A study of local chain dynamics in concentrated polystyrene solutions using fluorescence anisotropy decay

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The local dynamics of polymer chains in concentrated and semi-dilute solutions are investigated using synchroton-excited fluorescence anisotropy decay. A small amount (less than 1%) of monodisperse polystyrene labelled with anthracene in the middle of the chain is embedded in a mixture of monodisperse unlabelled chains and toluene. Two different labelled chains (with molecular weights respectively 30 000 and 300 000) and unlabelled chains of various molecular weights (ranging from 23 000 to 1 300 000) were used, and the polymer weight fraction of the mixtures was varied from 0.01 to 0.51. It is shown that segmental motions are affected by the polymer weight fraction when it exceeds 0.15, but remains unaffected by the molecular weight of the labelled chain and that of the matrix. In the whole range of concentrations, the orientation autocorrelation function obeys the same generalized diffusion and loss model as in dilute solution. The evolution of the characteristic time for segmental motions as a function of the concentration should provide rather direct access to the evolution of the friction coefficient.

(Keywords: dynamics; fluorescence anisotropy decay; concentrated polymer solutions)

INTRODUCTION

The dynamics of moderately concentrated entangled polymer solutions have been widely investigated using various techniques[1]. The most important features of this semi-dilute regime can be described within a single model, based on the 'reptation' idea[2], and on scaling arguments from the theory of critical phenomena[1].

The lowest 'critical concentration' of polymer solutions is associated with the overlap threshold of the coils. In the first approximation, it corresponds to a densely packed assembly of expanded coils (we consider good solvents only). This critical concentration c^*, which can be observed in elastic light or neutron scattering, is given by:

$$c^* \sim N/R_f^3 = N^{-4/5}a^{-3} \qquad (1)$$

where N is the number of statistical units, a is the Kuhn length, and R_f is the Flory radius. From a dynamic point of view, c^* should correspond to the threshold for deviation from the behaviour of dilute chains. Its evaluation depends somewhat on experimental technique.

Klein[3] introduced a slightly different definition of the critical concentration,

$$c^{**} = N^{-4/5}(18\pi^2)^{1/2}/A \qquad (2)$$

However, since expressions (1) and (2) differ only by a constant, and A is a molecular constant that cannot be evaluated directly, expressions (1) and (2) can be considered as equivalent scaling laws. The prefactor seems to depend somewhat on the experimental situation, and values ranging from 2 to 15 have been proposed in the literature, depending on the polymer, on the experiments taken into account, and probably also on the way data are plotted.

The scaling theories mentioned above suppose that the friction coefficient does not depend on the concentration. The degree of confidence one can put in this hypothesis depends on the desired precision, but one generally considers that it is not valid for weight fractions of polymer above 0.1. Thus, the range of validity of scaling laws is severely limited by the short actual range of the semi-dilute regime. The remaining concentrated regime (say from 0.1 to 0.9 weight fraction) is still poorly understood, in spite of its wide practical and conceptual interest. A rather detailed pulsed-field gradient spin-echo n.m.r. study of the diffusion of chains and probes in concentrated solution has been performed recently by von Meerval *et al.*[4].

In the present paper, we use fluorescence labelling to study in some detail the effect of molecular weight and concentration on chain dynamics, and to distinguish between intermolecular and intramolecular effects. Fluorescence anisotropy decay (FAD) experiments were performed on solutions containing a small amount (weight fraction less than 0.01) of polystyrene labelled with anthracene in the middle of the chain (PSAPS), embedded in a mixture of unlabelled polystyrene (PS) and toluene, with total polymer weight fractions ranging from 0.01 to 0.51. Because of this labelling technique and also the very small amount of labelled species required by the fluorescence experiment, it was possible to vary independently both the molecular weight of the probe and that of the matrix.

EXPERIMENTAL

The monodisperse unlabelled samples were provided by the Ecole d'Application des Hauts Polymères, Strasbourg, France. The monodisperse labelled polystyrenes were synthesized in our laboratory by C.

