Observation of single chain motion in a polymer melt

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Molecular motion of single polymer chains has been investigated in a melt sample of polytetrahydrofuran and compared with results for the same polymer in dilute solution. Using a high resolution neutron scattering technique motion over distances up to 30 Å has been observed with an energy resolution of 0.01 μeV ($\sim 10^7\,\mathrm{s}^{-1}$). The motion of the chains in the melt is described by the Rouse model and a friction factor per segment has been extracted from the data. This compares well with values obtained from viscosity and bulk relaxation measurements on similar polymers.

INTRODUCTION

Current molecular models of the dynamics of polymer melts are based on the reptating chain model discussed by de Gennes[1]. Polymer chains cannot pass through each other, so large scale motions are assumed to proceed via a snake-like motion of the chain along its own contour. These ideas of reptation have recently been extended and developed into a molecular theory of viscoelasticity in a series of papers by Doi and Edwards[2-4].

In this model a number of time and distance scales can be distinguished. The chain motion is impeded by the surrounding mesh of chains which are themselves moving. T_d, the disengagement time is the time taken for a chain to move out of its original cage. The supposedly much longer time T_r is the time taken for complete renewal of the chain conformation. In the Doi–Edwards discussion[2] the chain is conceived as being confined by the surrounding chains to a tube of radius a and length L such that $(aL)^{1/2}$ is the root mean square end to end distance of the chain.

The effects of the molecular models can be observed indirectly via such macroscopic properties as viscosity, diffusion coefficients and moduli, and their variation with molecular weight. Observation of the molecular motion can be made more directly via scattering of radiation. The two techniques so far available have been the quasielastic scattering of light (photon correlation spectroscopy) and of neutrons. Photon correlation spectroscopy observes the correlation function or intermediate scattering law, $S(\kappa, t)$*, while conventional neutron experiments observe the Fourier transform of this function, the scattering law, $S(\kappa, \omega)$.

These techniques cover widely differing and effectively non-overlapping ranges of the scattered wavevector, κ. (The range for light stretches up to 2×10^{-3} Å^{-1} and that for conventional neutron experiments extends down to about 10^{-1} Å^{-1} for dynamic measurements.) Both types of measurement have been applied to the observation of polymer motion in dilute solution[5-8]. The light scattering measurements cover, for large molecules, the range $\kappa \approx 1/R$ (where R = radius of gyration), and show the change-over from centre of mass diffusion to internal motion which appears to be well-described by Zimm[9,10] using a bead–spring model with hydrodynamic interactions through the solvent. The neutron scattering results cover the range $\kappa \approx 1/\sigma$, where σ is a step length within the polymer chain, and show the change-over from local bond motion at high κ to Zimm behaviour at lower κ values.

In the melt, light scattering can no longer be used for the observation of single chain dynamics, but the technique of substituting hydrogen for deuterium in a few chains allows these chains to be labelled for neutron scattering experiments[11]. At low κ the coherent structure factor, $S_{\mathrm{coh}}(\kappa)$, for the single chains becomes dominant so that the coherent scattering law $S_{\mathrm{coh}}(\kappa, \omega)$ can be observed directly if the experiments can be carried out at low enough values of κ. In conventional quasielastic neutron scattering the lowest values of κ are of order 10^{-1} Å^{-1}, but more important the energy resolution is of order 1 μeV (see below). This resolution limits the precision with which the motion of chains in dilute solution can be observed[6,7] so that the expected slower motion in the melt would be unobservable at the lower κ values. Indeed observation of the incoherent scattering law, $S_{\mathrm{inc}}(\kappa, \omega)$ for a flexible polymer[12] [poly(dimethyl siloxane)] shows the width of $S(\kappa, \omega)$ to be less than 0.1 μeV at $\kappa = 0.1$ Å^{-1}.

