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Stabilization Effect of Pressure on Free Radicals in Irradiated Polyacrylonitrile

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Synopsis

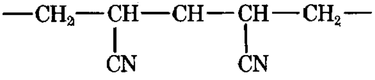
The influence of temperature and pressure on the decay of free radicals in γ-irradiated polyacrylonitrile (PAN) was studied by ESR method. The studies were carried out at temperatures between 90° and 160°C and pressures from 1 to 8000 atm. The rate constants and activation volumes for radical decay were determined. The stabilization effect of pressure on the decay of PAN radicals is discussed and compared with mechanical data.

INTRODUCTION

The stability of free radicals in a polymer matrix is closely connected with molecular motions in the polymer matrix. In the region of low temperatures, the molecular motions are markedly retarded, and free radicals are stable and do practically not decay. With increasing temperature, the mobility and thus also the reactivity of radicals increase.

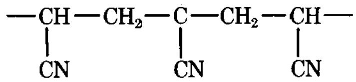
The significance of temperature in radical processes has been discussed many times. The effect of another thermodynamic variable—pressure—is also of importance because increasing pressure affects the change of internal spacing of molecules.

The first information on free radicals observed in γ-irradiated PAN appeared in Abraham and Whiffen.[1] Hasegawa[2] observed ESR spectra in pyrolized, UV, and γ-irradiated PAN. The ESR spectrum for irradiated PAN was assigned the following types of free radicals:



$$-CH_2-\underset{\displaystyle CN}{CH}-CH-\underset{\displaystyle CN}{CH}-CH_2-$$

and



$$-\underset{\displaystyle CN}{CH}-CH_2-\underset{\displaystyle CN}{C}-CH_2-\underset{\displaystyle CN}{CH}-$$

The same author[2] observed the central line assigned to the polyenyl radical.

The effect of high pressure on the stability and decay of free radicals in irradiated PAN has not been studied so far. Therefore, we decided to determine the pressure dependence of the rate constant for free-radical decay at 1–8000 atm and temperatures 90°–160°C. The backbone relaxation (α-process) is well resolved over the mentioned temperature range.

EXPERIMENTAL

The sample of polyacrylonitrile was an experimental homopolymer in powder form prepared by a free-radical mechanism using AIBN as initiator according to Colvin.[3] The molecular weight $\bar{M}_w = 91{,}000$ was determined viscometrically according to the relation[4]

$$[\eta]_{25}^{\mathrm{DMF}} = 2.43 \times 10^{-4}\, \bar{M}_w^{\,0.75}.$$

IR analysis confirmed the high degree of purity. The degree of crystallinity was established by an x-ray diffraction technique, amorphous content 50.8%.

The polymer powder was used to prepare cylinders (0.2 g) irradiated by gamma-rays from a Co-60 source, total dose 4.5 Mrad at −50°C. Irradiated samples were kept in liquid nitrogen. Immediately before measurement, the samples were taken from the cooling medium and the initial concentration of free radicals was determined by ESR method. The pressure measurement was performed in a pressure device described earlier.[5] After having been put into the pressure device, the irradiated sample was pressed to the respective pressure, heated to the required temperature, and held at this temperature for 20 min. On rapid cooling to 25°C and reducing the pressure to 1 atm, the sample was put into a cavity of the ESR spectrometer to determine the resulting spectrum. From the difference in concentrations of free radicals corresponding to the initial and resulting spectra, the total rate constant for radical decay in PAN was established.

An X-band ESR spectrometer ER-9, Carl Zeiss, Jena, was employed. Concentrations of free radicals were determined by a double integration of spectra and subsequent comparison with a Strong Pitch (Varian).

RESULTS AND DISCUSSION

Figure 1a shows the ESR spectrum after γ-irradiation at laboratory temperature. In the presence of air at 25°C, it undergoes no change for 30 min. With increasing temperature, the spectrum gradually decays, the intensity of the hfs lines at 80°C markedly decreases, and finally a spectrum consisting of one line only, which is considered to be due to a polyene free radical, is observed.

