Macromolecules **1983**, *16*, 736–739

drogen-bond network. We do not suggest that the hydrogen bonds are broken, but that they anchor the side groups so that usual side-group reorganization (in response to the monomer-to-polymer geometric transformation) are made difficult. Thus the side groups are distorted with strained bonds and, perhaps, the hydrogen-bond network is disrupted or substantially weakened. The energies involved should be about 0.4–0.7 eV/ru, which is in the range of the differences observed between thermal polymerization (1.6 eV/ru) and our photopolymerization (1.0 eV/ru) ΔH_p values. It is interesting to note that Desai et al.[14] obtain a very low value of 19 kcal/mol for the heat of polymerization of another diacetylene, *N*,*N*′-bis(2,4-dinitrophenyl)-2,4-hexadiyne-1,6-diamine (DNPNH). They attribute this to breaking of secondary hydrogen bonds on the DNPNH monomer sites during polymer formation. Based on available infrared data for our material, 4BCMU, we do not believe the hydrogen bonds are completely broken during reaction.

In summary, the energetics of 4BCMU polymerization are believed to be importantly influenced by an unfavorable side-group interaction in the polymer compared to that in the monomer. Our results could, therefore, suggest that a favorable polymer side-group interaction could lead to lower thermal activation energies and higher ΔH_p values.

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Registry No. 4BCMU, 68777-92-4.

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(19) The dimer formation process from the diacetylene excited state could also be temperature dependent and this temperature dependence could be different for different diacetylenes. We believe a temperature-dependent chain propagation is a more likely explanation.

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EPR Application to Polymers. 2. Spin Probing of Poly(phenylacetylene)

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ABSTRACT: Line shape changes in the electron paramagnetic spectrum of spin-probed poly(phenylacetylene) have been studied as a function of temperature. The line shapes have been simulated by using the stochastic Liouville theory of slow-motional effects on EPR spectra. Correlation times based on the moderate jump model have been calculated. It was found that the nitroxide spin probe exhibited anisotropic rotation whose anisotropy increased as temperature decreased. This has been interpreted as due to the intimate interaction between the nitroxide spin and the polymer chains which possess the π-delocalized electrons. The activation energy calculated from the temperature of rapid reorientation of the nitroxyl radical gives $E_a = 8$ kcal mol^{-1}.

Introduction

There has been considerable interest in the synthesis[1-3] and physical properties[4-6] of polyacetylenes mainly because of the fact that these materials are highly polyconjugated and can have organic semiconducting properties useful in electronic technology.[7]

In the present article we extend[8] our investigations of poly(phenylacetylene) (PPA) using the spin-probing EPR technique. This method provides information about the molecular motions and dynamics by studying the line shape of the electron paramagnetic resonance spectra of spin probes embedded in polymer matrices. In contrast to spin-probe studies,[9] where the paramagnetic molecule is present as a "guest", free to move within the polymer matrix at concentrations of 10–100 ppm, the same species in the spin-label studies is immobilized by being chemically bound to the polymer chain.[10] The former technique is much simpler than the latter and it would be the method of choice as long as comparable information were obtainable.

Although many polymers have been spin probed, very few spectral simulation studies have been carried out to fully understand polymer chain motions and dynamics. In this work, we report the first study of the EPR spin probing of poly(phenylacetylene). We demonstrate how the theory of slow-tumbling EPR spectra of nitroxides can

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be applied to give detailed comparison between the theoretical predictions and experimental results.

The slow-tumbling theory has been successful in the theoretical analysis of EPR line shapes in the slow or intermediate rotational regions. In these regions the radical is tumbling too slowly for the earlier relaxation theories[11,12] to apply, yet it is not tumbling slowly enough for the spectrum to have approached its rigid limit. If we define $\mathcal{H}_1(t)$ as the rotational-dependent perturbation in the spin Hamiltonian and τ_R as the rotational correlation time, then slow tumbling in magnetic resonance means the inequality $|\mathcal{H}_1(t)\tau_R| \ll 1$ is no longer fulfilled. Freed, Bruno, and Polnaszek[13] have developed a general approach based on the stochastic Liouville method, which can be used to simulate magnetic resonance line shapes for any process that involves Markoffian stochastic modulation of $\mathcal{H}_1(t)$. This method can describe EPR line shapes over the whole range of τ_R from the motional narrowing region $|\mathcal{H}_1(t)\tau_R| \ll 1$ through the rigid limit. One of the objectives of this work is to demonstrate the applicability of this theory to experimentally observable systems and to show its usefulness in understanding how EPR line shapes reflect molecular motions.

