E.s.r. study of free radicals in poly(vinyl carbazole)

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Poly(N-vinylcarbazole) was γ-irradiated at 77 K. The analysis of e.s.r. spectra showed that cation radicals centred at *N* were produced in the system. Hyperfine splitting constants are: a^N=0.57 mT and a_β^H=0.68 mT. The dependence of the rate constant of free radical decay on pressure (1–800 MPa) was studied at various temperatures (90–170°C). Activation volumes were determined for two characteristic pressure and temperature ranges. The results of e.s.r. measurements are compared with those obtained from dynamic–mechanical measurements.

INTRODUCTION

Although radical products of the degradation of many polymers were detected by the e.s.r. method, radicals formed in poly(N-vinylcarbazole) (PVCz) after γ-irradiation[1] have not yet been studied. The e.s.r. spectra of the irradiated monomer show that cation radicals with the unpaired electron spin associated mainly with a nitrogen atom[2] are produced in the system; at 90 K, cation radicals initiate polymerization and alkyl radicals occur in the polymer. The aim of this paper is the analysis of the e.s.r. spectrum of free radicals formed in solid PVCz under γ-irradiation, and to gain information on kinetic properties of these radicals and relate them to information about kinetics of molecular motions in the polymer matrix.

EXPERIMENTAL

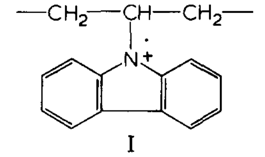
A commercial sample of PVCz, produced by BASF, *LUVIKAN* M-170, was used. Molecular weight $\bar{M}_n = 5 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.20$, $T_g = 225$°C, m.p. 320°C, density 1.186 g/cm^3.

Cylindrical samples of 6 mm in diameter and 6 mm in length were prepared by annealing at 200°C and 50 MPa. After annealing for 10 min, the sample was allowed to cool to room temperature (35 min) at the given pressure. The samples were γ-irradiated from a ^{60}Co source for 18 h with a total dose of 4 Mrad at room temperature. After measuring the initial concentration with an e.s.r. Varian E-4 spectrometer, the irradiated samples were transferred to a pressure-temperature device[3] and annealed under pressure. On cooling the sample under pressure to room temperature and pressure release, the resulting radical concentration was measured. From the difference between concentrations before and after sample annealing, the rate constant for free radical decay was determined.

Dynamic-mechanical measurements were carried out using a *RHEO-VIBRON*/DDV-II-C/ over the temperature range between −140°C and +200°C at the frequency of 110 c/s. The PVCz sample (7 cm long, 0.4 cm wide and 0.05 cm thick) was prepared on a pressure device at 250°C.

RESULTS AND DISCUSSION

E.s.r. spectra of radicals generated by γ-irradiation in PVCz were recorded at room temperature and atmospheric pressure, and again at room temperature after subjecting the sample to high pressure at various temperatures. This indicates that one type of radical prevails in the system; the radicals are also sufficiently stable at room temperature. Because of the small total width of the spectrum (5 mT), we assume that it concerns radicals of the type I with unpaired electron centred at the N atom.



I

The hyperfine splitting constant for the nitrogen atom is conditioned by considerable delocalization of unpaired electrons. Its value, e.g. in dihydrophenazine is 0.61 mT[4] and 0.75 mT in tetra-*tert*-butyl-hydrophenoxazine[5]. The shape of the spectrum (*Figure* 1) indicates that, besides the interaction of unpaired electron with nitrogen nucleus, there is also interaction with hydrogen nucleus in β-position and the lines overlap. The more precise determination of the constants of hyperfine interaction and the line width was done using a computer for minimization of the functional of the least-square method by the gradient method[6]. The construction of the theoretical spectrum (*Figure* 1) showed the shape of the line to be neither purely Gaussian nor Lorentzian in character. The resulting theoretical spectrum is in 50% Lorentzian and 50% Gaussian line shape. The hyperfine splitting constants obtained by the analysis of the spectrum are $a_N = 0.57$ mT and $a_H^\beta = 0.68$ mT. The line width used for constructing the theoretical spectrum is 0.94 mT. This value also includes the unresolved hyperfine interaction with protons of benzene nuclei. The values of these *hfs*

