Cyclization Dynamics of Polymers. 13. Effects of Added Polymer on the Conformation and Dynamics of Polystyrene Containing Evenly Spaced Pyrene Groups[†]

Mitchell A. Winnik,* Xiao-Bai Li,[‡] and J. E. Guillet

Lash Miller Laboratories, Department of Chemistry, and Erindale College, University of Toronto, Toronto, Ontario, Canada M5S 1A1. *Received July 19, 1983*

ABSTRACT: Steady-state fluorescence measurements of excimer formation in a polystyrene sample ($\bar{M}_n$ = 13 800) containing pyrene groups evenly spaced (ca. every 25–30 monomer units) have been carried out as a function of the concentration of unlabeled polymer. In cyclopentane, a Θ-solvent, hydrodynamic screening causes a decrease in the rate of excimer formation at elevated polymer concentration. In toluene, a good solvent, hydrodynamic screening effects are offset by excluded volume screening so that intramolecular excimer formation is much less affected than in cyclopentane. An important observation is that the changes in cyclization rates induced by increased polymer concentration are orders of magnitude *smaller* than the corresponding increases in shear viscosity of the solution.

This paper examines the effects of concentration on polymer conformation and dynamics. We use a labeled-chain technique which permits us to study the fluorescence of a trace concentration of these polymers in the presence of varying concentrations of unlabeled polymer.[1] The experiments measure the behavior of individual polymer molecules as affected by a mean field of invisible solvent and polymer molecules.

The polymer we examine is a polystyrene of $\bar{M}_n$ = 13 800 ($\bar{M}_w/\bar{M}_n$ = 1.3) with pyrene pendant groups *evenly spaced* every 25–30 monomer units, **3**. This polymer was prepared by the condensation of bishydroxy-terminated polystyrene (**1**) ($\bar{M}_n \sim 3000$) with pyrene-$CH_2CH(CO_2H)_2$ (**2**) (Scheme I). Since individual fluorescence experiments required less than 0.1 mg of labeled chain, fractionation of the condensation copolymer using analytical gel permeation chromatography columns yielded adequate (milligram) amounts labeled polymer.

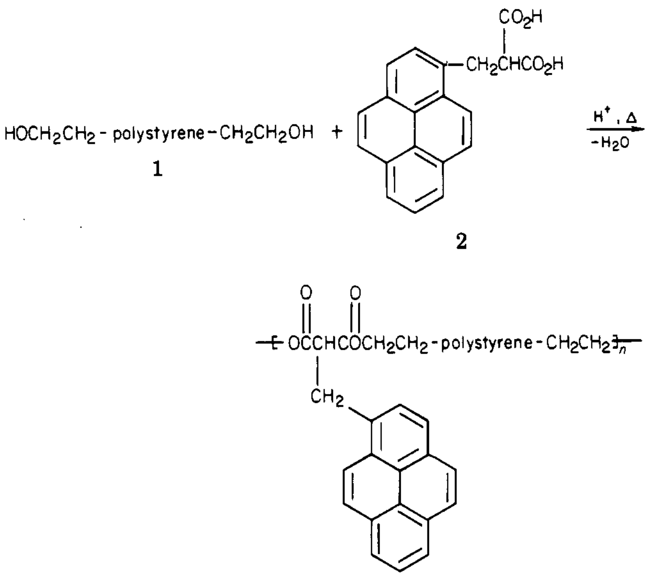
Samples were prepared by adding a solution of **3** to a known amount of polystyrene (PS) ($\bar{M}_n$ = 17 500, $\bar{M}_w/\bar{M}_n$ = 1.06) in small-diameter Pyrex tubes. The final concentration of **3** was approximately 10 ppm. The samples were outgassed on a vacuum line and sealed under vacuum. To ensure sample uniformity, the sealed tubes were annealed for 2 h at 80 °C and then cooled to room temperature. Samples were prepared containing up to 70% unlabeled polystyrene by weight.

Fluorescence measurements on these samples permit us to examine the influence of polymer concentration on the conformation and dynamics of the labeled chains. Under these conditions, with our low molecular weight polymer samples, entanglement contributions to chain dynamics are unimportant. This point is discussed in more detail below.

Experimental Section

The details of the synthesis of the pyrene-labeled polymer have been reported elsewhere.[2] The unlabeled polystyrene of $\bar{M}_n$ = 17 500, $\bar{M}_w/\bar{M}_n$ = 1.06, was purchased from Pressure Chemical Co. and used without further purification. Cyclopentane was refluxed over $LiAlH_4$ and distilled. Toluene was refluxed over sodium and distilled. 2-Butanone was dried over $CaSO_4$ and then distilled.

