# Relaxation spectrometry of polyethylene in urea–polyethylene complex by *BL* n.m.r. and e.s.r. measurements

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The molecular motions of polyethylene in urea–polyethylene complexes have been studied by e.s.r. and *BL* n.m.r. The e.s.r. spectra of alkyl free radicals located along the polymer chains were recorded and the temperature dependences of hyperfine splitting widths due to the $\beta$-protons ($\Delta H_{\beta_1}$, $\Delta H_{\beta_2}$) and linewidths were estimated. A decrease in ($\Delta H_{\beta_1} - \Delta H_{\beta_2}$) and narrowing (which appears over a wide temperature region) was found. The motional narrowing of line widths in the *BL* n.m.r. spectra were also found. Correlation times for the molecular motion of polyethylene molecules were calculated from this magnetic resonance data, taking into account the distribution of relaxation times according to Miyake's equation. It was concluded that the molecular motions studied by e.s.r. and n.m.r. were the same. Relaxation time spectra indicated higher activation energies (10 kcal) than those calculated for a system with a single correlation time.

## INTRODUCTION

The relation between the behaviour of trapped free radicals and the molecular motions of the trapping matrix of polymeric materials has been studied extensively. Close relations between the decay of radicals and relaxation processes in hydrocarbon polymers were reported[1]. The decay reaction of alkyl radicals in polyethylene has been analysed more precisely by the application of diffusion-controlled reaction theory, and the temperature dependence of the diffusion constant has been interpreted in connection with the relaxation process taking place in the crystalline regions of polyethylene[2,3]. The temperature dependences of $g$ values for peroxy radicals[4] trapped in irradiated polyethylene were discussed with respect to the local molecular motion of radical sites both for normal polyethylene and urea–polyethylene inclusion materials, and a more mobile character of radical sites in the latter than in the former was clearly demonstrated. Also, temperature dependences of the hyperfine splitting width due to interactions between $\beta$-protons and unpaired electrons in polyethylene radicals were successfully analysed and local motions of the radical sites were discussed[5]. The spin label method has also been widely applied to the studies of molecular motions in synthetic polymers and several useful interpretations have been presented[6].

In the application of magnetic resonance to the study of molecular motions, one of the usual methods is to calculate correlation times, for example by the application of the equation derived by Bloembergen, Purcell and Pound (BPP equation)[7]. However, the BPP equation was derived for a system with a single correlation time. Polymeric materials generally have a broad distribution of relaxation times and this must be taken into consideration. Miyake[8,9] pointed out that an apparent activation energy obtained from the n.m.r. correlation times of polymers by the use of Arrhenius equation was smaller than those obtained from viscoelastic or dielectric data and he derived a useful formula for n.m.r. correlation spectra. Here, the n.m.r. and e.s.r. correlation times of polyethylene molecules in a urea–polyethylene complex were analysed considering the distribution of the relaxation times.

## EXPERIMENTAL

High density polyethylene, Sholex 6050, was purified and used for preparing the urea–polyethylene inclusion compound (UPEC), by the method of Monobe and Yokoyama[10]. UPEC was subjected to $\gamma$-irradiation up to 3 Mrad under a vacuum of $10^{-4}$ torr and e.s.r. spectra of the alkyl free radicals trapped in the UPEC observed using an X-band spectrometer, JEOL ME-3. Broad line (BL) n.m.r. studies were also undertaken. The problem of the nuclear magnetic moment of protons in the urea molecules in UPEC was overcome using a deuterated urea–polyethylene complex (*d*-UPEC). The temperature dependences of the line width and second moment of *BL* n.m.r. spectra of *d*-UPEC and normal polyethylene were compared. Some previous published n.m.r. data[11] were used in the comparison with e.s.r. data.

