Stationary fluorescence depolarization study of mobility of rigid probes in bulk elastomers: Motion of dimethylanthracene and three *trans*-diphenylpolyenes inserted in polyisoprene, polybutadiene and random butadiene–styrene copolymers

J. P. Queslel, J. P. Jarry* and L. Monnerie

Laboratoire de Physicochimie Structurale et Macromoléculaire 10, rue Vauquelin 75231 Paris Cedex 05

Fluorescence depolarization is used to investigate the motions of four rigid probes of different sizes, 9,10-dimethylanthracene (DMA), 1,4-diphenylbutadiene (DPBD), 1,6-diphenylhexatriene (DPHT), and 1,8-diphenyloctatetraene (DPOT) inserted in a polyisoprene (IR 307), two polybutadienes (Diene 45 NF and Solprene 248) and three random butadiene-styrene copolymer matrices. Fluorescence anisotropy decay experiments have revealed that these motions follow the isotropic motional model. The correlation times were calculated, using this model, from stationary fluorescence depolarization measurements as a function of temperature. Large probes are shown to reflect the glass–rubber relaxation in agreement with the WLF law. The size dependence of the probe correlation times is also analysed.

(Keywords: fluorescence depolarization; chain dynamics; elastomers; polyisoprene; polybutadiene)

INTRODUCTION

The macroscopic properties of polymers result in part from the extent of motions which occur at the molecular level. The determination of the nature of these motions and the evolution of their characteristic times with temperature are therefore of some interest. Segmental motions of chains are associated with the glass–rubber transition, T_g. It has been established, mainly by dynamic mechanical experiments at low frequency[1], that their correlation times follow the time–temperature superposition principle known as WLF law. Many questions concerning the molecular mechanisms which govern this transition still exist.

The secondary transitions T_β, T_γ are normally attributable to motion of short segments of the chain backbone or to motion of substituent groups[2-7]. Their study is relatively difficult since they occur at rather low temperatures for the polymers which we are concerned with in this paper and which are in the rubbery state at room temperature. High frequency relaxation techniques such as fluorescence depolarization[8] and electron spin resonance[9] (e.s.r.) allow us to investigate chain dynamics generally through probe molecules of differing size whose motions are affected by matrix mobility. The experimental frequency window of the fluorescence technique is determined by the fluorescence lifetime of the probe, in the range 10^7–10^{10} Hz. Jarry and Monnerie have reported on a study of the glass–rubber transition in a bulk polyisoprene (IR 307) using either a fluorescent label inserted in the chain backbone or rigid probes inserted in the polymeric matrix[10]. It was shown that label and large probes reflect the glass–rubber relaxation in agreement with the WLF law and the nature and size of the segmental chain motions were subsequently analysed.

In the present paper, we have investigated the glass–rubber relaxation of polymers of different microstructure, namely a polyisoprene, two polybutadienes, and three random butadiene–styrene copolymers, through the mobilities of four rigid fluorescent probes, namely 9,10-dimethylanthracene (DMA), 1,4-diphenylbutadiene (DPBD), 1,6-diphenylanthracene (DPHT), and 1,8-diphenyloctatetraene (DPOT)[11].

Fluorescence depolarization technique

The rotational Brownian motion of a fluorescent molecule in an isotropic medium can be described by using the orientational autocorrelation function $M(t)$ defined by the following expression:

$$M(t) = \langle (3\cos^2 \theta(t) - 1)/2 \rangle \qquad (1)$$

where $\theta(t)$ is the angle through which the emission transition moment of the fluorescent molecule rotates between time zero and time t. The brackets indicate an average over all fluorescent molecules.

In a time-dependent fluorescence polarization experiment, the sample is excited by a short-duration pulse of vertically polarized light and the fluorescence is recorded in the horizontal plane at right angles to the direction of excitation. The $I_\parallel$ and $I_\perp$ components, respectively parallel and perpendicular to the electric

vector of the incident wave, are recorded as function of time.

It is thus possible to follow the decay of the emission anisotropy, as previously defined[12-14]

$$r(t) = [I_\parallel(t) - I_\perp(t)]/[I_\parallel(t) + 2I_\perp(t)] \tag{2}$$

The quantity $I_\parallel(t) + 2I_\perp(t)$ represents the total intensity $I(t)$ of fluorescence decay law which is generally exponential:

$$I(t) = I_0 e^{-t/\tau} \tag{3}$$

where τ is the lifetime of the fluorophore.

The time dependence of $r(t)$ reflects the motions modifying the orientation of the transition moments between the time of absorption ($t=0$) and the instant t corresponding to the time of emission. The initial value of the emission anisotropy r_0, called the fundamental anisotropy, depends on the angle α between the absorption and emission transition moments[15]

$$r_0 = (3\cos^2\alpha - 1)/5 \tag{4}$$

The emission anisotropy is directly related to the autocorrelation function defined in equation (1).

$$r(t) = r_0 M(t) \tag{5}$$

Fluorescent polarization measurements under continuous excitation[16] yield the mean anisotropy $\bar{r}$

$$\bar{r} = (r_0/\tau) \int_0^\infty M(t) \exp(-t/\tau) \mathrm{d}t$$
$$= (r_0/\tau)\bar{M}(\tau) \tag{6}$$

where $\bar{M}(\tau)$ is the mean autocorrelation function.

