

# Cyclization dynamics of polymers: 9. The effect of polymer concentration on the slowest internal relaxation mode of a labelled polystyrene chain

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A combination of steady-state and fluorescence decay techniques permits one to measure the dynamics of end-to-end cyclization of a polymer chain substituted at both ends with pyrene groups. In the limit of low concentration, the rate constant for cyclization,  $k_{cy}$ , can be identified with the slowest relaxation rate  $\tau_1^{-1}$  of a Rouse-Zimm chain. Experiments are reported which allow  $k_{cy}$  to be examined for two chain lengths of polystyrene substituted on both ends with pyrene groups. These chains have  $\bar{M}_n = 9200$  and 25 000 ( $\bar{M}_w/\bar{M}_n \leq 1.15$ ). Added unlabelled polystyrene polymer [PS] causes  $k_{cy}$  to decrease in cyclohexane just above the  $\theta$ -temperature, whereas in toluene, a good solvent,  $k_{cy}$  is largely unaffected, even at [PS] concentrations of 50 wt%. These results are explained in terms of frictional effects—hydrodynamic screening—dominating in the poor solvent, whereas other factors tend to have offsetting effects in the good solvent.

**Keywords** Polymer dynamics; cyclization; fluorescence; relaxation; concentration effects

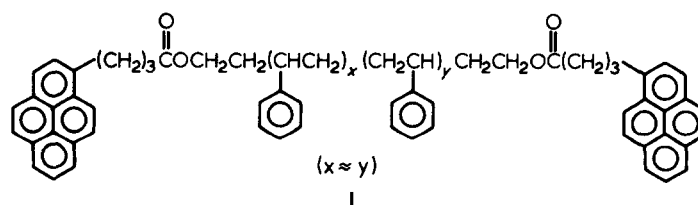
## INTRODUCTION

Polymer dynamics at high polymer concentrations has become an area of vital activity over the past several years, as new theoretical advances<sup>1-3</sup> have coupled with the development of new experimental techniques<sup>4-6</sup> to provide molecular-level measures of motion in the entangled state. Most of this activity has been focused on the translational diffusion of polymer molecules<sup>4-6</sup>. The internal dynamics of polymer chains traditionally have been studied by viscoelastic<sup>7</sup>, dielectric<sup>8</sup> and ultrasonic<sup>9</sup> relaxation as well as by flow birefringence<sup>10</sup> measurements. Although these experiments measure a bulk response of a polymer melt or polymer solution, they are normally interpreted in terms of models describing molecular responses. Ideally one would be able to test these models in terms of experiments which also operate at the molecular level. Insights into the molecular relaxation of polymer chains have been provided by n.m.r.<sup>11</sup>, vibrational spectroscopy<sup>12</sup>, e.s.r.<sup>13</sup> and fluorescence polarization and fluorescence depolarization<sup>14</sup> studies of suitably labelled polymer chains.

Luminescence quenching experiments provide another class of experiments for examining polymer dynamics via labelled chain experiments. Light is used to excite chromophores attached to the polymer chains. Motions which bring these excited chromophores close to quencher groups in the chain can be the rate-limiting step in the quenching process, which causes a decrease in the luminescence intensity and a shortening of the fluorescence or phosphorescence lifetime of the sample. In these experiments, the kinetics of cyclization provide a measure

of low-frequency chain dynamics. Our own experiments<sup>15</sup>, which examine pyrene excimer formation from pyrene groups attached to the ends of a polymer chain, fall into this class, as do the experiments of Cuniberti and Perico<sup>16,17</sup> in which pyrene groups are also incorporated along the polymer backbone. (The pyrene excimer technique was first applied to the study of cyclization of alkanes—see refs 18.) Also noteworthy are the phosphorescence quenching and triplet-triplet annihilation experiments of Mita, Horie and their coworkers<sup>19</sup>.

