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which will be conveniently written in the following form:

$$\langle X'(q,t)X^{*\prime}(q',0)\rangle = \langle X'(q,t+t')X^{*\prime}(q',t')\rangle = Nk_{\mathrm{B}}T\{2\zeta\delta(t) + \eta'(q,t) + \eta^{*\prime}(q,-t)\}\Delta(q-q') \quad \text{(II-3)}$$

where δ and Δ stand for the Dirac delta function and for the Kronecker delta, respectively. The above representation differs from the currently employed only in view of the term $\eta^{*\prime}(q,-t)$. This contribution was added to fulfil the symmetry property

$$g(q,t) = \langle X'(q,t)X^{*\prime}(q,0)\rangle = \langle X'(q,0)X^{*\prime}(q,-t)\rangle = g^*(q,-t) \quad \text{(II-4)}$$

otherwise no substantial change is implied, since $\eta^{*\prime}(q,-t) \equiv 0$ for $t > 0$ (see eq II-2). Multiplying the second and third members of eq II-3 by $\exp[+i\omega(t+t') - i\omega'(t')]$ and integrating over both t and t', we get

$$\langle X''(q,\omega)X^{*\prime\prime}(q',\omega')\rangle = \frac{Nk_{\mathrm{B}}T}{\pi}\left(\zeta - {}^{4}\!/_{3}\alpha(q)\sin q\frac{\omega\tau_0^2}{1+\omega^2\tau_0^2}\right)\Delta(q-q')\delta(\omega-\omega')$$

$$(X^{*\prime\prime}(q,\omega) = X''(-q,-\omega)) \quad \text{(II-5)}$$

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Polystyrene Dynamics in Dilute Solution: A Further Investigation by Electron Spin Resonance. Comparison with Other Techniques

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ABSTRACT: ESR relaxation measurements were carried out on dilute solutions of in-chain spin-labeled polystyrene in toluene in the temperature range 0–90 °C. There was some evidence for two different relaxation processes, in agreement with the "phase transition" observed at about 50 °C by several authors using different experimental techniques. Energy barriers to rotation were obtained after allowance was made for the viscous drag of the solvent, and the number of monomer units involved in each relaxation process was calculated by employing Kramers' rate constant for the crankshaft rotation and a three-state model. From comparison with results reported in the literature for local motion in polystyrene, differences have been shown to arise through both the internal barrier to rotation and the preexponential term.

Introduction

Studies of intramolecular motion of polystyrene in dilute solution have been carried out by several groups using ^{1}H,[1-4] ^{2}H,[2,5] and ^{13}C[3,6-15] nuclear magnetic relaxation, fluorescence depolarization,[16,17] Rayleigh scattering depolarization,[18-20] Raman line shape analysis,[21,22] and ultrasonic relaxation.[23-27] These measurements have clearly demonstrated the local character of the motions involved in the relaxation processes whose correlation time is independent of the molecular weight above a critical value of 10 000.

The single isotropic correlation theory was found inadequate to interpret the NMR[3,4,14] and fluorescence depolarization[16,17] data. On the other hand, the three-bond jump model for diamond lattice chains[28] has been proven to be successful in the description of the segmental reorientation of the chain backbone in terms of two correlation times. Ultrasonic absorption experiments have also

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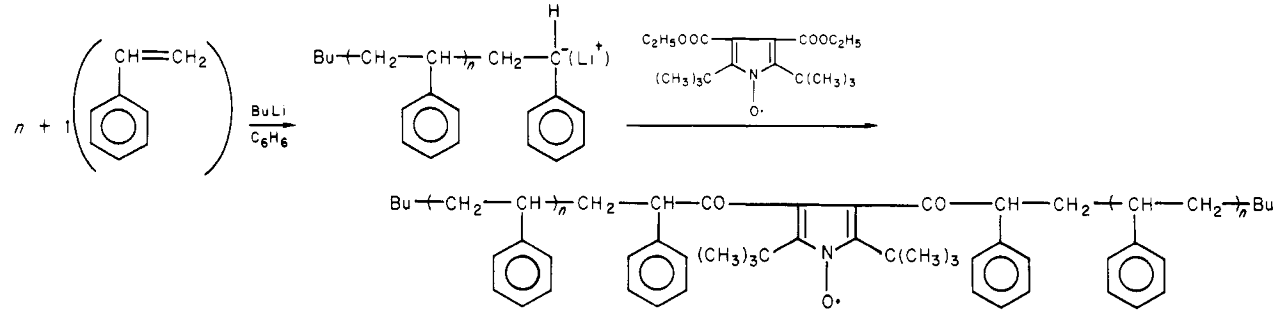
Scheme I



shown that at least two relaxation processes exist in the frequency range 1–150 MHz. Moreover, ^{13}C relaxation time values[2,3,9,10,12,13] were consistent with a rotation of the phenyl group about the C_α–C_{para} axis at a rate comparable to the segmental motion. The change of the temperature coefficient of the ^{1}H line width and ^{13}C T_1 values, which was observed in certain solvents at a critical temperature, has been assigned to long-range conformational changes,[10] and NMR results have been satisfactorily interpreted by a rotation of phenyl groups with a larger degree of freedom above the transition temperature.[10]

