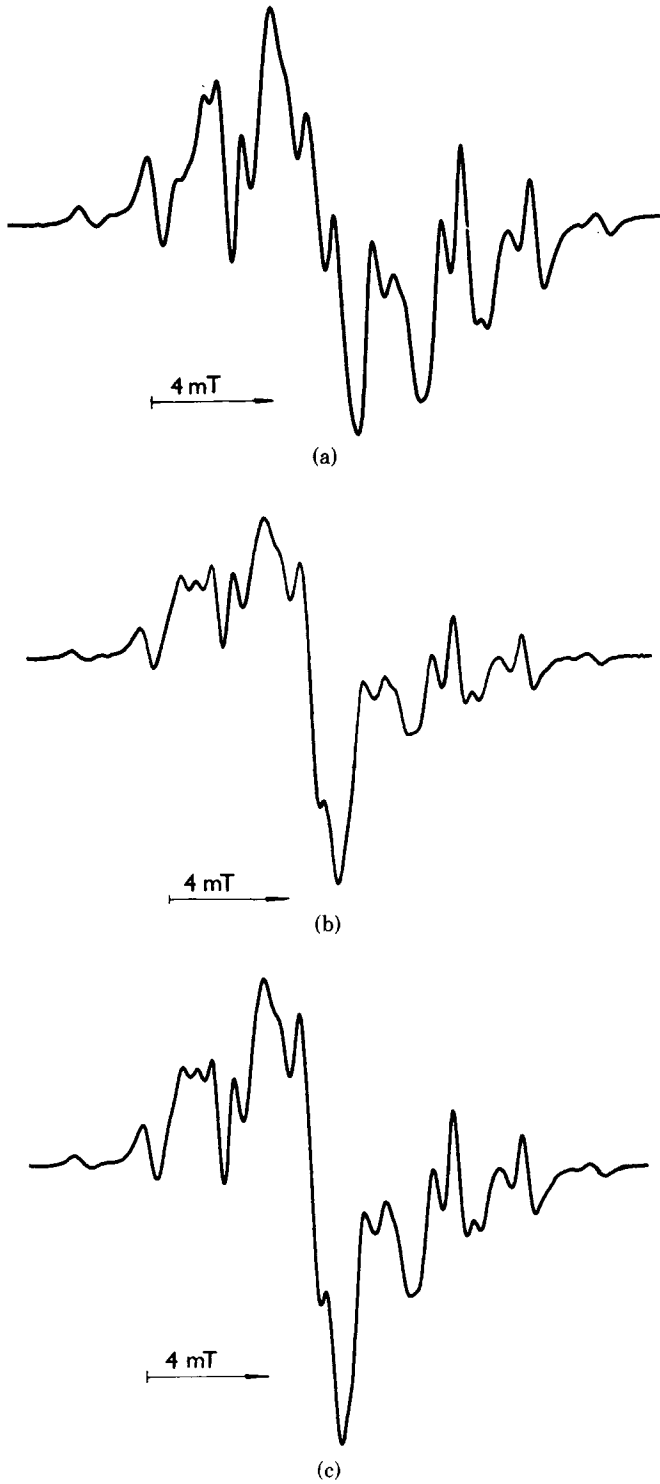
Fig. 1. ESR spectra of irradiated isotactic polypropylene: (a) immediately after irradiation (gain 2); (b) after oxidation (gain 2); (c) after the oxidation and annealing at 600 MPa and 70°C for 20 min (gain 2.5); (d) after oxidation and annealing at 100 MPa and 100°C for 20 min (gain 4).
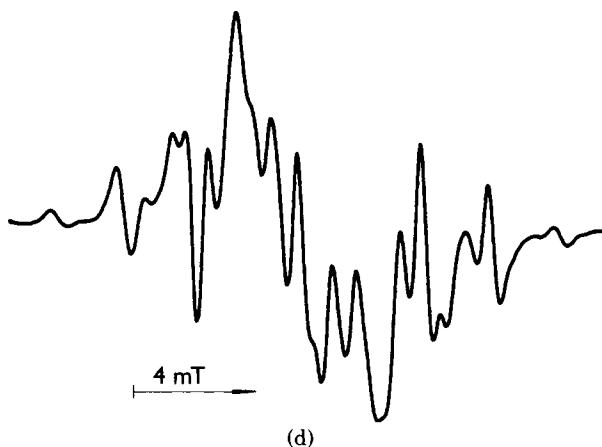
(d)

Fig. 1. (*Continued from previous page.*)

were automatically controlled. The difference between the EPR spectra recorded before and after compressing the polymer gave information about the influence of pressure on the decay of radicals. The concentration of radicals was determined on the basis of the lines corresponding to peroxy radicals. In the kinetic studies the particular peak height was measured as a function of time.

