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Electron Spin Resonance Study of Chain Motion of Spin-Labeled Poly(ethylene oxide) in Dilute Solution

C. Friedrich, F. Laupretre, C. Noël,* and L. Monnerie

Laboratoire de Physicochimie Structurale et Macromoléculaire, Associé au CNRS, ESPCI, 75231 Paris Cedex 05, France. *Received February 26, 1980*

ABSTRACT: The rotational correlation times τ_c of end-labeled poly(ethylene oxide) ($M_w = 9000$) were measured in a variety of solvents as a function of temperature. An expression of the correlation time has been found to be the same as that predicted by Kramers' theory in its dependence on solvent viscosity and temperature. The energy barrier for the rotation was found to be 1.45 kcal/mol. Assuming the transition to be that of the crankshaft and employing Kramers' expression, it appears that about one monomer unit may be considered as involved in the ESR relaxation process.

Introduction

The dynamic properties of macromolecules in dilute solutions constitute a problem of considerable interest. In recent years, many investigations have been carried out by techniques well adapted to the study of fast movements, e.g., dielectric relaxation,[1-3] fluorescence polarization,[4] ^{13}C and ^{1}H nuclear magnetic relaxation,[5-13] and line-shape analysis of the paramagnetic resonance of spin labels,[5,14-17] to find a description of the molecular motions under a variety of conditions.

In our previous paper[5] special attention has been paid to the information which can be derived from differences between the rotational correlation times τ_c determined for poly(ethylene oxide) (PEO) from ^{13}C NMR, ^{1}H NMR, and ESR measurements and from the dependence of these correlation times on the viscosity and nature of the solvent. The isotropic rotational model was found to be a satisfactory approximation for describing both ESR and ^{1}H and ^{13}C NMR relaxation measurements of PEO in dilute solution. When aromatic solvents or CCl_4, CH_2I_2, CH_2Br_2, $(CH_2Cl)_2$, and $(CH_2Br)_2$ were used in preparing PEO solutions, the viscosity dependence of the resulting PEO τ_c values was significantly different from that observed in CH_2Cl_2, $CHCl_3$, $CHBr_3$, $(CHCl_2)_2$ and $(CHBr_2)_2$ solutions. The τ_c values obtained in the first family of solvents were found the least viscosity sensitive.

In the present investigation, line-shape analysis of the paramagnetic resonance of spin-labeled PEO is carried out

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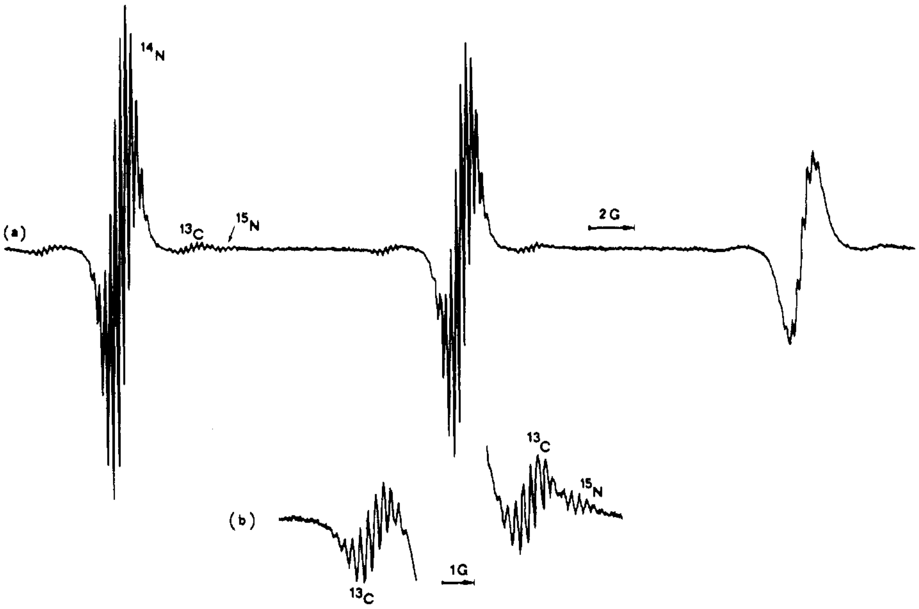
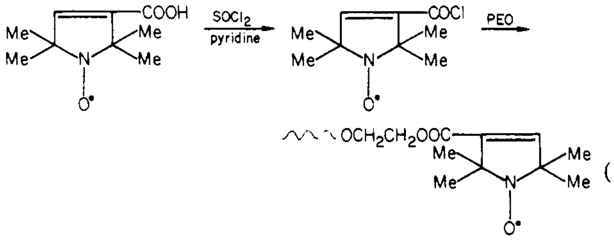