Recently, Bullock et al.[29-32] and we[33] have demonstrated that spin labeling provides a useful additional technique in the study of the dynamics of macromolecules in dilute solution. Besides, it has been proven that the ELDOR technique offers a strong alternative means to characterize labeled polymer motions.[34,35] Detailed information has been obtained on the dynamics of polystyrene chain in dilute solution, using nitroxide labels covalently bonded to either the chain ends[32,34,35] or a few phenyl groups per chain.[29-31] The purpose of the present work is to report an extension of this work to an "in-chain"-labeled polystyrene. In the first part of this paper, the ESR spectra and the related correlation times will be given as a function of temperature and viscosity. The second part will be devoted to a comparison with previous studies.

Experimental Section

The in-chain-labeled polystyrene (molecular weight 62 800, $\bar{M}_w/\bar{M}_n \leq 1.1$) was prepared anionically according to Scheme I. Basically, the method consists of adding a bifunctional deactivating reagent to the monofunctional "living" polymer, using butyllithium as the initiator and 2,5-di-*tert*-butyl-3,4-bis(ethoxycarbonyl)pyrrol-1-yloxy as the deactivating agent. The nitroxide spin label was a gift from Dr. A. Rassat.[36] The synthesis and the characterization of the in-chain-labeled polymer thus obtained has been reported elsewhere.[37]

Toluene was purified according to established procedure, dried, and distilled before use. Viscosities were obtained from ref 38 and 39 with the help of graphical interpolation and extrapolation. The activation energy, ΔH_η = 2.08 kcal mol^{-1}, was determined from a plot of log η against 1/T, where η is the solvent viscosity.

The X-band ESR measurements were performed on a Varian E4 spectrometer. The sample solutions were prepared in standard ESR tubes at a fixed composition of 10% by weight. Each solution was subjected to at least four freeze–pump–thaw cycles and sealed off under dynamic vacuum. An E-257 Varian variable-temperature controller was used to thermostat the cavity, and the temperature was determined by a copper–constantan thermocouple lowered into the cavity before and after each series of measurements. Field measurements were made with a direct-reading frequency meter (Radiall) and isotropic g values were measured by comparison with the spectrum of 1,1-diphenyl-2-picrylhydrazyl, for which g = 2.0036.

The isotropic nitrogen coupling constant, A_0, and g factor, g_0, were determined from the spectrum of the label in toluene. At 20 °C, the measured values of A_0 and g_0 were 4.60 and 2.0062, respectively, which compare favorably with the values of 4.58 and 2.0061 obtained by Rassat et al.[40] for the label in benzene solution. Previously g_{zz} and A_{zz} had been read from the 35-GHz rigid-limit spectrum of the label in toluene at 143 K, and g_{xx}, g_{yy}, A_{xx}, and A_{yy} had been determined by assuming an axial symmetry in the anisotropic g and hyperfine coupling tensors.[37] Computer simulations of both the 9.15- and 35-GHz rigid-limit spectra were performed according to standard methods.[41] They gave the more accurate set of magnetic parameters: A_{zz} = 13.68 G, $A_{xx} \simeq A_{yy} \simeq 0$; g_{zz} = 2.00206, g_{xx} = 2.01136, g_{yy} = 2.00517.

ESR Line-Shape Analysis. Theories relating the shape of ESR spectra of nitroxides to the rate of rotational motion have been presented by Freed[42] and Goldman.[43]

The dynamical properties of a spin probe are reflected in the transversal relaxation times $T_2(M)$, where M is the nuclear spin quantum number (^{14}N: M = +1, 0, −1). In the case of a nitroxide radical, the dominant relaxation mechanisms are the motional modulations of the hyperfine tensor and **g** tensor interactions. For an isotropic rotation of a label in a liquid, the theoretical spectrum has been predicted by Kivelson.[44] It consists of three Lorentzian lines. With the assumption that the nonsecular terms can be neglected, $T_2(M)$ is found to be

$$T_2(M)^{-1} = A + BM + CM^2$$

where

$$A = \tau({}^4\!/_{45}\Delta^2 H_0^{\,2} + {}^4\!/_{15}\delta^2 H_0^{\,2} + 3b^2/20) + K$$

$$B = {}^4\!/_{15} b \Delta H_0 \tau$$

$$C = (b^2/8)\tau$$

H_0 is the applied magnetic field, τ the correlation time, and

$$b = {}^2\!/_3[A_{zz} - {}^1\!/_2(A_{xx} + A_{yy})]$$

$$\Delta = (|\beta|/\hbar)[g_{zz} - {}^1\!/_2(g_{xx} + g_{yy})]$$

$$\delta = (|\beta|/\hbar)[(g_{xx} - g_{yy})/2]$$

K is a constant which takes into account the other contributions to $T_2(M)$, such as the spin rotational interactions, the unresolved proton hyperfine splitting, and instrumental broadening.