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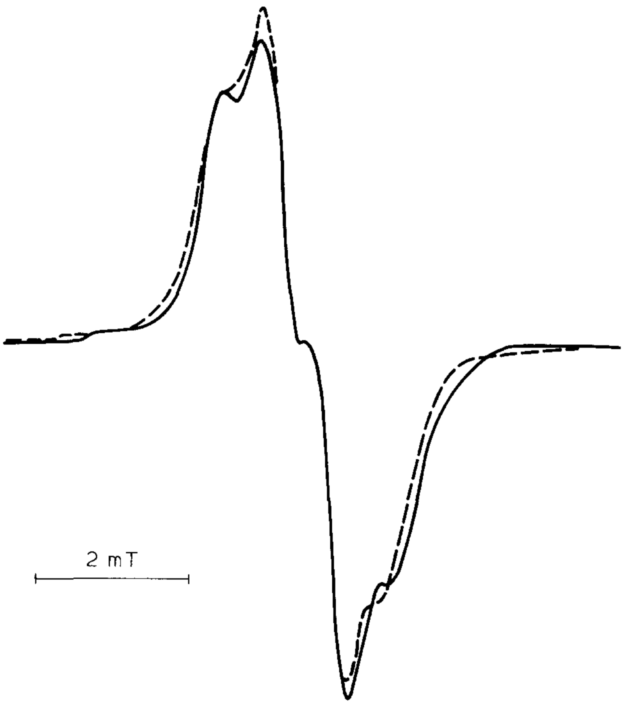

Figure 1 E.s.r. spectrum of free radicals of irradiated PVCz measured at room temperature. ——, experimental; – – –, theoretical

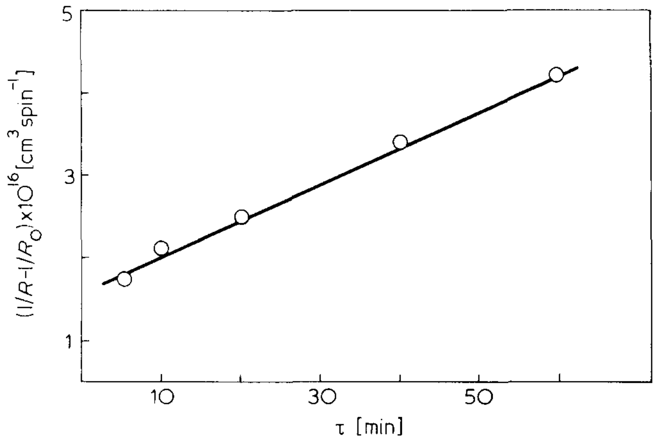

Figure 2 Time dependence of the reciprocal of the free radical concentration at 110°C and 300 MPa

constants can be determined from the calculation. The calculation of spin densities by the method of McLachlan[7] of the cation radical *I* shows that $\rho_N=0.26$, $\rho_{3,12}=0.16$ and $\rho_{8,10}=0.13$. (The parameters employed were: $h_N=1.5$, $k_{C-N}=0.8$). It follows from the calculation that, if for computing the *hfs* constants, McConnel's relation[8] is also used for N atom $a_x=Q^x\rho_x^\pi$ with the values $Q^N=2.2$ mT[9] and $Q^H=2.4$ mT[10], then $a_N=0.57$ mT, $a^H_{3,12}=0.4$ mT, $a^H_{5,10}=0.3$ mT. The contribution of the last two hyperfine interactions will be reflected in the spectrum indirectly as an apparent broadening of lines.

The time-dependence of the reciprocal of free radical concentration at 110°C and 300 MPa is a straight line (*Figure 2*): this demonstrates the validity of second-order kinetics. The rate constants for radical decay were determined on this basis. The pressure dependence of the rate constant for free radical decay (k) at various temperatures is shown in *Figure 3*. At 90°C, just a weak linear pressure dependence is observed. From 100°C the pressure dependence of k is very strong, i.e. at about 100°C a new transport mechanism begins to act. The mechanism is evidently closely connected with molecular motions in the given temperature interval.

