Segmental dynamics during the thermal polymerization of styrene: a kinetic fluorescence anisotropy decay study*

Jean-Louis Viovy and Lucien Monnerie
Laboratoire de Physicochimie Structurale et Macromoléculaire, Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris, 10, rue Vauquelin 75231 Paris Cedex 05, France

(*Received 2 January 1986; revised 11 May 1987; accepted 18 May 1987*)

The segmental dynamics of anthracene-labelled polystyrene chains is studied during the thermal polymerization process of styrene by means of fluorescence anisotropy decay. The characteristic time of conformational jumps starts to increase drastically after a conversion rate of *ca.* 15 wt%, due to the direct steric interaction between different chains. The shape of the orientation autocorrelation function remains rather independent of the polymer concentration. It is well described by the process of 'diffusive conformational jumps'.

The corresponding 'distribution of relaxation times' is significantly narrower than the one observed in depolarized Rayleigh scattering, indicating that multimolecular interactions affect this latter technique significantly. The variation of the correlation times as a function of the concentration is in agreement with the free-volume models for concentrated solutions proposed by Fujita and Mashimo.

However, the large difference between the concentration dependence of the conformational jump rate of the polymer chain and that of the reorientation time of styrene monomers rules out the idea of a single 'local viscosity' valid for all the species in the mixture.

(Keywords: polystyrene; thermal polymerization; glass transition; segmental motions; fluorescence anisotropy decay)

INTRODUCTION

The 'universal behaviour' of polymer solutions in the 'semidilute' regime (i.e. up to polymer weight fractions of about 0.15) has been studied extensively both experimentally and theoretically[1-3] and the overall dynamics is rather well described by the reptation model.

In contrast, the local dynamics is still poorly understood, especially in the concentrated range. Theoretically, very different approaches such as the local free volume concept[4-8] or generalizations of the reptation model[9,10] have been applied to such systems, but their unification has yet to be achieved. Experimentally, one is faced with the difficulties of making clean, well relaxed and highly concentrated solutions of high molecular weight polymers. In a recent series of experiments[11], we used fluorescence anisotropy decay to study segmental dynamics in semidilute and concentrated solutions of polystyrene (PS) in toluene. By using monodisperse samples of labelled and unlabelled PS, we have shown that the segmental dynamics is not affected either by the molecular weight of the labelled chain or by the molecular weight of the surrounding chains in the solution, for a wide range of molecular weights (23 000–1 300 000). However, owing to the practical difficulties quoted above, we could not reach polymer weight fractions higher than 0.50. A few years ago, Stevens, Patterson and co-workers demonstrated that optically clean and very concentrated solutions of polystyrene could be obtained by using thermal polymerization *in situ*. The kinetics of this reaction at 363 K has been studied in detail by Alms *et al.*[12]. The polymerization reaction is controlled by the rate of formation of radicals, and it leads to high molecular weight chains (about 1 000 000) with a rather high polydispersity. The polymer concentration increases linearly with time up to about 28%. The dependence above this concentration is also linear, but the rate is higher, due to a hindrance of the termination reaction by coupling. The reaction saturates after about 80 h; then the limiting step is the diffusion of the monomers towards the reactive ends.

Several spectroscopic techniques such as Raman scattering[13-15], n.m.r.[16] and the various aspects of light scattering[17-20] have been applied to styrene undergoing thermal polymerization a few degrees below the glass transition of the pure polymers. During these studies, different aspects of the dynamics have been addressed. Alms *et al.*[12] have measured the reorientation time of styrene in the first linear part of the reaction. It is found to increase rather slowly with polymer concentration. By using photon correlation spectroscopy, Patterson *et al.*[20] have measured the multimolecular rotational and translational correlation functions of the polymer for relatively high degrees of conversion. From a kinetic point of view, the reaction saturates after about 3×10^5 s, i.e. the concentration of polymer leaves the linear increase to approach asymptotically the 100% plateau. On the other hand, the reorientation time seems to continue an exponential increase long after the kinetic saturation, reaching a plateau after 10^6 s or more. However, such experiments are difficult to interpret on a molecular level,

---

* This paper is dedicated to Dr P. Thirion on the occasion of his retirement

0032-3861/87/091547–06$03.00

since they involve correlations between segments on the same chain, correlations between segments on different chains, and probably also correlations between a segment of a chain and the surrounding free monomers.