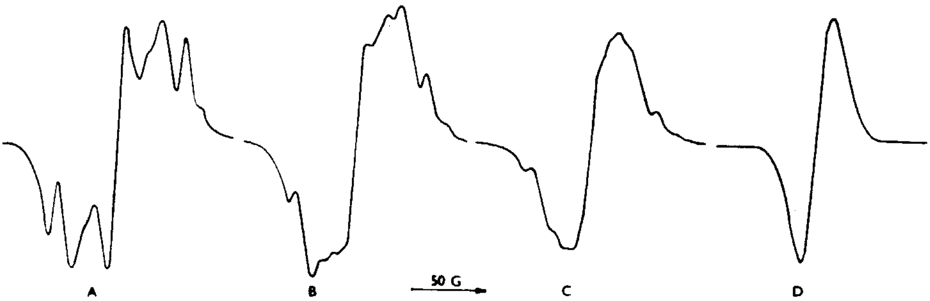


Fig. 1. ESR spectra of γ-irradiated polyacrylonitrile, recorded at room temperature: (a) immediately after the irradiation of the sample; (b) after holding the sample at 80°C and 3000 atm for 20 min; (c) after holding the sample at 100°C and 4000 atm for 20 min; (d) after holding the sample at 150°C and 7000 atm for 20 min.

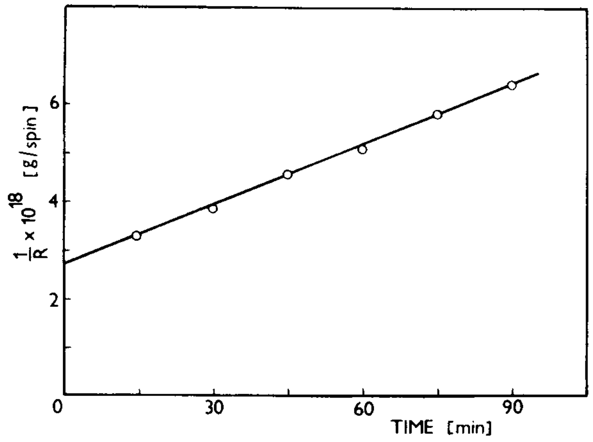


Fig. 2. Reciprocal of free-radical concentration as a function of time at 130°C and 3000 atm.

The spectra in Figures 1b, 1c, and 1d were recorded after annealing of the samples at various pressures and temperatures. The observed changes in the shape of spectra are caused by unequal stability of the radicals in the sample. No reliable analysis of the ESR spectrum of irradiated PAN has been done so far. Detailed analysis and interpretation of the spectrum are beyond the scope of the present paper.

Figure 2 shows the relation between the reciprocal of the concentration and the time at 130°C and 3000 atm. As follows from this dependence, free-radical decay is described by a second-order process. Dependences of the total rate constant for free-radical decay on pressure at the given temperatures are presented in Figure 3. At temperatures lower than 100°C, the dependence is

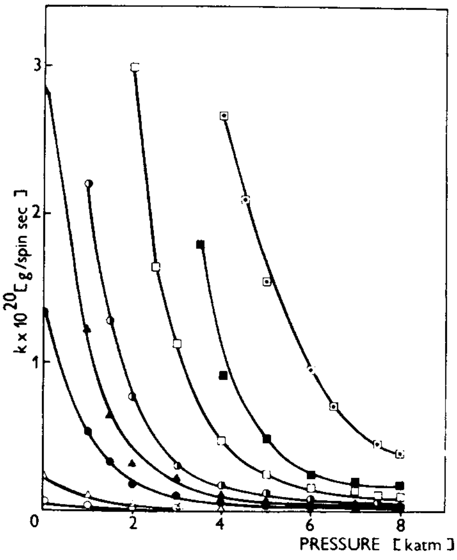


Fig. 3. Rate constants of free PAN radicals as a function of pressure at various temperatures: (○) 90°C; (△) 100°C; (●) 110°C; (▲) 120°C; (◐) 130°C; (□) 140°C; (■) 150°C; (⊡) 160°C.