One of the important applications of experiments involving labelled chains is the study of the influence of added (unlabelled) polymer upon the conformation and dynamics of the labelled chains. Preliminary experiments have been reported by the Genoa group<sup>17</sup> for the case of pyrene groups distributed along the backbone of poly(vinyl acetate) chains. They cited hydrodynamic screening and excluded volume screening as the major effects of adding unlabelled poly(vinyl acetate) to dilute solutions of the pyrene labelled chains. In the experiments we report here, we examine the influence of unlabelled polystyrene chains (the matrix chains) on the cyclization kinetics of polystyrene labelled on both ends with pyrene (Py) groups. These chains have the structure 1:



Trace quantities (1 ppm) of **1** were incorporated into solutions containing from 0.01 to 55 wt% ( $0.0001 \leq \phi_w \leq 0.55$ ) of unlabelled polystyrene. From the time-dependent and steady-state fluorescence properties of the test chain, we determined  $\langle k_1 \rangle$ , the mean rate constant for its end-to-end cyclization. The brackets  $\langle \rangle$  emphasize that real polymer samples have finite polydispersity and that experimental values represent an average over their molecular weight distributions. The term of theoretical significance is  $k_{cy}$ , the rate constant for diffusion-controlled cyclization for a chain of unique length. A knowledge of the details of excimer spectroscopy permits us to equate  $k_1$  with  $k_{cy}$ :



The theory of Wilemski and Fixman<sup>20,21</sup> relates the value of  $k_{cy}$  to the inverse of the slowest internal relaxation time  $\tau_1$  of a polymer chain. In terms of the bead-spring model,  $\tau_1$  is the slowest Rouse-Zimm time of the chain. Perico and Cuniberti<sup>22</sup> have shown that for partially draining finite chains, higher-order modes should enter into  $k_{cy}$ . Our experiments have shown, however, that even for quite short chains cyclization is dominated by a single relaxation process and that  $k_{cy} \approx \tau_1^{-1}$  for very dilute solutions of labelled polystyrene chains<sup>15b,23</sup>. Here we examine the effects of unlabelled chain concentration on the cyclization dynamics of labelled chains of structure **1**, and find that this relationship seems to break down when the total polymer concentration becomes substantial.

## EXPERIMENTAL

Py(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(polystyrene)CH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub>C(CH<sub>2</sub>)<sub>3</sub>Py (**1**) of  $\bar{M}_n = 3900$  ( $\bar{M}_w/\bar{M}_n = 1.09$ , Py-PS3900-Py) and  $\bar{M}_n = 9200$  ( $\bar{M}_w/\bar{M}_n = 1.13$ , Py-PS9200-Py) were prepared and purified as previously described<sup>15</sup>. Aliquots (0.30 ml) of a solution containing 0.1 mg of **1** in 10.0 ml toluene were added to polystyrene powder in Pyrex sample tubes. These tubes were prepared from 4 mm i.d. Pyrex tubing fitted with a 19/38 joint on the open end. These mixtures were rigorously degassed by the freeze-pump-thaw technique on a vacuum line at  $10^{-5}$  Torr and sealed under vacuum. They were annealed by heating at 80° to 100°C in the dark for 24 h. The PS samples were narrow dispersity standards from Pressure Chemical Co.: PS4000,  $\bar{M}_n = 4000$ ,  $\bar{M}_w/\bar{M}_n = 1.07$ ; and PS860000,  $\bar{M}_n = 860\,000$ ,  $\bar{M}_w/\bar{M}_n = 1.06$ . Some experiments were carried out in the presence of PS terminated on both ends with OH groups: HO-PS8900-OH,  $\bar{M}_n = 8900$ ,  $\bar{M}_w/\bar{M}_n = 1.2$ .

A polystyrene sample terminated on only one end with pyrene was prepared by initiation of styrene polymerization with sec-butyl-lithium in THF, termination with ethylene oxide, and esterification with pyrene-(CH<sub>2</sub>)<sub>3</sub>COCl. This sample had  $\bar{M}_n = 5900$  ( $\bar{M}_w/\bar{M}_n = 1.2$ , PS5900-Py).

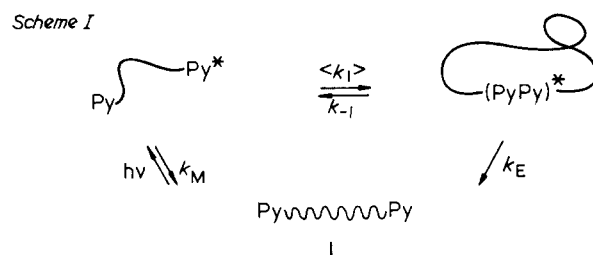
## DATA AND DATA ANALYSIS

In a labelled-chain experiment, one can examine a very dilute solution of a polymer chain containing a label (the 'test chain') in the presence of a vast excess of unlabelled

polymer (the 'matrix chains'). In our experiments polystyrene polymers tagged on both ends with pyrene (Py) groups were present at  $\sim 1$  to 2 ppm by weight ( $\sim 2 \times 10^{-6}$  M pyrene groups). Unlabelled polystyrene [PS] was added to the samples to give final solutions containing weight fractions ( $\phi_w$ ) of PS of 0.0001 to 0.55. Under these conditions bimolecular interactions between test chains can be completely neglected.