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Friedrich and J. F. Tassin following the method developed by Valeur and Monnerie[5]. The characteristics of the various samples used in the present study are gathered in *Table 1*.

The toluene used as solvent was purified by double distillation over sodium under reduced pressure. The samples were filtered and studied in sealed vessels to avoid evaporation of the solvent during the experiments.

The cyclosynchrotron LURE-ACO at Orsay, France, was the exciting source. The apparatus, which has been described elsewhere[6,7], has already provided interesting information about polymer dynamics in dilute solution[7,8] and in the melt[9].

The data have been treated according to an iterative reconvolution method, including nonlinear least-squares fitting[7,10].

RESULTS AND DISCUSSION

As usual for an anthracene covalently bonded to a polymer chain[5,8], the recorded decays of the total intensity present a clear non-exponential character. The deconvolution of this decay, which is a necessary intermediary in the deconvolution of the FAD, has been performed using an arbitrary three-exponential expression. The anisotropy is also non-exponential, because of the specific dynamic behaviour of flexible chains[7,8]. The orientation autocorrelation function (OACF) of polymer main-chain segments has been studied rather extensively in the last four years, theoretically and experimentally. In the case of flexible chains, it is now quite well understood. In particular, several studies[8,11] have shown that the expression proposed by Hall and Helfand[12] (HH), which presents promising theoretical features, also seems to describe the OACF of polymer main-chain segments rather well. In the case of FAD, a direct generalization of this model (generalized diffusion and loss expression, GDL) has been proposed in ref. 8 to account for the perturbation due to the probe. It improved further the agreement between experiment and theory. The OACF of polymer segments in the bulk state and in concentrated solution is less well known, but recent FAD experiments[13] indicated that it was also well described by the HH and GDL models.

In the present study, we fitted the experimental anisotropy decays using several models for polymer dynamics[8,12-14], and the same methods and criteria as in the previous studies[8,9]. The reader interested in these methods should refer to the original papers or to a review[7].

In the concentrated and semi-dilute solutions studied here, as in the dilute solutions and melts studied previously, the HH and GDL models provide good values for the reduced average of residuals, associated with good stability of the best-fit parameters and randomly distributed weighted residuals (see *Figures 1* and *2*). Since concentrated solutions are intermediate between dilute solutions and melts, this observation is not very surprising. It merely confirms the large range of applicability of the diffusion and loss models. However, the fitting provided by the GDL expression was slightly superior, and was obtained with better stability. Thus, we use the GDL expression throughout the following. As already emphasized[8,9], the physical interpretation of the parameters is the same in the two models, GDL and HH.

Table 1 Characteristics of the samples used in the present study

Type	Notation	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
Labelled[a]	PSA300	2.87	1.15
	PSA30	0.33	1.10
Unlabelled[b]	PS1300	13	1.28
	PS400	4.2	1.24
	PS23	0.239	1.16

[a] From our laboratory

[b] From the Ecole d'Application des Hauts Polymères

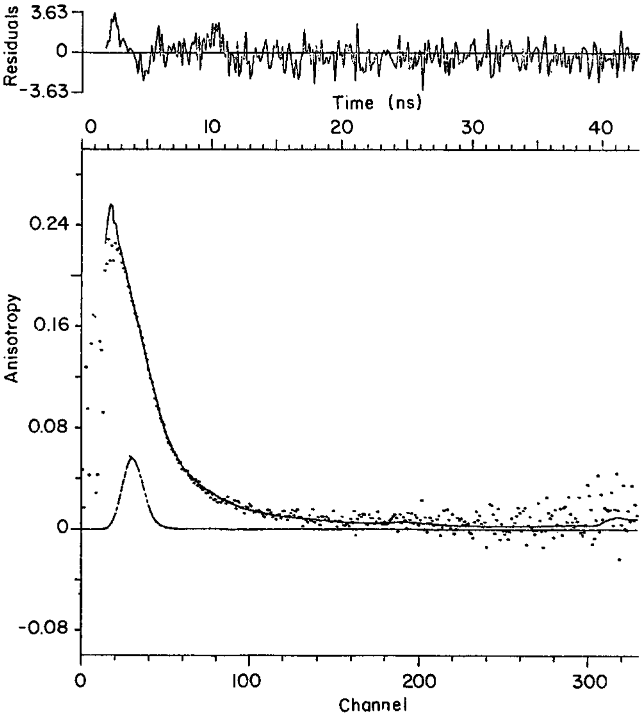

Figure 1 Experimental fluorescence anisotropy decay (dots) and best-fit reconvolution (full curve) for PSA300 in a PS420 matrix (weight fraction 0.28). The weighted residuals are given in the upper scale