Finally, Jeffrey and Stevens[16] have used ^1H n.m.r. to evaluate an average correlation time for the motion of the polymer for low and moderate conversion rates. However, this evaluation, which involves intrachain and interchain dipole–dipole coupling, could be only qualitative.

In the present paper, we report studies on polymer dynamics made by using synchrotron-excited fluorescence anisotropy decay (FAD). This technique provides an accurate and rather unambiguous sampling of the orientation autocorrelation function (OACF) of the polymer backbone of labelled chains[21-25]. Owing to the use of polymerization *in situ*, we were able to reach polymer weight fractions higher than in previous studies on monodisperse samples[11]. Since the latter studies have shown that for sufficiently high molecular weights ($M > 30\,000$) the polymer molecular weights do not play any significant role either in the shape of the OACF, or in the correlation time of the labelled chain, the relatively high polydispersity obtained in thermal polymerization should not affect the results discussed in the present paper.

EXPERIMENTAL

Sample

Styrene was purified by double distillation on sodium in vacuum, then transferred by a third distillation into quartz glassware, all containing a small quantity (under 1%) of polystyrene labelled with an anthracene group in the middle of the chain[26]. It was then degassed by the method of phase transitions, and finally transferred into the spectroscopic cell and sealed with no rupture of the secondary vacuum. The polymerization was achieved at 363 ± 0.5 K. In these conditions, the accuracy on the polymer concentration as a function of time is limited mainly by the accuracy of the temperature control system. In our experimental conditions, the polymer concentration is defined with an accuracy of about 4%.

Apparatus

The thermal chamber was placed into an SLM fluorescence apparatus operated in the single-photoelectron regime. The cyclosynchrotron LURE-ACO (Orsay, France) was used as the exciting source. This apparatus, and the techniques for data processing have been previously described[21-23]. Owing to the discontinuous schedule of operation of the synchrotron source, the whole polymerization could not be studied in a single experiment. Therefore, two samples were prepared and studied independently with different starting points relative to the schedule of ACO. These independent experiments also permit a check on reproducibility. Since no systematic deviations between the two samples have been observed, all the results have been gathered in *Table 1*.

Results

As usual for an anthracene covalently bonded to a polymer chain[21,26], the recorded decays of total intensity present a clear non-exponential character. The deconvolution of this decay, which is a necessary intermediary towards the deconvolution of the FAD, has been performed by using an arbitrary 3-exponential, because of the specific dynamic behaviour of flexible chains. The OACF of polymer main-chain segments has been studied quite extensively in the last few years, theoretically and experimentally. For flexible chains, it is now rather well understood. In particular, several studies have shown that the expression proposed by Hall and Helfand[27], which presents promising theoretical features, also seem to describe the OACF of polymer main-chain segments rather well[28]. For FAD, a direct generalization of this model (generalized diffusion and loss expression, GDL) has been proposed in reference 21. The corresponding expression for the anisotropy is

$$r(t) = r_0 \exp(-t/\tau_2) \exp(-t/\tau_1)[I_0(t/\tau_1) + I_1(t/\tau_1)]$$

where I_0 and I_1 are modified Bessel functions.