Experimentally $M(T)$ is calculated through equation (6) from the mean anisotropy $\bar{r}(T)$ and the fluorescence lifetime $\tau(T)$ measured as function of temperature T.

The results are represented in terms of the mobility parameter m

$$m = \bar{M}^{-1} - 1 \tag{7}$$

which increases from zero (molecular relaxation times much larger than the fluorescence lifetime) to infinity (relaxation times much smaller than the lifetime).

More quantitative information can be obtained from m by using a model of Brownian rotational motion to derive the correlation times of the molecular movements. The well-known isotropic model for a spherical body yields a monoexponential autocorrelation function.

$$M(t) = \exp(-t/\tau_{is}) \tag{8}$$

where τ_{is} is a unique isotropic correlation time which can be simply calculated through the following equation

$$\log \tau_{is}(T) = \log \tau(T) - \log m(T) \tag{9}$$

More specific models of chain dynamics exist[17-20] and they are suitable for the analysis of dynamics of fluorescent labelled chains in the melt[21-23].

To determine if the fluorescent probe mobilities are influenced by the glass–rubber transition of the polymeric matrix, we have compared the evolution of their correlation times with temperature with the predictions of the WLF law[1]

$$\log a_T = \log \tau_{is} + \text{constant} \tag{10}$$

$$\log a_T = -16(T - T_g)/(57 + T - T_g) \tag{11}$$

where T_g is the value of the glass–rubber transition temperature determined by d.s.c.

The fluorescence decay and stationary fluorescence depolarization apparatus are described elsewhere[24,25].

Materials

Polymers. The commercially available polymers, a polyisoprene (Shell IR 307), two polybutadienes (Firestone Diene 45 NF and Phillips Solprene 248), and three random butadiene–styrene copolymers (Phillips Solprene 1204, Firestone Stereon 704 and 705) were generously provided by Manufacture Française des Pneumatiques Michelin. Microstructure, styrene content, glass–rubber transition temperature, weight-average molecular weight and polydispersity of these polymers are reported in *Table 1*.

Samples were moulded and crosslinked with dicumyl peroxide. Crosslinking densities obtained by adjusting curing time and temperature were characterized by the average molecular weight M_c of network chains (between adjacent junctions) derived from measurements of the equilibrium swelling ratio in cyclohexane and through the classical Flory–Rehner equation[26,27]. Values of M_c are $2 \times 10^4, 5 \times 10^4, 12 \times 10^4, 3 \times 10^4, 7.5 \times 10^4, 21 \times 10^4$ for IR 307, Diene 45 NF, Solprene 248, Solprene 1204, Stereon

Table 1 Characteristics of polymers

Polymer designation	Microstructure of PI or PB phase			Styrene content w/w	$T_g{}^a$ (°C)	$M_w{}^b$ (g mol^{-1})	$M_w/M_n{}^b$
	% *cis*	% *trans*	% 1–2				
PI IR 307	92	5	3		−60	1 820 000	3.9
PB Diene 45 NF	37	51	12		−90	410 000	2.4
PB Solprene 248^c	37	51	12		−90	430 000	3.3
SBR Solprene 1204	24	43	33	27	−48	410 000	2.4
SBR Stereon 704	35	55	10	19	−72	300 000	2.0
SBR Stereon 705	33	57	10	26	−64	300 000	2.1

^{a} Determined by d.s.c
^{b} Measured by g.p.c. with reference to polystyrene standards
^{c} Binodal molecular weight distribution centred about 5×10^4 and 3×10^5 g mol^{-1}

704 and 705 samples respectively. After crosslinking, polymer sheets (2.4 mm thick) were carefully extracted with acetone for 15 h and then dried *in vacuo*.

The dynamic mechanical properties of the different polymers, namely the loss factor tan δ, were determined at low frequency (3.5 Hz) as a function of temperature from $-120°C$ up to 50°C in extension by using a Rheovibron viscoelastometer (Toyo Baldwin Co Ltd). Samples (0.5 mm thick) were kept in a nitrogen flow. Data are plotted in *Figure 1*. The peak occurring at around $-20°C$ for Solprene 248 could be attributed to the terminal zone loss of the fraction of chains of low molecular weight contained in this polymer.

Fluorescent probes. Four probes of ranging size were employed: 9,10-dimethylanthracene (DMA) and three *trans*-diphenyl-polyenes (DP). Their formulae and transition moments are shown in *Table 2*. Crosslinked polymers were swollen with solutions of the probes in benzene and then dried *in vacuo*. The final probe concentration in bulk samples was approximately 2×10^{-5} M.

Fluorescent labels. Polymer chains containing a dimethylanthracene (DMA) fluorescent group in their middle were prepared through monofunctional anionic chains deactivated with 9,10-bis(bromomethyl) anthracene[24]. For each type of polymer, the samples were obtained by mixing 1% of the labelled chain with 99% of the normal polymer.

