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EPR Application to Polymers. 3. EPR Studies of Poly(phenylacetylene) Using Different Nitroxide Spin Probes

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ABSTRACT: EPR line-shape analysis of spin-probed poly(phenylacetylene) in the slow-motional region has been performed in the temperature range 77–258 K where the outermost hyperfine extrema are separable. Two approaches were used to obtain the rotational correlation time, τ_R. In the first approach, the rotation is assumed to be isotropic, and τ_R was calculated by using the empirical formula $\tau_R = a(1 - S)^b$ for the three models of rotation, namely Brownian, moderate jump, and strong jump. The results showed that, depending on the model of rotation, activation energy of rotation decreased by a factor of three in going from the Brownian model to the strong jump model. In the second approach, the line shapes were simulated by using the stochastic Liouville theory of slow-motional effects on EPR spectrum. A systematic method has been developed to determine the axis of rotation, the anisotropy of rotation, and the model of rotation. All four spin probes used (Tempone, doxylcyclohexane, doxylcholestane, and Tempo palmitate) were found to undergo anisotropic reorientation. The model of rotation for Tempone was found to be moderate jump, while the models for the other three were Brownian. The apparently low activation energies (0.3–1.1 kcal/mol) calculated from EPR line-shape simulations in the low-temperature region have been explained in terms of the spin probes rotating in the "holes" of dimensions comparable to those of the probe in the polymer matrices. A comparison of the two approaches for calculating τ_R emphasizes the fact that accurate τ_R values of nitroxide spin probes in poly(phenylacetylene) could best be obtained from a simulation of EPR line shapes employing magnetic parameters determined from their rigid-limit spectra at 77 K.

Introduction

Many studies have been made on synthetic polymers using paramagnetic spin probes embedded in polymer matrices to study the molecular motions of the host polymers.[1] Experimental evidence has shown that the molecular motions of the probe are closely related to those of the host polymer.[2-9] We have used a nitroxide spin probe to study line-shape changes in poly(phenylacetylene)[10] and found that the nitroxide spin probe exhibited anisotropic rotation whose anisotropy increased as temperature decreased. In a recent study Meurisse et al.[11] studied the molecular motion of nitroxide spin probes in two aromatic–aliphatic polyesters and found that the ESR spectra of the nitroxide probes can be explained in terms of a change in the anisotropic rotation of the probes as they pass through the crystal–mesophase transition.

The objective of the present work is to examine the effect of temperature and different nitroxide spin probes on probing poly(phenylacetylene). In particular, we focus much of our attention on the lower temperature, slower tumbling spectra (5×10^{-9} s $< \tau_R < 10^{-7}$ s), in part because this is a region wherein the inhomogeneous proton broadening is of less significance in the spectral simulations. In this region, the typical nitroxide slow-motional spectrum has two well-separated outer hyperfine extrema with an overlapped central region. We have used two approaches to calculate the rotational correlation time. In the first approach, we used the simplified method of es-

timating correlation time[12] using separate deviations of high-field and low-field positions from the rigid-limit values. In the second approach, we determined the magnetic parameters of four nitroxide spin probes in poly-(phenylacetylene) at 77 K and calculated the correlation times by a computer simulation[13] of experimental line shapes using the stochastic Liouville theory.

The reason for choosing two approaches to calculate the rotational correlation time is as follows. In the first approach, τ_R was calculated from an empirical formula assuming that the rotation is isotropic and the model of rotation is known. Since neither of these two conditions is known a priori, the resulting τ_R and the activation energy values may not be reliable. In the second approach, the correlation times were determined from a computer simulating of experimental line shapes. A systematic method for determining the axis and the anisotropy of rotation and the model of rotation was given. The activation energies determined from the second approach were compared with those obtained from the empirical formula in an effort to find a correlation between the two approaches.

Experimental Section

The poly(phenylacetylene) was prepared, purified, and spin probed as described earlier.[10] The nitroxide spin probes were obtained from Molecular Probes, Junction City, OR. EPR spectra were recorded on a Bruker ER 200D-SRC spectrometer interfaced with an Aspect 2000 data system. The temperature was controlled by a Bruker ER 4111 VT variable temperature unit to 1 °C. The

