Studies of the mobility of probes in poly(propylene oxide): 1. Fluorescence anisotropy decay

Mamadou Fofana, Valerie Veissier, Jean Louis Viovy and Lucien Monnerie
Laboratoire de Physico-Chimie Structurale et Macromoléculaire, (LA CNRS 278), ESPCI, 10 rue Vauquelin, 75231 Paris Cedex 05, France

and G. P. Johari
Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada
(Received 22 June 1987; accepted 17 August 1987)

The fluorescence anisotropy decay of a rodlike probe, diphenylhexatriene (DPH), dissolved in 1,2-propanediol and in poly(propylene oxide) matrices with molecular weights 425 and 4000, is studied using the single-photon-counting technique and synchrotron radiation as the exciting source. The monomolecular reorientation correlation times are compared with previous light-scattering results. It is shown that combining these two techniques, which explore complementary time ranges, the shift factor and WLF parameters for molecular relaxation can be obtained without any further assumptions. The results are in agreement with those obtained from viscoelastic data. The validity of studies related to the glass transition and viscoelastic slowdown on a molecular level is confirmed, and the 'free-volume' unit for motions frozen during the glass transition is evaluated as $\simeq 2500$ Å^3. The very different behaviours of the monomer and polymer samples suggest that intramolecular (conformational) constraints lead to a much more 'catastrophic' coupling of motions than intermolecular ones.

(Keywords: glass transition; poly(propylene oxide); 1,2-propane diol; fluorescence anisotropy; free volume)

INTRODUCTION

In spite of numerous theoretical and experimental studies, the glass transition remains a rather poorly understood phenomenon on the molecular level[1]. The classical theories can be schematically separated into free-volume theories[2], applicable to any type of material, and entropic theories[3], more specifically designed for polymer glasses. This old problem now attracts renewed interest, as indicated by original approaches based on the thermodynamics of irreversible processes and the Mori formalism[4]. From the experimental point of view, this interest is expressed by a development of investigations on the molecular level, thanks to spectroscopic techniques. In this series of articles, we present experimental studies of local dynamics in 1,2-propanediol (PD) (monomer) and two polymers of this molecule, poly(propylene oxide) (PPO), with molecular weights 425 and 4000. These polymers have been intensively studied using different experimental techniques such as light scattering[5-8], Kerr effect[9], dielectric relaxation[10,11] and photon correlation spectroscopy[12]. In the present paper, we use the anisotropy of the fluorescence emitted by a rigid probe (1,6-diphenyl-1,3,5-hexatriene (DPH)) embedded in the monomer or polymer matrix to sample the molecular dynamics. This probe technique, which is more indirect, has the advantage of introducing an external size scale into the system.

EXPERIMENTAL

Samples

The fluorescent probe was scintillator-grade DPH (EGA). Optical densities below 0.1 at the maximum of the absorption peak for 10 mm optical-path cells were used to avoid energy transfer. 1,2-Propanediol was obtained from Prolabo and two samples of PPO, with molecular weights 425 and 4000, were purchased from Aldrich-Chemie. All samples were purified on active carbon until negligible residual fluorescence was observed in the experimental conditions used.

Apparatus

The experiments were performed using the cyclosynchrotron LURE-ACO (Orsay, France) as the exciting source. The excitation wavelength (378 nm) was selected using a double holographic grating, and the emission wavelength (448 nm) was selected using an interferential filter and/or a holographic grating, leading to essentially identical results. The polarized decays were recorded using classical single-proton electronics. (For a more detailed description of the experimental set-up, and of the sample handling, please refer to refs. 13–15.) The data were analysed at the CNRS 'CIRCE' computing centre, using a non-linear least-squares iterative algorithm[14,15].

0032-3861/88/020245-06$03.00
© 1988 Butterworth & Co. (Publishers) Ltd.