Figure 1. (a) ESR spectrum of end-labeled PEO in CHBr$_3$ solution at 41 °C. (b) Natural-abundance contributions from ^{13}C and ^{15}N.

in the viscosity range 0.4–27 cP at temperatures between 255 and 353 K in different solvents. An expression is obtained experimentally for the correlation time in which only the solvent viscosity enters as a property of the solvent. The expression is the same as that predicted by Kramers' theory in its dependence on solvent viscosity and temperature.

Experimental Section

The PEO used was Fluka poly(ethylene glycol) M 9000. The spin-labeled PEO was prepared with 3-(chlorocarbonyl)-2,2,5,5-tetramethylpyrroline 1-oxyl which reacts easily with the free hydroxyl groups of PEO according to eq 1. The experimental conditions were essentially those described by Törmälä et al.[18] The polymer sample was purified by four precipitations in ethyl ether from chloroform solution and then dried. The polymer thus obtained has a low polydispersity ($\bar{M}_w/\bar{M}_n \leq 1.1$) and a molecular weight of 9200, as determined by gel permeation chromatography. The density of spin-labels was kept below 1 nitroxide radical per 2000 monomer units to avoid contributions to line widths from spin exchange.



(1)

Reagent grade solvents were purified according to established procedures, dried, and distilled before use. Viscosities for the solvents were obtained from ref 19 and 20 with the help of graphical interpolation and extrapolation. The activation energy ΔH_η (Table I) was determined from a plot of log η against $1/T$, where η is the solvent viscosity.

The sample solutions [1% (w/v)] were prepared in standard ESR tubes. Each solution was degassed on a vacuum line by means of freeze–pump–thaw cycles.

ESR spectra were taken with a Varian E4 spectrometer. An E-257 Varian variable-temperature controller was used to thermostat the cavity, and the temperature was measured by a copper–constantan thermocouple lowered into the cavity before and after each series of measurements. Knowing the g value of the reference sample, g_R, we determined the g value of the sample under investigation, g_0, from the expression

$$g_0 = g_R + g_R(B_R - B_0)/B_0$$

Table I
Relaxation Parameters for Spin-Labeled PEO in Various Solvents

solvent	$a^N{}_{iso}$	ΔH_η, kcal/mol	$10^{11}\tau_0$, s	ΔH_a, kcal/mol
bromonaphthalene	14.5	4.28	$0.000\,48_5$	6.1_4
chloronaphthalene	14.5	4.23	$0.001\,7_1$	5.1_2
bromobenzene	14.47	2.84	$0.000\,97_8$	4.7_1
benzene	14.35	2.52	$0.004\,2_1$	3.7_2
chlorobenzene	14.5	2.11	$0.013\,1_6$	3.1_3
$(CH_2Br)_2$	14.5_5	2.68	$0.002\,3_1$	4.6_7
$(CH_2Cl)_2$	14.6	2.24	$0.006\,2_2$	3.5_4
$CHCl_3$	14.8_2	1.78_7	$0.008\,5_8$	3.2_5
$CHBr_3$	14.8_5	2.40	$0.006\,5_5$	4.1_7
$(CHBr_2)_2$	14.8	4.95	$0.000\,8_5$	6.3_3

where B_R and B_0 refer to the magnetic fields at the centers of the symmetrical central lines of the ESR spectra from the reference and the sample, respectively. In the calculation of the absolute values of g_0, 1,1-diphenyl-2-picrylhydrazyl was taken as the standard, with $g_R = 2.0036$. Field measurements were made with a direct-reading frequency meter (Radiall).

Theory and Method of Line-Width Analysis

The crystal and molecular structure of the free radical has been established by Kruger and Boeyens.[21] All the atoms in the ring and the oxygen of the nitroxyl function exist in one plane.

The ESR spectrum of end-labeled PEO in dilute solution is shown in Figure 1 with CHBr$_3$ as solvent. As expected, the principal feature is a triplet. However, each nitrogen line of the triplet shows further splittings due to interactions with the neighboring protons. The two lines on either side of the major three hyperfine lines represent the contributions made by the natural abundance of carbon-13. The arrows point to the natural-abundance contribution from ^{15}N.