Scheme I



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Samples were prepared in 3-mm-i.d. Pyrex tubes fitted with a female 19/38 joint. A weighed amount of unlabeled polystyrene was placed in the tube. Subsequently, a measured quantity of a solution of the labeled polymer **3** in cyclopentane, 2-butanone, or toluene was added, and the tube was attached to a vacuum line. The samples were outgassed by successive freeze–pump–thaw cycles and sealed under a vacuum of ca. 10^{-5} torr. They were then annealed at 80 °C for 2 h and allowed to cool to room temperature. The final concentration of **3** was ca. 10 ppm. Samples were prepared containing 1–70% unlabeled polystyrene by weight.

Fluorescence spectra were run with a right-angle geometry on a Hitachi Perkin-Elmer MPF-44B spectrometer. Lifetimes, where measured, were determined by the time-correlated single-photon-counting technique.

Results and Discussion

Fluorescence spectra of **3** in cyclopentane are shown in Figure 1. Two bands are observed, a structured blue fluorescence from isolated pyrene chromophores, and a broad green emission centered at 480 nm from pyrene excimers.[3] Pyrene excimers are formed from the encounter of an excited pyrene with a ground-state pyrene, and the intensity of excimer fluorescence (I_E) measures the number of pyrene groups that can diffuse together during the time in which one of the pyrene groups remains excited. The intensity of locally excited pyrene fluorescence (I_M) measures the number of excited groups that emit a photon before they encounter a second pyrene. The concentration of labeled chains is so low that all pyrene–pyrene encounters occur intramolecularly.

[†] Dedicated to Professor W. H. Stockmayer on his 70th birthday.

[‡] On leave from the Department of Chemistry, Nankai University, Tianjin, People's Republic of China; deceased February 1983.

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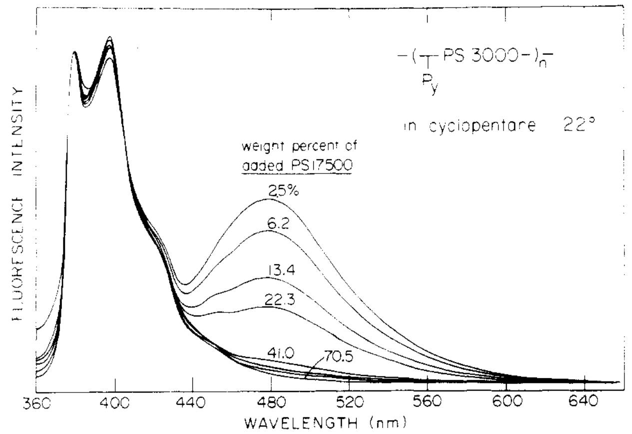
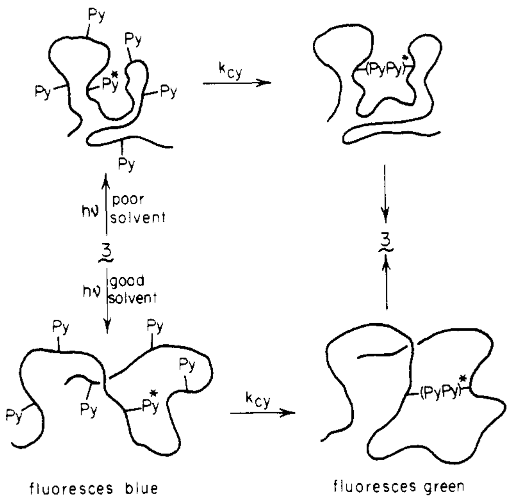


Figure 1. Fluorescence spectra of the probe polymer **3** in cyclopentane at 22 °C in the presence of varying amounts of polystyrene, $\bar{M}_n$ = 17 500.

Scheme II



Mechanism of Excimer Formation and Decay. Scheme II provides a simple mechanism for intramolecular excimer formation, in which k_1 is the rate constant describing cyclization. According to Scheme II, in a good solvent polymer chains are expanded, increasing the mean separation between pyrenes over that in a poor or Θ-solvent. One anticipates less excimer formation in a good solvent than in a poor solvent. Comparison of Figure 1 and 2 indicates that at low polymer concentration, substantially more excimer is observed in cyclopentane (a Θ-solvent for polystyrene at 22 °C) than in toluene.