RESULTS AND DISCUSSIONS

The ESR spectra of free radicals in irradiated IPP are the topic of several papers.[3-5] However, there is no good agreement among the interpretations of the spectra up to now. All the same, there are some interpretations that explain the origin of the predominating radical.[6]

According to Fischer and Hellwege,[3] the 17-line ESR spectrum of irradiated IPP recorded at room temperature corresponds to radical of the allyl type:

$$-CH_2-CH-CH=C-\overset{\cdot}{C}H-CH-$$
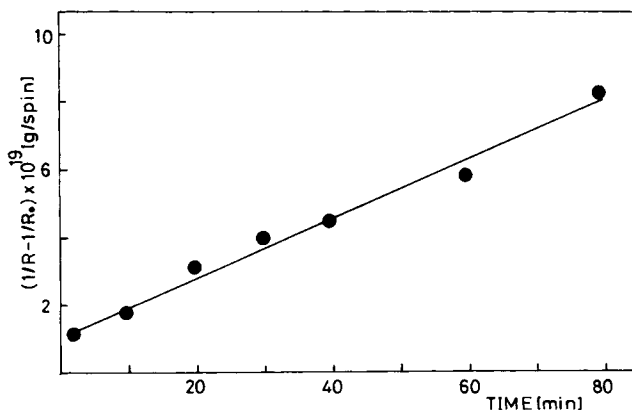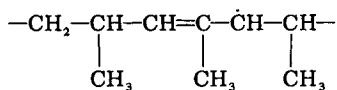
$$CH_3 \qquad CH_3 \qquad CH_3$$

Fig. 2. Time dependence of the reciprocal of the free radical concentration at 70°C and 600 MPa.

The spectrum in Figure 1 is of equal character as observed by the above authors, the only difference being that it already bears the marks of changes which arise in the spectrum in the course of free radical decay. In this case, the radicals were generated at room temperature, and, for this reason, the decay of radicals took place during irradiation of the polymer. The spectrum of equal sample irradiated at lower temperatures exhibits the known 17-line structure. The change in spectrum observed during the free radical decay gives evidence that, besides the predominating type of radical, other types of free radicals are present.[1] In the scope of this study, attention is concentrated on that part of spectrum which was formed after diffusion of oxygen into polymer. This composite spectrum corresponds to peroxy radicals (ROO·) the concentration change of which is studied in this work. A considerable contribution of peroxy radicals to the spectrum is to be observed after the 24-h action of oxygen on an irradiated sample [Fig. 1(b)]. Provided the sample is thermostatted under pressure, the composite spectrum corresponding to peroxy radicals vanishes [Figs. 1(c), 1(d)]. It is known that the peroxy radicals decay much more rapidly than the hydrocarbon radicals,[7] and for this reason the decay of hydrocarbon radicals (R·) may be neglected in this case. This considerable difference between the rate constants of the peroxy and hydrocarbon radicals enables us to obtain information about the influence of pressure on the decay of peroxy radicals.

The plot in Figure 2 shows that the decay of radicals is governed by the law of the second-order reactions. The rate constants of the decay of peroxy radicals given in this paper have been determined according to the law of the second-order reactions. The rate constant of the decay of peroxy radicals is significantly dependent on pressure from 60°C upwards (Fig. 3). This dependence is, however, quite different from the pressure dependence of the rate constant of the decay of hydrocarbon radicals in IPP.[1]

It has been ascertained in foregoing papers that there is a striking difference between the pressure dependence of free radical decay in amorphous polymers and that in semicrystalline polymers. Amorphous polymers, for instance, poly(methyl methacrylate)[8] and polystyrene[9] exhibit a considerable pressure dependence at low pressure (1–300 MPa) while this dependence is poor in the region of higher pressures (400–1000 MPa).