Table I
Parameters a and b[12] for Different Models of Rotation

model	line width, G	a	b	τ_R ($S = 0.99$)
Brownian	0.3	2.57×10^{-10}	-1.78	9×10^{-7}
diffusion	3.0	5.40×10^{-9}	-1.36	3×10^{-7}
moderate	0.3	6.99×10^{-10}	-1.20	3×10^{-7}
jump	3.0	1.10×10^{-9}	-1.01	1×10^{-7}
strong	0.3	2.46×10^{-9}	-0.589	3×10^{-7}
jump	3.0	2.55×10^{-9}	-0.615	1×10^{-7}

magnetic field sweep was calibrated with a Bruker ER 035M NMR gaussmeter with an accuracy of 2 mG. The frequency was measured with a Model 5342 A Hewlett-Packard frequency counter. Both microwave power and modulation amplitude were verified to be at least 10 times below the onset of broadening. The scan speed and time constant were also carefully chosen so as not to introduce any artifact by scanning. The EPR spectra were simulated with an IBM 3033 computer using a program for slow-tumbling nitroxides.

Results and Discussion

The room-temperature EPR spectrum of powdered solid poly(phenylacetylene) is intrinsically paramagnetic with a peak-to-peak width of 15 G centered at $g = 2.0029$.[14] The spectrum of pure poly(phenylacetylene) without the nitroxide spin probe run under identical experimental conditions showed negligible (1.2%) EPR signal. The EPR spectra of poly(phenylacetylene) doped with nitroxide spin probes were recorded as a function of temperature. The spectra in the slow-tumbling region have two well-separated outer hyperfine extrema with an overlapped central region. Goldman, Bruno, and Freed[12] have developed a method that allowed the determination of τ_R of the order of microseconds using the ratio of the outer EPR hyperfine extrema separation at a given τ_R to the rigid-limit separation. In particular one needs only to measure $S = A_z'/A_z$, where A_z' is one-half the separation of the outer hyperfine extrema and A_z is the rigid-limit value for the quantity. As motion becomes more rapid, A_z' decreases monotonically from its rigid-limit value of A_z. Thus S is a sensitive, monotonically increasing function of τ_R. This dependence can be expressed in the form

$$\tau_R = a(1 - S)^b \tag{1}$$

The variation of S with τ_R for different models[15] of isotropic rotational reorientation has been calculated by Goldman et al.[12] for an axial nitroxide with $A_\parallel = 32$ G, $A_\perp = 6$ G, $g_\parallel - g_\perp = 0.0041$. The parameters a and b used in our analysis are listed in Table I. Equation 1 is valid in the range 7×10^{-9} s $< \tau_R < 1 \times 10^{-7}$ s.

For this experiment, we have used four nitroxide spin probes of different size and shape. They are 4-oxo-2,2,6,6-tetramethyl-4-piperidinyl-1-oxy (Tempone), doxylcyclohexane, 4-hexadecanoyl-2,2,6,6-tetramethyl-piperidinyl-1-oxy (Tempo palmitate), and 4',4'-dimethyl-spiro[5α-cholestane-3,2'-oxazolidin]-3-yloxy (doxylcholestane), shown in Figure 1. We have taken the EPR spectra of these probes over a range of temperature from
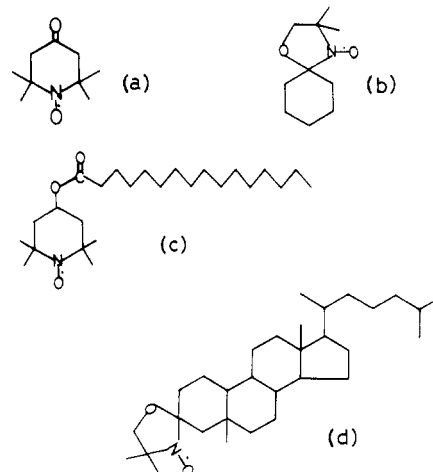

Figure 1. Molecular structures of the four nitroxide spin probes.

77 K up to a temperature where S is undefinable, since the outer lines begin to coverge to the motionally narrowed spectrum. These spectra are tabulated in Figures 4a, 5a, 6a, and 7a. The values of A' as a function of temperature and A_z at 77 K for each probe in poly(phenylacetylene) are given in Table II. τ_{R1} and τ_{R2} were calculated from eq 1 by using the a and b values of Table I and peak-to-peak Lorentzian widths of 0.3 and 3.0 G, respectively. If we define the rotational frequency as the reciprocal of the correlation time and assume that the tumbling of the probe can be treated as a typical rate process, we can then obtain an estimate of the energy barrier to rotation by plotting the natural logarithm of the rotational frequency as a function of the reciprocal temperature. The values of these activation energies are shown in Table III. For all models (Brownian, moderate jump, and strong jump) the activation energies of the four nitroxide spins probed on poly-(phenylacetylene) showed the same trend. Thus, the relative order of decreasing activation energy of poly-(phenylacetylene) with respect to the nature of the nitroxide spin was doxylcyclohexane, Tempo palmitate, Tempone, and doxylcholestane.