Table 1 Total intensity decay of PPO425: two-exponential fit

T (K)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ^2	$z_2\tau_2/(a_1\tau_1+a_2\tau_2)$
320.8	0.681×10^{-1}	6.91	0.188×10^{-1}	1.22	4.55	0.046
308.4	0.608×10^{-1}	7.54	0.178×10^{-1}	3.67	7.65	0.125
293.7	0.817×10^{-1}	7.68	0.243×10^{-1}	2.58	3.92	0.093
281.4	0.778×10^{-1}	7.74	0.130×10^{-1}	2.60	10.27	0.053
269.5	0.869×10^{-1}	7.82	0.147×10^{-1}	3.61	7.48	0.072
252.0	0.940×10^{-1}	8.32	0.339×10^{-1}	4.74	5.69	0.170

Table 2 Total intensity decay of PPO4000: two-exponential fit

T (K)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ^2	$a_2\tau_2/(a_1\tau_1+a_2\tau_2)$
320.8	0.793×10^{-1}	8.08	0.155×10^{-1}	1.67	4.82	0.039
308.4	0.828×10^{-1}	8.20	0.151×10^{-1}	2.21	6.45	0.047
293.1	0.864×10^{-1}	8.18	0.263×10^{-1}	1.75	6.05	0.061
283.3	0.909×10^{-1}	8.07	0.141×10^{-1}	0.182	11.80	0.0035
267.7	0.107×10^{0}	8.21	0.144×10^{-1}	3.93	7.46	0.060
253.0	0.101×10^{0}	8.56	0.294×10^{-1}	4.15	6.59	0.124

Table 3 Total intensity decay of PD: two-exponential fit

T (K)	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ^2	$a_2\tau_2/(a_1\tau_1+a_2\tau_2)$
308.3	0.249	3.57	0.124	0.301	34.06	0.040
292.2	0.736	4.23	0.264	0.655	10.32	0.053
282.5	0.365	5.59	0.201×10^{-2}	18.4	15.24	0.018
269.5	0.172	6.92	0.252×10^{-1}	2.78	3.47	0.055
251.6	0.503×10^{-1}	7.84	0.998×10^{-2}	3.23	3.42	0.075

RESULTS

Total intensity

In non-polar solvents, the total fluorescence intensity decay (FID) of DPH is known to be monoexponential. In the present experiments, we observed a weak non-exponential character, which seems to increase at low temperatures (see *Tables 1–3*). This character, which has been reported previously in the case of polar solvents[16], raises some delicate questions about the photophysics of DPH. We postpone this discussion, which requires further experimental work. This is legitimate because we are interested in anisotropy correlation times much longer than the additional short-time FID exponential, and because the relative amplitude of this latter exponential is small (generally smaller than 10%).

Fluorescence anisotropy decay (FAD)

To ascertain the type of orientational autocorrelation function relevant to the dynamics of DPH in the different matrices investigated, the 'reconvoluted' anisotropy corresponding to a given model $r(t)$:

$$R(t)=\frac{[r(t)\cdot s(t)]*F(t)}{I_{\parallel}(t)+2I_{\perp}(t)} \qquad (1)$$

was fitted to the experimental anisotropy:

$$R_{\mathrm{exp}}(t)=\frac{I_{\parallel}(t)-I_{\perp}(t)}{I_{\parallel}(t)+2I_{\perp}(t)} \qquad (2)$$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the experimental fluorescence decays with polarization parallel and perpendicular to the polarization of the exciting pulse, respectively, $F(t)$ is the experimentally recorded exciting pulse, $s(t)$ is the (fitted) total intensity decay, and $r(t)$ is the theoretical anisotropy. Current models are, respectively:

$$r(t)=r_0\exp(-t/\tau) \qquad (3)$$

for a spherical top,

$$r(t)=r_0[(1-a)\exp(-t/\tau)+a] \qquad (4)$$

for bounded rotation[17], and

$$r(t)=a_1\exp(-t/\tau_1)+a_2\exp(-t/\tau_2) \qquad (5)$$

for a more general asymmetric rotor[18]. As can be checked from *Tables 4–6*, expressions (3)–(5) lead to essentially equal results, apart from fluctuations due to the increasing complication of the hypersurface when the number of parameters increases, which may lead to slower convergence and extra rounding errors. Also, extra parameters may perform some 'noise' fitting, and slightly reduce χ^2. The small differences observed in *Tables 4–6* confirm that the FAD of DPH is monoexponential within experimental error, and justifies approximating this molecule by an elongated spherical top, or 'rod'.