However, there has recently been a new development in neutron scattering techniques. The neutron spin echo technique[13] simultaneously extends the wavevector range to 3×10^{-2} Å^{-1} and the effective limiting energy re-

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* $\boldsymbol{\kappa}$ is defined as the change in wavevector on scattering

$$\boldsymbol{\kappa} = \boldsymbol{\kappa}_i - \boldsymbol{\kappa}_f$$

and for elastic or quasielastic scattering, $\kappa = |\boldsymbol{\kappa}| = (4\pi/\lambda) \sin \theta/2$, where λ is the incident wavelength and θ the angle of scatter. ω is defined by the energy transfer on scattering:

$$h\omega = E_i - E_f = \frac{h^2}{2m}(|\boldsymbol{\kappa}_i^2| - |\boldsymbol{\kappa}_f^2|)$$

where i refers to the incident beam and f refers to the scattered beam.

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solution to 10^{-2} μeV (see below). First data for polymers in dilute solution confirm the power of the technique for the observation of polymer motion[14]. Here, we present the first data for a single labelled polymer chain in the melt.

The Doi–Edwards discussion makes a number of predictions about chain motion in the melt for different ranges of length (or κ) and different time-scales. For times longer than T_d and wavevectors κ of order $1/R$, the scattering from a polymer melt will be dominated by centre of mass diffusion. Doi and Edwards calculate both the coherent and incoherent intermediate scattering laws $S_{\mathrm{inc}}(\kappa, t)$ and $S_{\mathrm{coh}}(\kappa, t)$ for the interesting range $1/a > \kappa > 1/R$. In this range $S_{\mathrm{inc}}(\kappa, t)$ decays slowly as $1/\sqrt{t}$ and $S_{\mathrm{coh}}(\kappa, t)$ decay even more slowly with a relaxation time T_d.

Recently, Graessley[15] has used known physical characteristics of polymer systems such as the viscosity and the plateau modulus[16], G_N^0, to calculate values for the parameters in the Doi–Edwards theory. In particular he estimates that the tube diameter, a, is of order 34 Å for polyethylene and 83 Å for polystyrene. If these estimates are reliable they unfortunately put even the neutron spin–echo experiments in the range $\kappa > 1/a$. In this range only the local wriggling motion of the chain would be observed. The best estimates are that this will have the characteristics of the motion of a chain in solution but heavily damped and with no hydrodynamic interactions[16]. De Gennes[17] calculated $S_{\mathrm{coh}}(\kappa, t)$ for a Rouse chain and these results have been confirmed as part of a recent, more extensive, discussion by Akcasu *et al.*[18] of polymer chain motion. $S_{\mathrm{coh}}(\kappa, t)$ is a rather slowly decaying function $e^{-\sqrt{\Omega t}}$ and the correlation time Ω^{-1} varies as κ^4. In particular Akcasu *et al.* show that the initial time dependence of $S_{\mathrm{coh}}(\kappa, t)$ obtained as:

$$\Omega = \lim_{t \to 0} \frac{\mathrm{d}(\ln S(\kappa, t))}{\mathrm{d}t} \qquad (1)$$

is given by:

$$\Omega = \frac{1}{12}\frac{k_B T}{\xi_0}\sigma^2\kappa^4 \qquad \mathrm{s}^{-1} \qquad (2)$$

where ξ_0 is a friction factor per step length σ.

The corresponding equation for dilute solution, where hydrodynamic effects are important is:

$$\Omega = \frac{1}{6\pi}\frac{k_B T}{\eta}\kappa^3 \qquad \mathrm{s}^{-1} \qquad (3)$$

i.e. the κ dependence is slower and only the solvent viscosity determines the prefactor.

In this paper we report neutron spin–echo experiments on bulk samples containing tagged chains. We investigate the magnitude and κ dependence of the inverse correlation time Ω. The results obtained allow us to discuss the nature of the molecular motion observed, and whether it is possible with this technique to penetrate the range $\kappa < 1/a$ and observe the confining effects of the surrounding tube.