Experimental Section

The nitroxide spin probe (Tempone) was purchased from Molecular Probes. Phenylacetylene monomer was obtained from Farchan Chemical Co. and was vacuum-distilled just prior to use. All solvents were reagent grade and used without further purification. Ten milliliters of degassed phenylacetylene was placed into a three-neck, round-bottom flask, equipped with a thermometer, a gas inlet adapter, and a Graham-type condenser. The apparatus was purged with dry nitrogen gas for 10–15 min while the contents of the flask were constantly stirred with a magnetic stirrer. The system was then heated to reflux by means of an oil bath. At the end of 30 h a dark brown viscous material was obtained, which was removed from the flask by extraction with benzene. The solution was then concentrated on a rotary evaporator and precipitated in cold (−10 °C) pentane. The resulting polymer was vacuum-dried to a constant weight at room temperature. The number-average molecular weight ($\bar{M}_n$) determined osmometrically was found to be 1600. A 1×10^{-4} M solution was prepared by dissolving Tempone in benzene solvent. Then, 1 mL of the above solution was mixed with 0.1 g of poly(phenylacetylene) until a homogeneous solution was formed. The benzene was then allowed to evaporate at room temperature and the resulting spin probe embedded polymer allowed to dry. It was then placed in a 3-mm glass tube, dried, and sealed under vacuum. EPR spectra were recorded with a Varian E-109 X-band spectrometer using 100-kHz field modulation. The temperature was varied with Varian's standard temperature accessory calibrated with a copper/constantan thermocouple, which showed it to be accurate within one degree. Most spectra were recorded under conditions where power saturation effects were negligible. The EPR spectra were simulated with an IBM 3033 computer using a program for slow-tumbling nitroxides.[14]

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 $g = 2.0029$.[15] 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 the nitroxide paramagnetic species 4-oxo-2,2,6,6-tetramethyl-4-piperidinyl-1-oxy (Tempone) were recorded as a function of temperature. The results depicted in Figure 1 reveal that these spectra are very different from those encountered in solutions at X-band near the incipient slow-tumbling region.[16] For example, in a nonviscous solvent nearly all nitroxides exhibit three equally spaced sharp hyperfine lines of nearly equal height. The sharp lines are caused by rapid isotropic tumbling motion, which averages away all anisotropic effects in the **g** tensor and the electron–nuclear hyperfine (**A**) tensor. If the rotational motion is slowed by increasing the solvent viscosity, averaging is incomplete. The result is unequal broadening of the three absorption lines and the spectrum becomes asymmetric. Figure 2a is a computer simulation of Tempone undergoing

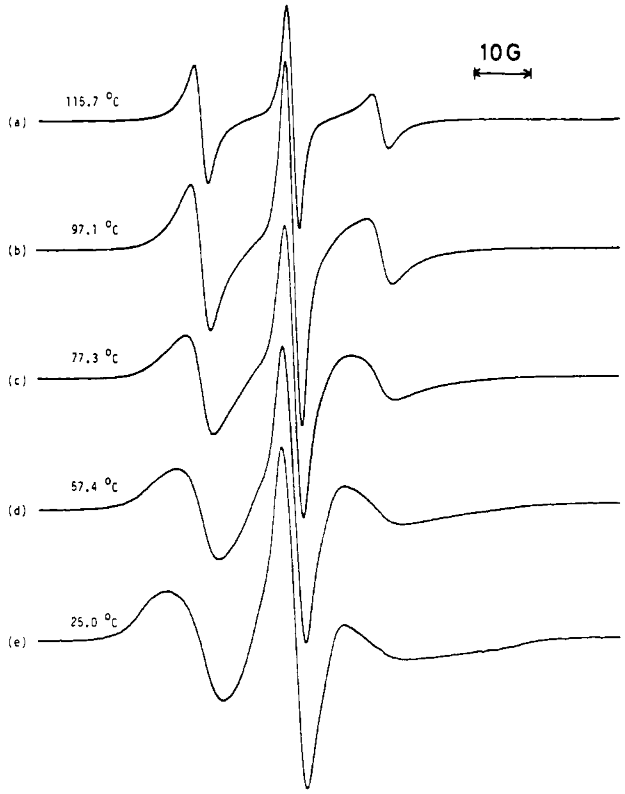

Figure 1. EPR spectra of Tempone in poly(phenylacetylene) at various temperatures.