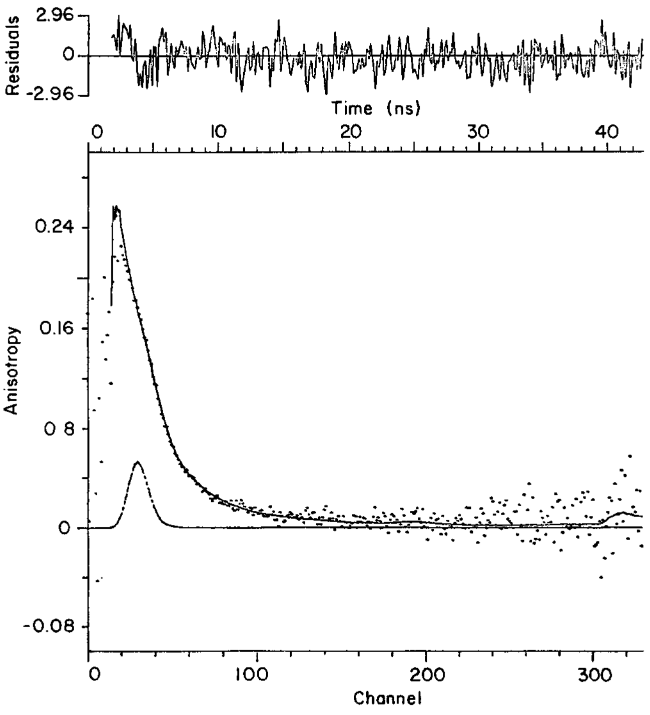

Figure 2 Experimental fluorescence anisotropy decay (dots) and best-fit reconvolution (full curve) for PSA300 in a PS23 matrix (weight fraction 0.28)

The expression for the anisotropy corresponding to the GDL model is:

$$r(t)=r_0\exp(-t/\tau_2)\exp(-t/\tau_1)[I_0(t/\tau_1)+I_1(t/\tau_1)] \quad (3)$$

where r_0 is a molecular constant, related to the average orientation of the transition moments of the anthracene group. For an excitation in the $S_0 \rightarrow S_1$ band, the theoretical value for r_0 is 0.4. However, the actual value is lower, due to fast electronic delocalization, and r_0 has to be fitted. The τ_1 term, which contains modified Bessel functions, is associated with a correlated diffusion of conformational excitations along the chain. In terms of diffusion processes, it corresponds to a 'memory' induced by the connectivity of the chain. The exponential term with a decay constant τ_2 corresponds to all the processes able to damp the diffusion of excitations, such as non-correlated (localized) conformational jumps, torsion fluctuations, etc. The two correlation times characterize the polymer chain motions. τ_1 can be considered as an average jump time for conformational dynamics, and the ratio τ_2/τ_1 reflects the range of the memory effects.