The characteristic term τ_1 is associated with cooperative conformation jumps, which diffuse along the chain. The physical meaning of the loss term $\exp(-t/\tau_2)$ is still not clear. It should correspond to a slow process corresponding to cooperative conformational jumps, since experimental values of τ_2/τ_1 are generally higher than ten. This expression, which accounted successfully for the experimental OACF of a variety of polymer systems[11,23-25] also recently received further theoretical support[29]. The best-fit parameters using the GDL model are gathered in *Table 1*. As expected, correlation times

Table 1 Best-fit parameters using the GDL and WW models

Elapsed time (10^3 s)	Polymer weight fraction (g/g)	GDL model					WW model			
		χ^2	r_0	τ_1 (ns)	τ_2 (ns)	τ_2/τ_1	χ^2	r_0	τ (s)	β
2.7	7.5×10^{-3}	1.07	0.168	(0.10)	2.6	(26)	1.00	0.234	(0.13)	(0.37)
6.8	1.8×10^{-2}	1.99	0.155	(0.11)	4.2	(37)	1.62	0.287	(0.05)	(0.26)
16.9	4.6×10^{-2}	1.04	0.193	(0.11)	2.5	(23)	1.00	0.322	(0.11)	(0.37)
23.2	6.3×10^{-2}	0.97	0.195	(0.11)	2.5	(23)	0.95	0.253	(0.12)	(0.41)
92.5	0.254	1.09	0.206	0.33	7.9	24	1.14	0.269	0.65	0.44
111	0.306	0.92	0.210	0.48	7.0	15	0.93	0.249	1.05	0.53
114	0.310	1.01	0.208	0.52	6.9	13	1.01	0.246	1.12	0.55
171	0.516	1.01	0.214	2.87	106.0	37	1.02	0.230	8.89	0.62
173	0.520	1.10	0.215	3.9	58.0	15	1.09	0.225	10.2	0.62
201	0.630	1.22	0.214	7.22	(210)	29	1.05	0.232	21.9	0.61
529	(0.95)	1.44	0.233	(330)	(749)	(2.3)	1.44	0.234	(501)	(0.88)
601	(0.95)	1.57	0.235	(196)	(6×10^3)	(30)	1.56	0.237	(1073)	(0.70)

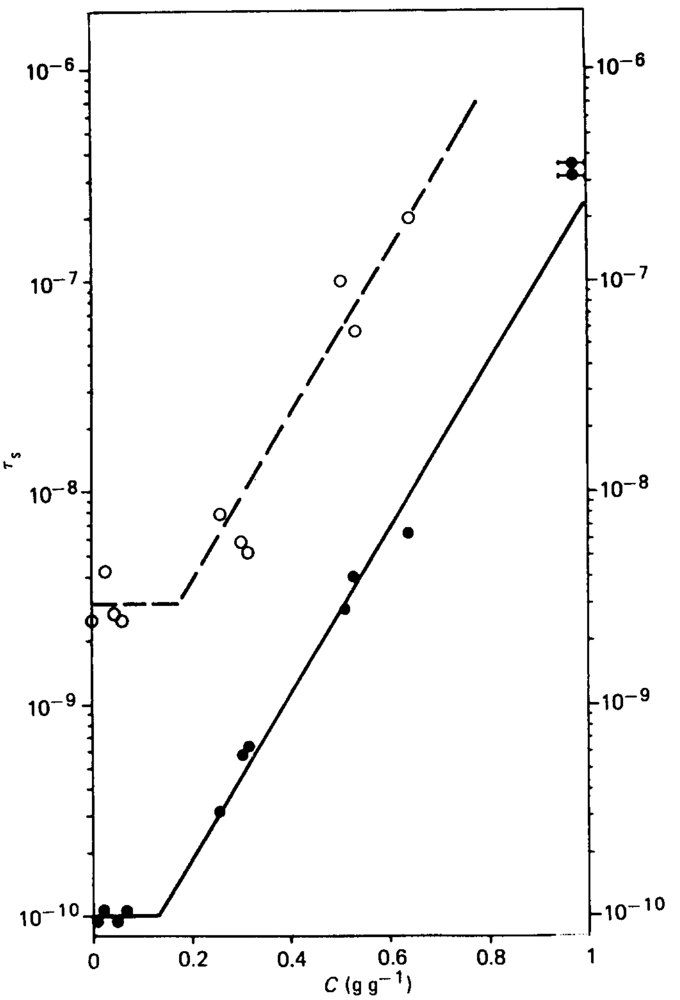

Figure 1 Evolution of the correlation times τ_1(●) and τ_2(○) as a function of the polymer weight fraction