RESULTS AND DISCUSSION

Fluorescence lifetimes

Fluorescence lifetimes at 20°C were determined by time-dependent fluorescence polarization experiments for the four probes inserted in the six polymeric matrices. The
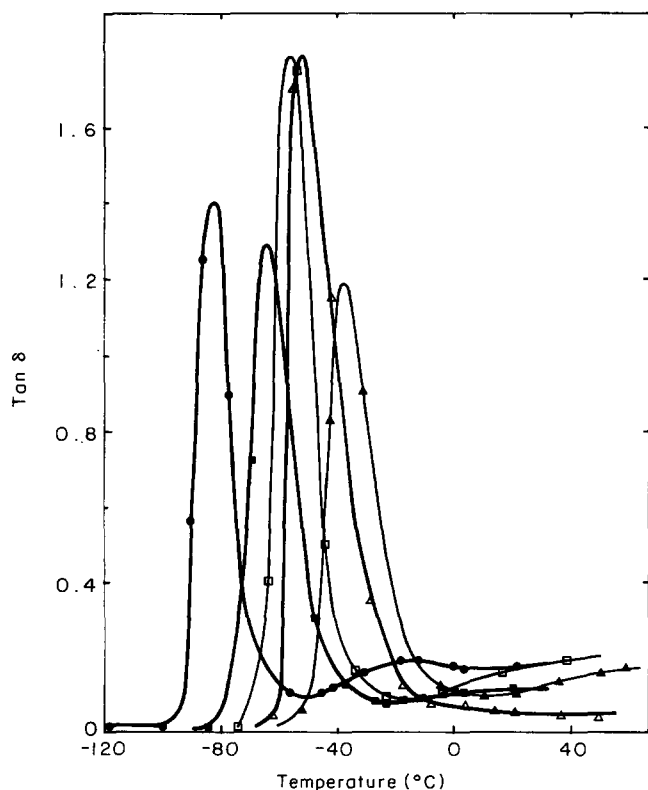
Figure 1 Dynamic loss tangent *versus* temperature for IR 307 (△), Solprene 248 (●), Solprene 1204 (▲), Stereon 704 (■), Stereon 705 (□)

Table 2 Formulae, approximate lengths (Å), and transition moments (double arrows) of the probes DMA, DPBD, DPHT and DPOT[a]

DMA 6.5 Å	
DPBD 11.5 Å	
DPHT 14 Å	
DPOT 16.5 Å	

[a] DMA, 9,10-dimethylanthracene; DPBD, 1,4-diphenylbutadiene; DPHT, 1,6-diphenylhexatriene; DPOT, 1,8-diphenyloctatetraene

decays of total intensities were found to be monoexponential as described by equation (3). Their curves were analysed by the modulating function method[28,29].

Fluorescence lifetime values at 20°C are presented in *Table 3*. They are approximately independent of the nature of the polymeric matrix.

The total intensity under continuous excitation is proportional to the fluorescence lifetime, which can be shown by integration with respect to time of equation (3). From the determination of the fluorescent lifetimes at 20°C by decay experiments and from the measurements of the total intensity at different temperatures by stationary experiments, it is therefore possible to obtain the values of fluorescence lifetime over a wide range of temperature. Typical curves are presented in *Figure 2* for the four probes inserted in Diene 45 NF. Logarithms (10 as a base) of τ (in nanoseconds) are plotted with respect to $T - T_g$, T_g having been determined by d.s.c. and, as expected, τ decreases with increasing temperature.

Mobility parameter m

Calculation of m from the measured mean anisotropy $\bar{r}$, through equations (6) and (7), implies some knowledge of the fundamental anisotropy r_0 at the temperature of the measurements. Such a requirement leads to some difficulty, for the fluorescence polarization technique under continuous excitation does not yield the r_0 determination in the temperature range where the probes undergo a motion during their fluorescence lifetime. However, at temperatures low enough to freeze the probe motion, this technique allows one to measure r_0. Values of r_0 obtained at $-60°C$ for DPBD, DPHT and DPOT in the various matrices are reported in *Table 4*. In the case of the DMA probe, the situation is different because the probe motion is not completely frozen at $-60°C$, whereas for polymer chains covalently labelled with DMA, the motion of the label is frozen at $-60°C$. For this reason, the