The line widths were analyzed according to the general expression[22]

$$T_2^{-1}(m_1,m_2,...,m_n) = A + \sum_{i=1}^{n} B_i m_i + \sum_{i=1}^{n} C_i m_i + \sum_{i \neq j=1}^{n} E_{ij} m_i m_j \quad (2)$$

where A, B, and C are functions of the spectral densities and various inner products of the g and hyperfine tensors. E involves the cross product of the hyperfine coupling tensors for ^{14}N and ^{1}H. Fortunately, it is possible to obtain an expression which depends only on m_I, the component of the ^{14}N nuclear spin and the anisotropy of the coupling tensor to ^{14}N. Explicitly

$$T_{2(+1)}^{-1} + T_{2(-1)}^{-1} - 2T_{2(0)}^{-1} = 2C_N \qquad (3)$$

With the ratios $T_{2(0)}/T_{2(+1)}$ and $T_{2(0)}/T_{2(-1)}$ defined as R_+ and R_-, respectively, it is readily shown that

$$R_+ + R_- - 2 = 2C_N T_{2(0)} \qquad (4)$$

Omitting nonsecular contributions and, in accordance with earlier studies of PEO in dilute solutions,[5,12] considering the coefficients in eq 2 as those appropriate for isotropic tumbling, eq 4 becomes

$$R_+ + R_- - 2 = {}^1/_4 \tau_c b^2 T_{2(0)} \qquad (5)$$

where τ_c is the rotational correlation time and $b = (4\pi/3)[T_z - a^N_{iso}]$. The parameter b was obtained by measuring the separation between the outermost lines in the rigid-limit ESR spectrum of powdered labeled PEO and combining this measurement with the isotropic solution value of a^N, as described in an earlier study.[5] $T_{2(0)}$ was determined by measuring $\Delta\nu$, the peak-to-peak width of the central hyperfine component. If the individual lines are expected to be Lorentzian in shape, then $T_{2(0)}^{-1} = 3^{1/2}\pi\Delta\nu$. R_+ and R_- are obtained from the ratios of peak-to-peak intensities, Y, of the relevant lines

$$R_\pm = [Y(0)/Y(\pm 1)]^{1/2}$$

It is necessary to correct the observed $T_{2(0)}$ and $R_\pm$ for the inhomogeneous broadening due to unresolved couplings. The correction procedure involves spectral simulations from which appropriate correction curves are constructed, and the value of the hydrogen hyperfine coupling constant is found to be $a^H = 0.2$ G.[23] There is a negligible dependence of a^H on solvent nature. On the other hand, from Table I, a trend of increasing nitrogen hyperfine coupling constant, a^N_{iso}, with increasing solvent polarity is apparent.

Results and Discussion

In order to determine the apparent activation energy, ΔH_a, for the ESR relaxation process, we plotted values of ln τ_c against the reciprocal of the absolute temperature, $1/T$ (Figures 2 and 3). For each solution, τ_c values fit an expression of the Arrhenius type

$$\tau = \tau_0 \exp(\Delta H_a/RT) \qquad (6)$$

where τ_0 is the preexponential factor. Table I gives the values of ΔH_a and τ_0.

From Figure 2, it is apparent that the τ_c values determined by ESR measurements are longer than those obtained by dielectric relaxation.[1] On the other hand, in accordance with earlier studies,[5,17] under identical solvent and temperature conditions, ^{13}C and ^{1}H NMR and spin-labeling technique are in qualitative agreement.

The calculated value of the apparent activation energy for PEO in chloroform is 3.25 kcal mol^{-1} (Table I), which compares favorably with the value of 4.1 kcal mol^{-1} quoted by Hermann[11] from NMR experiments in the same solvent. Whereas Braun and Törmälä[14] have reported for the apparent activation energy of spin-labeled PEO in benzene solution a high value of 11.6 kcal mol^{-1}, the value of 3.7$_2$ kcal mol^{-1} given in Table I is comparable to, although slightly higher than, the values of 2.4 and 2.7 kcal mol^{-1} obtained by dielectric relaxation measurements[1] in the same solvent for PEO of molecular weights 1000 and 9000, respectively.