The variation of S with τ_R has been calculated with $A_\parallel = 32$ G and $A_\perp = 6$ G, $g_\parallel - g_\perp = 0.0041$, assuming isotropic reorientation. This assumption is highly unlikely for nitroxide spin probes in poly(phenylacetylene), since we have observed anisotropic rotation for Tempone in poly(phenylacetylene).[10] In addition, the most important requirement in analyzing slow-tumbling spectrum is to have accurate values for the magnetic tensor A and g determined individually from the same system. For these reasons we have determined the magnetic parameters of all four nitroxide spin probes in poly(phenylacetylene) from their rigid-limit spectra at 77 K in order to simulate the variable temperature spectra with accurate values of the magnetic parameters. To determine the magnetic parameters from the rigid-limit spectra one must simulate theoretical spectra and compare these to the experimental spectra. The rigid-limit computer simulations of Tempone,

Table II
A' for Four Spin Probes in Poly(phenylacetylene) at a Variety of Temperatures

Tempone			doxylcyclohexane			Tempo palmitate			doxylcholestane		
temp, K	$2A_z'$, G	S	temp, K	$2A_z'$, G	S	temp, K	$2A_z'$, G	S	temp, K	$2A_z'$, G	S
77	66.45	1	77	66.10	1	77	68.44	1	77	66.679	1
120	66.13	0.9952	180	65.16	0.9858	110	68.29	0.9978	116	66.342	0.9949
170	64.54	0.9713	230	64.345	0.9734	164	67.48	0.9860	158	66.232	0.9933
220	62.88	0.9463				223	66.93	0.9779	188	66.011	0.9900
260	62.33	0.9380							224	65.285	0.9791
									258	65.433	0.9813

Table III
Activation Energies of Spin-Probed Poly(phenylacetylene)
Calculated from Least-Square Fit of ln τ_R vs. T^{-1}

system	E_1, kcal/mol	E_2, kcal/mol
Brownian Model		
Tempone	2.070	1.585
doxylcyclohexane	2.727	2.122
Tempo palmitate	2.216	1.711
doxylcholestane	1.197	1.001
Moderate Jump Model		
Tempone	1.396	1.176
doxylcyclohexane	1.839	1.575
Tempo palmitate	1.495	1.270
doxylcholestane	0.807	0.743
Strong Jump Model		
Tempone	0.684	0.717
doxylcyclohexane	0.902	0.960
Tempo palmitate	0.733	0.773
doxylcholestane	0.396	0.453

Table IV
Magnetic Parameters of Different Nitroxide Spin Probes in
Poly(phenylacetylene)

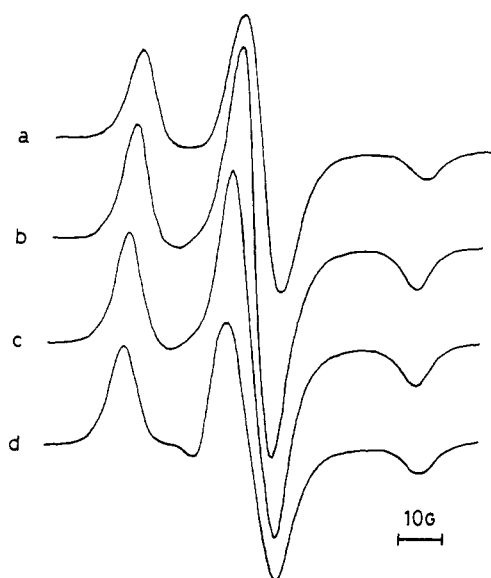|	Tempone	doxyl-cyclo-hexane	Tempo palmitate	doxyl-choles-tane
g_x	2.0093	2.0086	2.0097	2.0088
g_y	2.0059	2.0058	2.0060	2.0058
g_z	2.0022	2.0022	2.0023	2.0022
$\langle g \rangle$	2.0058	2.0055	2.0060	2.0056
A_x	6.4	5.3	7.3	5.4
A_y	4.4	5.3	4.5	5.3
A_z	33.23	33.34	34.22	33.34
α	5.5	4.9	4.9	4.9
β	0.2	0.2	0.2	0.2