EXPERIMENTAL

Experiments were carried out at the high flux reactor at the Institut Laue–Langevin, Grenoble, France, using the backscattering spectrometer IN10[21] and the spin–echo spectrometer IN11[13,19,20].

IN11[21] makes possible the measurement of energy changes down to 0.01 μeV on scattering from a sample, by changing and keeping track of the neutron beam polarization non-parallel to the magnetic guide field. The resultant neutron beam polarization, when normalized against a purely elastic scatterer, e.g. a glassy polymer, is directly proportional to the cosine Fourier transform of the coherent scattering law, $S_{\mathrm{coh}}(\kappa, \omega)$, which is to say the intermediate scattering law, $S_{\mathrm{coh}}(\kappa, t)$, is measured directly. IN10, the backscattering spectrometer, measures in the frequency regime, giving the total scattering law ($S_{\mathrm{coh}}(\kappa, \omega) + S_{\mathrm{inc}}(\kappa, \omega)$) for the sample, convoluted with the machine resolution function. The equivalent of the inverse correlation time is the half-width at half maximum height ($\Delta\omega$) of $S(\kappa, \omega)$, which is directly proportional to Ω. In order to evaluate $\Delta\omega$, the machine resolution fuction is convoluted with a model $S(\kappa, \omega)$ for the sample and the resulting function is fitted to the experimental data. The resolution function is measured using the elastic incoherent scattering from a vanadium standard. Using IN10, it is possible to resolve energy changes greater than 10% of the 1 μeV resolution width for $\kappa > 0.07$ Å^{-1}.

Samples

Polytetrahydrofuran (PTHF) and polytetrahydrofuran-d_8 (PTDF) were prepared as described below. Carefully purified tetrahydrofuran (Analar ex. BDH Ltd, $\nless$99.5% purity, $\ngtr$0.1% water) was polymerized using antimony pentachloride as an initiator following the procedure described in ref 22). G.p.c. analysis indicated the molecular weight to be about 50 000 with a broad distribution. The deuterated analogue was prepared from tetrahydrofuran-d_8 (ex. Merck, Sharpe and Dohme, $\nless$99 atom % D) following the same basic procedure. N.m.r. examination indicated that the polymer contained less than 1% PTHF and g.p.c. analysis gave a molecular weight of about 50 000. (The radius of gyration of the PTDF in CS_2 (a good solvent) was measured using small-angle neutron scattering, and was found to be 140 Å.)

A sample of PTDF containing 3% PTHF was prepared by mixing the polymers in solution and precipitating out the product.

The bulk samples (3% PTHF in PTDF, 100% PTDF and 100% PTHF) were prepared by melting the sample and pressing in a mould to give discs 3 mm thick and 30 mm in diameter. These were contained in aluminium foil envelopes. The 3% PTHF/PTDF sample was measured at 110°C and 150°C on IN11, and at 110°C on IN10. The 100% PTDF sample was measured under similar conditions and the results subtracted in order to account for the background. The same (deuterated) polymer has also been observed on both IN11 and IN10 in dilute solution (25 mg cm^{-3}) in a good solvent, CS_2. The samples were contained in quartz cells for IN11 and aluminium cells for IN10. In each case measurements were made of the background (sample containers plus solvent).

Data analysis

Data are obtained from IN11 in the form of normalized polarization $P_N(t)$ against Fourier time (at a given scattered wavevector, κ) which is identical to the intermediate scattering law:

$$P_N(t) = S_{\mathrm{coh}}(\kappa, t)/S_{\mathrm{coh}}(\kappa)$$

For the small energy transfers involved for the melt samples, in the κ range of IN11, it was found that $S_{\mathrm{coh}}(\kappa, t)$ was satisfactorily described by a simple exponential of the form $S_{\mathrm{coh}}(\kappa, t) \propto \mathrm{e}^{-\Omega t}$ such that the initial slope Ω defined in equation (1) was given by:

$$\Omega = \frac{\mathrm{d} \ln (S(\kappa, t)}{\mathrm{d}t}$$

At the lowest κ values of these particular measurements ($\kappa \sim 0.05$ Å^{-1}) it was possible only to put an upper limit on the value of Ω.

