Relaxation processes and mobility of spin labelled polyethylene

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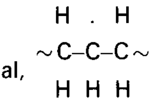

$$\sim\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\cdot}{C}}-\underset{H}{\overset{H}{C}}\sim$$

A high density polyethylene was spin-labelled by the reaction of the alkyl type free radical, $\sim\underset{H}{\overset{H}{C}}-\underset{H}{\overset{\cdot}{C}}-\underset{H}{\overset{H}{C}}\sim$ with 2,4,6-tri-t-butyl nitrosobenzene as a spin-trapping reagent. Extrema separations and line widths of e.s.r. spectrum of nitroxide free radicals were obtained and used in order to calculate correlation times of the motion of the label in a wide temperature range. Spin rotational frequencies of free radicals were compared with the correlation frequencies obtained from a relaxation map which revealed α-, β- and γ-relaxation processes in solid polyethylene. It was concluded that the motional narrowing of the line width in the high temperature region 283–343 K with an activation energy of 9.2 kcal/mol, was caused by the β-relaxation process, which is normally attributed to the large scale segmental motion over the whole molecular chain in the amorphous phase. The decrease of the extrema separation in the higher temperature region 353–383 K was conisdered due to the same mechanism of the relaxation observed in the 283–343 K region in the case of the line width study. These e.s.r. techniques gave lower activation energies of β-relaxation process than those obtained by dielectric and mechanical relaxation measurements. This discrepancy was interpreted in terms of the distribution of relaxation times. The relaxation spectrum for the β-process was discussed based on the Miyake equation.

INTRODUCTION

The spin probe[1,2] and the spin label method[3] have been studied for several polymers by many authors. They have calculated the rotational correlation times by using Freed's[4] or Kivelson's[5] equations and they have suggested that the mobility of spin molecules were reflecting the molecular motions of solid polymers. For example, spin probe studies of solid polyethylene have been reported by Kusumoto *et al.*[6] They observed the effect of annealing on the molecular motion at the surface of a crystallite of solution grown polyethylene by estimating the rotational frequencies of the spin probe. On the other hand, Bullock *et al.*[7] labelled polyethylene with stable nitroxide radicals by using chemical reactions involving small amounts of CO groups in polyethylene chains with the amines and attributed the mobility of the label molecule to the relaxation processes in solid polyethylene. They concluded that the motions of the label in the temperature regions 220–350 K and 350–380 K reflected the β- and α-relaxation processes, respectively, because the n.m.r. activation energies were in good agreement with the results obtained from the spin label study. However, the rotational relaxation frequencies of spin label estimated by e.s.r. technique seem to be higher by 1–5 orders of magnitude than those of α- and β-processes observed by the other relaxation measurements. The activation energies of 5.7 and 11.3 kcal/mol obtained by the spin label method also seems to be lower than those of 20 and 46 kcal/mol estimated from a relaxation map for the β- and α-relaxation processes, respectively. It is well known that the magnetic resonance techniques give lower activation energies than those obtained by dielectric and mechanical relaxation measurements, generally. Miyake[8,9] interpreted these phenomena in terms of the distribution of correlation times, and then derived n.m.r. correlation time spectra of amorphous polymers. Törmälä[14,15] concluded that the motions of spin labels and spin probes in poly(ethylene oxide) reflect γ-process by comparison with the dielectric frequencies and apparent activation energies. However, this kind of simple comparison of the data of magentic resonance method and those of dynamic mechanical measurements must be very careful because the distribution of relaxation times must not be neglected for polymer study. In a previous paper[10], the real activation energy and correlation time spectra for relaxation process were determined by the analysis of e.s.r. and n.m.r. line width data of polymers in urea–polyethylene complex. The aim of the present paper is to analyse the temperature dependence of the line width of e.s.r. spectra of spin label and the distribution of the relaxation times with regard to the relaxation process in solid polyethylene.