## CORRELATION TIME IN MAGNETIC RESONANCE STUDIES

The temperature dependence of the line width of the magnetic resonance spectrum has been discussed with respect to the molecular motion of the matrix containing the observed magnetic centre. The BPP equation was also used to estimate the correlation time associated with the molecular motion attributed to motional narrowing of the line widths of magnetic resonance spectrum. However, BPP theory was developed for a system exhibiting

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random Brownian motion with a single correlation time. A polymeric material has a rather broad distribution of the relaxation times, and the simple application of the BPP equation is therefore not appropriate. Miyake[9] proposed a useful device to overcome this problem 20 years ago. According to BPP theory modified by Gutowsky and Meyer[12], the correlation time. $\tau_c$, of the molecular motion may be estimated by the following equation:

$$\langle\Delta\omega^2\rangle - \langle\Delta\omega^2\rangle_F = \frac{2}{\pi\alpha}(\langle\Delta\omega^2\rangle_R - \langle\Delta\omega^2\rangle_F)\tan^{-1}(\alpha\tau_c/T_2) \tag{1}$$

where $\langle\Delta\omega^2\rangle_R$ and $\langle\Delta\omega^2\rangle_F$ are the second moments at rigid and free states, respectively, and $T_2$ is spin–spin relaxation time. $\langle\Delta\omega^2\rangle$ is the second moment observed in the transition temperature region. The constant $\alpha$ in equation (1) is a line shape parameter which is assumed to be unity. According to Miyake's theory modified by Kakudate[13], the distribution of the correlation time, $I(\tau_c)$, must satisfy the following equation:

$$\langle\Delta\omega^2\rangle - \langle\Delta\omega^2\rangle_F = \frac{2}{\pi\alpha}(\langle\Delta\omega^2\rangle_R - \langle\Delta\omega^2\rangle_F)\int_{-\infty}^{\infty}\tan^{-1}(\alpha\tau_c/T_2)I(\tau_c)d\log\tau_c \tag{2}$$

where the distribution of the correlation time $I(\tau_c)$ is assumed to be a symmetric function, the relaxation spectrum, $I(\tau_c)$, in the transition temperautre region, may then be expressed by equation (3):

$$I(\alpha/\sqrt{\langle\Delta\omega^2\rangle}\cdot a(T)) \simeq [2\langle\Delta\omega^2\rangle/(\langle\Delta\omega^2\rangle_R - \langle\Delta\omega^2\rangle_F)]\left\{1+\frac{d\log a(T)}{d\log\sqrt{\langle\Delta\omega^2\rangle}}\right\}^{-1} \tag{3}$$

where $a(T)$ represents the shift factor at any particular temperature, $T$, and $\tau_c$ at that temperature can be expressed by the following equation:

$$\tau_c(T) = a(T)\tau_c(T_r) \tag{4}$$

where $T_r$ is a reference temperature and the above equation implies the temperature–time superposition principle[14]. Equation (4) indicates a temperature dependence of $\tau_c$ also. Since Arrhenius type relations can generally be adopted for the temperature dependence of $\tau_c$, equation (5) can be written:

$$\tau_c(T) = A\exp(E/RT) \tag{5}$$

where $A$ is a constant. Thus, the shift factor $a(T)$ can be expressed by the following equation:

$$a(T) = \exp\{(E/R)(1/T - 1/T_r)\} \tag{6}$$

Therefore, if the activation energy is known, $I(\tau_c)$ can be obtained according to equation (3) using the value of $a(T)$ estimated above.

Gutowsky and Holm[15] treated the phenomenon of the spin exchange in the case of high resolution nuclear magnetic resonance by solving the modified Bloch equation and derived a relation between peak separation and correlation time, $\tau$, of the molecular motion causing the change in peak separation. This was expressed by the following equation:

$$\frac{1}{\tau} = \sqrt{2}\pi\{(\Delta\nu_o)^2 - (\Delta\nu)^2\}^{1/2} \tag{7}$$

where $\Delta\nu_o$ and $\Delta\nu$ are the separations of peaks at slow and intermediate rates of exchange, respectively. The application of equation (7) to e.s.r. spectroscopy is valid where $\Delta\nu_o$ and $\Delta\nu$ can be understood as the hyperfine separation due to the rigid and mobile states of the radical sites, respectively. Ohnishi *et al.*[16] applied equation (7) to allylic polyethylene radicals, with equation (7) modified:

$$\Delta\nu = \Delta\nu_o\sqrt{1-\frac{1}{2\pi^2\tau^2\Delta{\nu_o}^2}} = \Delta\nu_o\sqrt{1-\frac{1}{2\pi^2\tau^2\Delta\nu^2+1}} \tag{8}$$

$$\omega = \omega_o\sqrt{1-\frac{2}{\tau^2\omega^2+2}} \quad \begin{pmatrix}\omega = 2\pi\Delta\nu\\ \omega_o = 2\pi\Delta\nu_o\end{pmatrix} \tag{9}$$