Results and Discussion

ESR Results. The spectra of the "in-chain"-labeled polystyrene in toluene solution are shown in Figure 1. They appear as a superposition of two types of lines. Indeed, above 30 °C and below 80 °C, the spectra show a splitting at the high-field peak of the triplet, which gives a clear indication of two different environments for the label. Subspectra differ by the values of their isotropic nitrogen coupling constant, A_0, and g factor, g_0. Because of the environment's effects, at high temperature A_0 is slightly smaller and g_0 is slightly larger than at low temperature. The interplay of these A- and g-value shifts causes the spectra to overlap asymmetrically, so that at 9.5 GHz only the high-field lines are resolved. The ratio of the two components in the final line shape depends on temperature, suggesting that polystyrene undergoes a transition between 30 and 70 °C. This temperature range effectively corresponds to the "phase transition" evidenced

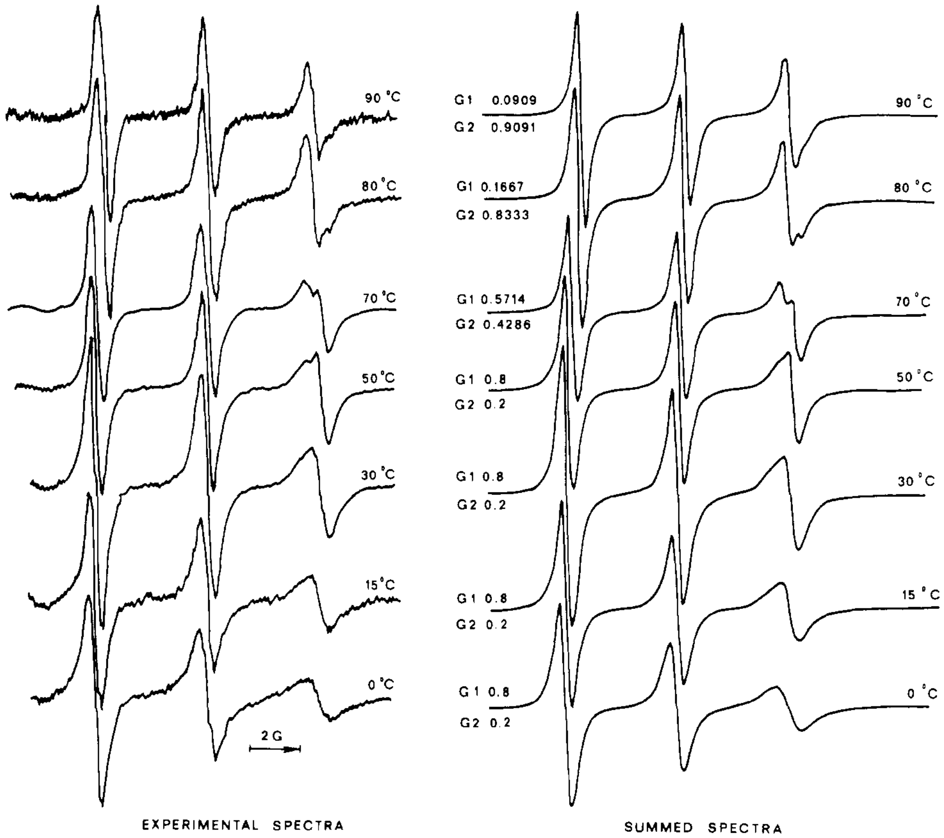


Figure 1. Experimental and summed spectra of in-chain-labeled polystyrene in toluene dilute solution.

by several authors using different experimental techniques as reviewed in ref 45.

In order to verify that these composite spectra represent sums of two spectral components and to determine the ratios of these two components in the final line shape, the spectra can be synthesized by summing the two putative spectral components.

Extrapolation at low and high temperature gives A_{0_1} = 4.65 G, A_{0_2} = 4.3 G, and $g_{0_2} - g_{0_1} = 9.26 \times 10^{-5}$.