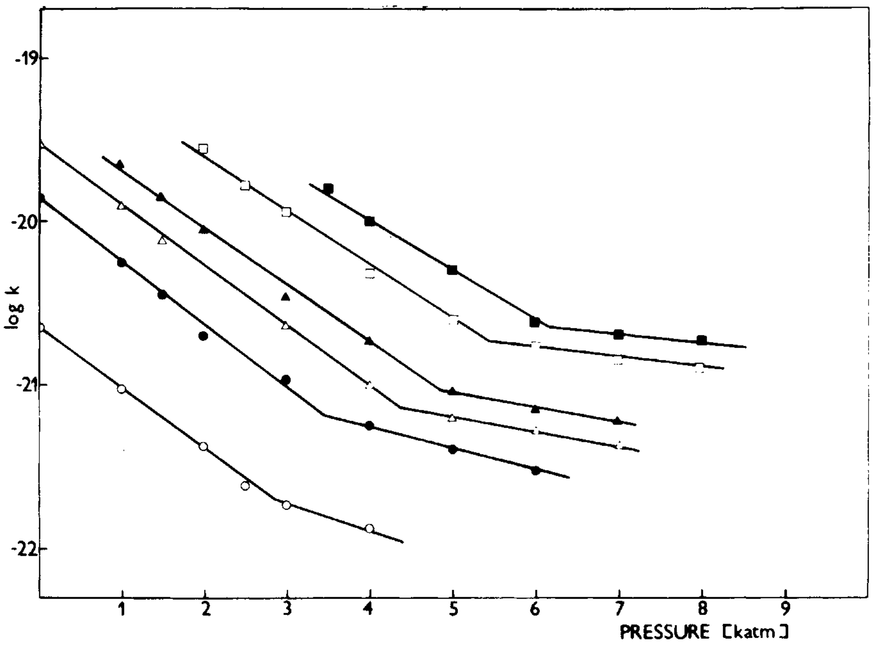


Fig. 4. Pressure dependence of logarithm of rate constants at various temperatures: (○) 100°C; (●) 110°C; (△) 120°C; (▲) 130°C; (□) 140°C; (■) 150°C.

linear since the molecular motions enabling decay are not so sensitive to pressure and decrease in the free volume.

Transition between the region where the pressure slightly affects decay of radicals and the region of marked influence is at about 100°C. Above this temperature, the values of the rate constants decrease rapidly with increasing pressure. Within this domain, molecular motions are retarded with decreasing volume and do not enable motion of the radical center any more.

Information on molecular motions can be obtained from the results of mechanical and dielectric relaxation measurements available in the literature. According to Minami,[6] tan δ for undrawn conventional PAN over the temper-

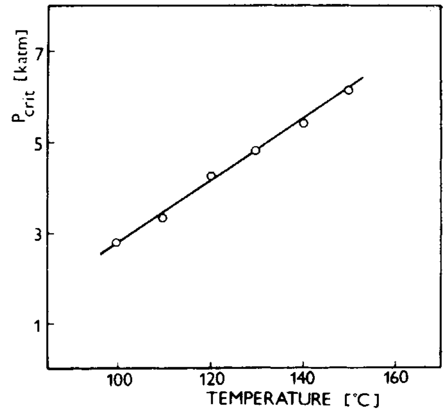


Fig. 5. Temperature dependence of critical pressure p_{cr}.

ature range between 0° and 200°C has two maxima: one around 160°C (α_{I}) and the second, around 110°C (α_{II}). The α_{I} peak is attributed to the molecular motion in the amorphous phase and the α_{II} peak, to the motion in the crystalline phase. This ensues from the fact that in the amorphous PAN, no α_{II} peak is observed. On the other hand, with increasing degree of orientation, the α_{I} peak decreases. This statement is in agreement with the observations of Bohn et al.[7] who found by x-ray analysis that the lattice space increases above 87°C.

The comparison of our results (Fig. 3) with those obtained from mechanical relaxation measurements for PAN shows strong correlation. The rate constant for free-radical decay depends on pressure within the region of α_{II} relaxations. Hence, the free-radical decay is made possible by molecular motions corresponding to relaxations in the α_{II} region.

On the basis of the data in Figure 3, log k was plotted against pressure for various temperatures in Figure 4. The dependence consists of the two linear parts being determined by two different activation volumes at the given temperature. The activation volume for the region of lower pressures is about 26 cm^3/mole and approximately 6 cm^3/mole for the domain of higher pressures. A marked difference in the activation volumes points to the change in the mechanism of the decay reaction as a consequence of the pressure effect.

Intersection of the linear parts of the dependence in Figure 4 gives the value of the critical pressure p_{cr}, the temperature dependence of which is shown in Figure 5. Below the p_{cr} value at the given temperature, the motions prevail which need a relatively large free volume. It can be mainly the macromolecular segment motions on the surface of the crystalline region. Pressure higher than p_{cr} causes such a decrease that these motions cannot take place. The mechanism of decay will change, which will be reflected in a decrease in the activation volume.

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