Here, we will discuss the distribution of correlation times for alkyl radicals in UPEC, by applying equation (8). As for *BL* n.m.r., an equation similar to (2) can be written, and equation (9) can be rewritten taking into account the distribution function of correlation times, $I(\tau_c)$:

$$\omega = \omega_o\int_{-\infty}^{\infty}\sqrt{1-\frac{2}{\omega^2a^2(T){\tau_c}^2+2}}\cdot I(\tau_c)\mathrm{d}\log\tau_c \simeq \omega_0\int_{\frac{\sqrt{6}}{3a(T)\omega}}^{\infty}\frac{I(\tau_c)}{\tau_c}\mathrm{d}\tau_c \tag{10}$$

An equation similar to (3) can then be obtained:

$$I\left(\frac{\sqrt{6}}{3a(T)\omega}\right) \simeq \frac{\omega}{\omega_o}\left(1+\frac{\mathrm{d}\log a(T)}{\mathrm{d}\log\omega}\right)^{-1} \tag{11}$$

For e.s.r. experiments the temperature dependences of correlation time and shift factor, $a(T)$, were also assumed to be Arrhenius-type as in equations (5) and (6). Thus $I(\tau_c)$ can be obtained for a known activation energy, as in the case of broad line n.m.r.

The aim of the present paper is not only the determination of $I(\tau)$ but also a consistent discussion of the accurate application of magnetic resonance to polymer science.

## RESULTS AND DISCUSSION

### *Variation of e.s.r. and n.m.r. parameters with temperature:*

Alkyl free radicals are trapped on a main chain polyethylene unit in UPEC when subjected to $\gamma$-