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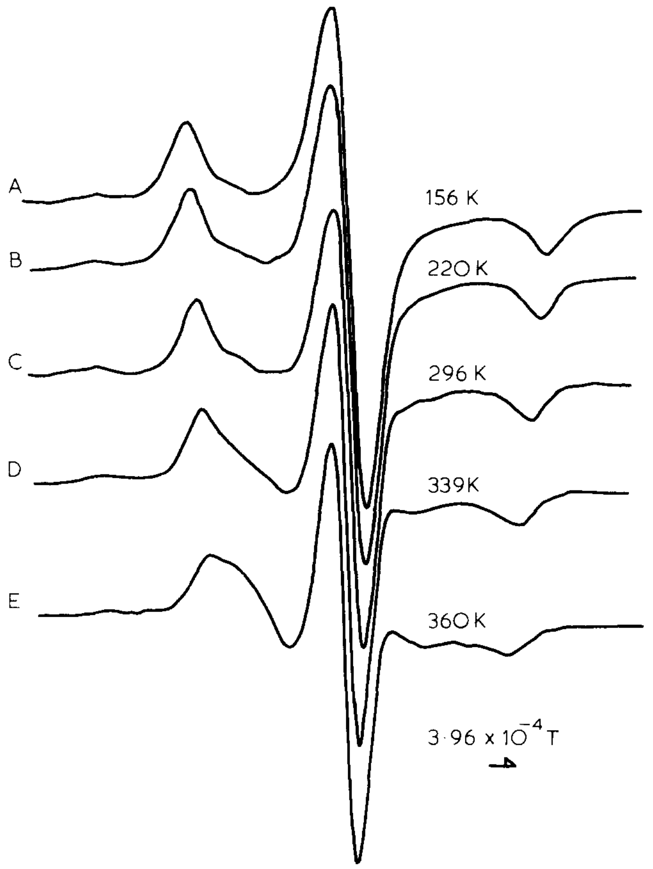


Figure 1 E.s.r. spectra of nitroxide free radicals trapped in polyethylene matrix: (a) 156 K; (b) 220 K; (c) 296 K; (d) 339 K; (e) 360 K

EXPERIMENTAL

Preparation of spin-labelled polyethylene

A high density polyethylene, Sholex 6050 (Showa Electric Co. Ltd) was used for this study. The sample was purified by dissolving in boiling toluene, precipitated by cooling, washed in acetone, and dried in a vacuum oven. 2,4,6-tri-t-butyl nitrosobenzene, spin trapping reagent, was introduced into the samples by swelling the powdered polyethylene in benzene solution of the reagent. The samples were dried again thoroughly *in vacuo* at 10^{-3} mmHg.

Irradiation technique

The samples were subjected to ^{60}Co γ-irradiation at room temperature under a vacuum of 10^{-4} mmHg. The total dose was 2.5 Mrad with a dose rate of 0.1 Mrad/h.

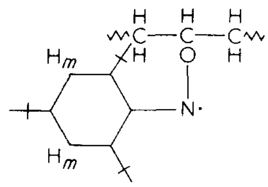
E.s.r. observation

E.s.r. spectra were recorded with a JEOL ME-2 spectrometer (X-band) with field modulation of 100 kHz. An online spectrum computer JEOL EC-6 was connected to the spectrometer, and the data were punched out on paper tape by an A–D converter. The analyses of the line shape were conducted by the electronic computer HITAC 8400.

RESULTS AND DISCUSSION

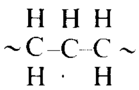
Variation of e.s.r. spectra of labelled nitroxide free radicals in solid polyethylene

Figure 1 shows the change of e.s.r. spectra of free radicals produced in irradiated polyethylene containing the spin trapping reagent with temperature of observation. In a previous paper[11], it was reported that the triplet spectra in *Figure* 1 was attributed to the nitroxide radicals,



(I)

produced by the reaction of the alkyl type free radical,



$$\begin{matrix} \mathrm{H} & \mathrm{H} & \mathrm{H} \\ \sim\mathrm{C} - & \mathrm{C} - & \mathrm{C}\sim \\ \mathrm{H} & \cdot & \mathrm{H} \end{matrix} \qquad \text{(II)}$$

with the spin trapping reagent. It is clear that the extrema separation (Δ) and the line width (ΔH_{msl}) of this triplet spectra are decreasing with increasing temperature.