Temperature effects

The temperature dependence of the correlation times of DPH in different matrices is reported in *Tables 4–6*, and plotted in an Arrhenius representation in *Figures 1–3*. At high temperatures, log(τ) is approximately linear in $10^3/T$, and the apparent activation energies (48 kJ mol^{-1} for

Table 4 Fluorescence anisotropy decay of PD: one-exponential, Kinosita and two-exponential fits

T (K)	Fit	a_1	τ_1 (ns)	a_2	τ_2 (ns)	χ^2
308.3	1E	0.362	2.01			1.65
	K	0.368	2.13	-0.943×10^{-2}		1.43
	2E	0.729	2.57	-0.373	3.18	1.32
292.2	1E	0.353	4.87			2.75
	K	0.352	4.86	0.1×10^{-3}		2.77
	2E	0.353	4.87	0.1×10^{-2}	0.601	2.75
282.5	1E	0.366	8.51			1.81
	K	0.367	8.54	-0.458×10^{-3}		1.81
	2E	0.277	8.53	0.893×10^{-1}	8.45	1.81
269.5	1E	0.359	23.8			1.94
	K	0.390.	27.2	-0.335×10^{-1}		1.77
	2E	0.312	23.9	0.468×10^{-1}	23.3	1.94
251.6	1E	0.359	140			1.33
	K	0.367	127	-0.872×10^{-2}		1.33
	2E	0.330	156	0.283×10^{-1}	60.4	1.33

Table 5 Fluorescence anisotropy decay of PPO425: one-exponential fit

T (K)	a	τ (ns)	r_0	χ^2
320.8	0.372	0.975	0.37	1.34
308.4	0.367	1.77	0.37	2.03
293.7	0.359	4.57	0.36	1.09
281.4	0.336	11.5	0.34	2.71
269.5	0.333	35.4	0.33	2.35
252.0	0.334	254	0.33	1.67

Table 6 Fluorescence anisotropy decay of PPO4000: one-exponential fit

T (K)	a	τ (ns)	r_0	χ^2
320.8	0.354	1.47	0.35	1.49
308.4	0.342	2.53	0.34	2.74
293.1	0.341	6.73	0.34	1.95
283.3	0.329	13.5	0.33	1.98
267.7	0.325	50.3	0.33	2.01
253.0	0.330	285	0.33	1.81

PPO425 and 46 kJ mol^{-1} for PPO4000) are compatible with those reported by Baur and Stockmayer[10] and by Yano *et al.*[11] Notice that these values are much higher than the activation energy for the relaxation reported by Pathmanathan *et al.*[19] (19 kJ mol^{-1}). The behaviour at lower temperatures is definitely non-Arrhenian. This suggests that DPH can move only when the surrounding molecules undergo the type of molecular motions involved in the glass transition.

Molecular-weight effects

To eliminate the 'trivial' effect of T_g shifts on the mobility, we plotted log (τ) as a function of $T-T_g$ in *Figure 4*. (The T_g values of the different samples, reported in *Table 7*, were obtained using a DuPont d.s.c. apparatus, a heating rate of 5 K min^{-1} and cyclohexane calibration.) The reduced correlation time in the monomer is much larger than in the polymers, whereas the difference of mobility between PPO425 and PPO4000 is very weak. These observations clearly demonstrate that