The additional broadening, K, was estimated by seeking the minimum, high-temperature limiting line width, and maintained constant under the whole range of temperature: −10 to +90 °C. Although it is a very simple approximation, it was first assumed that the label in its two environments is affected by isotropic rotational diffusion motions defined by the same average correlation time τ. Therefore, the only two parameters involved in the simulations were the correlation time τ and the ratio G of the two spectral components. The results of this procedure are shown in Figure 2. It is immediately apparent that correlation times τ thus obtained cannot be fitted to a simple Arrhenius expression over the range of temperature studied. This being so, the problem was approached in the following way. It is clear from Figure 1 that at high temperatures as well as at low temperatures spectra can be regarded as typical of only one environment for the labels. Therefore, in order to interpret the data by a two-correlation-time process, the exponential behavior of τ toward $1/T$ observed at low temperature was extrapolated at higher temperatures. In the same manner, the exponential behavior of τ toward $1/T$ observed at high temperature was extrapolated at lower temperatures. Two straight lines, $\ln \tau_{\mathrm{LT}} = f_{\mathrm{LT}}(1/T)$ and $\ln \tau_{\mathrm{HT}} = f_{\mathrm{HT}}(1/T)$, were thus obtained. Then, for each experimental spectrum between 0 and 90 °C, best curve fitting with two correlation times τ_1 and τ_2 was looked for, using τ_{LT} and τ_{HT} as starting values for τ_1 and τ_2, respectively. The results of these simulations are given in Figure 3.

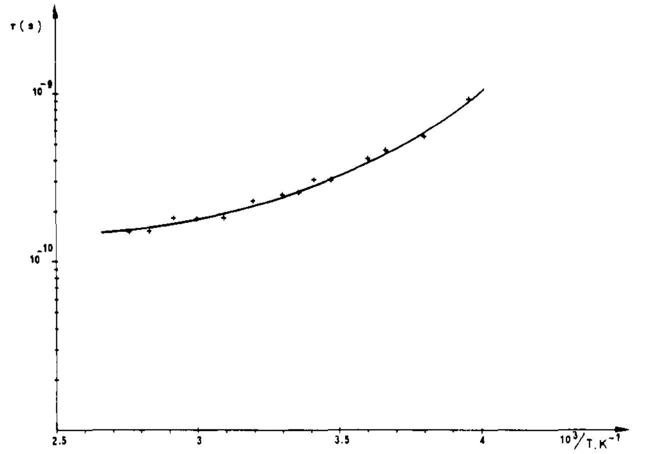


Figure 2. Temperature dependence of the average rotational correlation time τ.

Correlation times can be fitted to Arrhenius expressions of the normal form

$$\tau_i = \tau_{0i} \exp(E_i/RT) \tag{1}$$

where E_1 = 4.10 kcal/mol, $\tau_{0_1} = 2.46 \times 10^{-13}$, E_2 = 2.6 kcal/mol, and $\tau_{0_2} = 3.36 \times 10^{-12}$. From the variation as a function of temperature of the ratio G of the two spectral components (Figure 1), the activation energy of the transition is calculated as $E \simeq 14$ kcal/mol. Although it is impossible to give an exhaustive interpretation of the observed phenomena in terms of molecular conformation of the chain, these results corroborate well with the interpretation previously advanced to account for the transition observed for polystyrene in dilute solution.[45] The tran-

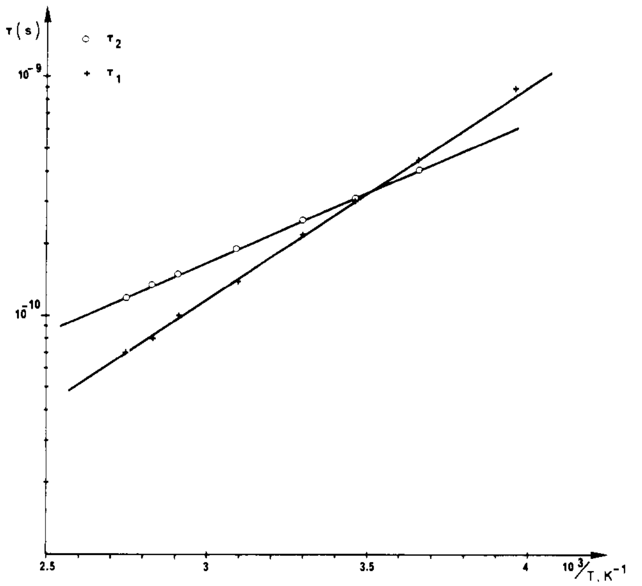


Figure 3. Least-squares Arrhenius plots, log τ_i against $1/T$, for in-chain-labeled polystyrene in toluene dilute solution.

sition is probably due to a simple modification in the conformation of the benzene rings with respect to the chain which is accompanied by a rotational movement of the backbone bonds. It could lead to an overall change in the conformation of the chain, increasing temperature causing a higher flexible structure.