The fluorescence spectrum of Py-polystyrene-Py (**1**)  $\bar{M}_n = 3900$  is shown in Figure 1, in dilute solution in pure toluene, and in the presence of 40 wt% PS4000. These spectra are arbitrarily normalized at the 0-0 band of the pyrene fluorescence. It is clear that the added unlabelled polystyrene causes a decrease in the relative excimer intensity in the two samples.

Both fluorescence decay and steady-state fluorescence measurements were carried out on all samples. In toluene solution at 22°C, when the [PS] concentrations were sufficiently small ( $\phi_w < 0.1$ ), the intensity decay of the blue pyrene fluorescence  $I_M(t)$  was a single exponential over two decades of the intensity decay. In cyclohexane at 36°C, the Py-PS9200-Py sample fluorescence decays should be fitted to the sum of two exponential terms. The corresponding excimer  $I_E(t)$  could be fitted to a difference of two exponentials with essentially the same decay parameters. At high PS concentrations a parasitic fluorescence with a short decay time, emanating from an impurity in the PS, complicated the fluorescence decay analysis.



The experimental results can be interpreted in terms of Scheme I, where  $k_E$  and  $k_M$  represent respectively the reciprocal lifetimes of the excimer and locally excited pyrene. The rate constant  $k_{-1}$  describes excimer dissociation. For the polymers examined here, excimer dissociation is unimportant for experiments carried out at 22°C, but is significant in some of the experiments carried out at 36°C.

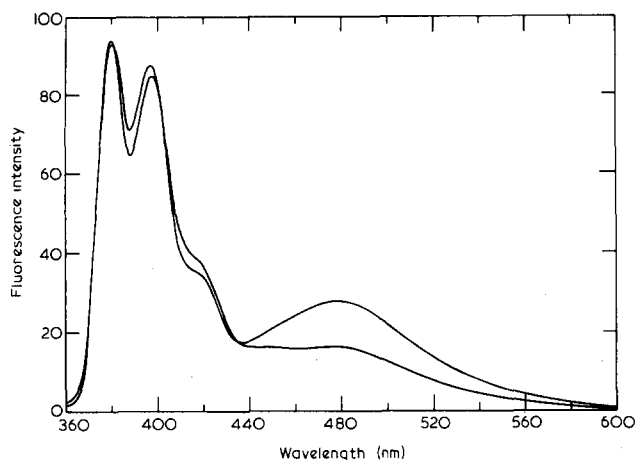
For experiments in toluene at 22°C, pyrene fluorescence decays were single exponential. Rate constants could be obtained from the expression

$$\langle k_1 \rangle = \lambda_1 - \lambda_{\text{model}} \quad (1)$$

where  $\lambda_1$  is the fluorescence decay rate of the blue pyrene fluorescence in **1** and  $\lambda_{\text{model}}$  is that for a sample of PS substituted at only one end with pyrene, in a solution of the same concentration of unlabelled polymer. Relative values of the cyclization rate constants could also be calculated from the expression

$$\frac{(I_E/I_M)}{(I_E/I_M)_0} = \frac{\langle k_1 \rangle / (k_{-1} + k_E)}{\langle k_1 \rangle_0 / (k_{-1} + k_E)_0} \quad (2)$$

where the subscript 0 refers to the dilute solution limit. The application of equation (2) is somewhat delicate.



**Figure 1** Fluorescence spectrum of Py-PS3900-Py ( $1 \times 10^{-6}$  M) in toluene and in 40 wt% PS4000 in toluene. The curves have been normalized at the (0,0) band of pyrene fluorescence to emphasize the decrease in excimer emission in the presence of added PS4000

While  $k_E$  is unaffected by high concentrations of unlabelled chains,  $k_{-1}$  decreases as the matrix chain concentration increases. In toluene at 22°C,  $k_{-1}$  is of the order of  $0.01k_E$ ; this consideration could be neglected. In cyclohexane at 36°C,  $k_{-1,0}$  is of the order of  $0.2k_E$ , decreasing to  $0.05k_E$  when  $\phi_w = 0.1$ . The changes in  $k_{-1}$  must be taken into account in analysing the steady-state experiments at 36°C.