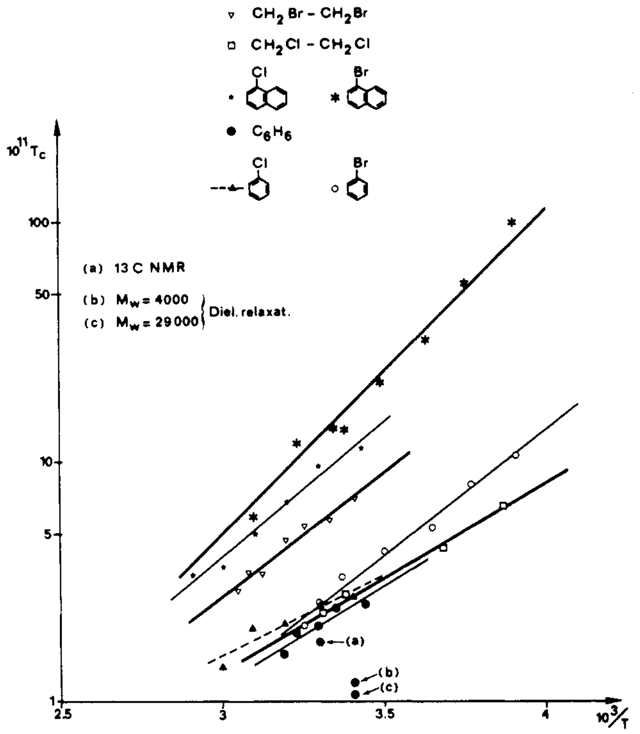


Figure 2. Least-squares Arrhenius plots of ln $(10^{11}\tau_c)$ against $1/T$ for end-labeled PEO in various solvents of series I.

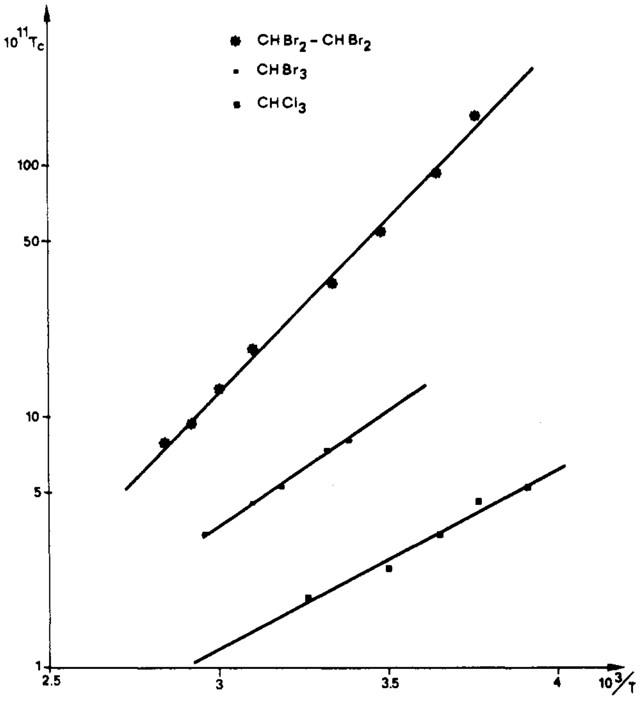


Figure 3. Least-squares Arrhenius plots of ln $(10^{11}\tau_c)$ against $1/T$ for end-labeled PEO in various solvents of series II.

These comparisons and earlier results indicating that NMR,[5,7] ESR,[5,14] and dielectric[1] correlation times are practically independent of chain length for a degree of polymerization larger than 30 lead us to associate some form of local conformational motion of the polymer backbone. Further, although the relaxation of PEO depends on the solvent nature,[5,6] the change from a fluid

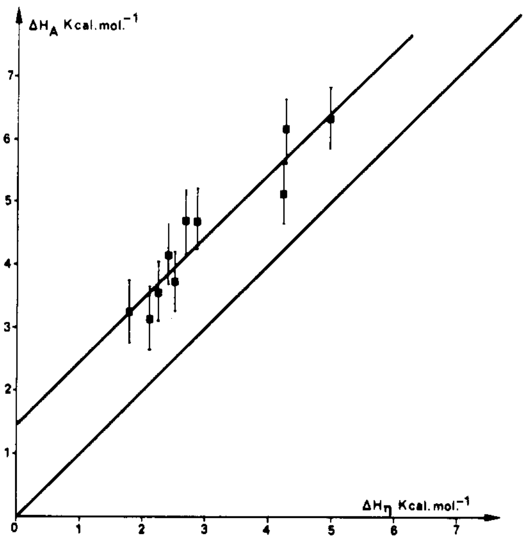


Figure 4. Relationship between the apparent activation energy for the ESR relaxation process, ΔH_a, and the activation energy for the solvent viscosity, ΔH_η.

solvent to a viscous one results in a much higher apparent activation energy and longer correlation times. Thus, the rotational mobility of the terminal segment appears to be mainly determined by (a) the internal energy barriers to rotation and (b) the viscous drag of the solvent medium.