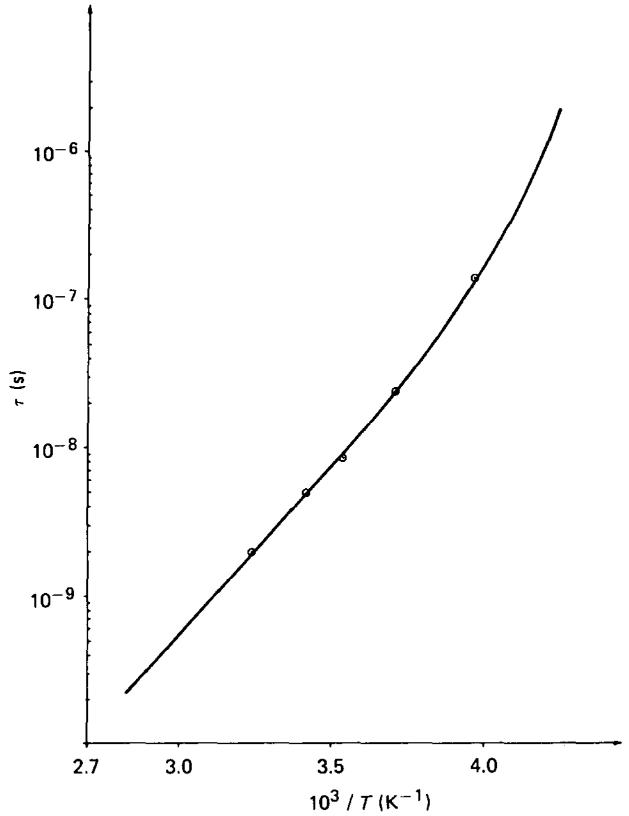

Figure 1 Correlation time of DPH in 1,2-propanediol *versus* $10^3/T$

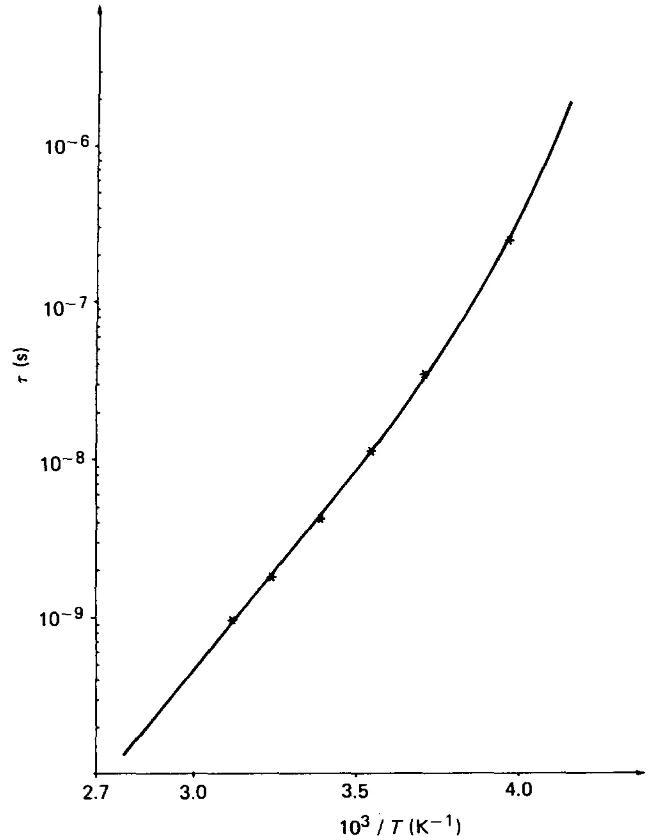

Figure 2 Correlation time of DPH in PPO425 *versus* $10^3/T$

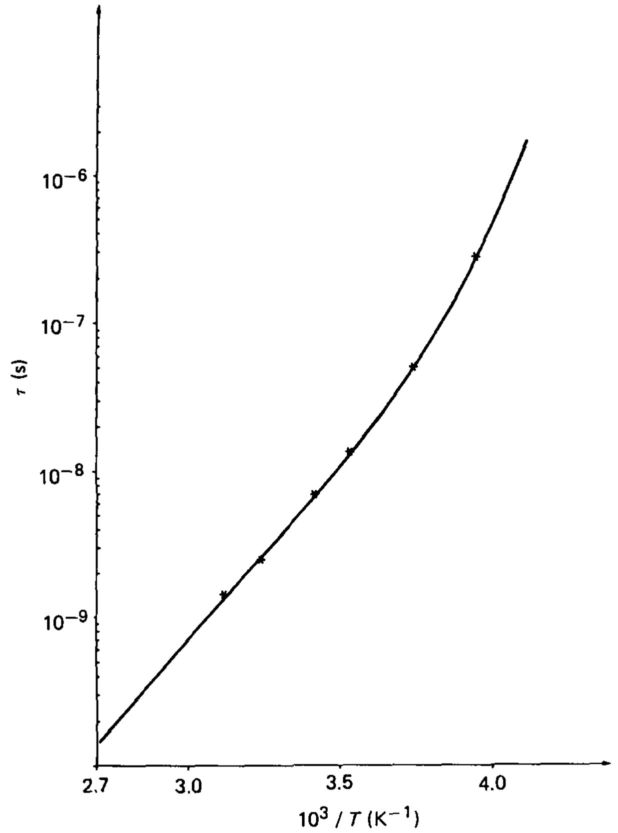

Figure 3 Correlation time of DPH in PPO4000 *versus* $10^3/T$

the T_g shift as a function of the molecular weight is not the whole story of M_w effects. At the present time, it is not clear if purely entropic theories are able to predict correctly the type of 'second-order' effect on the mobility observed here. It is our feeling, however, that the glass-forming nature of PD is due mainly to intermolecular specific interactions which are not included in the entropic theories of glasses. Finally, it is worth noticing that the similarity between the behaviours of PPO425 and PPO4000 is consistent with the result already quoted by Wang *et al.*[12] for a temperature domain very close to T_g.