Fluorescence decay curves of Py-PS9200-Py in cyclohexane at 36°C were non-exponential. In the [PS] concentration range of  $\phi_w \leq 0.1$ , the locally excited pyrene fluorescence  $I_M(t)$  and excimer fluorescence  $I_E(t)$  decays could be fitted, respectively, to sums and differences of two exponential terms. A full analysis of these decay curves<sup>15b,24</sup> in conjunction with measurements of  $\lambda_{\text{model}}$  under identical conditions gave values for all four rate constants in Scheme I. In this way the variation of  $k_{-1}$  with [PS] could be assessed. Under the same conditions  $\langle k_1 \rangle$  values could also be obtained *via* steady-state measurements, and these turned out to be in excellent agreement with those determined from the fluorescence decay measurements.

At higher [PS] concentrations, estimates of  $\langle k_1 \rangle$  could be obtained from equation (1) by setting  $\lambda_1$  equal to the long-time decay in the  $I_M(t)$  and  $I_E(t)$  measurements for Py-PS9200-Py samples. Alternatively  $\langle k_1 \rangle$  values could be obtained from steady-state fluorescence measurements. For Py-PS25000-Py, fluorescence decay experiments in the presence of added [PS] were not very useful for determining  $\langle k_1 \rangle$ :  $\lambda_1$  was so close in magnitude to  $\lambda_{\text{model}}$  that data analysis using equation (1) was unsatisfactory. Here equation (2) could be applied to data obtained from steady-state fluorescence measurements, using  $k_{-1}$  values obtained for lower molecular weight chains. Fortunately,  $k_{-1}$  does not depend upon chain length<sup>15b,23,24</sup>.

## DISCUSSION

### Review of dilute solution behaviour

In the limit of dilute solution in a  $\theta$ -solvent, the bead-and-spring model provides a theoretical framework for

relating the rate constant for diffusion-controlled end-to-end cyclization of a polymer chain,  $k_{\text{cy}}$ , to its slowest internal relaxation time,  $\tau_1$ . Exploitation of the model leads to the relationship  $k_{\text{cy}} \approx \tau_1^{-1}$ , and predicts that  $k_{\text{cy}}$  should decrease with chain length  $N$  as  $N^{-3/2}$  power<sup>20-22</sup>. Both predictions have been verified experimentally for polystyrene chains of 50 to 2000 backbone carbons.

In good solvents and at finite polymer concentrations, the theoretical predictions are not clear cut. Not only do excluded volume effects enter the picture, but the partially draining nature of finite chains swollen in a good solvent complicate evaluations of the hydrodynamic interactions in the bead-and-spring model. One can visualize the interplay of dynamic and configurational contributions as follows: the bead-spring model leads to the suggestion that the cyclization rate constant, at least for very long chains, is proportional to the ratio of the translational diffusion coefficient  $D$  to the mean-squared radius of gyration  $R_G^2$  of a polymer<sup>20,22</sup>:

$$k_{\text{cy}} \propto D/R_G^2 \quad (3)$$

Note that for polymers in a  $\theta$ -solvent, equation (3) also predicts that  $k_{\text{cy}} \sim N^{-3/2}$ .

Polymers swell in a good solvent.  $R_G^2$  is larger<sup>1</sup>. At comparable solvent viscosities,  $D$  is smaller<sup>1</sup>. Both predict that cyclization should be slower in a good solvent than in a poor solvent. This also has been confirmed experimentally<sup>15b</sup>. For chains of high enough molecular weight,  $D/R_G^2$  in a good solvent should decrease as  $(N^{-3/5}/N^{6/5})$ , i.e.  $k_{\text{cy}} \sim N^{9/5}$ . Experiments on polystyrene chains of  $50 \leq N \leq 2000$  yield values of  $k_{\text{cy}}$  for which a plot of  $\log k_{\text{cy}}$  versus  $\log N$  is concave downwards. These data give no indication for the asymptotic behaviour suggested for very long chains<sup>15b</sup>.