Table 3 Lifetimes, τ, at 20°C. Values in nanoseconds

Polymers	DMA	DPBD	DPHT	DPOT
IR 307	10.1	3.6	6.8	6.2
Diene 45 NF	10.1	2.7	6.4	6.1
Solprene 248	10.2	3.8	6.5	6.1
Solprene 1204	10.1	3	6.1	6.3
Stereon 704	10.2	3.5	6	6.2
Stereon 705	10.1	2.6	5.9	6.2
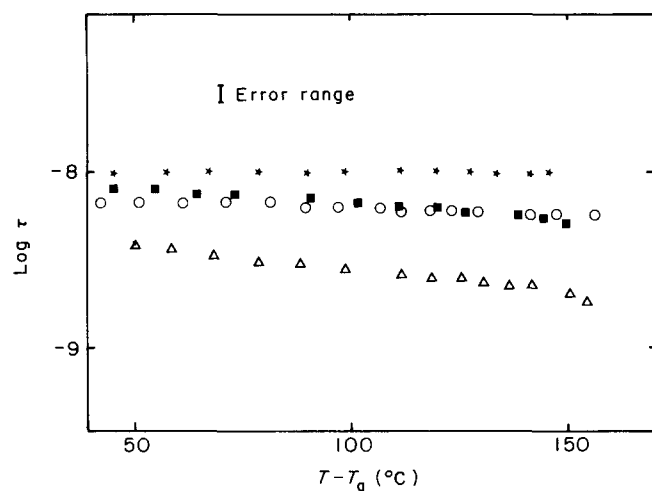
Figure 2 Logarithmic plot of lifetime τ versus temperature for the four probes inserted in Polybutadiene Diene 45 NF: DMA (★), DPBD (△), DPHT (■), DPOT (○)

Table 4 Values of the limit anisotropies r_0

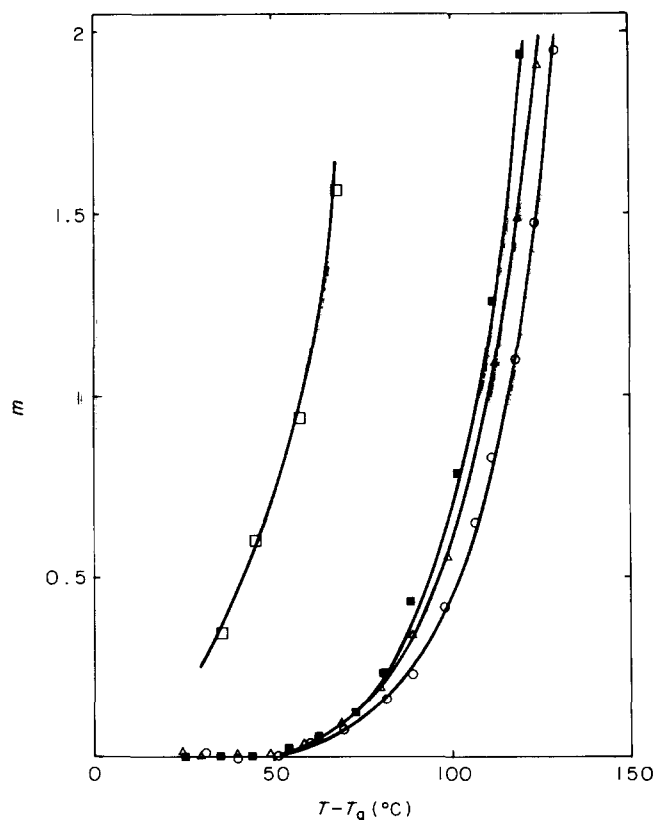| Polymers	DMA	DPBD	DPHT	DPOT
IR 307	0.24	0.31	0.32	0.32
Diene 45 NF	0.21	0.32	0.33	0.34
Solprene 248	0.20	0.31	0.32	0.33
Solprene 1204	0.22	0.28	0.32	0.32
Stereon 704	0.22	0.29	0.34	0.35
Stereon 705	0.23	0.29	0.34	0.37

r_0 value for DMA in a given matrix has been chosen to be equal to that of the corresponding DMA-labelled polymer. These values are given in *Table 4*. Furthermore, it has previously been shown by the fluorescence anisotropy decay technique[10] that r_0 values of DPBD, DPHT, DPOT probes in IR 307, as well as that of DMA-labelled polyisoprene are constant in the temperature range considered here. We assume that such a constancy of r_0 is also valid for the other elastomer matrices under investigation and thus the values of r_0 given in *Table 4* have been used to calculate m from $\bar{r}$.

Typical plots of the mobility parameter m versus reduced temperature $T - T_g$ for Diene 45 NF are shown in *Figure 3*. The behaviour of the three DP probes is quite different from that of DMA. The rotational mobility of the DP probes appears to reflect the glass–rubber relaxation. The onset of mobility occurs at about $T - T_g = 50°C$. This shift of T_g value illustrates the time–temperature superposition principle[1]: the higher the frequency of the experimental technique the higher the temperature at which the transition is observed. The smaller DMA probe exhibits a higher mobility which vanishes only well below $T_g + 50°C$. As previously reported for fluorescent and spin probes[9,10,30], the dynamic behaviour of a guest molecule depends on its relative size compared with that of the