Both for electron spin relaxation and ^{13}C NMR relaxation of polystyrene in solution[12,30,32] and for dielectric relaxation of para-substituted polystyrenes in solution[46,47] correlation times have been found proportional to solvent viscosity. Such an effect can be discussed more quantitatively by using Kramers' theory[48] for the diffusion of a particle over a potential barrier. Helfand[49] has applied this theory to conformational transitions in polymers. In the limit of high viscous damping and for the crankshaft motion, the correlation time τ is related to the solvent viscosity, η, and the temperature, T, by

$$\tau \simeq \frac{1}{k} = \frac{12\pi^2}{(\gamma_A\gamma_B)^{1/2}}\sum_i r_i^2 a\eta \exp(E^*/RT) \qquad (2)$$

where k is Kramers' rate constant for the motion of some monomer units over a potential barrier E^* from a position A to C, r_i is the distance of the ith moving unit from the shaft axis, and γ_A and γ_B are the curvatures of the potential for the rotation at A and B. The monomer unit is treated as a sphere of radius a.

In order to investigate the effect of the solvent viscosity η on the relaxation processes, the observed values of log (τ_1/η) and log (τ_2/η) are plotted against $1/T$ in Figure 4. The plots lie fairly well on straight lines described by

$$\tau_i = \tau'_{0i}\eta \exp(E^*_i/RT) \qquad (3)$$

were $E^*_1 = 2.02$ kcal/mol, $\tau'_{0_1} = 1.45 \times 10^{-9}$, $E^*_2 = 0.52$ kcal/mol, and $\tau'_{0_2} = 1.98 \times 10^{-8}$.

Under these conditions, E_i can be written as the sum of the activation energy for the toluene viscosity, E_η, and the height of the internal potential barrier, E^*_i

$$E_i = E_\eta + E^*_i \qquad (4)$$

The value of E_η is 2.08 kcal.

The number of monomer units involved in the ESR relaxation processes can be obtained according to the treatment applied by Mashimo[46] to dielectric relaxation data, that is using Kramers' rate constant for the crankshaft rotation and a three-state model.

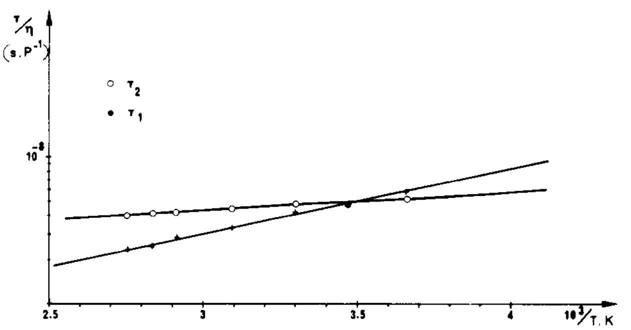


Figure 4. Plots of log (τ_i/η) against $1/T$.

Experimental equations 1 and 4 demonstrate the diffusion-controlled character of the relaxation process.[49] Therefore as correlation times in magnetic resonance are normally concerned with second-order spherical harmonics of the position coordinates, the ESR and dielectric correlation times observed for the same motional model are related by

$$\tau_{\text{diel}}/\tau_{\text{ESR}} = 3$$

This is equivalent to reducing the relaxation times τ_1 and τ_2 in the equation given by Mashimo[46] by a factor 3. The modified inequality reads

$$\frac{1}{9}\left[\frac{12\pi^2 a\sum_i r_i^2}{(\gamma_A\gamma_B)^{1/2}}\right]\eta \exp(E^*_i/RT) \le \tau_i \le \frac{1}{3}\left[\frac{12\pi^2 a\sum_i r_i^2}{(\gamma_A\gamma_B)^{1/2}}\right]\eta \exp(E^*_i/RT) \qquad (5)$$

The value of $(\gamma_A\gamma_B)^{1/2}$ can be determined by assuming the form of the potential u to be

$$u = \tfrac{1}{2}E^*_i(1 - 3\cos\theta)$$

where E^*_i is the experimental value. Then

$$(\gamma_A\gamma_B)^{1/2} = 6.3 \times 10^{-13}\ \text{erg/rad}^2$$

for relaxation process 1 and

$$(\gamma_A\gamma_B)^{1/2} = 1.6 \times 10^{-13}\ \text{erg/rad}^2$$

for relaxation process 2. Using a value of 3 Å for a, we obtain

$$7.7\ \text{Å}^2 \le \underset{1}{\sum_i r_i^2} \le 23\ \text{Å}^2$$

$$27\ \text{Å}^2 \le \underset{2}{\sum_i r_i^2} \le 80\ \text{Å}^2$$

Taking the mean value of r_i to be 4 Å, which was assumed to be a reasonable value,[46] it appears that about one monomer unit may be considered as involved in the ESR relaxation process which is dominant below 80 °C. On the other hand, our results suggest a value of 2–5 for the number of monomer units involved in the relaxation process observed at high temperature, which is consistent with a more flexible structure.