For the solution data, as a good first approximation, the data were fitted to $S_{\mathrm{coh}}(\kappa, t)$ as calculated by Dubois-Violette and de Gennes[10] for the case of scattering from infinitely long chains in the dilute limit, using the Zimm model[9]. $S(\kappa, t)$ is in this case a universal function of the (effectively) normalized time coordinate (Γt). The inverse correlation time, Γ, is given by:

$$\Gamma = \frac{\sqrt{3}}{6^{3/2}\pi} \frac{k_B T}{\eta} \kappa^2 \qquad \mathrm{s}^{-1} \tag{4}$$

where η is the solvent viscosity and k_B is the Boltzmann constant. Γ is proportional to the initial slope Ω defined in (1) such that:

$$\Omega = \sqrt{2}\Gamma \tag{5}$$

Combination of equations (4) and (5) yields Ω given in equation (3).] The error bars in the Ω values extracted from the IN11 data and presented in the Figures are related to the counting statistics in the $S(\kappa, t)$ data. The limiting Ω values are the reasonable extremes of fitting the various model curves to the data.

Earlier experiments on bulk samples using IN10[12] have shown the data to be best fitted using the Rouse bead–spring model. In order to extract $\Delta\omega$, (half-width at half maximum height of $S(\kappa, \omega)$) the function was convoluted with $S(\kappa,\omega)$ obtained by Fourier transforming the expressions for $S_{\mathrm{coh}}(\kappa, t)$ as given in ref 17. The resulting function was then fitted to the experimental points.

There is a large uncertainty in the $\Delta\omega$ values extracted by fitting the Rouse model, because the κ range for IN10 falls inevitably in a region where this model must break down. The previous data for which the Rouse model provided the best fit were obtained for poly(dimethyl siloxane), an extremely flexible polymer. In this case the Rouse model might be valid to higher κ values. It has been shown that the value of $\Delta\omega$ depends heavily on the model used to extract it[12]. As with the solutions, the data observed at high enough κ might be expected to give Lorentzian correlation functions. To give some idea of the uncertainty in the κ values obtained from $S(\kappa, \omega)$ data via $\Delta\omega$, error bars were estimated by fitting both Lorentzian and Rouse models to the same data.

Similarly for dilute polymer solutions experience has shown the best fits to lie between Zimm and Lorentzian models[6–8]. In this case the error bars span the $\Delta\omega$ values obtained from these two fits. Before data from IN10 and IN11 can be compared consideration must be given to the model used in the IN10 fitting procedure to obtain the relationship between $\Delta\omega$ and Ω. For a simple Lorentzian it is clear that $\Delta\omega = \Omega$ since on Fourier transforming

$$S(\kappa, \omega) \propto \frac{\Delta\omega}{(\Delta\omega)^2 + \omega^2}$$

one obtains $S(\kappa, t) \propto \mathrm{e}^{-\Delta\omega t}$ and hence

$$\Delta\omega = \Omega = \lim_{t+0} \frac{\mathrm{d}}{\mathrm{d}t} \ln S(\kappa, t).$$

For the Zimm model an inverse correlation time, Γ, has been defined in equation (4) which is directly proportional to the initial slope Ω (equation 5). The relationship between $\Delta\omega$ and Γ ranges from $\Delta\omega/\Gamma = 0.85$ for coherent scattering and $\Delta\omega/\Gamma = 1.1$ for incoherent scattering[10] This shift is too small to observe within the accuracy of the experiment, especially considering the mixed coherent and incoherent scattering on IN10. Thus the values of $\Delta\omega$ obtained from fitting the Zimm model are approximately equal to Γ, but must be multiplied by $\sqrt{2}$ in order to obtain Ω.