Addition of unlabeled polymer to dilute solutions of the labeled chains results in a decrease in excimer formation. This decrease is much more pronounced in cyclopentane than in toluene. Interpretation of these results requires a more detailed consideration of the mechanism of excimer formation and decay.[3-5]

Scheme III takes into account the possibility that unlabeled polystyrene (PS) might quench pyrene fluorescence (with a second-order rate constant k_{qM}) or quench pyrene excimer fluorescence (k_{qE}). In addition, it recognizes that excimer dissociation (k_{-1}) can occur. The terms k_M and k_E describe, respectively, the reciprocal lifetimes (τ_M^{-1}, τ_E^{-1}) of the locally excited pyrene and excimer. At room temperature $\tau_M \approx 200$ ns and $\tau_E \approx 45$ ns, with some variation in different solvents. This scheme leads to the equation

$$\frac{I_E}{I_M} \propto \frac{\phi_E}{\phi_M} = \frac{k_{fE}}{k_{fM}}\left(\frac{k_1}{k_E + k_{-1} + k_{qE}[\mathrm{PS}]}\right) \qquad (1)$$

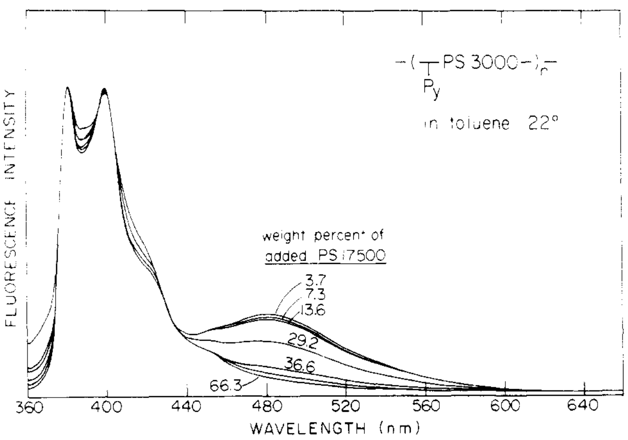
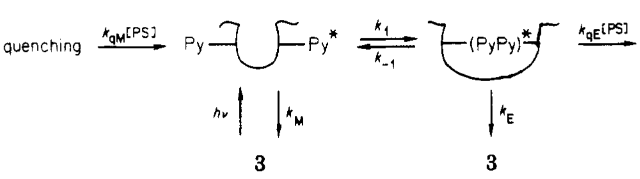


Figure 2. Fluorescence spectra of **3** in toluene at 22 °C in the presence of varying amounts of polystyrene, $\bar{M}_n$ = 17 500.

Scheme III



where ϕ_E and ϕ_M are the quantum yields of excimer and pyrene fluorescence and k_{fE} and k_{fM} are their respective radiative rate constants.

Previous experiments have indicated that k_{qE}[PS] term is negligible over the entire range of these experiments.[6] Values of k_{qM}[PS] are significant, but these, as eq 1 indicates, do not affect interpretation of I_E/I_M values. At 22 °C, the value of k_{-1} is ca. 20% that of k_E.[7] It describes a process with a diffusion component, ring opening, and its magnitude is sensitive to frictional (viscosity) effects.[8] One of the consequences of adding unlabeled polymer to solutions of **3** is that k_{-1} decreases. Since k_E is insensitive to [PS], k_{-1} makes a negligible contribution to the experiment for [PS] ≥ 10% by weight.[8] At lower PS concentrations changes in k_{-1} makes a small contribution to the [PS] sensitivity of the I_E/I_M values.

Cyclization to form pyrene excimers is a diffusion-controlled process.[3,4] Consequently k_1 is sensitive to friction effects. One of the important consequences of increased polymer concentration is to increase the local friction coefficient (f), causing a decrease in k_1.

Meaningful values for k_1 and k_{-1} can be obtained only from a detailed analysis of the fluorescence decay curves $I_M(t)$ and $I_E(t)$. This is a delicate and difficult task since our measurements show that these decays are more complex than simple kinetic models such as Scheme III predicts. Polydispersity effects contribute as do multiple relaxation times due to excimer formation from pyrene pairs remote along the chain contour. Nonetheless estimates can be made for k_1 by comparing the mean experimental lifetime ($\bar{\tau}_M$) of the pyrene decay with $k_M + k_{qM}$[PS] values obtained in separate experiments. Since $\bar{\tau}_m$ is on the order of 120–150 ns when [PS] = 0, k_1 values under those conditions are on the order of 2×10^6 s^{-1}, depending, of course, on solvent viscosity. In other words, the experiments reported in this paper probe chain relaxation times on the time scale of 0.5 μs to approximately 50 μs.