### Cyclization dynamics in semidilute and concentrated solution

The dependence of  $\langle k_1 \rangle$  upon matrix chain concentration is shown in Figure 2 for the labelled chains of  $\bar{M}_n = 9200$  and  $\bar{M}_n = 25000$ . The most striking feature of the data is that  $\langle k_1 \rangle$  shows a very different dependence on [PS] in a good solvent (toluene, 22°C) than in a poor solvent (cyclohexane, 36°C). In cyclohexane, addition of even small amounts of unlabelled PS causes a decrease in the cyclization rate, amounting to about a factor of 4 at  $\phi_w = 0.5$ . In toluene, the changes are more modest, and for the labelled chain of  $\bar{M}_n = 25000$ ,  $\langle k_1 \rangle$  barely changes at all.

The second significant point to notice is that at [PS] concentrations above  $\phi_w = 0.2$ ,  $\langle k_1 \rangle$  takes very similar values in both solvents. Some correction ought in principle to be applied to the data to account for solvent viscosity ( $\eta$ ) and temperature differences between the two sets of experimental conditions. At zero [PS] concentration, an  $\eta_1 T_2 / \eta_2 T_1$  correction can be applied rigorously. This factor is modest, and its applicability at finite [PS] concentration is problematic. We prefer at this point not to apply any corrections to the data we report.

The third feature of the data is that the length of the matrix chains seems not to influence the cyclization dynamics, even though it profoundly affects the macroscopic viscosity of the polymer solutions. For example, values of  $\langle k_1 \rangle$  have been determined for Py-PS9200-Py

in the presence of PS chains of  $\bar{M}_n=17\,500$  and  $\bar{M}_n=860\,000$  ( $\bar{M}_w/\bar{M}_n < 1.1$  for both) as well as in the presence of HO-PS8900-OH where hydrogen bonding between the ends of different chains causes transient networks to be formed. These different polymers affect the cyclization rate of the test chain similarly.

The cyclization dynamics of Py-PS25000-Py have been examined only in the presence of PS of  $\bar{M}_n=17\,500$ . The gross features of the dependence of  $\langle k_1 \rangle$  upon  $\phi_w$  are essentially the same as those observed for Py-PS9200-Py, even though here the matrix chains are somewhat shorter than the test chains.

Entanglement effects are unlikely to play any role in determining the behaviour depicted in Figure 2. These chains are too short. For PS,  $\bar{M}_w=25\,000$  represents the onset for entanglements to be an important contributor to the polymer melt viscosity. Even longer chains are necessary to observe these effects in the presence of a diluent.

Hydrodynamic screening and excluded volume screening effects are more likely to be the source of the behaviour shown in Figure 2. For example, if we assert that equation (3) continues to apply at finite matrix chain concentrations, we would identify  $D$  with the self-diffusion coefficient ( $D_{\text{self}}$ ) of the labelled chain.  $D_{\text{self}}$  decreases with increasing polymer concentration  $c$  because of an increase in the microscopic friction coefficient  $f$ ,  $f=f_0(1+k_f c + \dots)$ , where  $k_f$  is a constant greater than zero\*<sup>25</sup>:

$$D_{\text{self}} = \frac{kT}{f} = \frac{kT}{f_0(1+k_f c + \dots)} \quad (4)$$

$$\langle k_1 \rangle \sim \frac{D_{\text{self}}}{R_G^2} = \frac{kT}{R_G^2 f_0(1+k_f c + \dots)} \quad (5)$$

From this perspective, one can understand the dynamic behaviour in a poor solvent near the  $\theta$ -temperature. Here  $R_G^2$  changes only weakly if at all with increasing polymer concentration.  $D_{\text{self}}$  decreases, initially as  $c^{-1}$  (i.e. as  $\phi_w^{-1}$  at low  $c$ ), and  $\langle k_1 \rangle$  decreases with increasing [PS]. In a good solvent  $R_G$  decreases with increasing polymer concentration<sup>25</sup>. The decrease in  $D_{\text{self}}$  will be offset by a corresponding decrease in  $R_G^2$  which by itself would tend to increase  $\langle k_1 \rangle$ .

Two serious issues remain to be resolved. First, for the relatively short chains examined here, the changes in  $R_G^2$  by themselves are too small to account for the large differences in cyclization rates in toluene and cyclohexane at low [PS] concentration. Another factor must contribute.