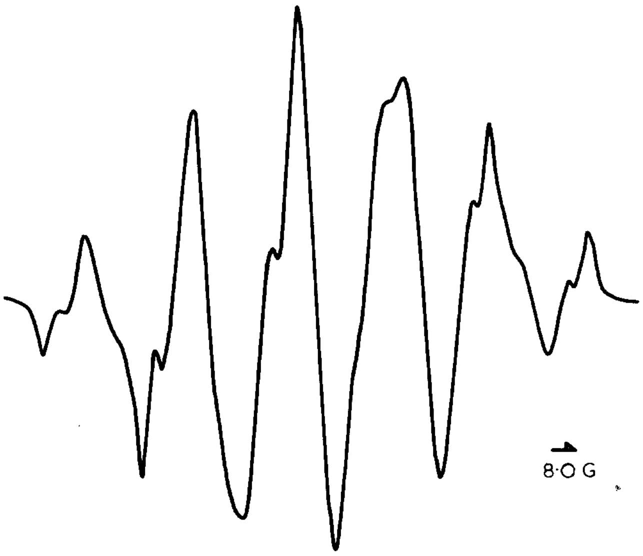

*Figure 1* E.s.r. spectra of alkyl radicals trapped in UPEC at 149.5K

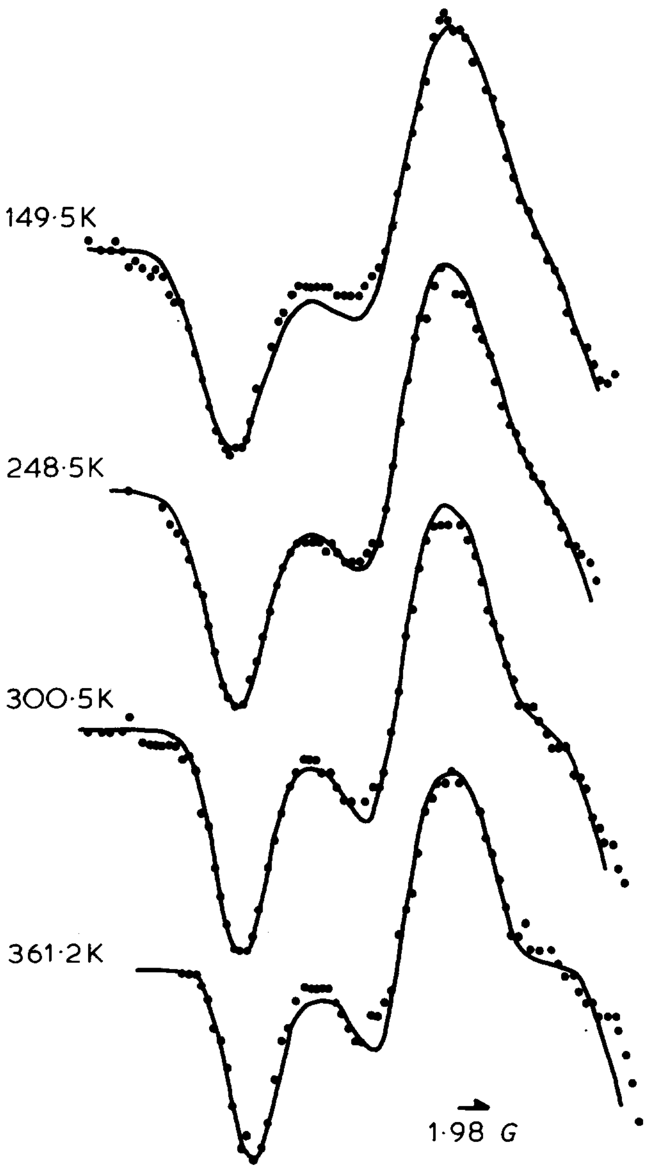

*Figure 2* Variation of outermost line shapes at low magnetic field with observation temperature: . . ., experimental; ——, calculated

irradiation[2]. The e.s.r. spectrum of the alkyl radicals appears as a sextet spectrum as shown in *Figure* 1. Detailed investigation of the sextet spectrum of alkyl radicals in polyethylene showed that the hyperfine interaction between the unpaired electron and $\alpha$ proton was anisotropic and the principal values of the hyperfine tensor were obtained[17]. Another study of the same radical showed that hyperfine splittings due to two $\beta$ protons, $\Delta H_{\beta_1}$ and $\Delta H_{\beta_2}$, were not the same and the temperature dependences of these quantities were also investigated[5]. Here, computer simulation was applied to spectra observed at various temperatures in order to examine the anisotropic parameters and line widths of the spectra which were assumed to be Gaussian. Detailed simulation of the component at low magnetic field were carried out. *Figure* 2 shows some of these results: the full lines are the simulated curves; the dashed curves represent the spectra observed. By finding the simulation curves which best fit the observed spectra, line widths could be determined for various observation temperautres. The temperature dependence of the e.s.r. line width is illustrated by the filled circles in *Figure* 3, and clearly begins to narrow at ~180K.

Broad line n.m.r. studies were undertaken previously[11], when deuterated urea materials were used in order to observe the proton magnetic resonance caused by the protons in polyethylene molecules only. The temperature dependence of the n.m.r. line width is shown by the open circles plotted in *Figure* 3; motional narrowing appears at temperatures higher than 140K, at lower temperatures than that for e.s.r. line width. This is quite reasonable when the difference in observing frequency is taken into consideration, i.e. both narrowings may be caused by the same molecular motion.

As mentioned above, the variation of hyperfine splitting with temperature can be analysed using equation (7), and the data was arranged accordingly. The variation of the hyperfine splittings with temperature was reported in our previous paper[5] and the experimental data obtained there have been used in this paper. In addition $\Delta\nu$ in equation (7) corresponds to the difference in hyperfine splittings between two $\beta$ protons in neighbouring methylene groups $(\Delta H_{\beta_1} - \Delta H_{\beta_2})$; the values of this quantity at various temperatures are plotted as open squares in *Figure* 3, and it can be seen that $(\Delta H_{\beta_1} - \Delta H_{\beta_2})$ decreases gradually to 210K and then drops abruptly.