For the Rouse model, the relationship between $\Delta\omega$ (as defined by de Gennes[17]) and Ω (as defined by equation 2) is $\Delta\omega/\Omega = 0.24$ for coherent scattering. Although no explicit form for Ω_{inc} is available to us, the Zimm case described above would lead one to suspect a somewhat larger ratio for $(\Delta\omega/\Omega)_{\mathrm{inc}}$. These arguments show that the conversion from $\Delta\omega$ to Ω is strongly model dependent. For consistency, the following relationships have been used in the conversion from $\Delta\omega$ to Ω.

Model used to obtain $\Delta\omega$	$\Delta\omega/\Omega$	
Lorentzian	1	
Zimm	$1/\sqrt{2}$	averaged coherent and incoherent values
Rouse	0.3	

RESULTS AND DISCUSSION

Figure 1 shows the coherent structure factor $S_{\mathrm{coh}}(\kappa)$, calculated for a sample of PTDF containing 3% PTHF chains using the Debye theory[23] and estimating R in the θ conditions of bulk samples to be 100 Å. This coherent intensity is given relative to a shifted baseline which represents the incoherent scattered intensity from the mixture[23]. Shown on the same graph is the total coherent intensity $S_{\mathrm{coh}}(\kappa)$ obtained from the IN11 experiments normalized at $\kappa = 0.08$ Å^{-1} and relative to the same baseline. The excellent agreement shows that the pure $S_{\mathrm{coh}}(\kappa, t)$ is indeed measured by the spin–echo measurements. *Figure 1* also draws attention to the fact that a mixture of $S_{\mathrm{inc}}(\kappa, \omega)$ and $S_{\mathrm{coh}}(\kappa, \omega)$ will inevitably be observed on the IN10 spectrometer where no distinction can be made between neutrons scattered coherently or incoherently. At higher κ values $S_{\mathrm{inc}}(\kappa, \omega)$ will dominate.

A comparison has been made of IN10 data from the sample containing labelled chains and from a purely homogenous sample for which $S_{\mathrm{inc}}(\kappa, \omega)$ is dominant. Within experimental error the scattering was identical, confirming that at high κ values $S_{\mathrm{inc}}(\kappa, \omega)$ and $S_{\mathrm{coh}}(\kappa, \omega)$ are qualitatively similar. De Gennes[17] predicts a ratio of 3:2 for the full width at half maximum of $S_{\mathrm{inc}}(\kappa, \omega)$ to $S_{\mathrm{coh}}(\kappa, \omega)$.

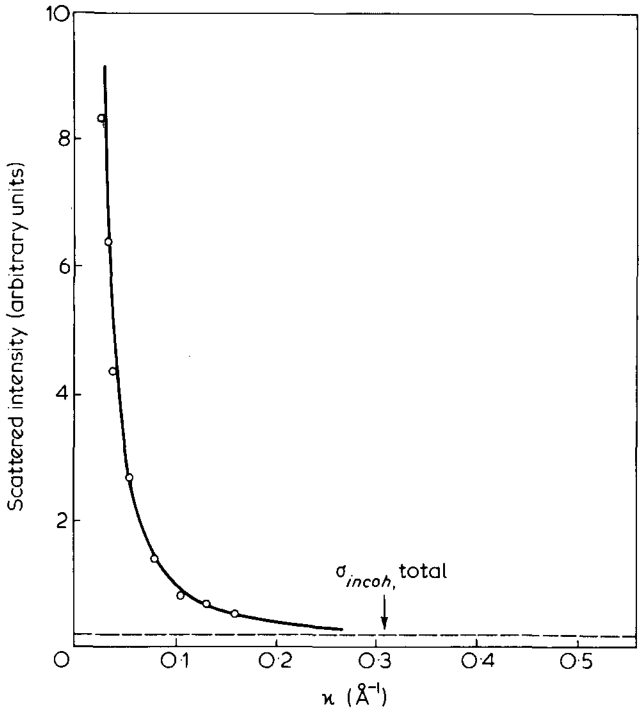

Figure 1 Full line represents the coherent structure factor for a PTDF sample containing 3% PTHF chains, calculated using the Debye theory, and plotted relative to a shifted baseline which represents the calculated incoherent scattered intensity from the mixture. The points show S_{coh} (κ) evaluated using IN11 data relative to the same shifted baseline

This would predict a vertical shift of 0.4 for the data in *Figures 2* and *3*, which falls within the error bars of the measurements).