One possibility is that excluded volume operates to suppress end-to-end cyclization. This view is supported by recent theoretical studies by Oono and Freed<sup>26</sup>. They report that the radial distribution function, at short end-to-end separations, is much more sensitive to excluded volume effects than is  $R_G^2$ . In our laboratory we have observed strong solvent effects on the cyclization equilibrium constant in accord with their predictions<sup>27</sup>. From this point of view, one says that the addition of unlabelled

polymer screens the excluded volume effects and presumably relaxes the constraints against chain end proximity.

The second serious problem is associated with the connection between  $k_{\text{cy}}$  and  $\tau_1$ , the slowest internal relaxation time of the test chain. From the theory of Wilemski and Fixman<sup>20</sup>, one identifies  $k_{\text{cy},0}$  with  $\tau_{1,0}^{-1}$ . Experiments (*vide supra*) tend to confirm this point of view. What happens at finite polymer concentrations is not yet clear. Chain relaxations in separate chains are coupled. Viscoelastic and birefringence experiments, which look at the bulk solution properties, are interpreted to yield the conclusion that  $\tau_1$  increases substantially with increasing polymer concentration, both in good and poor solvents, with the magnitude of the increase being nearly as large as the increase in the solution viscosity<sup>7</sup>.

Muthukumar and Freed<sup>28</sup> have developed a theoretical treatment of hydrodynamic screening effects on chain dynamics in terms of the bead-spring model. For the  $p$ th mode of internal relaxation, they show that

$$\tau_p = \tau_{p,0}(1 + Acp^{-k} + \dots) \quad (6)$$

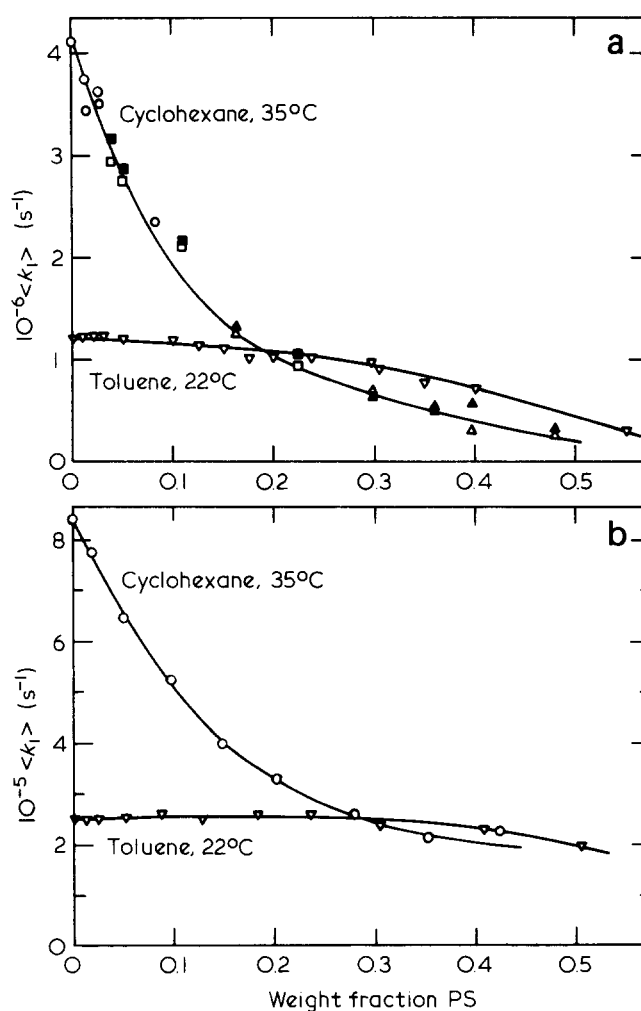


Figure 2 A plot of  $\langle k_1 \rangle$  vs. the weight fraction of PS. (a) Test chain of  $\bar{M}_n=9200$  in the presence of unlabelled PS of  $\bar{M}_n=17500$  ( $\circ, \bullet$ ),  $\bar{M}_n=860\,000$  ( $\square, \blacksquare$ ), and HO-PS-OH of  $\bar{M}_n=8900$  ( $\bar{M}_w/\bar{M}_n=1.3$ ) ( $\triangle, \blacktriangle$ ). (b) Test chain of  $\bar{M}_n=25\,000$  in the presence of PS of  $\bar{M}_n=17\,500$  ( $\circ$ ). Open points refer to steady-state measurements; closed points to fluorescence decay measurements