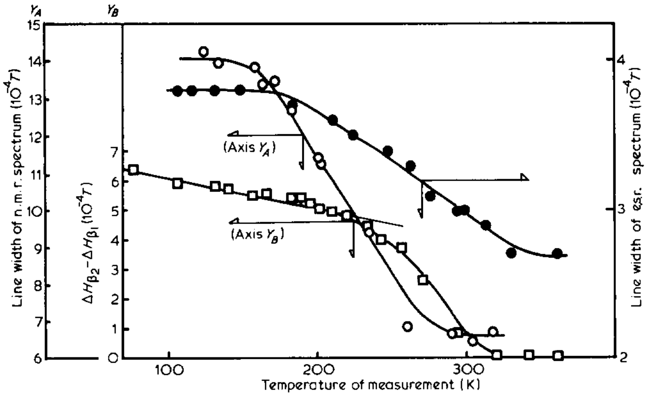

*Figure 3* Variation of line widths and $(\Delta H_{\beta_1} - \Delta H_{\beta_2})$ with observation temperature: ○, *BL* n.m.r. line width; ●, e.s.r. line width; □, $(\Delta H_{\beta_1} - \Delta H_{\beta_2})$

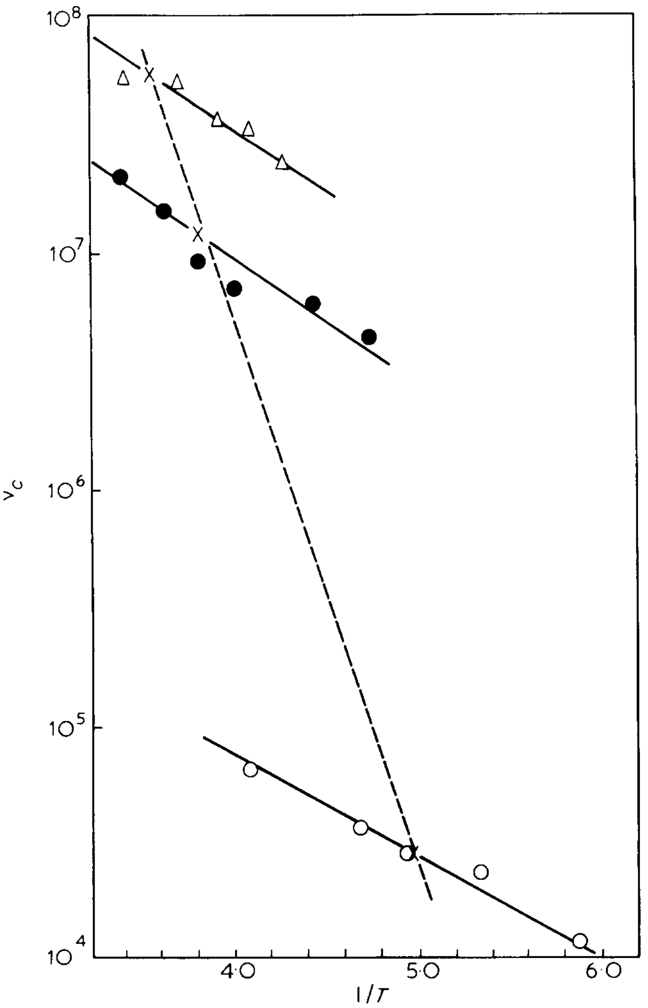

*Figure 4* Correlation frequencies $\nu_c$ as a function of the inverse of temperature: ○, *BL* n.m.r. line width; ●, e.s.r. line width; △, $(\Delta H_{\beta_1} - \Delta H_{\beta_2})$; x, representative correlation frequencies obtained by the respective studies (see text)

*Correlation times calculated from equations derived for the single correlation time system*