dramatically increase when the polymer weight fraction exceeds 0.15. As in previous studies[21–23], we observed that τ_1 is obtained with a better accuracy than τ_2, due to the exponential decay of the fluorescence intensity. This decay decreases the number of fluorescence photons at long times, and thus leads to a poorer accuracy on the slow component. However, within experimental error, the ratio τ_2/τ_1, which characterizes the shape of the OACF, does not seem to vary in the conversion range lower than the saturation. This behaviour suggests that the increase in the average correlation time is not due to important changes in the elementary conformational processes, more likely these processes are slowed down due to an increase in some mean 'friction'.

By using the polymerization rates determined by Alms *et al.* at the same temperature[12], the evolution of the correlation times as a function of polymer concentration can be deduced from the results in *Table 1* and are shown in *Figure 1*. The concentration corresponding to the two last points is only indicative, since no study of the reaction kinetics after saturation is available. In each case log τ seems to vary rather linearly as a function of the weight fraction above about 15% conversion. It has been shown in a previous study[11] that this concentration corresponds to the onset of direct intermolecular segment–segment friction. The evolution of τ_1 and τ_2 above $C_0 = 15\%$ will be discussed in the section on the free-volume approach.

For comparison we also present in *Table 1* best-fit parameters obtained by using the phenomenological Williams–Watts (WW) expression[30], used by Patterson *et al.* in their light-scattering study[19]. As can be checked from the values of the weighted residuals χ^2, the two models fit the data equally well. The evolution of the best-fit correlation times as a function of elapsed time is also similar for the two models, although the WW results suffer from a large scattering, probably related with the already observed instability of this model upon changes in the experimental window[21] (see *Figure 2*). Thus, this evolution should be accepted with good confidence, at least on the account of its weak model-dependence.

The continuous increase of β, the WW exponential expansion parameter, with the conversion rate observed in our fitting apparently contradicts the stability of τ_2/τ_1 (GDL) since β and τ_2/τ_1 can be considered as dimensionless 'shape parameters' in the WW and GDL models, respectively. In our opinion the behaviour of β is merely a consequence of the 'curve-fitting' nature of the WW expression. In a more detailed check of the different available models of polymer dynamics, using experimental FAD curves, we have already observed that although this expression was generally able to provide good values of χ^2, the values of the fitting parameters were sometimes physically unreasonable and changed with changes in the fitting window[21]. If one is willing to use the WW model in spite of its arbitrary character, the most reliable value for β corresponding to the OACF should correspond to the centre of the experimental window, i.e. $0.5 \leqslant \beta \leqslant 0.6$.

COMPARISON WITH PREVIOUS RESULTS

In *Figure 3*, our results are compared with n.m.r. and light scattering results. The general features of our data and of the results by Jeffrey *et al.*[16] (dotted line) are the same, but