Analysis of line width

The line shapes of the outer peaks in *Figure* 1 seem to be quite sensitive to the anisotropy of coupling constant due to the nitrogen nucleus; in other words, the pattern is the so-called amorphous pattern. However, the central line seems to be symmetrical and purely Gaussian in shape. For simplicity, it was assumed that the anisotropy due to the nitrogen nucleus in the central line was negligible. A well resolved triple-quartet (each component of the triplet with separation of 10.5×10^{-4} T was composed of four lines with separation of 1.8×10^{-4} T) is observed at temperatures higher than 410 K. This subsplitting was caused by coupling due to one proton (H_x) in polymer chain and two protons at *meta* positions in benzene ring (H_m). Though these couplings are small and unresolved at lower temperature, it is recognized that they cause inhomogeneous broadening of spectral lines and cannot be ignored in line width analysis. The central lines are shown expanded in *Figure* 2. We obtained the theoretical line shapes assuming that the relative intensities of the quartet lines were binomial and each component was Gaussian in line shape. These line shapes were recorded on an X–Y plotter and compared with observed spectra in order to get the best fit. The broken lines in *Figure* 2 show examples of the calculated line shape. By this method, line width, ΔH_{msl}, of the central lines observed at various temperatures can be determined quite accurately.

Variations of line widths and extrema separations

Figure 3 shows the variation of line widths of central lines and the extrema separations with temperature. The

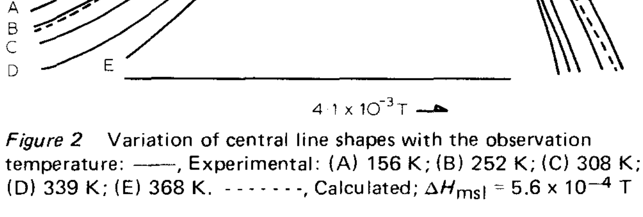


Figure 2 Variation of central line shapes with the observation temperature: ——, Experimental: (A) 156 K; (B) 252 K; (C) 308 K; (D) 339 K; (E) 368 K. -------, Calculated; $\Delta H_{msl} = 5.6 \times 10^{-4}$ T

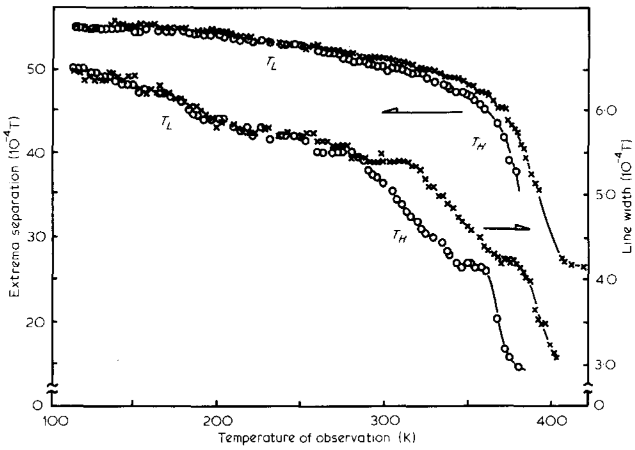


Figure 3 Variations of line widths and extrema separations with the observed temperature: x, first heating; ○, second heating