Figure 2. Rigid-limit (77 K) spectra of the following spin probes in poly(phenylacetylene): (a) Tempone, (b) doxylcyclohexane, (c) Tempo palmitate, (d) doxylcholestane.
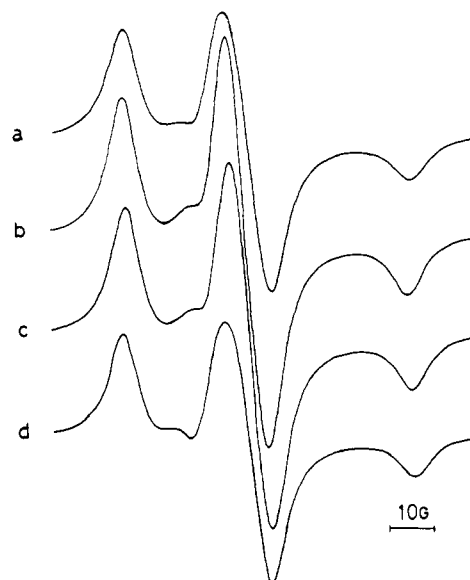
Figure 3. Simulated spectra of Figure 1 using the rigid-limit program.

doxylcyclohexane, Tempo palmitate, and doxylcholestane in poly(phenylacetylene) were simulated by the general methods of Lefebre and Maruani[16] adapted to nitroxides by Polnaszek.[17] The simulation employs Simpson's numerical integration over θ in 85 intervals and over ϕ in 40 intervals. Figure 2 shows the four experimental spectra of the four nitroxide spin probes at 77 K. Since the nitroxide spin probes are not deuterated, the central region of the rigid-limit spectra is not as well resolved compared to that of the deuterated nitroxide spin probe[18] because of inhomogeneous broadening by the 12 protons. The parameters A_z and g_z can be determined directly from the separation between the two outer hyperfine extrema which is $2A_z$, while g_z corresponds to the midpoint of the two extrema. The line width and g_x, g_y, A_x, and A_y are varied to fit the experimental spectra until the line shape of the central portion is simulated. In all cases Lorentzian line shape gave the best overall fit. The reason the center of the spectrum has a Lorentzian shape is perhaps due to some residual motion at 77 K and, therefore, the condition for the validity of a rigid limit $|H_1|\tau_R \gg 1$ is not as strong for the center of the spectrum (A about 5 G) as it is for the outer part of the spectrum (A about 33 G). This may be the cause of the orientationally dependent line width

needed to fit the spectrum. The form for the orientationally dependent intrinsic line width is assumed to be

$$T_2^{-1} = \alpha + \beta \cos^2 \theta$$

where θ is the polar angle relative to the z axis of the nitroxide. These α and β values are listed in Table IV; α values were found to range from 4.9 to 5.5 G, and β value was 0.2 G. The intrinsic line width for the parallel (z) orientation can be determined from fitting the low-field peak. The magnetic parameters that gave the best fit are listed in Table IV. These magnetic parameters were used in the simulations in Figure 3.

The values of A_x in Table IV deserve some comments. In all cases, they are higher than those of A_y. If one simulates the rigid-limit spectrum of Tempone in poly(phenylacetylene) by reversing the values of A_x and A_y keeping everything else constant, one gets the simulated plot in Figure 8. This comparison indicates that the assignment of the A_x and A_y values is unambiguous.