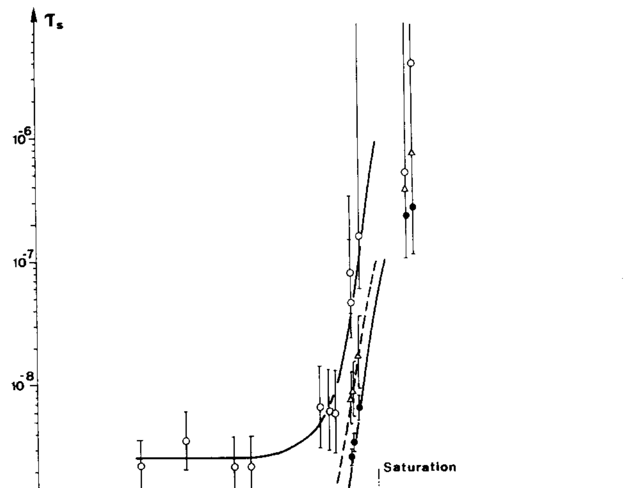

Figure 2 Evolution of the relaxation times τ_1(●), τ_2(○) (GDL model) and τ(△) (WW model) for a labelled polystyrene chain in styrene during thermal polymerization

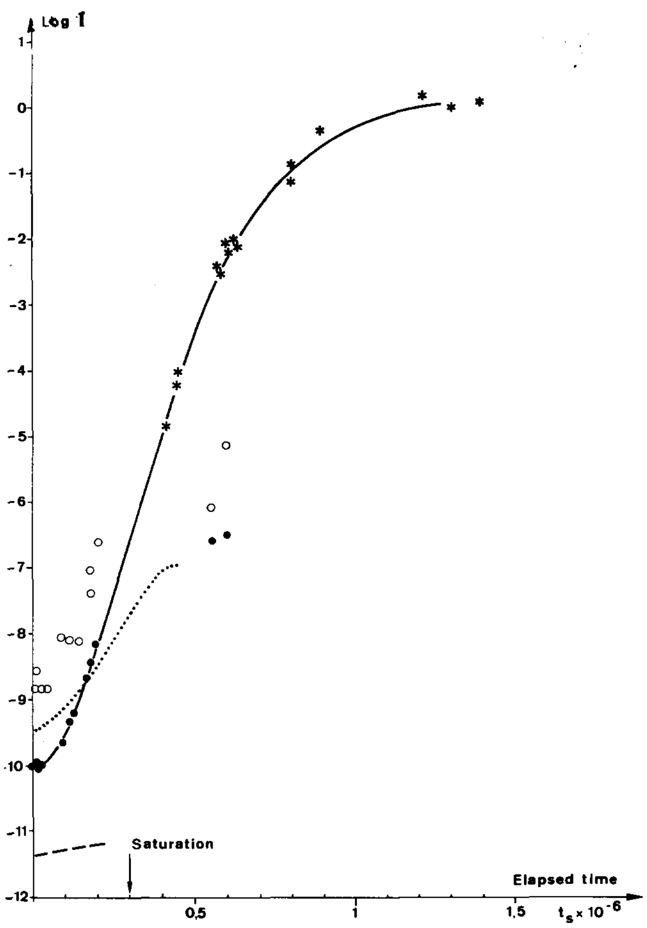

Figure 3 Comparison of correlation times as a function of elapsed time during thermal polymerization. FAD correlation times τ_1(●) and τ_2(○) correlation time of styrene, light scattering (broken line)[12]; correlation time of polystyrene, light scattering (★)[20]; ^{1}H correlation time of polystyrene, n.m.r. (dotted line)[16]

the agreement is only qualitative. It is probable that the ^{1}H dipole–dipole interaction dominant in the experiments by Jeffrey *et al.* sampled a combination of correlation functions more complicated than the polymer backbone OACF.

Depolarized Rayleigh scattering (DRS), which measures multimolecular orientation correlation functions, may also be compared to the FAD experiments. Following generalized hydrodynamics, the average multimolecular orientational correlation time τ_{multi} (measured by DRS) should be related with τ_{mono} (measured by FAD or n.m.r.) by the following expression

$$\tau_{\text{multi}} = \tau_{\text{mono}}((1+\mathcal{N}f)/(1+\mathcal{N}g)) \qquad (1)$$

where $\mathcal{N}$ is Avogadro's number and f and g are static and dynamic coupling factors. The factor $(1+\mathcal{N}f)/(1+\mathcal{N}g)$ is rather difficult to evaluate experimentally. Values between 1 and 5 have been reported, depending on the studied molecules. Thus, a comparison between FAD and DRS may involve some arbitrary time shift in a log plot. Since DRS integrates over the polarizability anisotropy of all the species in the sample, it can provide accurate information on the dominant species only. Thus Patterson *et al.* have been able to study the reorientation of free styrene at the beginning of the polymerization on one hand[12], and the polymer reorientation at the end of the polymerization process on the other[20].