moving polymer segments involved in the glass–rubber relaxation. If the probe is larger than a critical size, its mobility is modulated by the same free volume fluctuations as the polymer segments, and it reflects the glass–rubber transition. Probes smaller than the critical size start to move below T_g and their mobility may be related to secondary transitions.
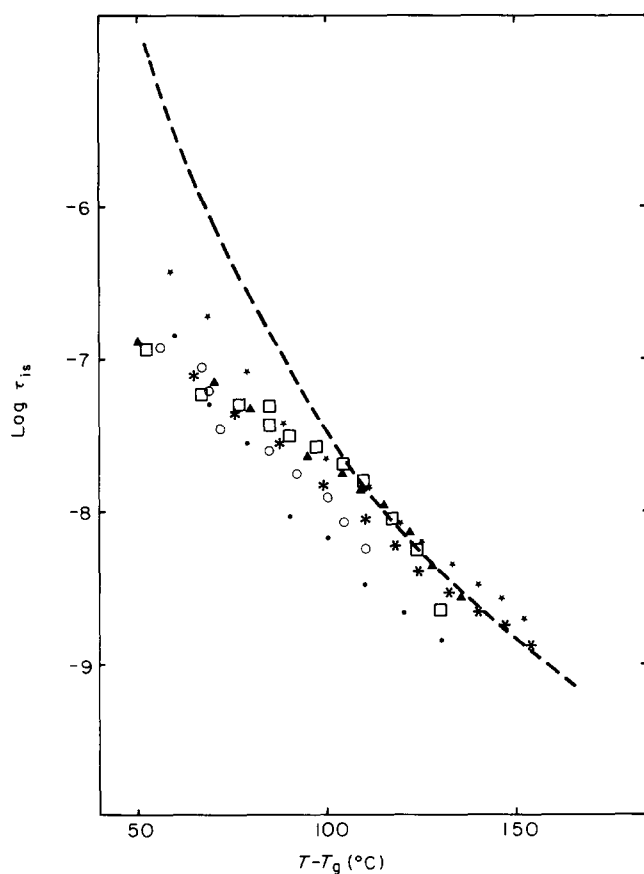
Correlation times

For the four probes, fluorescence anisotropy decay experiments at room temperature show that $M(t)$ is monoexponential and that an isotropic motional model is valid. These behaviours are in agreement with those reported previously[10,14]. The correlation times τ_{is} can therefore be calculated from equation (9) as a function of temperature. The evolution of the correlation times for the four probes in Diene 45 NF are shown in *Figure 4*. The conclusion already reached in view of the mobility curves still holds. The DMA probe behaviour differs markedly from that of the other probes. As expected from size considerations, the DMA correlation times are smaller. This particular behaviour is confirmed when the DMA probe is inserted in the five other matrices, as shown in *Figure 5*. The use of reduced temperature $T - T_g$ (d.s.c.) has the advantage of suppressing the difference in T_g of the polymeric matrices. In this frame of coordinates, the WLF law (equation (11)) is represented by a unique curve which can be directly compared with the evolution of the correlation times (equation (10)). The constant in equation (10) is adjusted to have $\log a_T$ values in the vicinity of $\log \tau_{is}$ at high temperatures. It is clear that the small DMA probe does not follow the WLF law represented by the broken line in *Figure 5*. Indeed, it has been shown that the DMA probe experiences an in-plane

Figure 3 Mobility parameter m versus temperature for the four probes in Diene 45 NF: DMA (□), DPBD (△), DPHT (■), DPOT (○)
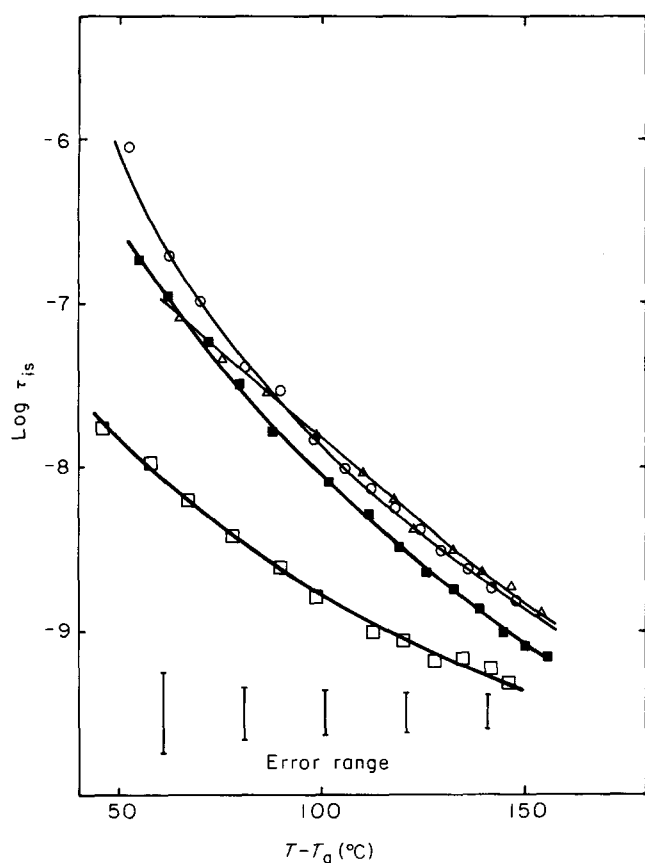
Figure 4 Logarithmic plot of correlation time τ_{is} *versus* reduced temperature $T - T_g$ d.s.c. for the four probes: DMA ($\square$), DPBD ($\triangle$), DPHT ($\blacksquare$), DPOT ($\bigcirc$), in Diene 45 NF

