Comparison between end-bond and internal-bond relaxation of polystyrene in dilute solution: an investigation by time-dependent fluorescence polarization

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Fluorescence anisotropy decay experiments are described for polystyrene containing a fluorescent dye label either inserted in the middle of the chain or bonded to the chain end. A comparison between the end-bond relaxation and the internal-bond relaxation is thus possible and shows that the former is four times faster than the latter. The mean relaxation time and the correlation times θ and ρ (introduced in our jump model) are compared and carefully examined as a function of viscosity. A comparison with electron spin resonance experiments is presented.

Keywords Fluorescence polarization; fluorescence anisotropy decay; polymer dynamics; polystyrene; dilute solution; viscosity effect

INTRODUCTION

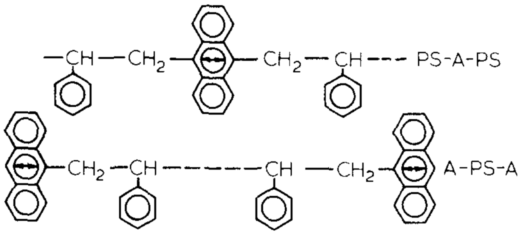
Most of the investigations on polymer dynamics deal with internal motion of chains. Nevertheless, motion of the end bond is of particular interest when information on the chemical reactivity of a reactive group bonded to the chain end is required. Such reactivity is involved in fast intermolecular reactions[1].

Techniques involving fluorescent dye labels or spin labels are suitable for the comparison between the relaxation of an internal bond and that of the end bond. Bullock *et al.*[2] have performed electron spin resonance (e.s.r.) studies on polystyrene containing nitroxide radicals attached either to the chain ends or the side of the chain (phenyl group). A comparison between end and internal mobility was also investigated by stationary fluorescence polarization using dye-labelled poly(methyl methacrylate)[3,4] or polystyrene[5,6].

In the present paper, we report time-dependent fluorescence polarization experiments carried out with polystyrene containing an anthracene group either inserted in the middle of the chain or bonded to the chain end. Our previous investigation on the former[7] will be taken into consideration. The emission anisotropy decay curves will be analysed in relation to our theoretical jump model[8-10].

EXPERIMENTAL

The polystyrene samples under study have the following structure:



The double arrow indicates the common direction of the absorption and emission transition moments for the first singlet state.

The preparation of PS–A–PS polystyrene is described in an earlier paper[11].

The sample of A–PS–A polystyrene was prepared by adding a monofunctional deactivating reagent (9-chloromethyl anthracene) to the bifunctional 'living' polymer initiated by naphthalene sodium.

The average molecular weights of these samples were determined by gel permeation chromatography (g.p.c.):

	$\overline{M}_n$	$\overline{M}_w$
PS-A-PS	52 000	69 000
A-PS-A	66 000	95 000

These molecular weights are high enough to avoid contribution of the overall rotation of the macromolecules.

In both cases, excess of free fluorophore was carefully removed by several precipitations in methanol or soxhlet extraction by methanol.

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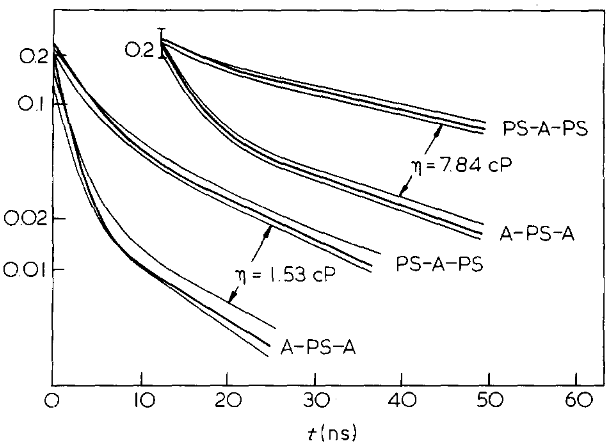

Figure 1 Examples of anisotropy decay curves. The theoretical curves are drawn as bold lines

Experiments were done in mixtures of ethyl acetate and tripropionin (glyceryl tripropionate), as proposed in an earlier paper[7], and in α-chloronaphthalene in order to compare our results with those of Bullock *et al.*[2] Polymer concentrations were less than 0.1%, which corresponds to an anthracene concentration of less than 10^{-5} M.