As expected, the reorientation of free styrene, τ_{styrene}, (broken line in *Figure 3*) is more than one decade faster than that of the labelled chains. More surprisingly, the evolution of the two correlation times τ_1 and τ_{styrene} is very different. This discrepancy stresses the danger of concepts such as 'local viscosity'. Different species in the medium seem to be rather differently affected by the concentration of the chains, so that each one is sensitive to a specific 'friction coefficient'.

Since FAD and photon correlation spectroscopy have very different experimental windows, it has not been possible to compare the chain orientation correlation functions (OCF) obtained by the two techniques in the same concentration range. However, since the shape of these OCF does not seem to vary rapidly with the elapsed time, the comparison remains interesting. In particular, the width of the distribution of correlation times (reflected by the β parameter in a WW fitting) is larger in DRS than in FAD. This is not surprising, since DRS samples a mixture of mononuclear and multimolecular correlations.

Lastly, it may be interesting to note that on *Figure 3* the straight line $\log(\tau_1) = f(t)$, which can be drawn through our FAD correlation times obtained before the saturation of the reaction, seems to extrapolate rather naturally towards the depolarized light scattering correlation times obtained after the saturation. Considering the number of decades involved in this extrapolation, this agreement may be fortuitous.

THE FREE-VOLUME APPROACH

In spite of its phenomenological character the free-volume theory of glass-forming liquids[31] has been applied with some success to concentrated polymer–diluent systems[4–8]. In the following, we apply to our data the treatment proposed by Mashimo[7,8], which is closely related to the earlier model developed by Fujita[4,5]. In this approach, the friction coefficient, ξ, is given by

$$\xi = X \exp[1/f_v(T, \phi)] \qquad (2)$$

where f_v is an average fractional free volume and ϕ is the volume fraction of the solvent. By using rather simple free-volume arguments, Mashimo was able to express $f_v(T, \phi)$ as a function of the fractional free volumes of the polymer and of the solvent respectively:

$$f(T,\phi) = \alpha(T) + \phi \,.\, \sigma(T)$$
$$\sigma(T) = (1+\alpha(T))(1+\beta(T))^{-1}\beta(T) \qquad (3)$$

In expression (3), $\alpha(T)$ is the fractional free volume of the polymer, and $\beta(T)$ the fractional free volume of the solvent:

$$\alpha(T) = V_{\text{fp}}/V_{\text{op}}$$
$$\beta(T) = V_{\text{fs}}/V_{\text{os}} \qquad (4)$$

where the subscripts f and o indicate free volume and van der Waals volumes respectively.

Following (2) and (3), the correlation time for conformation jumps, τ_1, is given by

