Pressure dependence of free radical decay in γ-irradiated main chain liquid crystalline polymers

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A decay of free radicals in γ-irradiated rigid main chain thermotropic polymer BRY 856 was studied. The dependence of the rate constant for free radical decay over the pressure region between 1 MPa and 800 MPa was determined in the temperature range between 80°C and 230°C. Activation volumes of free radical decay were established. A decrease in activation volume at temperatures above the glass transition temperature of the polymer was observed and attributed to rotational structural order along the long axis of the macromolecules.

(Keywords: e.p.r. spectroscopy; high pressure; liquid crystalline polymers; activation volumes)

Introduction

Investigation of the kinetics of free radical decay in solid polymers provides information not only about the reactivity of macroradicals but also about the efficiency of transport mechanisms and related molecular motions.

Liquid crystalline rod-like polymers are represented by one type of polymer with unusual physical properties which were investigated in detail by Wendorff *et al.*[1–3]. Their model proposed that the ordered state displays a well defined three-dimensional long range order, whereas the molecular long axis of the blade-like molecules is orientationally disordered.

The aim of this paper was to obtain information on a particular polymer via measurements of the influence of external pressure on the transport of free radicals in the system ordered in an unusual way.

Experimental

The samples used were produced by Bayer AG Leverkusen under the trade name BRY 856. The polymer consists of 52 wt% *p*-hydroxybenzoic acid, 21 wt% hydroquinone, 22 wt% diphenyl carbonate and 4,4'-biphenyldiol and terephthalic acid in small concentrations. The samples were prepared by polycondensation and the comonomers were arranged statistically along the polymer chain.

The cylinder-like samples (5 mm diameter and 6 mm long) were γ-irradiated by a ^{60}Co source at -50°C using a total dose of 10.5 kGy. The initial concentration of free radicals was measured after irradiation with an EPR Varian E-4 spectrometer. The sample was then put into a press[4,5] and annealed under pressure for 20 min. On rapid cooling of the sample to 25°C and reducing pressure to 0.1 MPa the concentration of free radicals was again measured. The total concentration of free radicals was obtained by double integration of the first derivative of the e.p.r. spectra and comparison with a Strong Pitch standard (Varian). From the difference in concentration of free radicals corresponding to the initial and final spectra, the rate constants for macroradical decay were determined in samples of BRY 856.

Results and discussion

The e.p.r. spectrum shown in *Figure 1* is a superposition of two singlets. The broad singlet has a line width, $\Delta H_{1/2} = 1.5$ mT and a g-factor = 2.0045 and the narrow singlet has $\Delta H_{1/2} = 0.51$ mT and a g-factor = 2.0032. From the analogous broad singlet in the e.p.r. spectrum of polycarbonate[6,7] we may assign a phenoxy-type free radical C_6H_4–O· (I) to the broad singlet. A radical of polyene-type is probably assigned to the narrow singlet. The kinetic data reported here relate to the total free radical concentration. The dependence of the reciprocal of the free radical concentration on time is almost linear, indicating second-order kinetics[8]. The rate constants were therefore determined accordingly. *Figure 2* shows the pressure dependence of the logarithm of the rate constant for free radical decay. This dependence was studied over the temperature region between 80°C and 230°C. The activation volumes were determined according to the relation $(\partial \ln k/\partial P)_T = -\Delta V^*/RT$ and are listed in *Table 1*. As can be seen, the activation volumes decrease with increasing temperature. We found that over 200°C the values of ΔV^* are extremely low; this can be explained by postcrystallization and irreversible plasticity under high pressure annealing[9]. The changes in activation volumes are caused

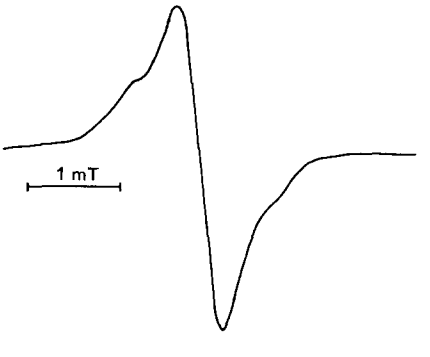

Figure 1 E.p.r. spectrum of γ-irradiated BRY 856 after sample annealing for 20 min at 110°C and 400 MPa

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Table 1 Activation volumes in BRY 856 obtained at pressures between 1 MPa and 800 MPa and temperatures between 80°C and 230°C

Temperature (°C)	80	90	110	120	130	150	190	210	230
Activation volume ($cm^3\ mol^{-1}$)	9.8	9.5	8.7	7.3	7.7	7.7	5.2	1.7	0.5

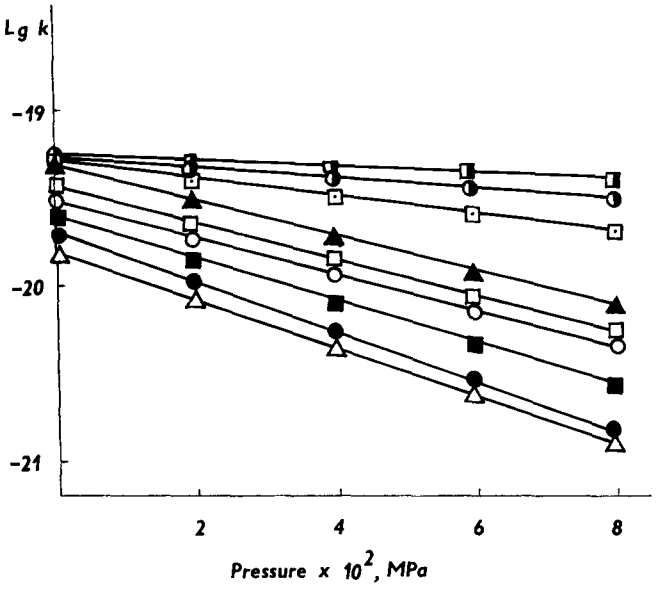

Figure 2 Pressure dependence of the logarithm of the rate constant for free radical decay in γ-irradiated BRY 856 at various temperatures (°C): (△) 80; (●) 90; (■) 110; (○) 120; (□) 130; (▲) 150; (⊡) 190; (◑) 210; (◨) 230

by a change in the degree of structural order of the polymers having an extraordinary plasticity far below the glass transition temperature, T_g. The T_g of BRY 856, obtained by d.s.c. measurement, is 90°C[1]. The transition area begins between 70°C and 80°C and ends between 100°C and 110°C. Above the glass transition the system is arranged according to the Wendorff model and therefore only one region of free radical decay is observed throughout the pressure interval of 1–800 MPa in our experiment. The rod-like molecules are ordered in a regular parallel structure. Owing to the remarkable irreversible plasticity of the polymer under high pressure, the equilibrium parallel structure of rods is readily formed.

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