\* Hervet *et al.*<sup>25</sup> report that  $D_{\text{self}}$  values for a PS chain of  $M=245\,000$  (in a good solvent) determined by the forced Rayleigh technique, show a slight increase over the concentration range  $3 \times 10^{-3}$  to  $1 \times 10^{-2}$  g ml<sup>-1</sup>, accompanying a decrease in chain dimensions. We thank a referee for reminding us of these results.

where  $A$  is related to the second virial coefficient of the polymer and  $\kappa$ , a constant, takes the value 0.5 in a  $\theta$ -solvent and 0.6 to 0.8 in a good solvent. Birefringence experiments by Schrag's group<sup>10</sup> confirm these predictions for long chains at concentrations up to  $\phi_w = 0.01$ .

If we identify  $\langle k_1 \rangle$  with  $\tau_1$ , we can examine whether the corresponding behaviour

$$\langle k_1 \rangle^{-1} = \langle k_1 \rangle_0^{-1} (1 + Ac + \dots) \quad (7)$$

is satisfied. In a good solvent, toluene, our data indicate that  $\langle k_1 \rangle$  is almost independent of  $c$ , perhaps for the reasons cited above. Equation (7) does not apply to the data.

Our data in cyclohexane near the  $\theta$ -temperature fit the form predicted by equation (7). These are plotted in Figure 3. While the initial slope for Py-PS25000-Py is steeper than that for Py-PS9200-Py, the  $A$  values are determined from the slope-to-intercept ratio. We find  $A = 6.6 \text{ ml g}^{-1}$  for the longer chain and  $A = 10.8 \text{ ml g}^{-1}$  for Py-PS9200-Py. The shorter chain has the larger value of  $A$ . This result is inconsistent with the formulation of Muthukumar and Freed.

These results suggest that at finite polymer concentration the end-to-end cyclization experiment and the viscoelastic and birefringence experiments look at fundamentally different aspects of chain dynamics. These latter experiments are sensitive to dynamic coupling among chains extending over distances far greater than the dimensions of a single chain. The fluorescence experiment looks at factors affecting the rate of cyclization of

individual chains. The way in which the matrix chains influence these motions remains to be elucidated.

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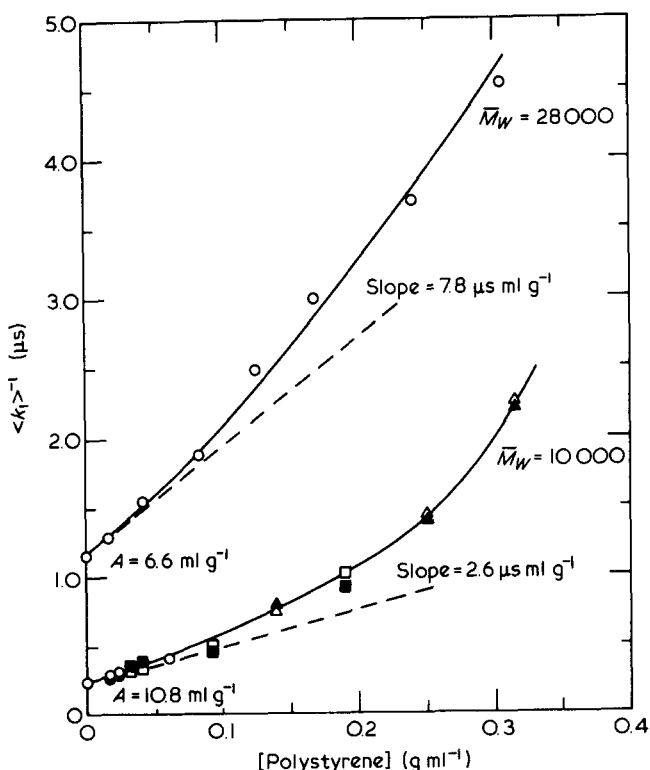


Figure 3 A plot of  $\tau_1 \propto \langle k_1 \rangle^{-1}$  vs. concentration of PS chains in cyclohexane at 36°C. Data are taken from Figure 2