DISCUSSION

The time domain available to FAD is sufficient to reveal the non-Arrhenian character of the dynamics, and to promote the use of a WLF approach, as in Ferry[2]. According to free-volume models, the mobility of polymer segments should follow the WLF equation:

$$\log(a_T) = \log[\tau_c(T)/\tau_c(T_g)] = -\frac{C_1^g(T-T_g)}{C_2^g+T-T_g} \tag{6}$$

where a_T is the shift factor, $\tau_c(T)$ the correlation time at temperature T and T_g is the glass transition temperature, determined by d.s.c., for instance. A similar expression holds for any arbitrary reference temperature T_0:

$$\log[\tau_c(T)/\tau_c(T_0)] = -\frac{C_1^0(T-T_0)}{C_1^0+T-T_0} \tag{7}$$

The WLF equations (6) and (7) depend on the chosen reference temperature, and the following correlations can be written:

$$\begin{gathered} C_1^0C_2^0 = C_1^gC_2^g \\ T_0 - C_2^0 = T_g - C_2^g = T_\infty \end{gathered} \tag{8}$$

where T_∞, often called the 'Vogel' temperature, is the temperature at which the free volume in the system is zero. It represents a point of infinite viscosity and infinite correlation time for the supercooled liquid. In a previous paper, Bokobza *et al.*[20] have emphasized the advantages of rewriting the WLF equations as:

$$\begin{aligned} \log[\tau_c(T)] &= \log[\tau_c(T_g)] - C_1^g + C_1^gC_2^g\frac{1}{T-T_\infty} \\ &= A + \frac{B}{T-T_\infty} \end{aligned} \tag{9}$$

Indeed, applying this representation to our FAD results for PPO425 or PPO4000 using the T_∞ value reported by Ferry leads to a good linearity (the results for PPO425 are plotted in *Figure 5*), but we observed that rather different values of T_∞ would also lead to equally straight lines within experimental error. This lack of sensitivity is due to the rather narrow experimental window of FAD. In order