annealing has no effect on the temperature region T_L, but it shifted the temperature region T_H to the lower temperature side. This can be interpreted in terms of the rearrangement of molecular chains due to heat treatment of the first run as mentioned in a previous paper[11]. We will discuss the case of the second run, in which nitroxide radicals are occluded by polymer main chains because of melting in the first run. It is well known that extrema separations are reflecting the anisotropy parameter ($2A_{zz}$) due to the interaction of the nitrogen nucleus and its variation reflects the circumstances of the motion of the spin labels. We can see more than two temperature regions, in which extrema separations decrease remarkably with increasing temperature in *Figure* 3. The change in the region lower than 353 K (T_l) is rather gradual, but the one in the higher temperature region, 353–383 K, (T_H) is quite remarkable. These two transition regions seem to be corresponding to the transitions in the region of 220–350 K and 350–389 K, respectively as observed by Bullock *et al.*[7]. Motional narrowing of line widths was observed as shown in *Figure* 3. We can also see more than three temperature regions, in which the decreasing of line width is remarkable. It is interesting that the changes of line widths are similar to those of extrema separations.

Comparison of spin rotational motion with the mobility of polymer chains

It is important and meaningful to compare the time constant of spin rotation of the labels obtained by the e.s.r. method with that of the molecular motion of polymer chains obtained by other methods. Deviation of extrema separations ($2A_{zz}$) from the value for rigid state ($2A^{\circ}_{zz}$) was used to calculate correlation times. Spin rotational relaxation times, τ_R were calculated by Freed's[4] equations using Brownian diffusion, moderate jump and large jump models. Since line widths in the region of T_H were estimated to be 3.0–4.0 × $10^{-4}T$ as described in *Figure* 3, the following equations in the case of line width of 3.0 × $10^{-4}T$ were applied.

$$\tau_R=a\left(1-\frac{A_{zz}}{A^{\circ}_{zz}}\right)^b$$

$$\begin{array}{lll} a=5.4\times10^{-10}\ \mathrm{s} & b=-1.36 & \text{(Brownian diffusion)} \\ a=1.10\times10^{-9}\ \mathrm{s} & b=-1.01 & \text{(moderate jump)} \\ a=2.55\times10^{-9}\ \mathrm{s} & b=-0.615 & \text{(large jump)} \end{array} \qquad (1)$$

In order to make clear comparison in a relaxation map, the values of τ_R were converted into spin rotational frequencies, f_{τ_R} by using the relation:

$$f_{\tau_R}=\frac{1}{2\pi\tau_R} \qquad (2)$$

The relation between line width and correlation frequency may be given by

$$(\Delta\nu)^2=M^2+(R^2-M^2)\frac{2}{\pi}\tan^{-1}\left(\frac{\alpha\Delta\nu}{\nu_c}\right) \qquad (3)$$

according to treatment of Gutowsky and Meyer[12], where M is the line width in free rotational motion state, R is the line width in rigid state. ν_c is a correlation frequency giving the average rate of change in structural configuration. α means a line width parameter and $\Delta\nu$ is the observed line width at the transition temperature region. The line widths are all given in frequency scale. By this equation, the correlation frequencies of spin labels were calculated over a wide temperature range as shown in *Figure* 4. The difference of the values of spin rotational frequencies calculated by the respective models of Freed's equation, equation (1), is relatively small and these values are in good accord with that obtained by the extrapolation of the spin rotational frequencies estimated from the line width data. Therefore, it can be considered that the decrease of extrema separation in the higher temperature region 353–383 K was caused by the same mechanism as that of the relaxation observed in the region 283–343 K in the case of the line width study. The correlation frequencies in the case of the second heating were plotted in the relaxation map[13] made by the data obtained in the other relaxation measurements as shown in *Figure* 5. Correlation frequencies estimated for the lower temperature region, T_L, from line width data are not consistent with any of the α-, β- and γ-processes. On the other hand, in the higher temperature region, T_H, (283–343 K for line width, 353–383 K for extrema separation) the order of frequencies were in good agreement with the extrapolated curve for β-relaxation process.According to the above