Information on molecular motions can be obtained especially from relaxation studies. Pochan *et al.*[11] studied dielectric relaxation spectra of PVCz. They found four relaxation regions. The authors attribute α-relaxation (225°C) to glass transition, β-relaxation (80°C) is assigned to carbazole wagging motions, γ-relaxation (−60°C) has been associated with a rotational liberation of pendant carbazole group, and δ-relaxation (−160°C) is assigned to the localized backbone motion. β- and α-relaxation interest us since the kinetic process studied take place here.

Further information on molecular motions is provided by measurements of mechanical relaxations. *Figure* 4 shows the results of measurements. The maximum of β-relaxations lies at about 90°C and α-relaxation has a maximum at 240°C. The dashed line in *Figure* 4 denotes extrapolation of α-relaxations. With regard to the frequency of measurement (110 c/s), temperature around 100°C can be considered as the beginning of the α-process. At this temperature, pressure begins to influence intensively the rate constant for free radical decay. Pressure dependence of k reflects thus the beginning of the release of molecular motions which are responsible for α-relaxation. From 100°C, the molecular segment backbone motions are successively released as the temperature increases. At 170°C, the motions are very intensive and, therefore, the radical decay can be observed at high pressure only.

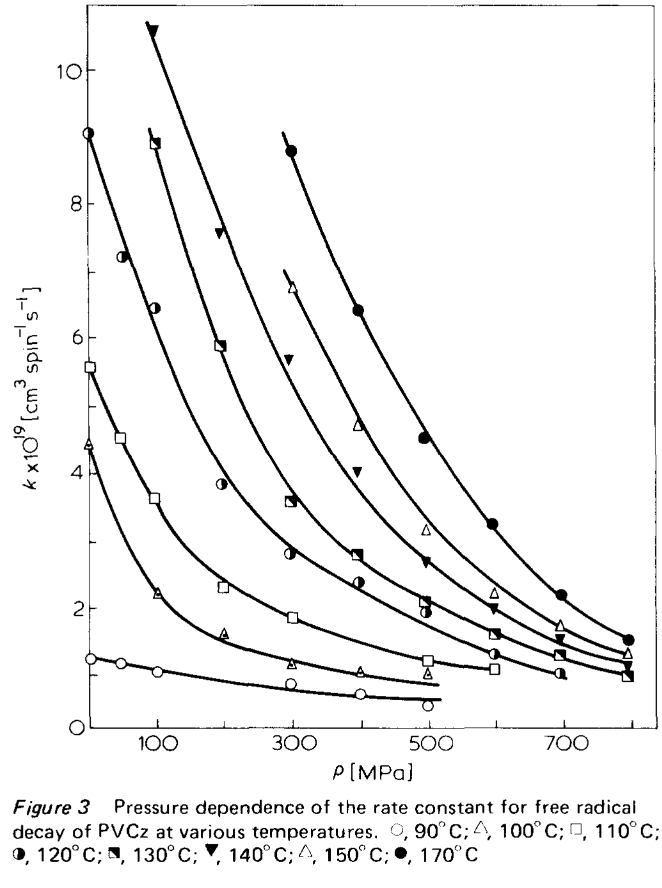

Figure 3 Pressure dependence of the rate constant for free radical decay of PVCz at various temperatures. ○, 90°C; △, 100°C; □, 110°C; ◑, 120°C; ◪, 130°C; ▼, 140°C; △, 150°C; ●, 170°C

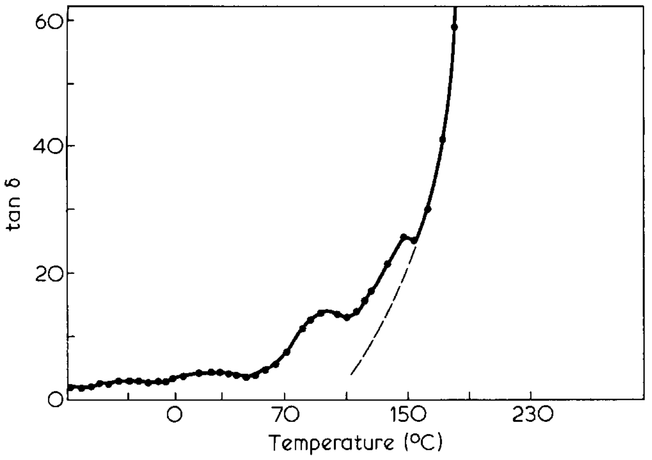

Figure 4 Temperature dependence of the mechanical loss tangent at 110 c/s for PVCz