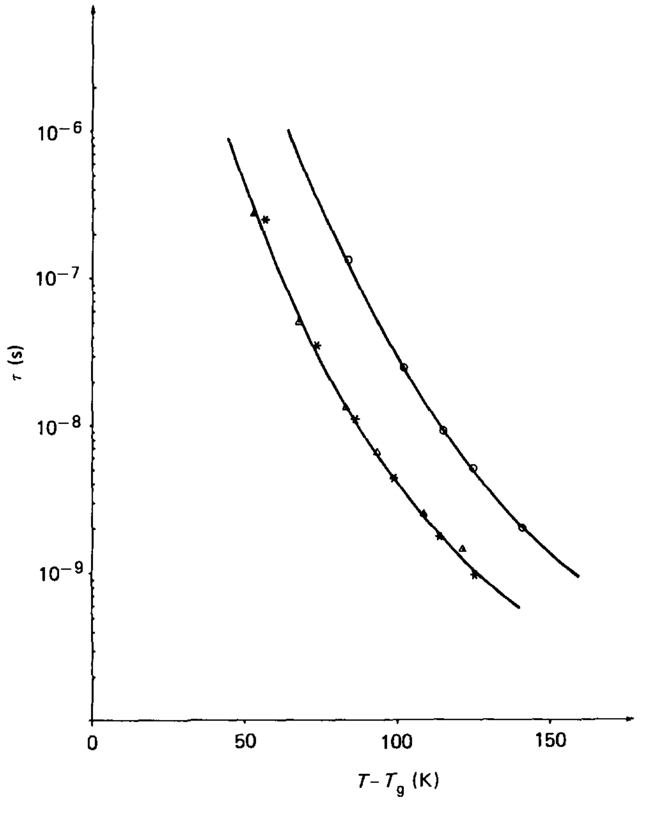

Figure 4 Correlation time of DPH in different matrices *versus* $T-T_g$

Table 7 Glass transition temperature of polymer matrices

Polymers	PD	PPO425	PPO4000
T_g (K)	167.5	195.5	200

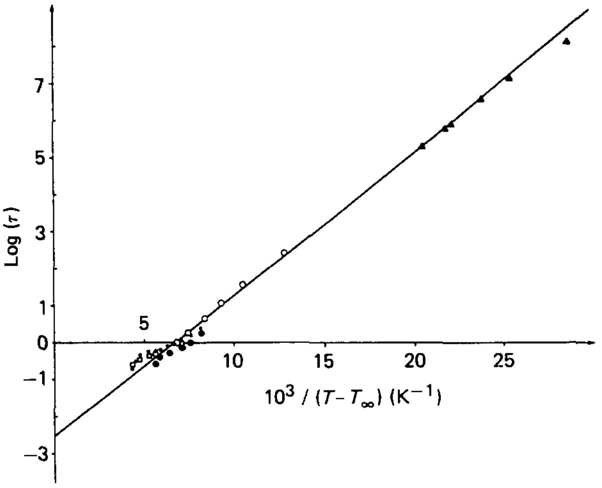

Figure 5 Logarithms of correlation times *versus* $10^3/(T-T_\infty)$ in PPO425: DPH (○); light scattering, from ref. 5 (∗, polarized; □, depolarized), ref. 11 (●) and ref. 12 (▲)

to make our discussion of the dynamics more critical, we compare our results with several light-scattering experiments reported in the past[5–7]. Light-scattering (LS) techniques are particularly interesting here, because they provide dynamical information in time domains complementary to this of FAD. Photon correlation spectroscopy explores very slow motions, while Fabry–Perot interferometry explores a time range which overlaps slightly with FAD in the nanosecond region, and extends into the picosecond domain. It must be remembered that LS and FAD techniques do not sample the same correlation functions: depolarized Rayleigh scattering (or photon correlation) is sensitive to a chain multimolecular orientation correlation function, and polarized Rayleigh scattering or photon correlation reflect translational multimolecular correlation functions. Finally, our experiment reflects the oriention al autocorrelation of a DPH probe. Although the different correlation times quoted above are not expected to be identical, it is well known (and well justified theoretically) that multimolecular and monomolecular correlation functions differ by a frequency-independent correlation factor of order unity, which only introduces a shift between the different light-scattering correlation times. Finally, the reorientation time of DPH must have the same temperature evolution as the light-scattering correlation times, if this probe is large enough to be embedded in the molecular motions associated with the primary relaxation.

Indeed, as already suggested by the high-temperature apparent activation energies, this hypothesis seems nicely supported by the data plotted in *Figure 6* (PPO425). More surprisingly, within an experimental uncertainty of a factor of ~2 or less, FAD data interpolate between the low-frequency and high-frequency light-scattering data without any vertical shift. This indicates that the size of the elementary mobile chain unit of PPO has roughly the same size as DPH (which is reasonable on molecular grounds). Knowing the length of a DPH molecule (≃17 Å), one can deduce that the 'free-volume' unit for molecular motions approximately corresponds to the volume swept by DPH during a reorientation, i.e. about 2500 Å^3.

The experimental slope obtained using the whole set of correlation times without shift leads to a coefficient $C^g{}_1 \simeq 16.2$, equal to the value obtained from viscoelasticity[2] within experimental error. One can argue rightly that we are not comparing independent results there, since our determination of C_1^g uses the viscoelastic T_∞ value as an input. To check the consistency of viscoelastic and spectroscopic results more critically, we now propose a direct determination of the WLF parameters from spectroscopic data, following the method recalled in ref. 20. If an arbitrary reference temperature T_0 is chosen, equation (1) leads to:

$$-1/[\log(\tau/\tau_0)] = 1/C_1^0 + C_2^0/(T-T_0)C_1^0$$

Therefore, a plot of $-1/[\log(\tau/\tau_0)]$ as a function of $1/(T-T_0)$ should be linear, and should give access to the WLF coefficients. Using $T_0 = 252$ K and $\tau_0 = 254$ ns, *Figure 5* is obtained. The WLF parameters corresponding to the full set of spectroscopic correlation times for PPO425 are:

$$C_1^0 = 5.158, \qquad C_2^0 = 80.8°, \qquad C_1C_2 = 417°$$

or, equivalently,

$$C_1^g = 17.2 \pm 1 \quad (16.2), \qquad C_2^g = 24.3 \pm 1° \quad (24°),$$

$$T_\infty = 171 \pm 2\,\text{K}\ (174\,\text{K})$$

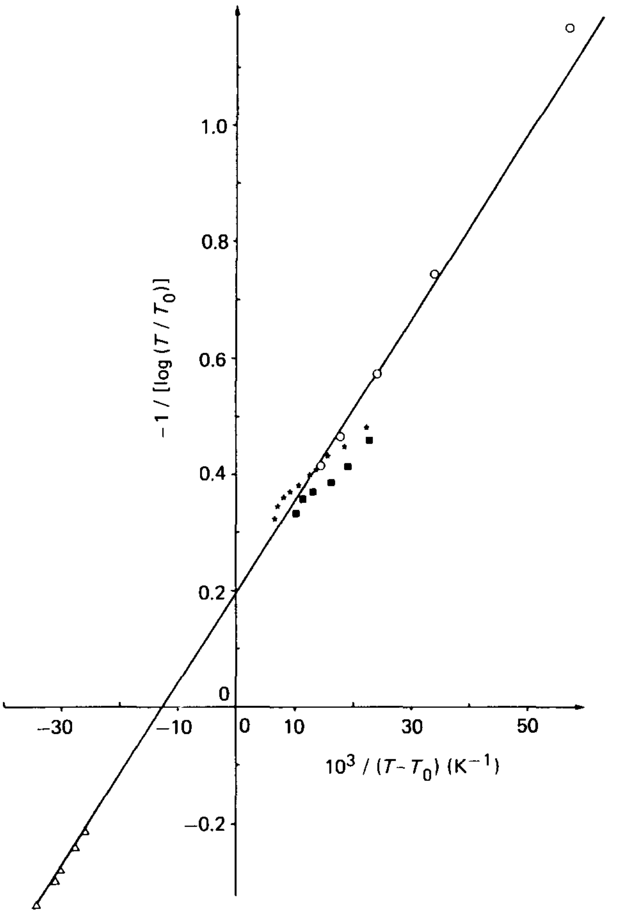

Figure 6 Graphical determination of the WLF parameters of PPO425 using spectroscopic data and relation (10): DPH (○); light scattering, from ref. 5 (∗), ref. 11 (□) and ref. 12 (△). ($T_0 = 252$ K)

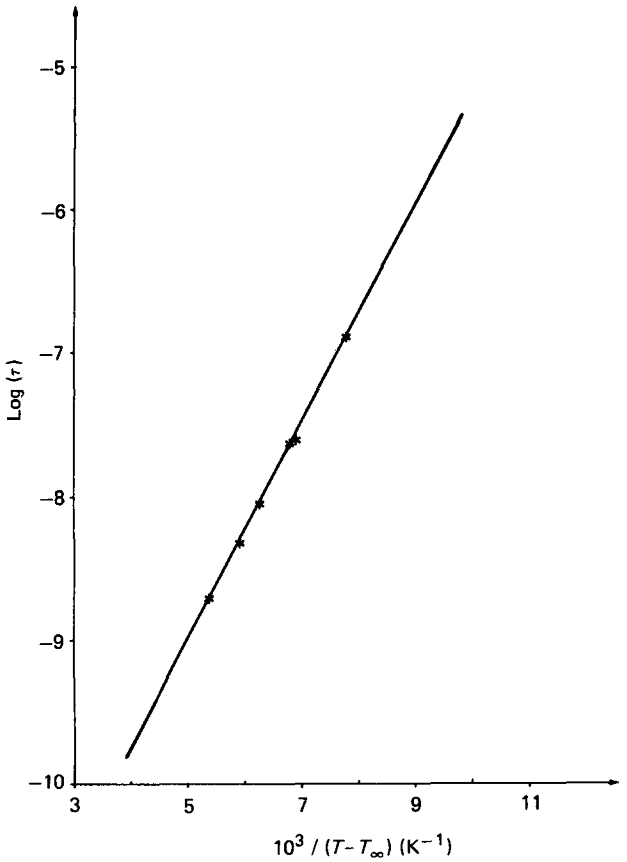

Figure 7 Log(τ_{FAD}) *versus* $10^3/(T-T_\infty)$ for DPH in propanediol

Very similar results were obtained for PPO4000. The independent values reported by Ferry, given in parentheses, show agreement which is very reasonable as regards the intrinsic weakness of the graphic method, which emphasizes the error on the reference point (other reasonable reference choices lead to variations in the parameters reflected in the errors quoted above). We attribute this rather good result to the fact that, as regards the huge time interval sampled by spectroscopic methods, the complications of the correlation functions used and the associated shifts become rather negligible. Used with some care, spectroscopic methods are still able to give an accurate description of the phenomenological behaviour of glass-forming materials, while giving access to molecular information on this process, such as the size of the elementary unit involved in the critical slowdown.