Figure 2 shows Ω data from IN10 and IN11 experiments and compares a dilute solution of 2.5% PTDF in CS_2 at 30°C with a melt sample of 3% PTHF in PTDF at 110°C. The slight discontinuity in IN11/IN10 data overlap may arise from the dominance of $S_{inc}(\kappa, \omega)$ for IN10. For the melt sample the model dependence of the $\Delta\omega$ to Ω conversion may be crucial. Qualitatively the behaviour in the melt and in dilute solution are similar, with a somewhat faster κ dependence of Ω in the melt. The limits on a straight line fit to the data in *Figure 2* would give $\kappa^{2.4 \leq n \leq 2.8} \propto \Omega$ for solution and $\kappa^{3.2 \leq n \leq 3.8} \propto \Omega$ for the melt, but since the experimental κ-range is clearly transitional between Rouse–Zimm motion and local bond rotations, such power laws are not meaningful[7,8,18]. The vertical shift between the two sets of data corresponds to an increase in Ω by a factor of about 20 in going from melt to dilute solution. The absolute values of Ω predicted by the Zimm[10,18] and Rouse[17,18] theories were given in equations (2) and (3). For dilute solution assuming hydrodynamic interactions Ω varies as T/η for a given κ.

The value of η, the solvent viscosity, extracted from these data at $\kappa = 0.05$ Å^{-1} is 0.25 ± 0.3 cp which corresponds reasonably well with the handbook value[24] for CS_2 at 30°C of 0.34 cp. In the melt the solvent viscosity is replaced by a friction factor per step length, ξ_0, divided by σ^2 as shown in equation (2). Without assuming a value for σ the quantity ξ_0/σ^2 extracted from the data at $\kappa = 0.132$ Å^{-1} is 3×10^6 dyne s cm^{-3}. Values for ξ_0 defined for a given step length are obtained from values of the bulk modulus and listed for PTHF but for poly(dimethyl siloxane) (PDMS) and for natural rubber at the same temperature ξ_0/σ^2 gives 6.5×10^5 dyne s cm^{-3} and 6.8 $\times 10^5$ dyne s cm^{-3}, respectively. We have compared the incoherent scattering from PDMS with that for PTHF. The PTHF was found to move 2 or 3 times more slowly, so that a somewhat larger value for ξ_0/σ^2 in this polymer is to be expected when compared to PDMS. It is perhaps surprising that friction factors obtained from such different methods of observation fall so closely together in magnitude.

Figure 3 shows in detail the values of Ω obtained from IN11 measurements at two temperatures. Given the present resolution of the apparatus it does not seem likely to us that values of Ω at lower κ are accessible. It is difficult