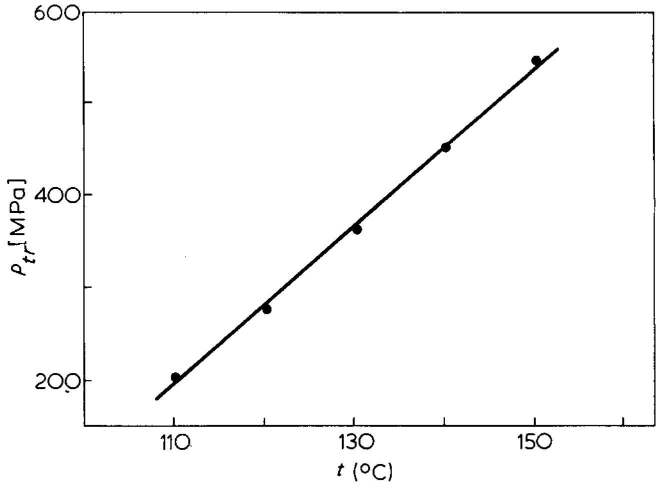

Figure 6 Temperature dependence of the transition pressure (p_{tr})

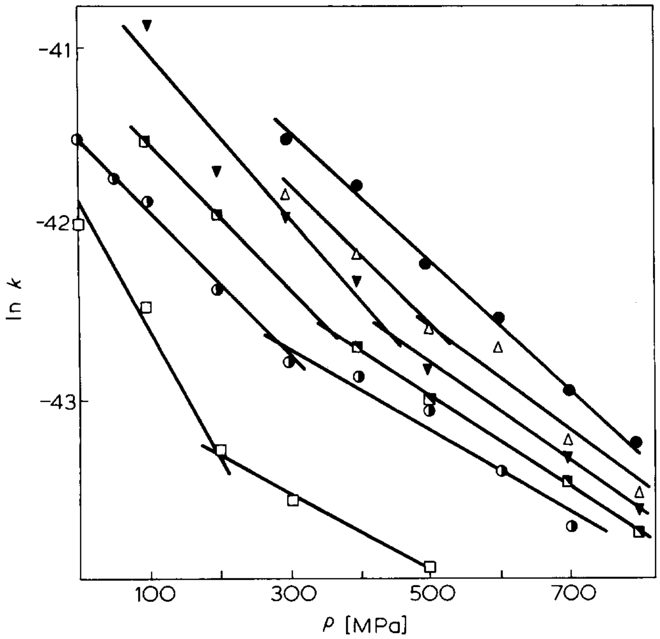

Figure 5 Pressure dependence of the logarithm of the rate constant for free radical decay at various temperatures. □, 110°C; ◑, 120°C; ◪, 130°C; ▼, 140°C; △, 150°C; ●, 170°C

Figure 5 shows the effect of pressure on free radical decay in the logarithmic scale. A break seen in the plot at lower temperatures is greatest at 110°C, and then gradually disappears. The activation volumes corresponding to the two mechanisms of decay at 110°C are:

$V_{\mathrm{I}} = 8.4\ \mathrm{cm^3\ mol^{-1}}$ (for 700–300 MPa) and

$V_{\mathrm{II}} = 12.2\ \mathrm{cm^3\ mol^{-1}}$ (for 300–0.1 MPa).

The point of intersection of the two linear parts (*Figure* 6) gives, at constant temperature, the value of the transition pressure p_{tr}. *Figure* 6 shows the temperature dependence of p_{tr}. It is linear, and shows how the temperature shifts the boundary between the two mechanisms of free radical decay to higher pressure.

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