$$1/\ln(\tau_1/\tau_1^\circ) = \alpha(T) + \phi \,.\, \sigma(T) \qquad (5)$$

Since τ_1° is unknown, Mashimo suggested referencing the

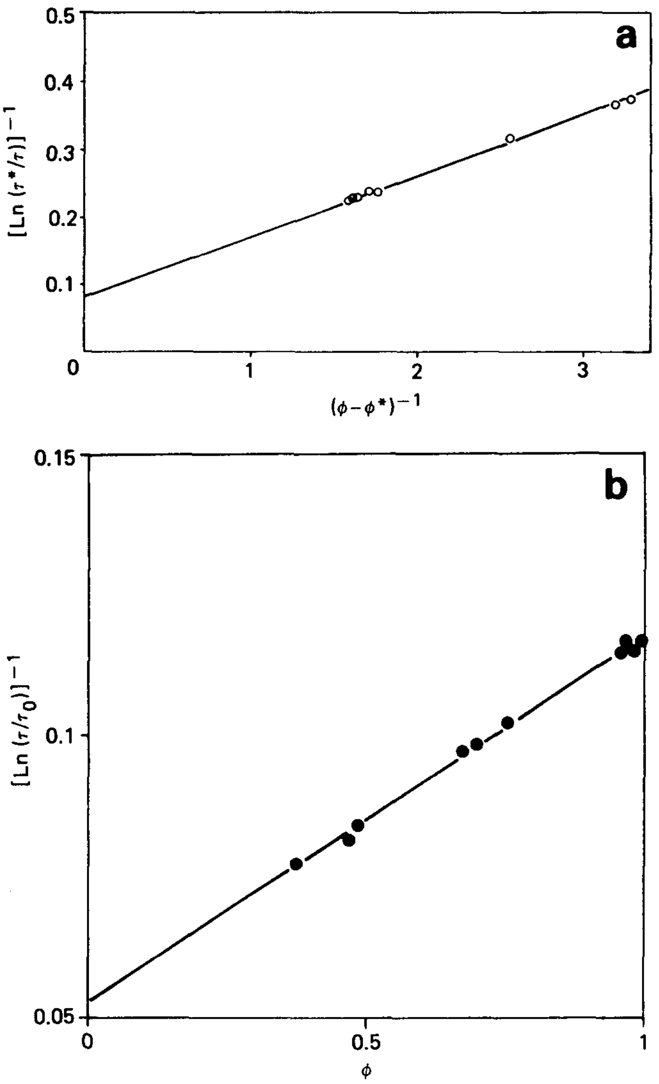

Figure 4 Graphical determination of $\alpha(T)$ and $\beta(T)$, following Mashimo[7]

results to an arbitrary weight fraction ϕ^*:

$$1/\ln(\tau_1^*/\tau_1) = 1/\ln(\tau_1^*/\tau_1^\circ) + [1/\ln(\tau_1^*/\tau_1^\circ)]^2[1/(\phi-\phi^*)][\sigma(T)]^{-1} \quad (6)$$

Equation (6) indicates that when the experimental data $(\ln(\tau_1^*/\tau_1))^{-1}$ are plotted against $(\phi-\phi^*)^{-1}$, a straight line should be obtained, which gives the values of $1/\ln(\tau_1^*/\tau_1^\circ)$ from its intercept on the ordinate axis and $\sigma(T)$ from its slope. Indeed, that is what we observe (*Figure 4a*). τ_1° can be deduced from the value of $\ln(\tau_1^*/\tau_1^\circ)$, and inserted into equation (5). Then, plotting $1/\ln(\tau_1/\tau_1^\circ)$ as a function of ϕ gives a straight line with an intercept $\alpha(T)$ and a slope $\sigma(T)$. Finally, the experimental values for the fractional free volumes are

$$\sigma(T) = 0.053 \pm 0.01$$

$$\beta(T) = 0.10 \pm 0.01$$

The value obtained for $\alpha(T)$ is higher than the 'universal' value at the glass transition

$$\alpha(T_g) \simeq 0.0355 \pm 0.005$$

However, the Fujita–Mashimo theory is rather crude, and numerous reasons can be invoked to explain this discrepancy. On the other hand, more detailed theories, such as the one proposed by Vrentas and Duda[6] contain molecular quantities that are difficult to define accurately, such as the size of the 'jumping unit'. However, the linear behaviour of our data in *Figure 4* is in qualitative agreement with a free volume approach.