Table I summarizes some of the previous studies on local motion of polystyrene and compares them with our present results. Concordance of correlation times observed at 52 °C for nitroxide substitution in the system ring at the position meta[50] or para[29,31] has led Bullock et al. to the conclusion that segmental reorientation is the main factor controlling τ in side-chain-labeled polystyrene of high

Table I
ESR Relaxation Parameters for Spin-Labeled Polystyrenes in Toluene

labeling site	ref		E, kcal/mol	E^*, kcal/mol	τ_0	$\tau_0' = \tau_0/\eta_0$	$(\gamma_A\gamma_B)^{1/2}$	Σr_i^2, Å^2
in-chain	this work	2	2.6	0.52	3.36×10^{-12}	1.98×10^{-8}	1.6×10^{-13}	27-80
		1	4.10	2.02	2.46×10^{-13}	1.45×10^{-9}	6.3×10^{-13}	7.7-23
side-chain	32		4.31	2.23	3.9×10^{-13}	2.29×10^{-9}	7×10^{-13}	13.5-40
end-chain	32		3.54	1.46	6.3×10^{-13}	3.7×10^{-9}	4.5×10^{-13}	14-42

Table II
Activation Energies for Local Motion in Polystyrene

technique	ref	labeling site	solvent	E, kcal/mol	E^*, kcal/mol
ELDOR	35	end-chain	THF	2.87	1.22
fluorescence depolarization	52	side-chain	ethylbenzene	3.35	1.25
	17	in-chain	tripropionin	6.7	1
	17	end-chain	tripropionin	8.3	2.4
dielectric relaxation	46	poly(*p*-chlorostyrene)	toluene	4.9	2.82
	46	poly(*p*-chlorostyrene)	ethylbenzene	5.0	2.9
ultrasonic relaxation	26	polystyrene	toluene		2.57
	27	polystyrene	ethylbenzene		~0
^{19}F NMR	51	poly(*p*-fluorostyrene)	C_6D_6	6.7	4.2
	51	poly(*m*-fluorostyrene)	C_6D_6	6.7	4.2
^{13}C NMR	3	polystyrene	hexachlorobutadiene	6	2.9[a]
	12	polystyrene	THF	6.45	4.8
	14	polystyrene	toluene	4.6	2.5_2[a]
^{1}H NMR	4	polystyrene	hexachlorobutadiene	6.94	3.8_3[a]
	4	polystyrene	CCl_4	5.98	3.3_5[a]
	4	polystyrene	$CDCl_3$	4.54	2.6_3[a]

[a] From the Arrhenius plot of the correlation time ρ.

molecular weight. Our results lend further support to this statement since the activation energy E^*_1 of 2.02 kcal/mol found for the relaxation process which is dominant below 80 °C compares favorably with the activation energy E^* of 2.23 kcal/mol obtained by Bullock et al. for the side-chain-labeled polystyrene in the same temperature range. On the other hand, the activation energies E^* determined for the end-chain-labeled polystyrene[32,35] are, as expected, smaller than those obtained for either in-chain- or side-chain-labeled polystyrene.

The preexponential factor τ_{0_1} associated with the relaxation process which is dominant below 80 °C for the in-chain-labeled polystyrene is comparable to, although slightly lower than, the values obtained by Bullock et al.[32] for the both side- and end-labeled polymers in the same solvent. As suggested by these authors, such a concordance is almost certainly the result of the high solvent power of toluene, in which the macromolecules are expected to be well extended.

Finally, the slightly greater number of monomer units involved in the ESR relaxation process of the side-chain- and the end-chain-labeled polystyrenes as compared to the in-chain-labeled polymer below 80 °C is probably due to the fact that the immediate surroundings of the terminal segments and the side groups of a macromolecule must be more or less different from those of its central segments. In fact, one might expect that a larger free volume is available for the terminal segments and the side groups than for the central segment.

Comparison with Other Techniques

From Tables I and II it is immediately apparent that the values of E^* determined from NMR measurements are higher than the range (0–2.9 kcal/mol) for the internal barrier quoted in the literature from other techniques. This difference may be associated with the different models used to explain the relaxation data. Indeed, results have been interpreted in terms of (i) a single isotropic correlation time τ,[32,35] (ii) distributions of correlation times[12,17,46] (the activation energy E is determined from a plot of log τ_m against $1/T$, where τ_m is the mean relaxation time), (iii) a more sophisticated model based on local jumps,[3,4,14] which leads to a nonexponential autocorrelation function with two correlation times ρ and θ (ρ is the correlation time characterizing conformational jumps and θ represents either slower modes of the chain or deviations from ideal lattice conditions; two different activation energies E can be derived from the plots of either log ρ or log θ against $1/T$), and (iv) a model based on three-bond crankshaft motions and a cutoff of coupling along the backbone.[51]