The pressure dependence of the rate constant of free radical decay observed for IPP has the character typical of semicrystalline polymers; i.e., it is almost linear in a wide region of pressures without any saturation effect characteristic of amorphous polymers. The plot in Figure 3 exhibits the character typical of amorphous polymers. This relationship shows saturation at higher pressures and may be divided into two regions. These two regions of decay are represented in Figure 4. The activation volume corresponding to the region of lower pressures is four times greater than that one corresponding to the region of higher pressures. The activation volume at 90°C is 10.6 cm³/mol for the region of lower pressures and 3 cm³/mol for the region of higher pressures. For comparison we give the plot of logarithm of the rate constant of the decay of hydrocarbon radicals against pressure (Fig. 5) based on the data published in Ref. 1. In this case, the activation volume is 4 cm³/mol for a wide pressure region.

The experimental results presented in this paper enable us to compare the pressure decay characteristics of two types of radicals of similar polymer to each other. It is obvious that the observed hydrocarbon radicals occur mainly in
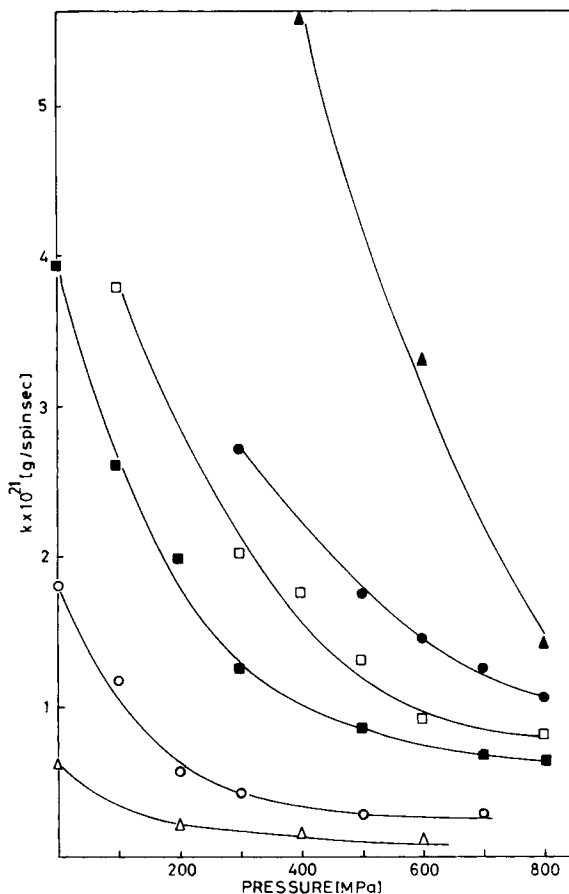
Fig. 3. Pressure dependence of the rate constant for peroxy (ROO·) radical decay at various temperatures: (△) 60°C; (○) 70°C; (■) 90°C; (□) 100°C; (●) 110°C; (▲) 120°C.

crystalline regions of IPP, and, for this reason, they are less sensitive to the action of pressure than the peroxy radicals occuring in amorphous regions of polymer. The molecular motions transporting the free valence are considerably limited in amorphous region by the effect of pressure. If a certain degree of compression has been reached, the increasing pressure affects the molecular motions only to a small extent and a saturation appears.

The molecular motions sensitive to the change in free volume control the process of decay in the region of lower pressures. If a critical degree of compression, i.e., saturation, has been reached, this efficacious mechanism comes to a standstill, and the decay is subsequently controlled by the molecular motions which are less sensitive to the change in free volume. The boundary between these two regions of decay is given by the point of intersection of two straight lines in Figure 4. Let us denote the pressure corresponding to this point of intersection p_{tr}. This point shifts to higher pressure values with increasing temperature (Fig. 6) and equals $(dT/dp) = 0.15$ (°C/MPa).