Figure 5 Logarithmic plot of correlation time τ_{is} *versus* reduced temperature $T - T_g$ for DMA probe inserted in IR 307 ($\bullet$), Diene 45 NF (*), Solprene 248 ($\bigstar$), Solprene 1204 ($\bigcirc$), Stereon 704 ($\blacktriangle$), Stereon 705 ($\square$). The broken line represents the WLF law (equation (11))

rotation in this temperature range[22]. Secondary transitions may influence the mobility of this probe. The correlation times associated with secondary transitions have an Arrhenius dependence with temperature[9], and it has been checked that the logarithm of τ_{is} (e as a base) *versus* the inverse of temperature has a linear behaviour. The activation energies of DMA motion in the various matrices are reported in *Table 5*. It was not possible to find the activation energies of these secondary transitions in the literature to compare with our values. However values of 6 Kcal mol^{-1} are consistent with what could be expected for short range motions. Morgan *et al.*[7] have investigated the secondary transitions of polyisoprene, polybutadiene and butadiene–styrene copolymer of different microstructure by dynamic mechanical measurements at 20 Hz. The temperatures determined by extrapolation of the curves log τ_{is} *versus* T at 20 Hz have been compared in *Table 5* with the loss factor maxima reported by these authors. Good agreement is reached, when one considers the difficulty of performing mechanical measurements at such low temperatures. It can be therefore concluded that the DMA probe reflects the motions involved in the secondary transition of the polymers investigated. These motions may be attributable to styrene lateral groups and also to short segments of the chain backbone[7].

The logarithms of correlation time *versus* temperature are plotted in *Figures 6, 7* and *8* for the DPBD, DPHT and DPOT probes respectively, inserted in the six polymers and compared with predictions of the WLF law (broken line).

Taking into account the error range (represented in *Figure 4*), it seems that the absolute values of the correlation times are rather insensitive to the nature of the polymeric matrix as only slight differences are evident. The behaviour at high reduced temperatures is in good agreement with WLF law. It can therefore be concluded that these large probes reflect the glass–rubber relaxation. A discrepancy which occurs at the low reduced temperature may signify that the probes begin to be slightly sensitive to secondary transitions.

The relaxtion times of the DP probes correspond to the rotation of their symmetry axis about a direction

Table 5 Characterization of secondary transitions by fluorescence depolarization of DMA probe compared with mechanical measurement data. E_a are the activation energies of DMA motions

	Fluorescence depolarization		Mechanical measurements at 20 Hz
Polymers	E_a (kcal mol^{-1})	T (K) extrapolated	T (K) maxima of tan δ
IR 307	8.2	135	
Cis PI[a]			100, 130
Trans PI[a]			155
Diene 45 NF	5.5	100	
Solprene 248	6.2	110	
Cis/trans/vinyl PB[a]			85, 130
Cis PB[a]			145
Trans PB[a]			90, 130
Solprene 1204	6.4	120	
Stereon 704	5.2	100	
Stereon 705	6.0	115	
SBR[a]			85, 125