The best-fit parameters obtained for the different samples are gathered in *Table 2*. Independent fitting of the three parameters r_0, τ_1 and τ_2/τ_1 leads to a certain scatter in the values of r_0 and τ_2/τ_1. Previous studies have already demonstrated that the two correlation times τ_1 and τ_2 were difficult to obtain together with accuracy[8,11,15]. In particular, the longer time τ_2 is rather poorly sampled in FAD due to the important Poisson noise in the tail of the decays. However, at the present level of experimental precision, no systematic evolution of the ratio τ_2/τ_1 as a function of the concentration or molecular weight is observed (*Table 2*). This is consistent with our previous finding that τ_2/τ_1 is not much affected when changing from dilute solution to polymer melt, and seems to remain in the order of magnitude of 10. This order of magnitude is also consistent with e.s.r. and n.m.r. experiments performed on various polymers[11,15]. Thus, we also fitted our data by setting the ratio $\tau_2/\tau_1=10$, to improve the precision in the main correlation time (right-hand side of *Table 2*). The corresponding values are plotted in *Figure 3*. There is a progressive evolution as a function of the concentration, but the correlation time does not depend on the molecular weight of the matrix and on the molecular weight of the labelled chain in the whole range explored. (One can check from the different critical concentrations c^{**} deduced from the data by Onogi *et al.*[16] that the increase in τ_1 cannot be associated with entanglements.) The full circles represent results obtained previously by Tardiveau[17] in the case of nearly monodisperse solutions with a molecular weight of about 60 000 (the original results have been shifted vertically, due to the use of another temperature (306 K) and another

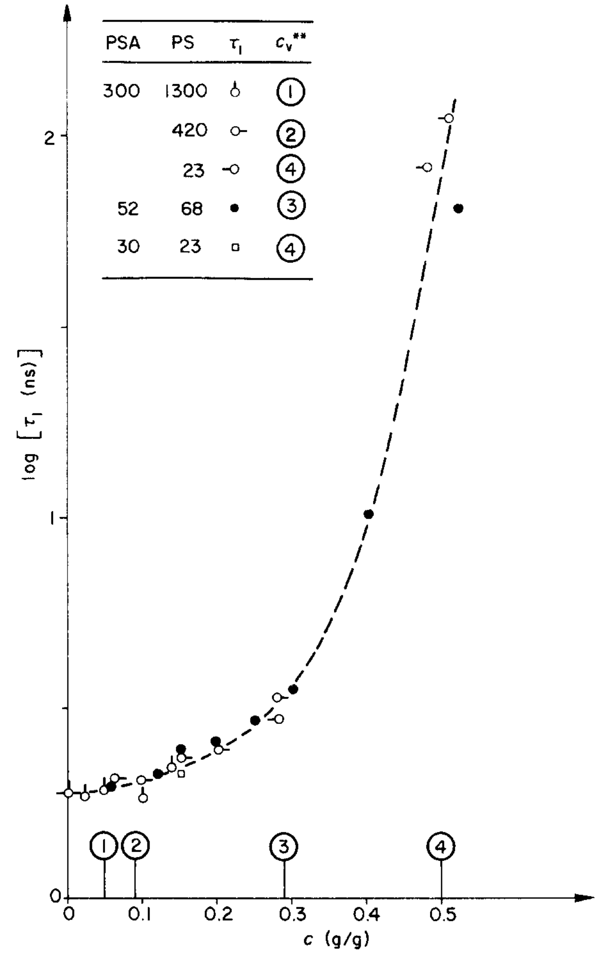

Figure 3 Evolution of the correlation time for segmental motion in different polystyrene–toluene mixtures

Table 2 Best-fit parameters obtained using the GDL model (323 K)

Labelled chain	Matrix Polymer	Matrix Weight fraction	τ_2/τ_1 free χ^2	τ_2/τ_1 free r_0	τ_2/τ_1 free τ_1	τ_2/τ_1 free τ_2/τ_1	$\tau_2/\tau_1=10$ χ^2	$\tau_2/\tau_1=10$ r_0	$\tau_2/\tau_1=10$ τ_1
PSA300	PS1300	0.14	1.60	0.138	0.501	5.8	2.11	0.150	0.34
		0.10	1.14	0.159	0.281	9.3	1.14	0.161	0.265
		0.05	1.31	0.200	0.338	9.4	1.64	0.211	0.269
		0.025	1.67	0.220	0.224	13	1.80	0.208	0.206
PSA300	PS420	0.28	1.35	0.363	0.520	13.8			
		0.20	1.14	0.231	0.274	18	1.47	0.250	0.520
		0.15	1.34	0.197	0.303	13	1.71	0.188	0.395
		0.10	1.38	0.189	0.345	9	1.49	0.193	0.369
		0.06	1.14	0.202	0.263	14	1.23	0.195	0.295
PSA300	PS23	0.51	1.55	0.210	1.82	13	1.74	0.206	2.05
		0.48	1.24	0.191	2.35	7	1.35	0.195	1.24
		0.28	1.29	0.262	0.472	13.3			
PSA300	pure solvent		1.53	1.66	0.225	13.3	1.71	0.157	0.280
PSA30	PS23	0.15	0.90	0.197	0.484	6	1.06	0.212	0.336