The EPR spectra of the four nitroxide spin probes in poly(phenylacetylene) were recorded from 110 to 258 K. Figures 4a, 5a, 6a, and 7a show experimental spectra of Tempone, doxylcyclohexane, Tempo palmitate, and doxylcholestane in poly(phenylacetylene) taken at a variety of temperatures. The theoretical simulation of these spectra were performed by using the stochastic Liouville theory of slow-motional effects on EPR spectra for $S = {}^1/_2$ and $I = 1$ for nitroxides. The rotational-diffusion tensor was taken as axially symmetric. The magnetic parameters used in the simulations were those listed in Table IV. For simulations where $\tau_R < 5 \times 10^{-9}$ s, we generally used an
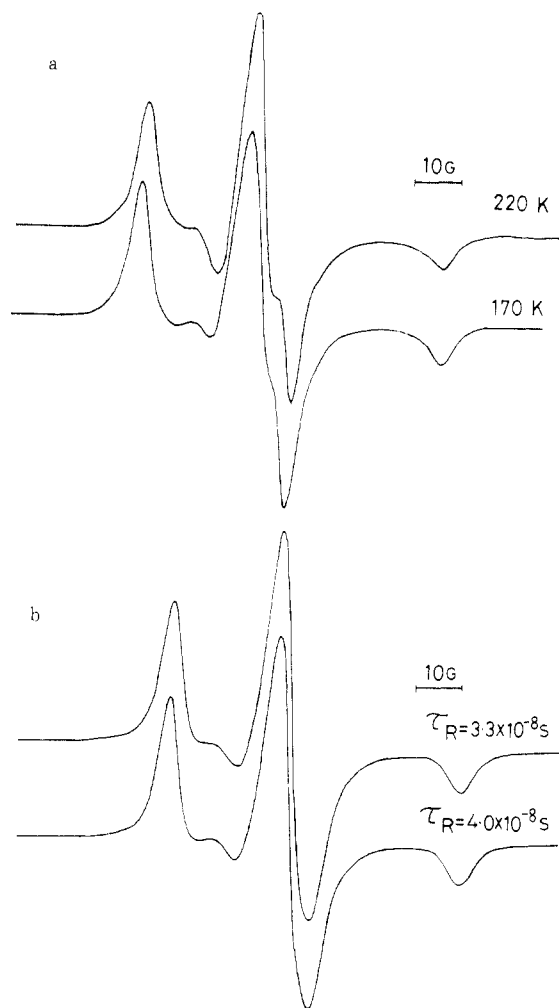
Figure 4. (a) Experimental spectra of Tempone in poly(phenylacetylene) at 170 and 220 K. Spectrometer settings were as follows: field set, 3364 G; scan range, 80–120 G; signal average, 5; modulation frequency, 100 kHz; modulation amplitude, 0.125–1.0 G; receiver gain, 3.2–6.3 × 10⁴; microwave power, 1.25 mW; microwave frequency, 9.444 GHz; digitization, 4000. (b) Simulated spectra of Figure 4a using the slow-tumbling program and the magnitude parameters in Table IV. The model for rotational reorientation is moderate jump diffusion. Correlation times are 3.3 × 10⁻⁸ and 4.0 × 10⁻⁸ s, respectively.
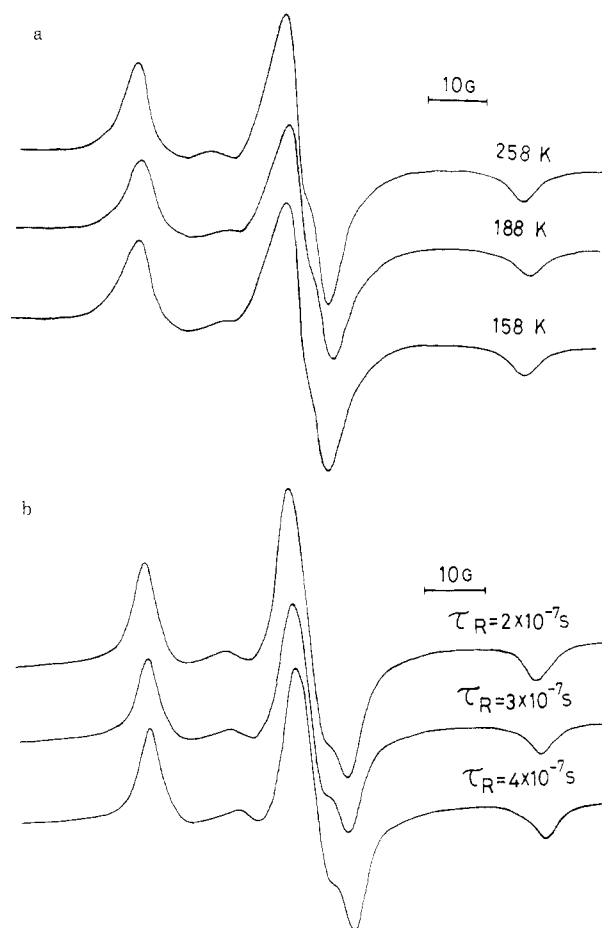

Figure 5. (a) Experimental spectra of doxylcholestane in poly-(phenylacetylene) at 158, 188, and 258 K. Spectrometer settings were as follows: field set, 3247 G; scan range, 100 G; signal average, 9; modulation amplitude, 0.8–1.0 G; receiver gain, 2–3.2 × 10²; microwave power, 0.65 mW; microwave frequency, 9.113 GHz; digitization, 4096. (b) Simulated spectra of part a using the slow-tumbling program and the magnetic parameters in Table IV. The model for rotational reorientation is Brownian diffusion. Correlation times are 2.0 × 10⁻⁷, 3.0 × 10⁻⁷, and 4.0 × 10⁻⁷ s, respectively.

