Influence of Pressure on Free Radical Decay in Irradiated Poly(ethylene terephthalate)

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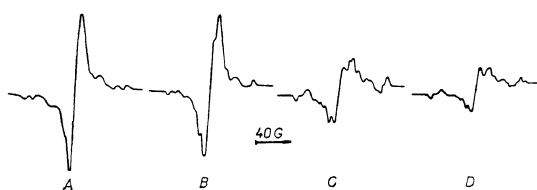
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Poly(ethylene terephthalate) (PET) Arnite produced AKZO Holland (mp 250°C *in vacuo*) was hot-pressed into a pellet ($6\phi \times 6$ mm) at 250°C, 500 atm, and cooled in 45 min. The pellet was irradiated with gamma-radiation for 4.6 Mrad at −50°C and the initial concentration of free radicals was determined by the ESR method. The pellet was then put into the pressing equipment[1,3], subjected to pressure, and heated to a constant temperature. The annealing was interrupted by a rapid cooling of the pressing equipment; the pellet was then put back into the ESR spectrometer to estimate the resulting concentration of free radicals. The rate constant of free radical decay was determined from the initial and resulting concentrations of the free radicals.
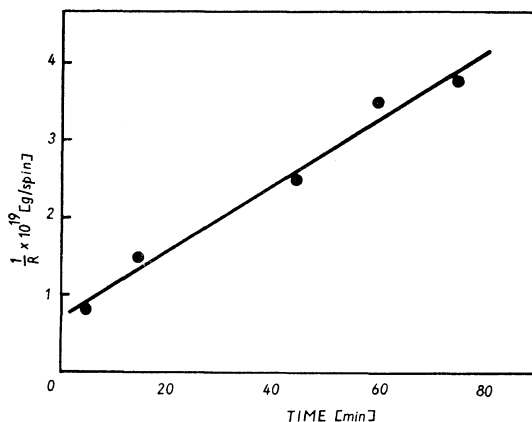
The ESR spectrum of free radicals after irradiation is shown in Figure 1A. The shape of the spectrum changes during the decay of the free radicals. Figure 1B shows the spectrum after 20 min annealing at 3000 atm and 80°C, Figure 1C after 20 min annealing at 1000 atm and 70°C, and Figure 1D after 20 min annealing at 3000 atm and 115°C. We do not intend to study the problem of the interpretation of these spectra. We shall just limit ourselves to the determination of the total concentration of free radicals.

The decay of free radicals obeys second-order kinetics (Figure 2) and we determined the rate constants of free-radical decay on this basis. The rate constant at 50°C depends on pressure only a little (Figure 3). The slope of the individual curves in the temperature region from 50°C to 80°C increases with temperature. In the pressure range from 2000 to 5000 atm and at temperatures between 50°C and 80°C the rate constant depends only slightly on pressure. With increasing pressure the free volume of the polymer decreases, especially in the amorphous
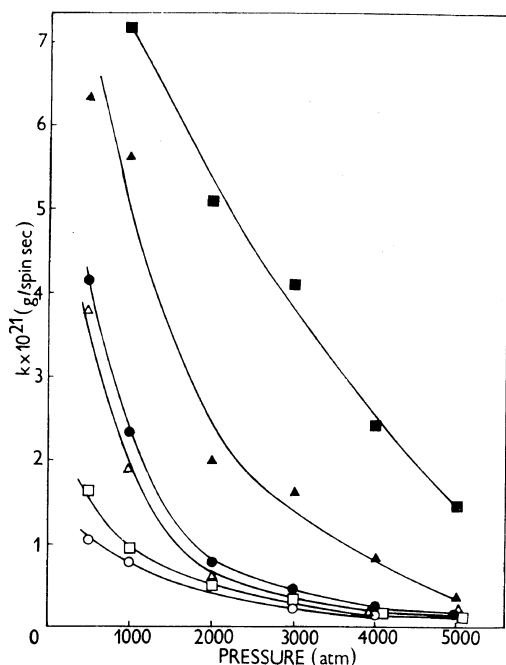

Figure 1. ESR spectra of irradiated poly(ethylene terephthalate) at room temperature: A, immediately after irradiation; B, after 20-min annealing at 80° and 3000 atm; C, after 20-min annealing at 70° and 1000 atm; D, after 20-min annealing at 115° and 3000 atm.

Figure 2. Reciprocal of the free-radical concentration as a function of time at 80°C and 4000 atm.

Figure 3. Rate constants of the free-radical decay as a function of pressure at different temperatures: ○, 50°C; □, 60°C; △, 70°C; ●, 80°C; ▲, 100°C; ■, 115°C.

regions; because of this, the molecular motion which allows the decay of free radicals is hindered. Further increase in pressure in the region from 2000 to 5000 atm does not affect the rate of decrease any more because the segmental motion that brings about the intensive decay has already been suppressed. The pressure dependence of the rate constant at 105°C shows a quite different character. The radicals which occur predominantly in the crystalline regions of the polymer decay at high temperatures. The dependence is almost linear, due to the mechanism of the pressure effect on the molecular motion in the crystalline phase. The molecular motion in the crystalline regions of the polymer is reduced proportionally to the pressure; no saturation appears, as in the amorphous phase where the free volume of the polymer decreases rapidly.

If we compare our results with those obtained from mechanical relaxations, a nice correspondence can be seen. Illers and Breuer[2] studied the dependence of G (dyn cm^{-2}) on temperature of PET upon varying the degree of crystallinity. Their results showed a narrow maximum at about 80°C for amorphous samples (0—2.5% of crystallinity) and a broad maximum at about 100°C for crystalline samples (33—46% of crystallinity). In principle, the results of our experiments are in good agreement with the course of the loss curve of the mechanical α-relaxation. The rate constant of decay is practically independent of pressure until the temperature reaches the value corresponding to the α-relaxation region. In the neighborhood of the maximum of the α-relaxations of the amorphous regions approximately 80°C) we can observe a remarkable effect of pressure on the free radical decay occurring in the amorphous regions. At higher temperatures (above 100°C) the pressure dependence of the rate constant is almost linear and its value is relatively high in the region of higher pressures (3000—4000 atm). At higher pressures and temperatures, free radicals decay mainly in the crystalline regions which are less sensitive to the effects of pressure than the amorphous regions.

REFERENCES

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