Fluorescence decay curves were recorded on our single photon decay fluorimeter, which has been described previously[7]. The sample is excited by a short-duration pulse of vertically polarized light at 380 nm and the fluorescence is observed at right-angles to the direction of excitation through a polarizer and a Balzers K2 optical filter. The $I_\parallel$ and $I_\perp$ components, respectively parallel and perpendicular to the electric vector of the incident wave, are recorded as functions of time. It is thus possible to follow the decay of the emission anisotropy, as defined by:

$$r(t)=\frac{I_\parallel(t)-I_\perp(t)}{I_\parallel(t)+2I_\perp(t)}=\frac{D(t)}{I(t)} \qquad (1)$$

where $I(t)$ represents the total intensity of fluorescence. The experimental decay curves $D(t)$ and $I(t)$ were analysed by the method of modulating functions, developed by one of the authors[12,13] in order to perform the deconvolution with respect to the flash profile and to determine the best fit decay parameters.

RESULTS AND DISCUSSION

In all cases analysis of $D(t)$ and $I(t)$ curves shows that a sum of two exponential terms is sufficient to obtain a satisfactory curve fit. On the basis of the amplitudes and time constants of these terms, curves can be reconstructed representing the emission anisotropy, $r(t)$, without making any *a priori* assumption regarding its theoretical form.

Fluorescence anisotropy decay curves were thus obtained for A–PS–A polystyrene in various ethylacetate–tripropionin mixtures at 25°C and compared with those of PS–A–PS polystyrene. *Figure 1* shows two examples of such a comparison. The results are represented by a cross-hatched zone corresponding to the confidence range in order to take into account the limited accuracy of the deconvolution process and the noise inherent in the experimental curves.

Figure 1 reveals that a rather satisfactory agreement is obtained in both cases with a function of the type[7,8,10]:

$$r(t)=r_0 e^{-1/\theta} e^{t/\rho} \mathrm{erfc}(t/\rho)^{1/2} \qquad (2)$$

This equation has been derived initially for a chain described in a tetrahedral lattice. The correlation time ρ corresponded to local jumps inside the lattice and the correlation time θ characterized discrepancies from the tetrahedral lattice.

As a matter of fact, such an equation is much more general. It deals with any orientational motion which can be described by a combination of two types of molecular processes. The first type corresponds to processes leading to diffusion of orientation along the chain (three-bond motion, crankshaft,...) and the second type to processes resulting in loss of orientation (large-scale isotropic motions, internal rotation angle fluctuations,...).

The correlation time ρ characterizes the rate of orientation diffusion and the correlation time θ reflects the loss of orientation. If several molecular processes are involved, ρ and θ are harmonic averages of the individual correlation times:

$$\frac{1}{\rho}=\sum_i \frac{1}{\rho_i}$$

$$\frac{1}{\theta}=\sum_j \frac{1}{\theta_j} \qquad (3)$$

Determination of the mean relaxation time $\langle\sigma\rangle$ and the correlation times θ and ρ

The anisotropy decay curves $r(t)$ can be analysed in terms of the mean relaxation time $\langle\sigma\rangle$ of the distribution of relaxation times $G(\sigma)$ defined as[7]:

$$\langle\sigma\rangle=\int_0^\infty \sigma G(\sigma)\,\mathrm{d}\sigma=\frac{1}{r_0}\int_0^\infty r(t)\,\mathrm{d}t \qquad (4)$$

and, using equation (2):

$$\langle\sigma\rangle=\frac{1}{r_0}\int_0^\infty \frac{A_1 \exp(-r/T_1)+A_2 \exp(-t/T_2)}{A'_1 \exp(-t/T'_1)+A'_2 \exp -t/T'_2)}\mathrm{d}t \qquad (5)$$

The calculation of the integral in equation (5) is inserted in the computer program.