For example, Heatley and Begum[9] have shown that the Cole–Cole distribution used in analysis of dielectric relaxation[46] or the log–χ^2 distribution used by Schaefer[8] leads to an activation energy E of 6.45 kcal/mol for backbone motions of polystyrene in pentachloroethane whereas a conformational jump model of chain dynamics gives E_ρ = 5.02 kcal/mol. In the same way, the analysis of the fluorescence anisotropy decay curves in terms of the mean relaxation time $\langle\sigma\rangle$ of the distribution of relaxation times $G(\sigma)$ defined as

$$\langle\sigma\rangle = \int_0^\infty \sigma G(\sigma)\, d\sigma = \left(\frac{1}{r_0}\right)\int_0^\infty r(t)\, dt$$

yields, for an in-chain-labeled polystyrene in tripropionin an activation energy E of 6.7 kcal/mol whereas a conformational jump model leads to E_θ = 7.8 kcal/mol and E_ρ = 4.6 kcal/mol.[17]

Besides, as mentioned by Gronsky et al.,[14] the intramolecular energies can be also affected by polymer–solvent interactions. Although the type of interaction occurring between certain solvents and the aromatic rings is still not unequivocally established, on the basis of NMR and ultraviolet spectral shifts,[53] chlorinated hydrocarbons and tetrahydrofuran have been distinctly revealed as solvents giving rise to specific interactions with polystyrene. The higher values obtained in these solvents for the internal barrier may be caused by increased steric restraints to rotation brought about by the specific polymer–solvent

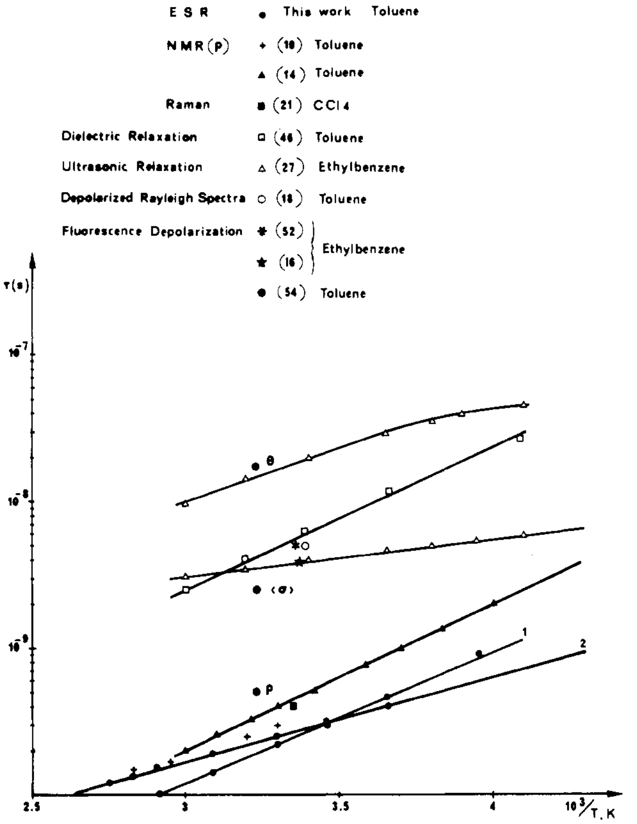


Figure 5. Arrhenius plots of the correlation times τ at various temperatures for local motion in polystyrene.

interactions. It is worth noting that the NMR,[14] dielectric,[46] and ultrasonic[26] values of E^* obtained at temperatures lower than 80 °C using toluene are in rather good agreement with the activation energy E^*_1 of 2.02 kcal/mol determined in this work for the ESR relaxation process which is dominant at low temperatures.

Comparison with other experimental techniques also yields discrepancies in the estimate of the preexponential factor τ_0. The preexponential factor obtained from ESR measurements for either in-chain (2.46×10^{-13}) or side-chain (3.9×10^{-13}) labeled polystyrene is about equal to the NMR preexponential factor (1.6×10^{-13}) determined in the same solvent, that is toluene.[14] On the other hand, $\tau_0 = 1.36 \times 10^{-12}$ is derived from dielectric relaxation experiments in toluene,[46] which is approximately an order of magnitude larger than τ_0 calculated from ESR and NMR data. As previously observed by Matsuo et al.,[51] certain techniques, such as fluorescence depolarization,[16,17,52] ultrasonic relaxation,[23-27] dielectric relaxation,[46,47] and depolarized Rayleigh spectroscopy,[18-20] yield correlation times which appear similar in magnitude, that is to say of the order of nanoseconds or about 10 times larger than the correlation times obtained over the same temperature range but by ESR (this work and ref 29–32 and 35), ELDOR,[34,35] or NMR[1-15,51] (Figure 5). A meaningful comparison of these techniques must take into account that in dielectric relaxation the coordinate function involved is the first-order spherical harmonics cos θ while in the description of the motions studied by NMR, ESR, and fluorescence depolarization, correlation times are normally concerned with the second-order spherical harmonics of the position coordinates. As for depolarized Rayleigh spectroscopy, the second rank tensor correlation function is measured. Thus assuming a diffusion-controlled character for the reorientation, a factor of 3 between the values of τ determined from dielectric relaxation measurements and NMR, ESR, and fluorescence depolarization data could be admitted. However, we would expect for correlation times obtained from fluorescence depolarization values close to NMR or ESR correlation times. A close examination of the time scales of motions probed by the different methods (Figure 5) shows that the above separation into two series of techniques is undoubtedly oversimplified.