Correlation times can be estimated from both e.s.r. and n.m.r. line widths (see above) using equation (1); they may also be estimated from hyperfine splittings using equation (7). Correlation times at various temperatures were plotted versus $1/T$ in *Figure* 4. The open circles show the results from n.m.r. study, filled circles are data from e.s.r. studies of line width and triangles are data from hyperfine splittings. The slopes of the respective plots obtained from e.s.r. and n.m.r. line width data and hyperfine splitting data at high temperatures in *Figure* 4 exhibit a similar activation energy, 2.3–2.4 kcal mol$^{-1}$. The motional narrowings observed from these 3 different approaches are probably caused by the same molecular motion, when the Arrhenius-type temperature dependence of the relaxation times and the smaller activation energy obtained by the magnetic resonance study are taken into account. However, the range of temperatures over which a decrease in hyperfine splitting widths occurs is lower than the range in which motional narrowings take place, as observed by e.s.r. and n.m.r. line widths. Hence the motional narrowing observed in this temperature region may be considered to be caused by a different molecular motion from that observed by e.s.r. and n.m.r. line width data. Thus we will now discuss the motional narrowings of e.s.r. and n.m.r. line widths and hyperfine splitting widths in the high temperature region which are attributed to the same molecular motion. Absolute values of the correlation times are different for the respective studies, as indicated in *Figure* 4. To deal with this problem the distribution of the correlation times in the polymer matrix was taken into account and a reasonable analysis of the data was made. *Figure* 3 shows that the narrowing of the line widths and the decrease in the values of $(\Delta H_{\beta_1} - \Delta H_{\beta_2})$ occur over a broad temperature range and this may arise from the distribution of the correlation times associated with the molecular motion.

*Correlation time spectra for the relaxation process of polyethylene in UPEC:*

As mentioned in the section on 'Correlation times in magnetic resonance studies', Miyake's idea of accounting for the distribution of correlation times in polymeric materials was adopted in our study. When $\int_{-\infty}^{\infty} I(\tau_c)\,\mathrm{d}\log\tau_c = 1$ and $I(\tau_c)$ is a symmetric distribution function with respect to $\tau_m$, the following equation is derived from equation (2):

$$\langle\Delta\omega^2\rangle_m - \langle\Delta\omega^2\rangle_F \simeq (\langle\Delta\omega^2\rangle_R - \langle\Delta\omega^2\rangle_F)\int_{\tau_m}^{\infty} I(\tau_c)\mathrm{d}\log\tau_c$$

$$= \frac{1}{2}(\langle\Delta\omega^2\rangle_R - \langle\Delta\omega^2\rangle_F) \qquad (12)$$

$\tau_m$ and $\langle\Delta\omega^2\rangle_m$ are the correlation time and the second moment at the maximum spectrum intensity, respectively. Using equations (12) and (1), the values of $\langle\Delta\omega^2\rangle_m$ and $\tau_m$ were determined and then the temperature at which the spectrum intensity was maximum (for an observed frequency $\nu_m$) was obtained from *Figure* 3. Such a value of $\tau_m$ is a representative correlation time, specifying the narrowing process associated with the molecular motion under consideration. The inverses of $\tau_m$ mentioned above are shown by crosses in *Figure* 4 for the various cases in our study; i.e. the line width of broad line n.m.r., the line width of e.s.r. and hyperfine separation of e.s.r. Three crosses in *Figure* 4 give us a straight line (broken line) with a slope corresponding to an activation energy of 10.5 kcal mol$^{-1}$. This value should be similar to that obtained from the temperature dependence of the average correlation time. We have calculated $I(\tau_c)$ by equations (3) and (6) from the line width data. $I(\tau_c)$ depends on the activation energy, $E$. *Figure* 5 shows comparisons of $I(\tau_c)$ calculated from n.m.r. and e.s.r. data for various values of $E$. When $E$ is small, $I(\tau_c)$ calculated from e.s.r. data and from n.m.r. data are quite different. A similar result is obtained for large $E$. However, when $E$ is 10 kcal mol$^{-1}$, $I(\tau_c)$ values from e.s.r. and n.m.r. coincide with each other. The slope of the broken line in *Figure* 4 is 10.5 kcal mol$^{-1}$ which is very close to 10 kcal mol$^{-1}$. Thus, it can be said that the activation energy which gives good coincidence between $I(\tau_c)$ values calculated from e.s.r. and n.m.r. data is the real activation energy for the molecular motion causing the narrowing of line width. In other words, the values of the activation energy calculated without consideration of the