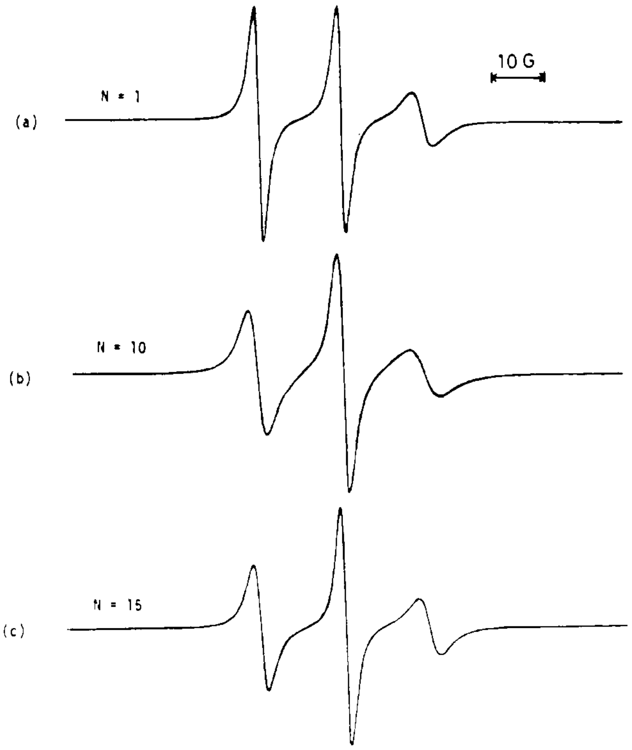

Figure 2. Effect of anisotropy on the simulated spectra in the incipient slow-tumbling region at $\tau_R = 3.16 \times 10^{-10}$ s.

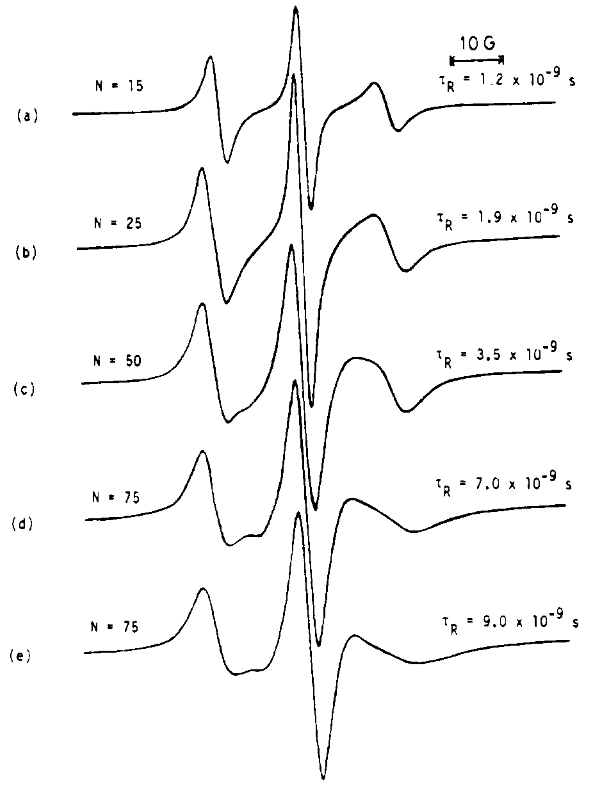

Figure 3. Simulated spectra of Tempone in poly(phenylacetylene) at various correlation times and anisotropy.

isotropic rotational diffusion. Molecular motion is not necessarily isotropic. Preferential motion about one axis is likely to occur for any elongated free radical, but the effects are particularly evident when the surrounding medium is anisotropic. The EPR spectrum is very sensitive to nitroxide mobility. The best way to make use of this sensitivity is to describe the motion quantitatively in terms of the shape of the spectrum.