L value of 10 and a K value of 4. Using the equations in the slow-tumbling program, we obtained NDIM = 87, JDIM = 28, NSY = 20, and NSY2 = 63. For $\tau_R > 5 \times 10^{-9}$ s, we increased the values of L and K to 22 and 8, respectively. We then obtained NDIM = 297, JDIM = 40, NSY = 38, and NSY2 = 234. With higher L and K values, we can simulate line shapes for $\tau_R = 4 \times 10^{-7}$ s.

For doxylcyclohexane, Tempo palmitate, and doxylcholestane we used the Brownian model with various τ_R values to fit the experimental spectra. For small nitroxides such as Tempone, it has been shown earlier that in the slow-motional region a moderate jump diffusion model gives a better fit than the Brownian model. For this reason, the spectra of Tempone in poly(phenylacetylene) were simulated by use of the moderate jump model. Below, we give a brief description of the determination of the axis of rotation and the anistropy of rotation (N) using information obtained from an analysis of the spectrum in the motional-narrowing region. (The exception to this is doxylcholestane, whose spectrum looks like a slow-tumbling spectrum even at 334 K.) At first N is assumed to be 1 and the value of τ_R is changed until the line width of the $M = 0$ line agrees with the line width of the of center

line. Keeping τ_R constant, N is varied from 1 to 30 for all the three axes of rotation until the experimental spectrum is simulated. The computer output will indicate that for a certain N value a particular axis of rotation will give the correct simulation (and thus the intensity ratio of the peaks). In this way the axis of rotation and the anistropy of rotation were determined.