It ensues from the obtained experimental results that the peroxy radicals occur in amorphous regions while the hydrocarbon radicals appear mainly in crystalline regions of the polymer. The process of oxidation is likely to proceed in the in-
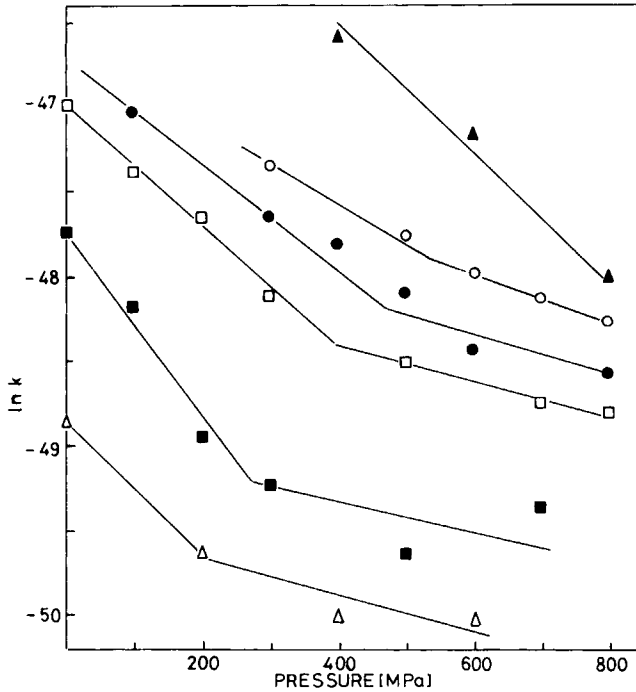
Fig. 4. Pressure dependence of the logarithm of the rate constant for peroxy radicals (ROO˙) decay at various temperatures: (△) 60°C; (■) (70°C); (□) 90°C; (●) 100°C; (○) 110°C; (▲) 120°C.

terface of both phases, oxygen diffuses into amorphous portion of the polymer and reacts with the free radicals occurring on the surface of crystalline regions, and afterwards the peroxy radicals migrate into amorphous regions. It means that the hydrocarbon radicals existing in crystalline regions migrate to the surface of these regions where they undergo oxidation, and the peroxy radicals thus formed pass into amorphous regions, where they decay.
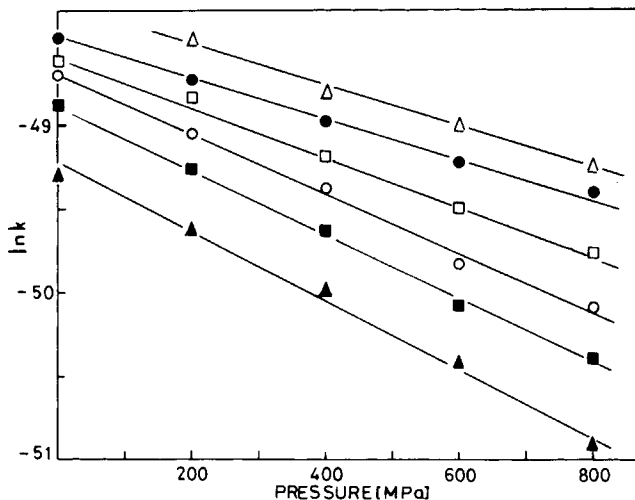

Fig. 5. Pressure dependence of the rate constant for hydrocarbon radicals (R˙) decay at various temperatures: (▲) 60°C; (■) 70°C; (○) 80°C; (□) 90°C; (●) 100°C; (△) 110°C.
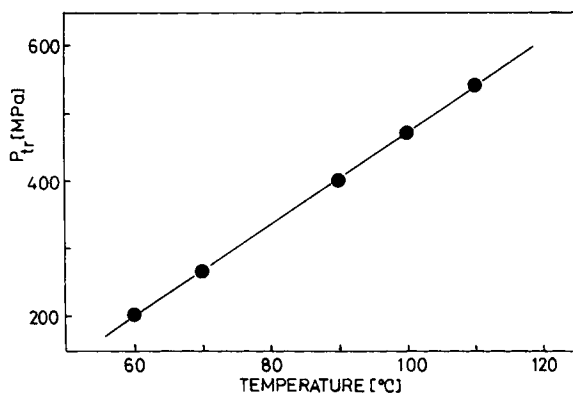
Fig. 6. Temperature dependence of the transition pressure p_{tr}.

The study of the pressure dependence of radical reactions in solid polymers affords useful information about the molecular mechanism of these reactions. At the same time, the free radicals serve as natural spin-probes. They provide us with information about molecular motions in their environment. The activation volumes represent an important parameter. They inform us about pressure sensitivity of the transfer mechanism of radical centers. If the free radicals exist in such medium where the molecular motions are retarded (e.g., ordered state, crosslinked molecules[10]), the activation volume is small. The situation is different if the environment of free radical is not in ordered state. In this case, there is sufficient free volume among the molecules for motion of the segments of macromolecules. This motion is very efficacious for the transfer of free valence and thus the free radicals very rapidly decay in such medium. If more detailed information about the activation volumes of different polymer structures are available, they will be of good use for elucidation of the molecular mechanism of radical reactions in solid polymers. For the time being, the present experimental data enable us to distinguish the reactions in disordered regions from the reactions in disordered regions of polymers.

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