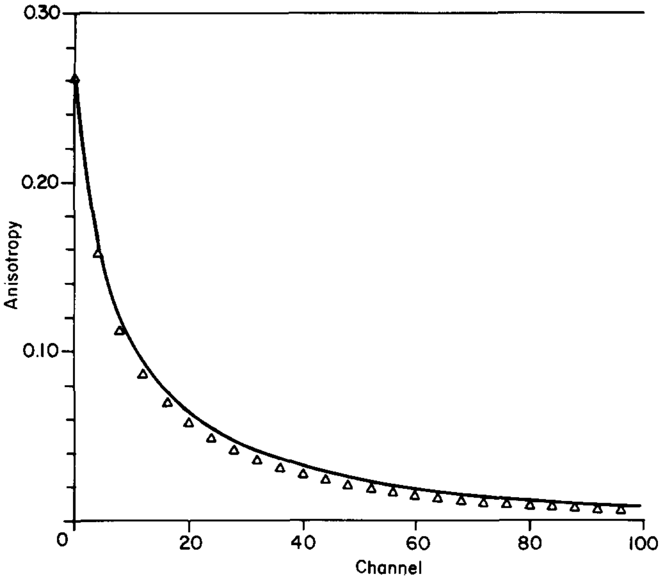

Figure 4 Best-fit orientation autocorrelation functions for PSA300 in a PS420 matrix (triangles) and in a PS23 matrix (full curve)

model (VJGM model[18]). The evolution as a function of concentration in both studies is very similar.

The effect of the molecular weight of the matrix has been checked more thoroughly by performing two experiments, one after the other, with optimized conditions for good reproducibility of all possible systematic errors, and a very high number of counts (underlined results in *Table 2*). In both experiments, the polymer weight fraction was 0.28, but the first sample (PSA300/PS420) was highly entangled, while the second was below c^*. As can be checked from both *Table 2* and *Figure 4*, the best-fit OACF obtained for both solutions are very similar. The small difference between the two values of τ_1 may reflect some effect of the chain ends, but it is not compatible with the very large difference expected from the scaling laws of entangled solutions. Also, it is noteworthy that τ_2/τ_1 is the same for the two experiments. Thus, entanglements do not affect the shape of the OACF, in the time and distance range explored by FAD. This finding is consistent with other recent results obtained using anthracene probes with alkyl tails[19] embedded in a polymer melt. In that latter case, we have shown that our FAD experiment is sensitive to dynamic processes occurring over a range of about 30 bonds along the backbone, which is smaller than the entanglement length.

CONCLUSIONS

This study, which covers a rather large range of viscosities and molecular weights, confirms quite unambiguously that the major conformational processes responsible for segmental chain reorientation are not affected by entanglements. However, when the concentration of a polymer solution is increased, the conformational jump time starts to increase dramatically when the polymer weight fraction exceeds 0.15. In this concentration domain, the probability that a monomer has a monomer from a different chain in its direct vicinity becomes rather large, whatever the molecular weight. We attribute the slowing down of the dynamics observed in FAD to an increase in the friction supported by the monomers, when solvent molecules in their neighbourhood are progressively replaced by other chain segments. Thus, this technique provides a very direct measure of the evolution of the friction coefficient as a function of concentration, independently of entanglements effects. Indirectly, it may also help to understand chain dynamics on a larger scale, and to separate friction and entanglements effects in the lower part of the concentrated regime. Indeed, it would be interesting to check if scaling theories are still relevant in this concentration range, provided the phenomenological frictional coefficient is rescaled according to experiments such as the ones presented here.

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