To determine the models of rotation we performed a theoretical simulation of the EPR line shapes as a function of τ_R and models of rotation by using the slow-tumbling program for nitroxides. The magnetic parameters chosen for the computer simulations were those for Tempone in poly(phenylacetylene). The rigid-limit spectrum was simulated under identical conditions in order to measure the shifts of the hyperfine extrema at various τ_R from their rigid-limit values. The parameter $R^{11,19} = \Delta H_{-1}/\Delta H_{+1}$ was calculated for each τ_R, where ΔH_{-1} is the shift of the high-field outer hyperfine extremum in the first derivative of the absorption curve relative to the rigid limit and ΔH_{+1} is the low-field shift. The range of theoretical R values for Brownian, moderate jump, and strong jump were calculated to be 1.1–1.6, 1.2–1.3, and 0.35–0.87, respectively. For the Brownian model, measurement of R should be made when the separation of the outer hyperfine extrema is greater than 52 G. For the strong jump model, the opposite trend is observed: the R values gradually decrease
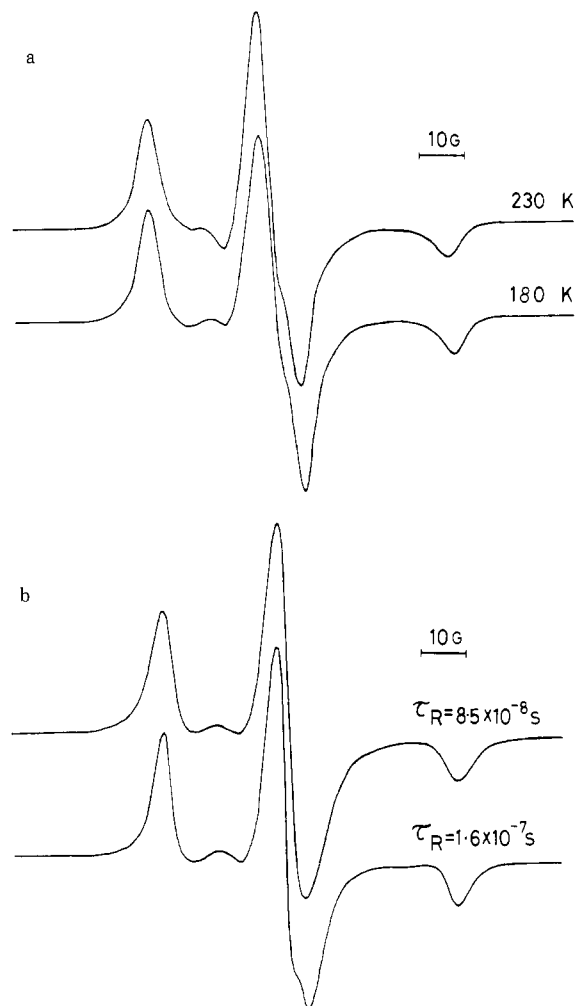
Figure 6. (a) Experimental spectra of doxylcyclohexane in poly(phenylacetylene) at 180 and 230 K. Spectrometer settings were as follows: field set, 3245 G; scan range, 120 G; signal average, 1; modulation amplitude, 0.2–0.8 G; receiver gain, 1.6–6.3 × 10^2; microwave power, 0.65 mW; microwave frequency, 9.443 GHz; digitization, 4000. (b) Simulated spectra of part a using the slow-tumbling program and the magnetic parameters in Table IV. The model for rotational reorientation is Brownian diffusion. Correlation times are 8.5 × 10^{-8} and 1.6 × 10^{-7} s, respectively.
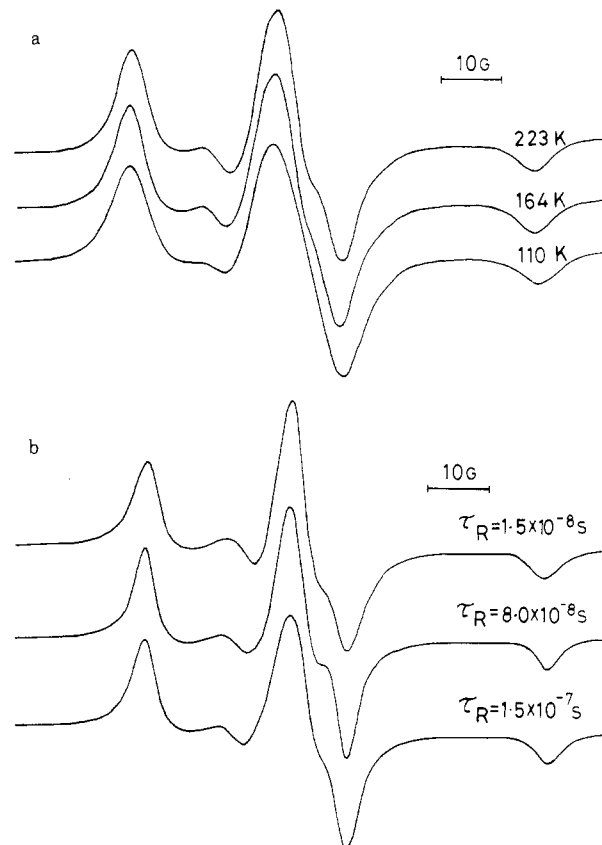
Figure 7. (a) Experimental spectra of Tempo palmitate in poly(phenylacetylene) at 110, 164, and 223 K. Spectrometer settings were as follows: field set, 3246 G; scan range, 100 G; signal average, 9; modulation frequency, 100 kHz; modulation amplitude, 0.2–1.0 G; receiver gain, 3.2–8.0 × 10^2; microwave power, 0.20 mW; microwave frequency, 9.111 GHz; digitization, 4096. (b) Simulated spectra of part a using the slow-tumbling program and the magnitude parameters in Table IV. The model for rotational reorientation is Brownian diffusion. Correlation times are 1.5 × 10^{-8}, 8.0 × 10^{-8}, and 1.5 × 10^{-7} s, respectively.

as correlation time increases. Measurements on the shifts for the strong jump model should be made when the outer hyperfine extrema separation is greater than 58 G. For the Brownian model, as correlation time increases, the R value gradually increases from 1.1 to 1.6. For the moderate jump model, the R value does not change much and oscillates between 1.2 and 1.3. The measurement on the shifts for the moderate jump model should be made when the outer hyperfine extrema is greater than 52 G. Applying the theoretical analysis of R on the EPR spectra of the four spin probes in poly(phenylacetylene), we found that the model of rotation for Tempone was moderate jump, while for the other three spin probes the model of rotation was Brownian.