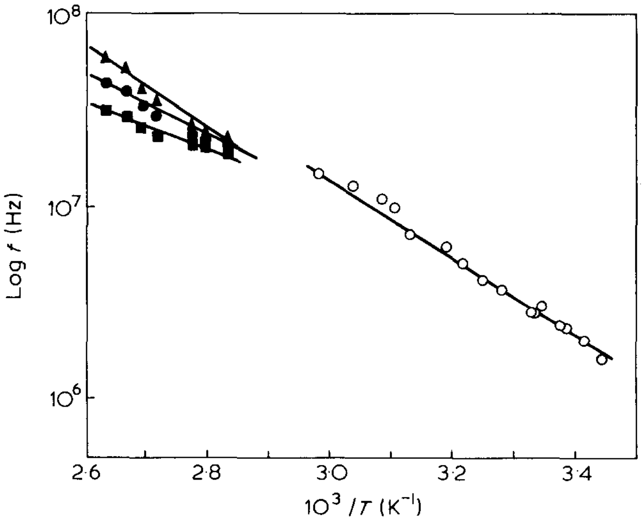


Figure 4 Rotational correlation frequencies f as a function of the inverse value of temperature: ○, line width; extrema separation: ▲, Brownian diffusion; ●, moderate jump; ■, strong jump

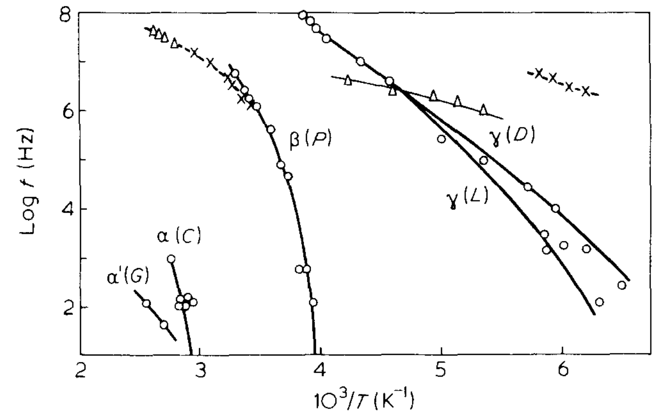


Figure 5 Composite plot for the relaxations in polyethylene: △, e.s.r. extrema separation (moderate jump); x, e.s.r. line width; ○, other relaxation measurement data (Wada map)

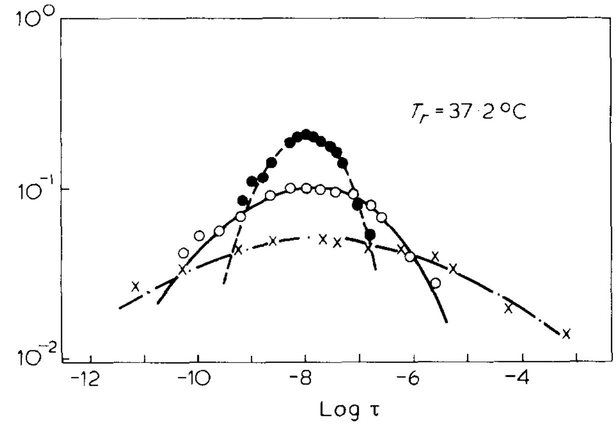


Figure 6 Calculated e.s.r. relaxation spectra of polyethylene with the assumed values of activation energies: ●, 10 kcal/mol; ○, 20 kcal/mol; x, 40 kcal/mol; (T_r = 37.2°C)

discussion it can be concluded that the motional narrowings of line width and extrema separation in these temperature regions were caused by β-relaxation process. However, relatively low activation energies of 9.2 kcal/mol (case of study of line width) and 7.6 kcal/mol (case of study of extrema separation assuming moderate jump) were obtained. These values are lower than the 20–30 kcal/mol of β-process in the relaxation map. This phenomenon will be discussed in the next section.

Correlation time spectra of β-process in polyethylene

When a distribution of relaxation times is neglected, the activation energy obtained in the magnetic resonance study is usually lower than that found by dielectric and mechanical measurements.