Finally, we consider PD, for which existing data are much more scarce. The correlation times (*Table 4* and *Figure 1*) show a significant non-Arrhenian behaviour, as for the polymer. Owing to the narrow experimental window of FAD, and to the lack of complementary spectroscopic experiments, a purely 'molecular' determination of the WLF parameter was not possible. However, we checked for the consistency of our data with the viscosity results analysed in paper 2 of this series[21] by plotting in *Figure 7* log(τ_{FAD}) as a function of $10^3/(T-T_\infty)$, where $T_\infty = 123$ K is taken from paper 2. A good linearity is observed, and the slope $C_1C_2 = 773°$ is also in good agreement with the value obtained from the macroscopic viscosity.

The comparison between the WLF coefficients of PD and PPO indicates that the latter compound is much more deeply non-Arrhenian than its monomer. Although the molecular significance of this observation is not clear, it suggests that the 'catastrophic' character of the slow down increases when passing from intermolecular interactions to intramolecular conformational constraints. A more quantitative discussion will be proposed at the end of paper 2, in which further studies using excimer fluorescence are presented.

ACKNOWLEDGEMENTS

We are indebted to Jean Claude Brochon and Fabienne Merola for their help in the use of the synchrotron facility, and to Bruno Amram and Isabelle Caucheteux for their contribution to the study of PD.

REFERENCES

1 Johari, G. P. 'Plastic Deformation of Amorphous and Semi-crystalline Materials', Les Houches Int. Spring School Lectures, (Eds. B. Escaig and C. G'Sell), Les Éditions de Physique, Les Ulis, France
2 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn., Wiley, New York, 1980; Cohen, M. H. and Grest, G. S. *Phys. Rev. B.* 1979, **20**, 1077
3 Gibbs, J. H. and Di Marzio, E. A. *J. Chem. Phys.* 1958, **28**, 373
4 Bengtzelius, U., Götze, W. and Sjölander, A. J. *J. Phys. C.* 1984, **17**, 5914
5 Huang, Y. Y. and Wang, C. H. *J. Chem. Phys.* 1975, **62**, 120
6 Wang, C. H. and Huang, Y. Y. *J. Chem. Phys.* 1976, **64**, 4847
7 Jones, D. R. and Wang, C. H. *J. Chem. Phys.* 1976, **65**, 1835
8 Lin, Y. H. and Wang, C. H. *J. Chem. Phys.* 1978, **69**, 1546
9 Beevers, M. S., Elliott, D. A. and Williams, G. *Polymer* 1980, **21**, 13
10 Baur, M. E. and Stockmayer, W. H. *J. Chem. Phys.* 1965, **43**, 4319
11 Yano, S., Rahalkär, R. R., Hunter, S. P., Wang, C. W. and Boyd, R. H. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1377
12 Wang, C. W., Fytas, G., Lilye, D. and Dorfmüller, T. *Macromolecules* 1981, **14**, 1363
13 Brochon, J. C. 'Protein Dynamics and Energy Transduction', (Ed. Shin' Ishi Ishiwata), Taniguchi Foundation, Japan, 1980
14 Viovy, J. L. and Monnerie, L. *Adv. Polym. Sci.* 1985, **67**, 99
15 Viovy, J. L. Doctorat d'état, Université Paris VI, 1983
16 Cehelnix, E. D., Cundall, R. B., Lockwood, J. R. and Palmer, T. F. *J. Phys. Chem.* 1975, **79**, 1369
17 Kinosita, K., Kawato, S. and Ikegami, A. *Biophys. J.* 1977, **20**, 289
18 Chuang, T. J. and Eisenthal, K. B. *J. Chem. Phys.* 1971, **55**, 2399
19 Pathmanathan, K., Johari, G. P. and Chan, R. K. *Polymer* 1986, **27**, 1907
20 Bokobza, L. *et al.* to appear
21 Bokobza, L., Pham-Van-Cang, C., Giordano, C., Monnerie, L., Vandendriessche, J. and De Shryver, F. C. *Polymer* 1988, **29**, 251