The results for the simulation were as follows. From the EPR spectrum of Tempone in poly(phenylacetylene) at 400 K we found that the intensity of the low-field line is about one-half the intensity of the center line. This implies that the nitroxide probe is undergoing anisotropic rotational reorientation ($N = 3$) with $z' = y$. This result seems to contradict the results in Table I of ref 10. A recalculation of the values in Table I (p 738 of ref 10) revealed an error in the column headings: "$z' = y$" and "$z' = x$" in Table I should be interchanged. Furthermore, "$z' = x$" on

the third line, second paragraph, p 738, should also be changed to "$z' = y$". Another error occurred in the bottom line of the fourth paragraph on p 738. The word "increases" should be changed to "decreases". Tempone is an ellipsoid with $a_y:a_x = 42:29$.[20] The anisotropy of rotation (N) of 3 and $z' = y$ can be interpreted as an ellipsoid embedded in poly(phenylacetylene) that rotates three times faster along its longer axis (the y molecular axis). The lower N value is a result of using the magnetic parameters in Table IV rather than those of perdeuterated Tempone in toluene as we have done in the past.[10] We have shown earlier[18] that it is very important to have accurate magnetic parameters before trying to determine anisotropic rotational diffusion from EPR relaxation data. Thus, if for a moment we suppose that the magnetic parameters of Tempone had not been measured in poly(phenylacetylene) and one chose to utilize the magnetic parameters obtained in toluene solvent, we would have obtained an N value of 7 instead of 3. Doxylcyclohexane, doxylcholestane, and Tempo palmitate were also found to undergo anisotropic reorientation; the values of N and z' are 11, 11, and 40 and $z' = y$, $z' = y$, and $z' = z$, respectively. It is observed that for these N values, only the Brownian diffusion model can give a better match for the separation of the hyperfine extrema separation. These N values and the axes of rotation were extrapolated into the slow-tumbling region and used for the simulation of EPR spectra in Figures 4–7. As noted earlier by Goldman et al.,[12] the primary effect of varying the value of N is to change the
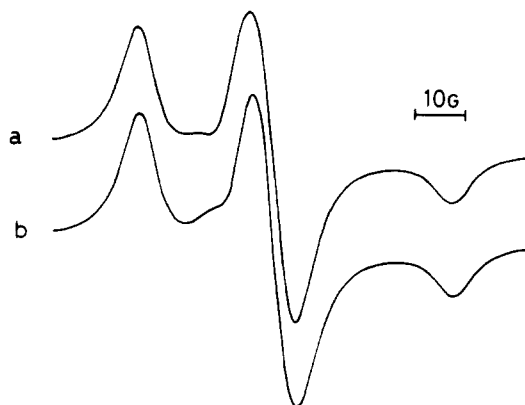
Figure 8. Effect of interchanging A_x and A_y values on the simulated rigid-limit spectra of Tempone in poly(phenylacetylene). In spectrum a, the values of $A_x = 6.4$ G and $A_y = 4.4$ G were used. In spectrum b, the values of A_x and A_y were interchanged.

Table V
Activation Energies of Spin-Probed Poly(phenylacetylene) Calculated from Line Shape Simulation at Low Temperatures

system	E_1, kcal/mol	rotational model
Tempone	0.3	moderate jump
doxylcyclohexane	1.1	Brownian diffusion
Tempo palmitate	0.9	Brownian diffusion
doxylcholestane	0.6	Brownian diffusion

relative amplitude of the low-field line; the N values determined in our experiment do give a very good match of the relative amplitude of the low-field line.

The values of τ_R so obtained yield a good Arrhenius-type plot vs. $1/T$ for the spectra taken at the lower temperature. These activation energies are listed in Table V. The τ_R values needed to fit a slow-motional spectrum with the moderate jump model are somewhat smaller than the τ_R values obtained by using a Brownian model. Thus, if the moderate jump diffusion model were used, the values of activation energy would be reduced somewhat. This is evident in the lower activation energy of Tempone.

The activation energies listed in Table V are all in the range of 0.3–1.1 kcal/mol. For Tempone in poly(phenylacetylene), it is 0.3 kcal/mol in the temperature range of 170–220 K. This is quite different from the rotational activation energies of 8 kcal/mol[10] obtained in the high-temperature range for Tempone in poly(phenylacetylene). This apparent anomaly in the rotational activation energies in the two temperature ranges has been explained in terms of the spin probe rotating in the low-temperature range (below T_g) in the "holes" of dimensions comparable to those of a probe in the polymer matrices[5] and is largely independent of the molecular motion of the polymer. At temperatures above T_g the spin probe motion is perturbed by molecular motions of the polymer chain and its segment, resulting in increased frequency and activation energy of the probe rotation.

The activation energies calculated by using the two approaches emphasize the fact that accurate τ_R values of the nitroxide spin probes could best be obtained through simulations of EPR line shapes with magnetic parameters of the nitroxide spin probes in poly(phenylacetylene) obtained from their rigid-limit spectra at 77 K.

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