Miyake[9] suggested that an apparent activation energy E obtained from the n.m.r. correlation time τ of high polymers by the use of the Arrehnius equation:

$$\tau = \tau_0 \exp(E/RT) \qquad (4)$$

was usually lower than those obtained from mechanical or dielectric data. He took the distribution of correlation times into consideration in such a complicated system as high polymers and derived correlation time spectra $I(\tau)$[16] as the following equation:

$$I\left(\frac{1}{\sqrt{\Delta\omega^2 a(T)}}\right) \simeq \frac{2\Delta\omega^2}{(\Delta\omega_R^2 - \Delta\omega_F^2)}\left(1 + \frac{\mathrm{d}\log a(T)}{\mathrm{d}\log\sqrt{\Delta\omega^2}}\right)^{-1} \qquad (5)$$

where $\Delta\omega_R^2$ is the second moment of n.m.r. spectrum in rigid state, $\Delta\omega_F^2$ is that in state of free rotation and $\Delta\omega^2$ is that at a temperature in the transition temperature range. $a(T)$ is called a shift factor and represented by:

$$\tau(T) = a(T)\tau(T_r) \qquad (6)$$

where T_r is a reference temperature. Substitution of equation (4) into equation (6) gives equation (7):

$$a(T) = \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right)\right] \qquad (7)$$

Kakudate *et al.*[16] made a study on correlation time spectra of α-, β- and γ-processes in polyethylene based on n.m.r. data by using equation (5) and obtained good results. Equation (5) can also be applied to the study of line width of e.s.r. spectrum. With the value of the activation energy, E, being assumed, the correlation time spectra for the relaxation process can be calculated by using equations (5) and (7). *Figure* 6 shows the correlation time spectra for the β-process obtained from the e.s.r. line width data using various values of the assumed activation energies. We can see that the broadness of the calculated relaxation spectrum is sensitive to the assumed value of the activation energy. In *Figure* 7, the solid line indicates correlation time spectra obtained by Kakudate *et al.*[16] from n.m.r. data and open triangle (△) mean that obtained by Saito *et al.*[17] in dielectric measurements. These experimental spectra do not agree well with the correlation time spectra calculated by using e.s.r. data and with the activation energy of 10 kcal/mol obtained from *Figure* 4. However, correlation time spectra obtained from e.s.r. data are in good agreement with the spectra obtained from dielectric and n.m.r. data when the activation energy is assumed to be 20 kcal/mol as shown in *Figure* 7. Therefore, it can be said that the value of the activation energy, 20 kcal/mol, must be the real activation energy of the molecular motion observed by e.s.r., n.m.r. and dielectric methods. The value of the activation energy (20 kcal/mol) is actually obtained from the relaxation map (*Figure* 5). From these results, it can be concluded that the motional narrowing of line width in the temperature region, T_H, is reflecting the β-relaxation process in polyethylene, which is normally attributed to the large scale segmental motion over the whole molecular chain in the amorphous phase.

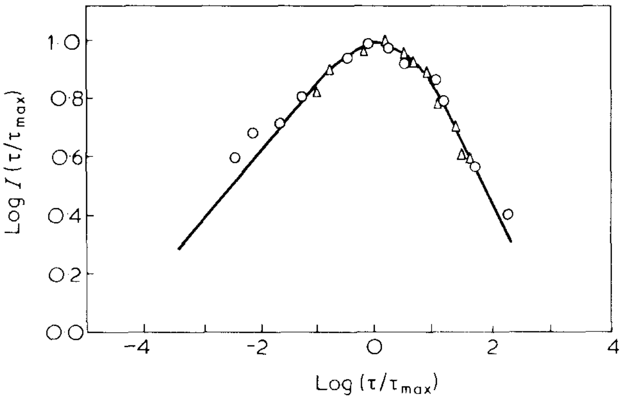


Figure 7 Comparison of the e.s.r., n.m.r. and dielectric relaxation spectra: ○, e.s.r.; ——, n.m.r.; △, dielectric

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