Analysis of $r(t)$ curves at long times permits determination of θ, since the long-time behaviour of $r(t)$ is:

$$r(t)\simeq r_0\,\mathrm{e}-^{t/\theta}(\pi t/\rho)^{-1/2} \qquad (6)$$

hence

$$\ln r(t)+\tfrac{1}{2}\ln t=-(t/\theta)+\text{constant}$$

Thus $\ln r(t)+\frac{1}{2}\ln t$ is plotted as a function of t and θ is deduced from the slope.

The correlation time ρ can be determined from the relation:

$$\langle\sigma\rangle=\frac{\theta}{1+(\theta/\rho)^{1/2}} \qquad (7)$$

Table 1 PS–A–PS polystyrene in ethylacetate–tripropionin mixtures at 25°C

Tripropionin content (%)	η(CP)	$\langle\sigma\rangle$(ns)	θ(ns)	ρ(ns)	θ/ρ
39.93	0.98	5.1	21.0	2.2	9.5
59.64	1.53	7.7	24.9	5.0	5.0
79.69	2.88	12.5	31.1	14.2	2.2
85.50	3.49	18.0	44.8	20.3	2.2
88.74	4.40	20.8	54.1	21.2	2.6
95.00	5.65	22.6	60.6	21.4	2.8
100.0	7.84	30.6	83.3	27.9	3.0

Table 2 A–PS–A polystyrene in ethylacetate–tripropionin mixtures at 25°C

Tripropionin content (%)	η(cP)	$\langle\sigma\rangle$(ns)	θ(ns)	ρ(ns)	θ/ρ
39.93	0.98	1.3	12.7	0.2	75
59.64	1.53	2.0	17.7	0.3	59
79.69	2.88	3.5	18.4	1.0	18
88.74	4.40	5.0	22.1	1.9	12
94.02	5.40	6.2	24.8	2.7	9.1
100.0	7.84	9.2	40.5	3.5	12

which is obtained by integration of:

$$\langle\sigma\rangle = \int_0^\infty e^{-t/\theta} e^{t/\rho} \operatorname{erfc}(t/\rho)^{1/2} \, dt$$

using Laplace transforms. Then, once $\langle\sigma\rangle$ and θ are known, ρ is calculated from the following equation:

$$\rho = \frac{\theta\langle\sigma\rangle^2}{(\theta - \langle\sigma\rangle)^2}$$

However, such a determination of ρ leads to unsatisfactory agreement with experimental results, the initial part of the theoretical curves lying beneath the corresponding $r(t)$ curves. This effect is particularly pronounced for low viscosities (i.e. when motions are rapid) and is due to the limiting bandwidth of the instrument. The values of r_0 resulting from the best fit of the experimental curves $D(t)$ and $I(t)$ are therefore lower than they should be. As proof, the value of r_0 for 9,10-dimethyl anthracene in propylene glycol in the glassy state (−60°C) is 0.25 at 380 nm (excitation wavelength)[14], which is in good agreement with the value 0.24 obtained in pure tripropionin with this same fluorophore inserted in a polystyrene chain. Therefore, it appears more reasonable to use such a value of r_0 for all the calculations of $\langle\sigma\rangle$ from equation (5) than ρ from equation (8).

The values of $\langle\sigma\rangle$, θ and ρ are reported in *Tables 1* and *2* for solutions of PS–A–PS and A–PS–A polystyrene in various ethylacetate–tripropionin mixtures at 25°C. Comparison of *Tables 1* and *2* reveals that the relaxation observed for the end-labelled A–PS–A polystyrene is, as expected, much faster than that of PS–A–PS polystyrene. The mean relaxation time of the latter is about four times larger, which is in agreement with stationary fluorescence polarization measurements performed on polystyrene labelled on the side chain and at the chain end by an anthracene group[5,6].