The EPR spectra were simulated in Figure 3 for $S = {}^1/_2$ and $I = 1$ nitroxide, using the computer program for slow-tumbling nitroxides.[14] The **g** and **A** tensors were taken as axially symmetric and moderate-jump diffusion was assumed. The moderate-jump model[16] was applied to analyze the spectra based on our experience in the past that very good agreement was achieved for this model, while the comparison was quite unsatisfactory for the Brownian and strong-jump models.[17,18]

A comparison of the spectra in Figures 1a and 2a shows that the intensity of the low-field line ($\tilde{M} = -1$) in Figure 1a is much less than that of the $\tilde{M} = -1$ line in Figure 2a, and the intensity of the high-field line ($\tilde{M} = +1$) in Figure 1a is much more than that of the $\tilde{M} = +1$ line in Figure 2a. $\tilde{M}$ is defined as the spectral index number. Usually nitroxides have **g** and **A** components such that in X-band measurements the central line is slightly shorter than the low-field line. The spectra observed in Figure 1 demonstrate just the opposite and clearly indicate anisotropic motion.

The spectra in Figure 2 were simulated by using different anisotropy (N) of the rotation. We define N as the ratio $R_\parallel/R_\perp$, where $R_\parallel$ is the rotational diffusion constant along the z' symmetry axis, $R_\perp$ is the rotational diffusion constant along the x' and y' axes, and the rotation is assumed to be axially symmetric. When $N = 1$, one gets the spectrum in Figure 2a, and when $N = 10$ and 15, spectra 2b and 2c. The feature that emerges from this simulation is that as N increases, the intensity of the low-field line increases relative to that of the center line.

Table I
Calculated $I(-1)/I(0)$ and $I(+1)/I(0)$ as a Function of N at $\tau_R = 3.16 \times 10^{-10}$ s

	$z' = z$		$z' = y$		$z' = x$	
N	$I(-1)/I(0)$	$I(+1)/I(0)$	$I(-1)/I(0)$	$I(+1)/I(0)$	$I(-1)/I(0)$	$I(+1)/I(0)$
10	1.017	0.229	1.474	0.293	0.765	0.428
1/10	1.069	0.610	0.964	0.458	1.091	0.411

Table I shows the effect of anisotropic rotational diffusion in which $N = 10$ and the rotational-diffusion tensor is axially symmetric, where the motion is described by two rotational-diffusion coefficients. We define the principal axes of the diffusion tensor as x', y', and z', with z' the symmetry axis. Then $R_\parallel$ is the rotational diffusion component about the z' axis while $R_\perp$ gives the component about the x' and y' axes. N is then $R_\parallel/R_\perp$.

A careful computer analysis of the EPR spectra taking $\tau_R = 3.16 \times 10^{-10}$ s and $N = 10$ is summarized in Table I. It can be seen from the data that $z' = x$ is the *only* choice that can explain our results. Here, τ_R is the rotational correlation time. The correlation time is a measure of the length of time over which molecules persist in a given orientation. The dramatic effect of N is illustrated in Figure 2, in which N varies from 1 to 15. One can see that $N = 15$ (Figure 2c) has the closest resemblance to Figure 1a.

The theory for simulating EPR line shapes by means of the stochastic Liouville approach is applied to the analysis of the EPR spectra of Tempone in poly(phenylacetylene). The stochastic Liouville method must be used to explain the EPR spectra when the motional narrowing theories break down. For isotropic solvents this occurs when the lines start to become asymmetric and/or the splitting constants begin to deviate from a constant value. Values of τ_R and N were obtained for five temperatures by fitting the experimental line shapes in Figure 1 to the computer-simulated line shapes in Figure 3. The criterion for the simulation is a match of the intensities of the three lines with the experimental spectra and the width of the center line. The computer simulation of the five experimental spectra in Figure 3 showed that as temperature decreases from 116 to 25 °C, N increases from 15 to 75. Our analysis of the rotational correlation times depends on the accurate values of the components of the **g** and **A** tensors in the spin-probed poly(phenylacetylene). Since we do not know these values accurately, we used the published values for Tempone in toluene.[17] Although the **g** and **A** components do not vary greatly from one system to another, the correlation time calculated from experimental spectra depends on the values assumed. In addition, the unresolved superhyperfine interactions with the nonequivalent protons in the nitroxide structures produce a complicated, inhomogeneous line broadening because the proton Zeeman interaction is comparable to the superhyperfine interactions. Unless the correct superhyperfine coupling constants for all protons in the nitroxide molecular structures are determined, the resultant inhomogeneous line broadening cannot be correctly included. It is perhaps due to these reasons that the intensities of the low-field lines in the spectra in Figure 3c–e do not agree very well with those observed in the experiment; cf. Figure 1.