The inability to account for the observed discrepancies may arise because the number of monomer units involved in the backbone rearrangements depends on the experimental technique employed.

The larger the number of monomer units required, the longer the correlation time observed. It has been shown that the low-frequency relaxation evidenced by ultrasonic measurements on polystyrene in ethylbenzene[27] involves about 20 monomer units while less than 10 monomer units seem to be affected by the high-frequency relaxation. The dielectric relaxation process[46] can be attributed to a conformation transition of the chain backbone in which 1–4 monomer units are involved. On the other hand, it appears that only one monomer unit may be considered as involved in the NMR relaxation process, which is in good agreement with the number of monomer units determined in this work for the ESR relaxation process observed below 80 °C.

There seems to be a general impression that a model based on a local jump of a chain[28] gives a better fit of fluorescence depolarization data than the simpler one based on a distribution of relaxation times. Indeed, from the recent fluorescence anisotropy decay experiments of Tardiveau[54] on polystyrene containing an anthracene group inserted in the middle of the chain, a value of 2.5 ns is obtained for the mean correlation time $\langle\sigma\rangle$ for 5% toluene solution at 36 °C. This corresponds to θ = 17 ns and ρ = 0.5 ns. Thus under the same experimental conditions and with the same model[28] to explain the relaxation data, the fluorescence depolarization correlation time ρ, which characterizes conformational jumps, appears only twice the correlation time ρ calculated from the NMR data of Gronsky et al.[14] and Inoue et al.[10,15] (Figure 5). As expected these correlation times ρ are similar in magnitude to the correlation times determined by ESR (this work) which probes the most rapid (or short range backbone) motions.

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Notes

Polarizabilities of Some Benzobisoxazole and Benzobisthiazole Rigid-Rod Polymers

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Introduction

The aromatic heterocyclic polymers considered in the present investigation are the *cis*-poly(benzobisoxazole) (PBO) shown in Figure 1, its trans modification, and the trans modification of the sulfur analogue, poly(benzobisthiazole) (*trans*-PBT). The electronic structures of these relatively rigid chain molecules are of considerable interest, for a variety of reasons. For example, charge distributions are relevant to both intramolecular[1,2] and intermolecular[1,3] energies of the chains, resonance stabilization is important with regard to conformational flexibility,[2] and energy band gap information is pertinent to electrical conductivity.[4] Also of considerable importance are polarizabilities, since they are needed for the interpretation of solution property studies such as flow birefringence measurements. Experimental studies of this type are carried out to obtain rheological time constants and orientation parameters relevant to the processing of these materials.[5] In this investigation, several theoretical approaches[6-9] are used to calculate repeat unit polarizabilities of the three polymers mentioned above.

Theory

The bond lengths and bond angles in the three repeat units were obtained from the X-ray structural studies conducted on model compounds by Fratini and co-workers.[10,11] The two PBO polymers have planar repeat units, but the *trans*-PBT repeat unit has the *p*-phenylene group rotated by 23.2°.[1,2,10,11] In this latter case, the plane of the phenylene ring was taken to be the plane of the molecule. For all three molecules, the plane of the molecule was in the xz plane, with the z axis coincident with the long molecular axis. The quantities of interest are the polarizability components α_{xx}, α_{yy}, and α_{zz}, their simple average $\bar{\alpha}$, and the anisotropic ratio defined by

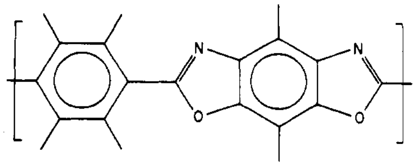

Figure 1. *cis*-PBO repeat unit.

$$\delta = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})^2} \right]^{1/2} \qquad (1)$$

The first method employed for all of these quantities was the quantum mechanical method of Marchese and Jaffé,[6] in which second-order perturbation theory is combined with the CNDO/S CI formalism[7] (complete neglect of differential overlap, configuration interactions). The second was the empirical scheme of Miller and Savchik,[8] in which the average polarizability is obtained by summing atomic hybrid components τ_A

$$\bar{\alpha} = (N/4)[\sum_A \tau_A]^2 \qquad (2)$$

in which N is the total number of electrons in the molecule. Pertinent values of τ_A for C, N, O, S, and H atoms are 1.428, 1.262, 1.290, 3.496, and 0.314 Å$^{3/2}$, respectively.[8] The

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