Effects of viscosity

By using mixtures of solvents of the same chemical nature (ethyl acetate and tripropionin), the effects of viscosity can be studied without significant perturbation due to changes in preferential solvation and chain conformation. Variations in the mean relaxation time as a function of viscosity are presented in *Figure 2*. The plot corresponding to PS–A–PS polystyrene is almost linear, though a slight curvature is observed for low viscosities, as reported and discussed previously[7]. On the other hand, the variations observed for A–PS–A polystyrene are linear.

A more detailed analysis of the relaxation phenomena is made possible by examination of the viscosity dependence of θ and ρ (*Figures 3* and *4*) which clearly illustrates the power of the decay technique.

Variations in θ as a function of viscosity are linear for both samples:

$$\theta = a + b\eta$$

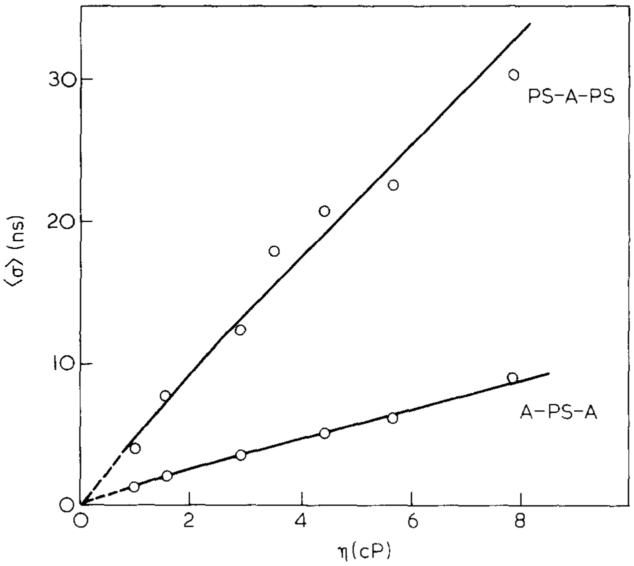

Figure 2 Plot of mean relaxation time *versus* viscosity

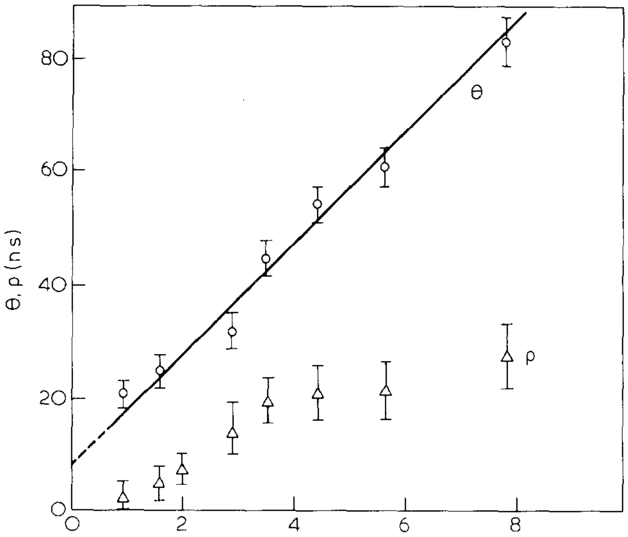

Figure 3 Plot of relaxation times θ (○) and ρ (△) *versus* viscosity (polystyrene PS–A–PS)

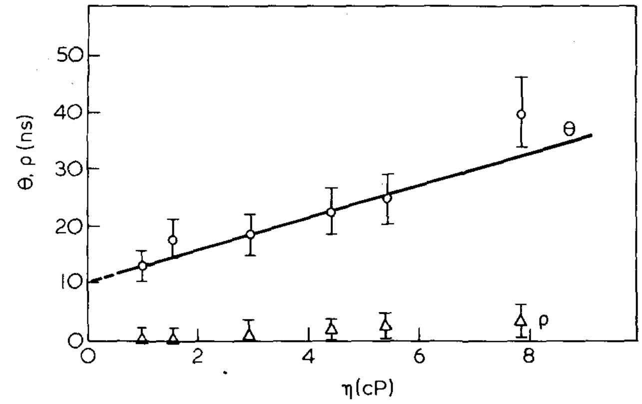

Figure 4 Plot of relaxation times θ (○) and ρ (△) *versus* viscosity (polystyrene A–PS–A)