Figure 4 shows the structure of Tempone with its axis system. The x axis is taken as being along the N–O bond, the z axis along the $2p_z$ orbital of the nitrogen, and the y axis perpendicular to the other two. The x', y', and z' axes are the principal axes of the diffusion tensor **R** and they are assumed in Table I either to be the same as the x, y,

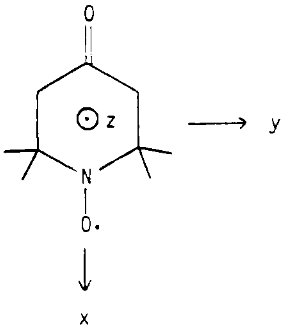

Figure 4. 4-Oxo-2,2,6,6-tetramethylpiperidinyl-1-oxy (Tempone) showing the molecular-fixed axis system.

and z axes or else to be a cyclic permutation of them. The computer simulation with anisotropic rotational diffusion with the fastest rotation about the molecular x axis, which is the N–O bond, gives the best fit to the experimental spectra in Figure 1. It seems that the N–O fragment loosely attaches itself to the polymer backbone and exhibits anisotropic rotation with the fastest rotation along the N–O bond. As the temperature is increased, thermal motion decreases the interaction of the N–O fragment with the polymer, as evidenced by a decrease in N.

The spectra we observed were different from those observed in other spin-probed polymer studies probably because those polymers did not have delocalized π electrons that are found on the backbone of poly(phenylacetylene). For example, the EPR spectra of spin-probed high-density polyethylene and poly(vinyl chloride) exhibited line shapes typical for isotropic rotation.[19] This may be attributed to the lack of intimate interaction between the nitroxide spin probe and the polymer chains, which do not possess π-delocalized electrons.

The possibility of a liquid crystalline environment is ruled out because liquid crystals tend to orient along a preferred orientation in the presence of a magnetic field.[20] To our knowledge the orientation of poly(phenylacetylene) is unaffected by the magnetic field. The EPR nitroxide spin probes in liquid crystals[21-23] have been studied in great detail. One of the obvious effects of the liquid crystal potential is to reduce the hyperfine splitting. The hyperfine splitting of the EPR spectra of Tempone in poly(phenylacetylene) in Figure 1a showed no evidence of such a reduction. One could argue that the anisotropy found in the spin-probe motion may be due to the rodlike conformations of the polymer molecule, but anisotropic motion of the nitroxide spin probe had been observed in isotropic liquids[17] like ethanol and acetone. The only difference is that in the latter the anisotropy remains constant with temperature change while in our study the anisotropy increases as temperature decreases. This effect could perhaps be attributed to the increasing importance of the interaction between the nitroxide spin probe and the polymer chains, which possess π-delocalized electrons as temperature decreases.

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 T^{-1}. For Tempone in poly(phenylacetylene) we have obtained an activation energy value of 7.8 ± 0.1 kcal mol^{-1}. Rabold[19] found that the energy barriers for rotation of the dissolved nitroxides in the polymers range from 7.8 to 18 kcal mol^{-1}, depending on the structure of the nitroxide and the polymer. In an EPR study of spin-labeled polystyrene, Bullock et al.[18] found that the rotational correlation times of nitroxide were in accord with the moderate-jump model and gave a low activation energy of 9 kcal mol^{-1}, which they attributed to a rotation about the C–N axis. This is very similar to our value of 7.8 kcal mol^{-1} based also on the moderate-jump model, indicating that a relaxation process with a very low activation energy is involved.

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