CONCLUSION

The thermal polymerization of styrene provides a method for making accurate fluorescence experiments on very concentrated solutions. By this means, we have shown that the shape of the orientation autocorrelation function of the polymer backbone in polymer solutions remains rather similar over a wide range of concentrations. On the other hand, the correlation time for conformation jumps increases dramatically with the polymer concentration above about 15%. This evolution can be qualitatively accounted for by using a free-volume approach, as proposed by Fujita or Mashimo. However, this description of polymer concentrated solutions is by no means complete. For instance, it cannot explain that the reorientation time of styrene and thus of polymer segments evolve differently as a function of the conversion rate.

In the 'free-volume' language, this observation might mean that the free volume is not 'equally available' to the different components in the mixture, contrary to what is usually assumed. More generally, this observation, which should be confirmed by further studies, suggests that the molecular dynamics in mixtures cannot always be described by using a single averaged 'local viscosity' or friction.

ACKNOWLEDGEMENT

We thank G. D. Patterson for suggesting this study.

REFERENCES

1 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell U.R., Ithaca, 1979
2 de Gennes, P. G. and Leger, L. *Ann. Rev. Phys. Chem.* 1982, **33**, 49
3 Osaki, R. and Doi, M. *Polym. Eng. Rev.* 1984, **4**, 35
4 Fujita, H. and Kishimoto, A. *J. Chem. Phys.* 1961, **34**, 393
5 Fujita, H. in 'Diffusion in Polymers' (Eds. J. Crank and G. S. Park), Academic Press, London, 1968, p. 98
6 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci. A2* 1977, **15**, 403
7 Mashimo, S. *J. Chem. Phys.* 1977, **67**, 2651
8 Mashimo, S. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 213
9 Graessley, W. W. and Edwards, S. F. *Polymer* 1981, **22**, 1329
10 Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
11 Viovy, J. L. and Monnerie, L. *Polymer* 1986, **27**, 181
12 Alms, G. R., Patterson, G. D. and Stevens, J. R. *J. Chem. Phys.* 1979, **70**, 2145
13 Chu, B., Fytas, G. and Zalczer, G. *Macromolecules* 1981, **14**, 395
14 Sears, W. M., Hunt, J. L. and Stevens, J. R. *J. Chem. Phys.* 1981, **75**, 1599
15 Chu, B. and Fytas, G. *Macromolecules* 1982, **15**, 561
16 Jeffrey, K. R. and Stevens, J. R. *J. Chem. Phys.* 1979, **71**, 2331
17 Jackson, D. A. and Stevens, J. R. *Molec. Phys.* 1975, **30**, 911
18 Coakley, R. W., Mitchell, R. S., Hunt, J. L. and Stevens, J. R. *J. Macromol. Sci. Phys.* 1976, **12**, 511
19 Patterson, G. D., Lindsey, C. P. and Stevens, J. R. *J. Chem. Phys.* 1979, **70**, 643
20 Patterson, G. D., Stevens, J. R., Alms, G. and Lindsey, C. P. *Macromolecules* 1979, **12**, 658
21 Viovy, J. L., Monnerie, L. and Brochon, J. C. *Macromolecules* 1983, **16**, 1845

22 Viovy, J. L. and Monnerie, L. *Adv. Polym. Sci.* 1985, **67**, 99
23 Voivy, J. L. and Monnerie, L. *Macromolecules* 1985, **18**, 1130
24 Viovy, J. L., Frank, C. W. and Monnerie, L. *Macromolecules*, in press
25 Viovy, J. L. and Monnerie, L. *Makromol. Chem. Suppl.* 1985, **13**, 91
26 Valeur, B. and Monnerie, L. *J. Polym. Sci., Polym. Phys. Edn* 1976, **14**, 11, 29
27 Hall, C. K. and Helfand, E. *J. Chem. Phys.* 1982, **77**, 3275
28 Weber, T. A. and Helfand, E. *J. Chem. Phys.* 1983, **87**, 2881
29 Lin, Y. Y., Jones, A. A. and Stockmayer, W. H. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 2195
30 Williams, G. and Watts, D. C. *Trans. Farad. Soc.* 1970, **66**, 80
31 Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164