In order to investigate the relative importance of these two factors in determining the segmental rotational mobility of spin-labeled PEO in dilute solution, we plotted the activation energy ΔH_a against the activation energy for the solvent viscosity, ΔH_η (Figure 4). The plot lies on a straight line described by

$$\Delta H_a = \Delta H_\eta + E^*$$

where E^* takes a value of 1.45 kcal mol^{-1}.

Under these conditions, the correlation time is of the form

$$\tau = \tau_0 \exp[(\Delta H_\eta + E^*)/RT] \qquad (7)$$

and, as shown by Mashimo[2] for poly(p-chlorostyrene) dielectric relaxation data, the effects can be discussed more quantitatively using Kramers' theory.[24] Indeed, such a dependence on solvent viscosity and temperature is foreseen in the Helfand's analysis[25] of the Brownian diffusion of a segment over a potential barrier and in the limit of high viscous damping, which gives, for the crankshaft motion

$$\tau \approx \frac{1}{k} = \frac{2\pi}{(\gamma_A\gamma_B)^{1/2}} \sum_i r_i^2 \xi_i \exp(E^*/RT) \qquad (8)$$

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, ξ_i is the frictional coefficient, and γ_A and γ_B are the curvatures of the potential for the rotation at A and B, respectively. When the monomer unit is treated as a sphere of radius a, the frictional coefficient ξ_i may be expressed as

$$\xi_i = 6\pi a\eta$$

where η is the solvent viscosity.

The correlation time is therefore

$$\tau \approx \frac{12\pi^2}{(\gamma_A\gamma_B)^{1/2}} \sum_i r_i^2 a\eta \quad \exp(E^*/RT) \qquad (9)$$

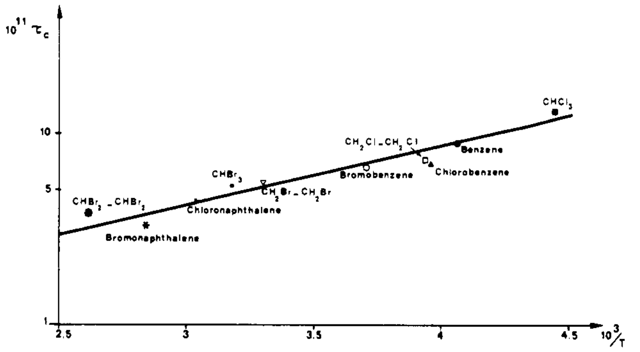


Figure 5. Plot of ln $(10^{11}\tau_c)$ against $1/T$ at η = 1.5 cP for all solutions of PEO.

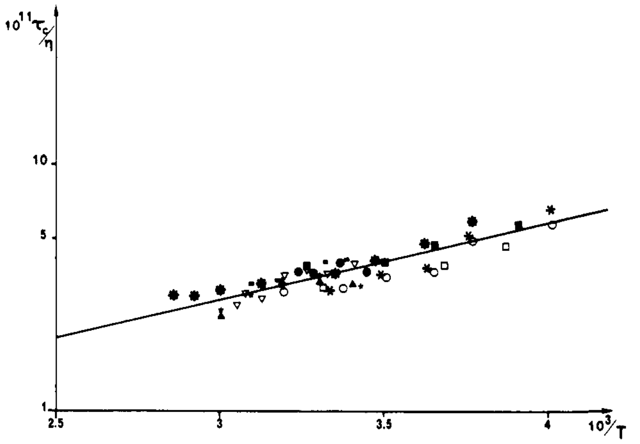


Figure 6. Plot of ln $(10^{11}\tau_c/\eta)$ against $1/T$. Line calculated from eq 11 with the viscosity in units of centipoise.

As seen in Figure 5, dependence of correlation time on temperature, at constant viscosity, is described by

$$\tau_c = 0.49 \times 10^{-11} \exp(E^*/RT) \text{ at } \eta = 1.5 \text{ cP} \qquad (10)$$

that is to say

$$\tau_c = 33 \times 10^{-11}\eta \exp(E^*/RT) \qquad (11)$$

where the viscosity is in units of poise.