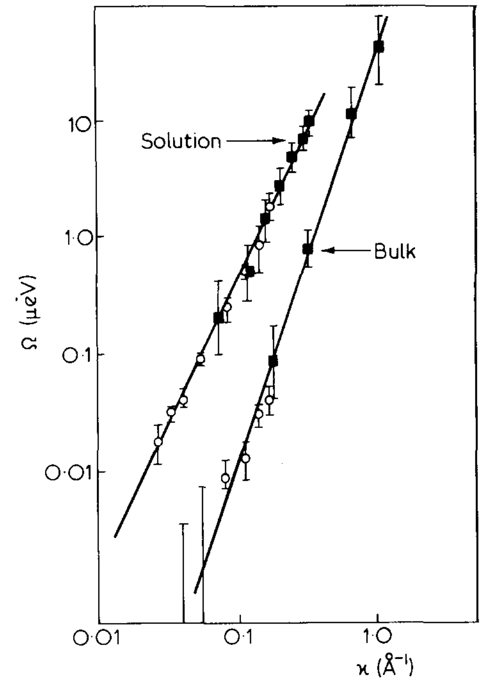

Figure 2 Data obtained from IN10 (■) and IN11 (○) for both a dilute solution of PTDF/CS_2 measured at 30°C and a melt sample of 3% PTHF/PTDF, measured at T = 110°C. The full lines are drawn as guides for the eye

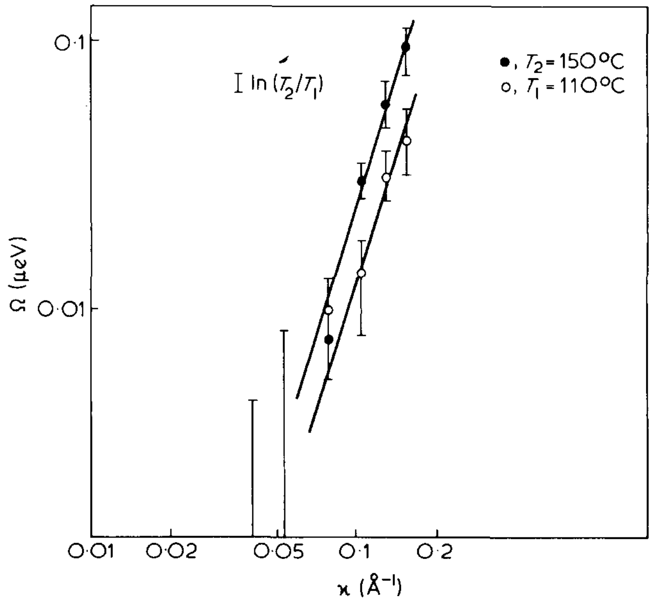

Figure 3 Results obtained from IN11 on the melt sample of 3% PTHF/PTDF measured at 110° and 150°C

to discuss quantitatively the temperature dependence shown in *Figure 3* since ξ_0 itself varies with temperature[16]. The ratio of the absolute temperatures for the two experiments would alone give rise to the small vertical shift marked in *Figure 3*. The experimental shift appears somewhat larger confirming that ξ_0 in these experiments is probably temperature-dependent.

CONCLUSIONS

The motion observed for melt polytetrahydrofuran is similar to that observed for dilute solutions, but with the damping factor increased by an order of magnitude. The friction coefficient extracted from the melt data falls well within the range of values obtained from bulk physical measurements for similar polymers. The similarity of the behaviour to that in dilute solution confirms that a similar type of motion is being observed while the increased κ dependence of the inverse correlation time, Ω, indicates a Rouse behaviour in the melt.

A Rouse-type wriggling motion is expected when the observation range falls within the tunnel diameter, a, of the Doi–Edwards model, i.e. when $\kappa > 1/a$. For $\kappa < 1/a$ an entirely different behaviour is expected with a slow relaxation time T_d which is κ independent. Such behaviour is certainly excluded by our data for $\kappa > 0.03$ Å^{-1}.

The IN11 spectrometer allows for the first time observation of the correlated motion in a polymer chain over distances between 10 and 30 Å. Only a factor of 2 improvement in energy resolution is foreseen for IN11 in the near future, and the rate of motion cannot be increased more than a factor of 2 or 3 by varying T or ξ_0. Thus the observable motion will remain limited to values of $\kappa > 0.03$ Å^{-1}. The calculated values of the tunnel diameter, a, are greater than 30 Å so it appears unlikely that neutron experiments on bulk samples will penetrate beyond the range of Rouse-like wriggling motion to observe the confining effects of the surrounding tunnel.

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