The constant a is the part of the orientation loss which is independent of the viscosity. It may be interpreted as deviations of valence angles and internal rotation angles from the ideal values that they would have in the case of motions within a tetrahedral lattice in which no loss of orientation can occur. Thus, the constant a appears to be an intrinsic constant depending solely on the chemical structure of the chain. The fact that a has about the same value for both samples (see extrapolation of $\theta(\eta)$ curves in *Figures 3* and *4*) is consistent with this interpretation.

The constant b reflects the influence of viscosity on large-scale isotropic motions or on the fluctuations of *trans* or *gauche* positions around equilibrium.

Although the determination of ρ is less accurate, *Figure 3* clearly reveals nonlinear variations as a function of viscosity for PS–A–PS polystyrene. At viscosities greater than 4 cP, the values of ρ seem to reach a plateau. Similar behaviour has been also observed in n.m.r. relaxation experiments performed with polystyrene in the same mixtures of solvents[15]. Magee's theory[16] for small molecules might help in the interpretation of this behaviour: at high viscosities, the influence of the viscosity on rotation vanishes when these rotations mainly occur within the solvation shell.

Finally, it is worth noting that viscosity influences the end-bond motions to a smaller extent than the internal motions as shown by *Figures 2*, *3* and *4*.

Comparison with e.s.r. experiments

Fluorescence decay curves were also recorded at 30°C using α-chloronaphthalene as a solvent in order to compare our results with those of Bullock *et al.*[2] The values of the characteristic times (i.e. the correlation time τ_c for e.s.r., assuming isotropic rotations, and the mean relaxation time $\langle\sigma\rangle$ for fluorescence polarization) are reported in *Table 3* for comparison.

The difference in end and internal mobility appears to be about the same in both techniques. The slightly smaller difference observed in Bullock's experiments can be explained by the fact that a label attached to the side of the chain is more mobile than a label inserted in the chain[7]. We can conclude from the consistency between the two techniques that the motions of an internal bond of a polystyrene chain is about four times slower than those of the end bonds.

Table 3 Comparison of fluorescence polarization and e.s.r. results for polystyrene in α-chloronaphthalene solution at 30°C

Technique	Reference	Labelling site	Correlation time (ns)
Fluorescence Polarization	This work	in-chain	$\langle\sigma\rangle = 9.6$
		end-chain	$\langle\sigma\rangle = 2.3$
E.s.r.	2	side-chain	$\tau_C = 3.81$
		end-chain	$\tau_C = 1.06$

On the other hand, the discrepancy between the absolute values of the characteristic times of the two techniques should be noted. This discrepancy is even larger for solutions in toluene ($\langle\sigma\rangle = 2.3$ ns, $\tau_c = 0.24$ ns, at 36°C). A detailed comparison between the information given by fluorescence polarization and e.s.r. is difficult because the characteristic frequency of e.s.r. is larger; thus, the phenomena that are actually observed occur at shorter times than in fluorescence polarization. In addition the principles of e.s.r. lead us to think that this technique reflects more local motions.

CONCLUSION

Analysis of chain relaxation by the fluorescence anisotropy decay technique confirms that the rotational motions of the end bonds of a polystyrene chain are four times faster than those of the internal bonds, as previously observed by stationary experiments. The fluorescence decay technique provides further information thanks to the determination of the correlation times θ and ρ. Comparison between internal-bond and end-bond relaxations is in good agreement with e.s.r. experiments despite the shorter absolute values of correlation times observed by this technique.

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