As illustrated in Figure 6 for all solutions of PEO, the experimental values and those calculated from eq 11 are quite similar. Random errors dominate the small differences previously observed[5,6] between the two classes of solvents. From our earlier ESR study of PEO[5] there is general agreement that, at constant temperature, correlation time is proportional to the solvent viscosity. The narrow temperature range investigated in that study had led us to interpret such a result in terms of the Stokes–Einstein law. However, contrary to data reported here, this view would not predict the exponential dependence of the correlation time on temperature.

The experimental eq 7 demonstrates the diffusion-controlled character of the relaxation process.[25] Therefore, the ESR and dielectric correlation times observed for the same motional mode are related by

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

If the transition observed in the ESR measurements is assumed to be of a crankshaft type, the number of monomer units involved in the relaxation process can be obtained from Kramers' expression for the rate constant.

The preferred conformation of the poly(ethylene oxide) chain is known to be[26,27]

$$-O-C-C\overset{g}{-}O\overset{t}{-}C\overset{t}{-}C-$$

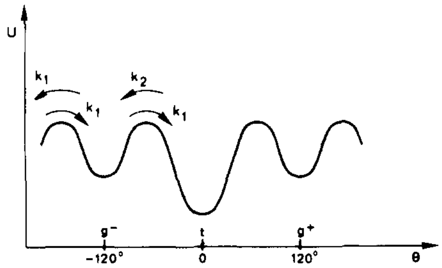


Figure 7. Schematic potential energy for rotational isomers of poly(ethylene oxide).

Let us assume that the potential energy for the conformational transitions between the three isomers g^+, g^-, and t of PEO has the form illustrated in Figure 7, in which upper states g^+ and g^- are degenerate. According to the site theory of relaxation,[28] two dielectric correlation times $\tau_{1\mathrm{diel}}$ and $\tau_{2\mathrm{diel}}$ are derived

$$\tau_{1\mathrm{diel}} = 1/3k_1$$

$$\tau_{2\mathrm{diel}} = 1/(k_1 + 2k_2)$$

where k_1 is the rate constant for transition from state g^+ to g^- and k_2 that from state t to state g^+.

It is noticeable that $\tau_{1\mathrm{diel}}$ and $\tau_{2\mathrm{diel}}$ are not very different. When k_2 takes a value between zero and k_1, $\tau_{2\mathrm{diel}}$ takes a value between $1/3k_1$ and $1/k_1$

$$1/3k_1 \le \tau_{1\mathrm{diel}} \le \tau_{2\mathrm{diel}} \le 1/k_1$$

and, if only a mean relaxation time τ_{diel} is observed, we have

$$1/3k_1 \le \tau_{\mathrm{mdiel}} \le 1/k_1$$

Therefore, for the correlation times τ_c deduced from the ESR measurements reported here, we get

$$1/9k_1 \le \tau_c \le 1/3k_1$$

Thus, using eq 9 we obtain

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

The estimation of the radius a can be obtained from our previous data.[5] The value of $(\gamma_A\gamma_B)^{1/2}$ can be determined by assuming the form of the potential U to be

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

where E^* is the experimental value of 1.4_5 kcal mol^{-1}. Then

$$(\gamma_A\gamma_B)^{1/2} = 4.53 \times 10^{-13}\ \mathrm{erg/rad^2}$$

Using these values in the inequality (12) and experimental results of eq 11, we obtain

$$1.2 \times 10^{-16}\ \mathrm{cm^2} \le \sum_i r_i^2 \le 3.8 \times 10^{-16}\ \mathrm{cm^2}$$

By comparing these results to the description of reorientational motions of the PEO chain,[27] it appears that about one monomer unit may be considered as involved in the ESR relaxation process.

It is worth noting at this point that both for dielectric relaxation of para-substituted polystyrene[2,3] and for electron spin relaxation of polystyrene,[15,16] which probe the most rapid chain motions, correlation times are proportional to solvent viscosity. In the case of poly(*p*-chlorostyrene) Mashimo[2] has calculated a value of 1–4 for the number of monomer units between the two collinear bonds in quite the same way as the present one, that is, by assuming the transition to be that of the crankshaft and employing Kramers' rate constant for the transition and the three-state model. Such a value is in satisfactory agreement with the number of 9–13 bonds obtained by Stockmayer et al.[13] from their NMR study of poly(*p*-fluorostyrene).

The conclusion to be reached as a result of these studies is that for methods which probe the most rapid chain motions, such as ESR, NMR, and dielectric dispersion, the dominant processes seem to be of the diffusion-controlled type and correspond to simple flexible structures. Indeed, the values of the number of monomer units involved in the relaxation process are very small (1–5) and do not differ much from each other.

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