[a]From ref. 7
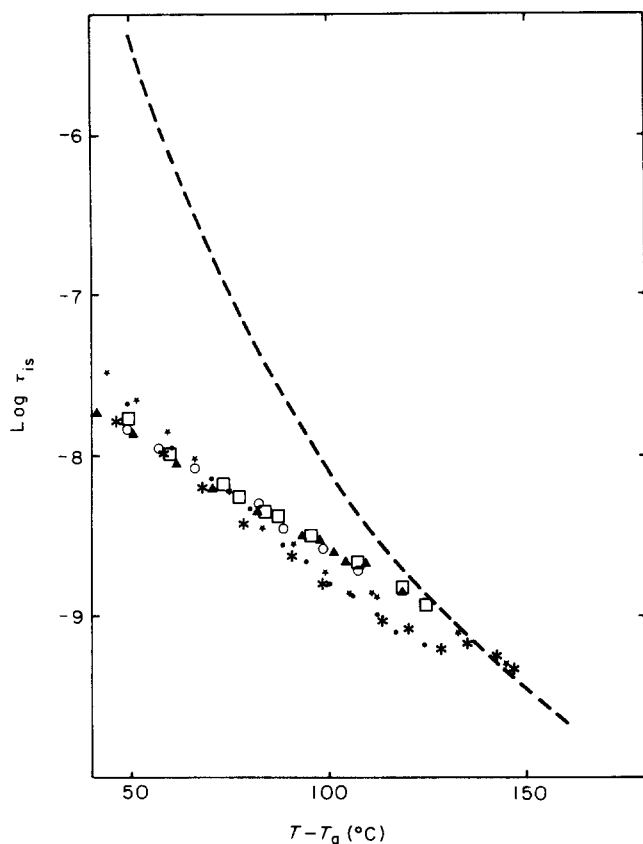
Figure 6 Logarithmic plot of correlation time τ_{is} *versus* reduced temperature for DPBD probe inserted in the six polymeric matrices. Same symbols as in *Figure 5*
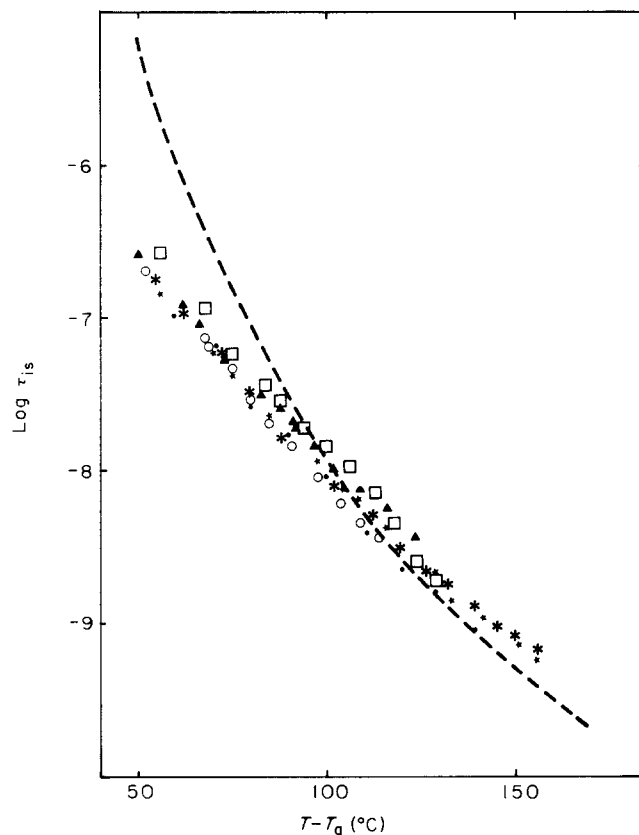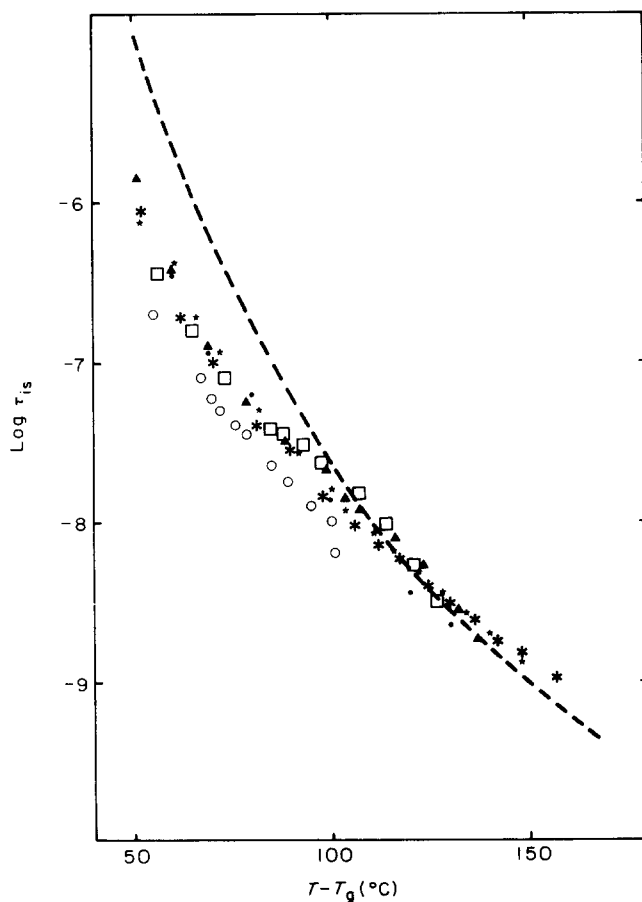

Figure 7 Logarithmic plot of correlation time τ_{is} *versus* reduced temperature for DPHT inserted in the six polymeric matrices. Same symbols as in *Figure 5*

perpendicular to it, since their absorption and transition moments lie along this axis. Besides, Jarry and Monnerie[10] have shown that the Perrin theory[31] for prolate ellipsoids accounts for both size and temperature effects on the correlation times of the DP probes in IR 307. This theory relates the correlation time of an ellipsoid probe with its main axes a and b ($b < a$) and the local viscosity $\eta(T)$ which describes the local friction acting on the probe molecule by the following expression:

$$\tau_{is} = 8\pi\eta a^3 (9kT\{2\log(2a/b) - 1\})^{-1} \qquad (12)$$

k is the Boltzmann constant and a reasonable value of b for DP probes was found equal to 2.5 Å. Thus by using this expression it is possible to calculate what would be the length of a DP probe, the relaxation time of which has a given value in environmental conditions defined by T and η. Such a calculation can be used to estimate how many monomers are involved in the motions observed through fluorescence polarization of the DMA labels.