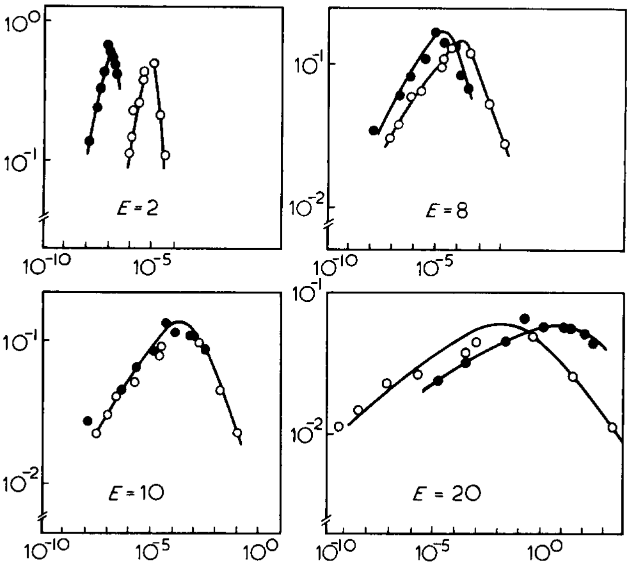

***Figure 5*** Calculated e.s.r. and n.m.r. relaxation spectra of polyethylene in UPEC with assumed values of activation energies ($T_r$ = 183.5K); ○, *BL* n.m.r. line width; ●, e.s.r. line width; horizontal axis, relaxation time (s); vertical axis, relaxation strength

distribution of correlation time (2.3–2.4 kcal mol$^{-1}$) does not represent the real value of the activation energy for the observed molecular motion. Furthermore, it can be said that the molecular motions observed in e.s.r. and n.m.r. studies are the same. Equation (11) was applied to the calculation of the distribution function $I(\tau)$ from the temperature dependence of the hyperfine splitting. The calculated distribution of correlation times using an activation energy of 10 kcal mol$^{-1}$, is shown by the open squares in *Figure* 6 together with the distribution for the line width studies. The three curves are in close coincidence with each other. This implies that the variation in hyperfine splitting of the e.s.r. spectrum of alkyl radicals trapped in UPEC also reflect the molecular motion causing the narrowing of e.s.r. and n.m.r. line widths. Thus, it is quite reasonable that the mobility of free radicals trapped in polymer solids is closely related to the relaxation processes of polymer materials. It is interesting that the relaxation spectra (the distribution of the relaxation times) in the polymer can be determined by the analysis of the observed e.s.r. and n.m.r. line widths.

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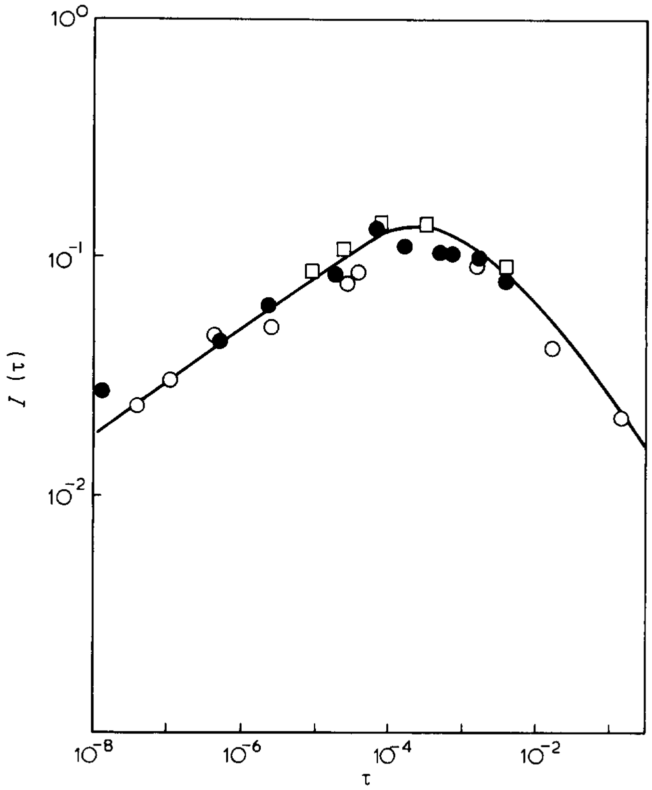

***Figure 6*** Comparison of the relaxation spectra obtained by the respective studies (activation energy, 10 kcal mol$^{-1}$): ○, *BL* n.m.r. line width; ●, e.s.r. line width; □, ($\Delta H_{\beta_1} - \Delta H_{\beta_2}$)

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