A more complete study of the mobility of labelled chains of the different polymers characterized in *Table 1* will be presented in a subsequent paper[32]. However, the relaxation times ρ of the DMA-labelled polymers, measured at ($T_g + 100°C$) are reported in *Table 6* as well as those of the DP probes in the same conditions. For the labelled polymers, the relaxation time ρ has been calculated assuming the model of orientational diffusion along the chain backbone[17] which describes the segmental dynamics of a polymer chain. The length a_s of an 'equivalent DP probe' which would have, in these conditions, a correlation time τ_{is} equal to ρ is given for

Figure 8 Logarithmic plot of correlation time τ_{is} *versus* reduced temperature for DPOT inserted in the six polymeric matrices. Symbols as in *Figure 5*

Table 6 Correlation times of free probes and labels at $(T_g + 100°C)$, length a_s of 'equivalent DP probes' and number, n, of monomer units involved in the label motion

	DPBD $a = 11.5$ Å	DPHT $a = 14$ Å	DPOT $a = 16.5$ Å	DMA label		
	τ_{is} (ns)	τ_{is} (ns)	τ_{is} (ns)	ρ (ns)	a_s (Å)	n
IR 307	6	8	13	7	13	3
Diene 45 NF	14	10	15	44	25	5.5
Solprene 248	21	10	15	37	24	5
Solprene 1204	11	8	9	33	26	7
Stereon 704	20	12	19	214	42	10
Stereon 705	23	14	19	123	33	8

each polymer in *Table 6*. From a_s and the average dimension of a monomer unit, it is possible to estimate the number, n, of monomer units involved in the motion investigated through the DMA label. The corresponding n values are reported in *Table 6*. They gradually increase from polyisoprene to SBR. There is no relationship between n and the glass transition temperature of the polymer. However n values are higher for SBR compounds than for pure diene polymers, and may be due to the steric intramolecular constraints arising from the aromatic side groups.

CONCLUSION

The stationary fluorescence depolarization technique was used to investigate the glass–rubber transitions of six crosslinked polymers: a polyisoprene, two poly-butadienes and three random butadiene–styrene copolymers. Four probes were used in this study. Their motions appear to be isotropic. It was shown that the smallest probe, DMA, is mainly sensitive to secondary relaxations. The larger probes, DPBD, DPHT and DPOT, exhibit correlation times which evolve with temperature and follow the WLF law. It was therefore concluded that the mobility of these probes reflects the glass–rubber transition. By making use of the Perrin formula for ellipsoids and making comparisons with the correlation times of DMA-labelled chains, the number of monomer units involved in the motion of the label has been estimated for each polymer.

REFERENCES

1   Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn., Wiley, New York, 1970
2   McIntyre, A. D. *J. Appl. Polym. Sci.* 1961, **5**, 195
3   Baccaredda, M. and Butta, E. *J. Polym. Sci.* 1961, **51**, 539
4   Gupta, R. E. *J. Phys. Chem.* 1962, **66**, 1
5   Angelo, R. J., Ikedo, R. M. and Wallach, M. L. *Polymer* 1965, **6**, 141
6   Kraus, G., Childers, C. W. and Gruver, J. T. *J. Appl. Polym. Sci.* 1967, **11**, 1581
7   Morgan, R. J., Nielsen, L. E. and Buchdahl, R. *J. Appl. Phys.* 1971, **32**, 4653
8   Monnerie, L. and Jarry, J. P. *Ann. New York Acad. Sci.* 1981, **366**, 328
9   Tormala, P. *J. Makromol. Sci. Rev., Makromol. Chem.* 1979, C17, 297
10   Jarry, J. P. and Monnerie, L. *Macromolecules* 1979, **12**, 927
11   Queslel, J. P. *Thesis*, Université Paris VI, 1982
12   Jablonsky, A. Z. *Naturforsch.* 1961, A16, 1
13   Gordon, R. G. *J. Chem. Phys.* 1966, **45**, 1643
14   Tao, T. *Biopolymers* 1969, **8**, 609
15   Perrin, F. *J. Phys. Rad.* 1926, **7**, 390; *Ann. Phys.* 1929, **12**, 169
16   Perrin, F. *Ann. Phys.* 1929, **12**, 769
17   Valeur, B., Jarry, J. P., Geny, F. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 667, 675
18   Jones, A. A. and Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **15**, 847
19   Bendler, J. J. and Yaris, R. *Macromolecules* 1978, **11**, 650
20   Hall, C. K. and Helfand, E. *J. Chem. Phys.* 1982, **77**, 3275
21   Jarry, J. P. *Thesis*, Université Paris VI, 1978
22   Viovy, J. L. *Thesis*, Université Paris VI, 1983
23   Viovy, J. L., Monnerie, L. and Brochon, J. C. *Macromolecules* 1983, **16**, 1845
24   Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 11
25   Jarry, J. P., Sergot, P., Pambrun, C. and Monnerie, L. *J. Phys. E.* 1978, **11**, 702
26   Flory, P. J. and Rehner, J. *J. Chem. Phys.* 1943, **11**, 512
27   Flory, P. J. *Chem. Rev.* 1944, **35**, 51
28   Valeur, B. and Moirez, J. *J. Chem. Phys.* 1973, **70**, 500
29   Valeur, B. *Chem. Phys.* 1978, **30**, 85
30   Kumler, P. L. and Boyer, R. F. *Macromolecules* 1976, **9**, 903
31   Perrin, F. *J. Phys. Rad.* 1934, **5**, 497
32   Paper in preparation