Concentration Effects on Cyclization in a Θ-Solvent. The theory of diffusion-controlled end-to-end cyclization was first treated by Wilemski and Fixman,[9] with important further contributions by Doi[10] and by Perico and

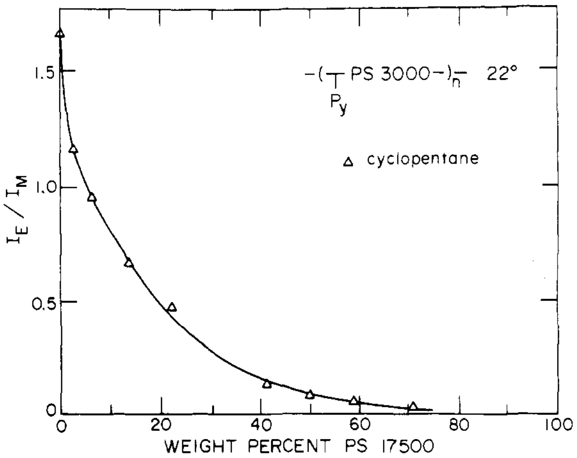


Figure 3. Plot of I_E/I_M vs. weight percent of polystyrene ($\bar{M}_n$ = 17500) in cyclopentane at 22 °C.

Cuniberti.[11] They provide considerable insights into the cyclization process. For example, in terms of the Rouse–Zimm model, the cyclization rate constant k_{cy} is related to the ratio of the translational diffusion coefficient (D) and the mean-squared radius of gyration R_G.[9,11]

$$k_{cy} \sim D/R_G^2 \qquad (2)$$

Dimensional factors are contained in the R_G^2 term. Expansion of the chain should result in a decrease in the cyclization rate. Frictional effects are contained in the D term; k_{cy} should vary as the inverse solvent viscosity. Where comparison to experiment has been possible, the predictions of the theory have been substantiated for dilute solutions of polymers in Θ-solvents.[4,7,12]

A simple-minded extension of this model to cyclization at finite polymer concentration might equate D with the self-diffusion coefficient. Since $D_{self} = kT/f$ and f increases with polymer concentration (c) according to

$$f = f_0(1 + \kappa_f c + ...) \qquad (3)$$

k_{cy} should decrease with increasing polymer concentration, initially as $1/c$. In a Θ-solvent, R_G^2 is essentially independent of c.

In Figure 3 we show the concentration dependence of I_E/I_M for 3 in cyclopentane at 22 °C in the presence of unlabeled PS of similar molecular weight. At 22 °C, cyclopentane is a Θ-solvent for PS. The decrease of I_E/I_M with increasing PS is substantial and resembles a $1/c$ dependence. A curious feature of the results is that even at very high polymer concentrations, the decrease in I_E/I_M is relatively modest. It decreases by a factor of 15 under conditions in which the bulk solution viscosity increases by several orders of magnitude. One learns that the motion described by k_1 is much less sensitive to polymer concentration than is the low-frequency shear viscosity.

Concentration Effects on Cyclization in Modest and Good Solvents. In a good solvent R_G^2 decreases with increasing polymer concentration.[13] One would anticipate from eq 2 that PS concentration would affect R_G^2 and D in ways that should in part offset one another. Experiments in dilute solution have indicated that eq 2 is inadequate to describe cyclization rates of polymers in good solvents.[4,14] Excluded volume considerations lead to important correlation effects.[15] Cyclization probability in good solvents is decreased not only by the increase in R_G^2. It is also affected by the presence of a "correlation hole" in the end-vector distribution function, which suppresses the probability of the two chain ends being in proximity.

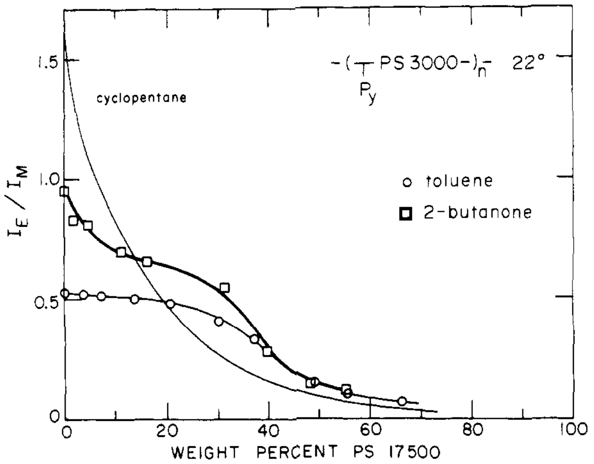


Figure 4. Plot of I_E/I_M vs. weight percent of polystyrene ($\bar{M}_n$ = 17500) in toluene (○) and in 2-butanone (□) at 22 °C. The thin solid line presents the data in cyclopentane for comparison.

We have previously shown for end-labeled polystyrene in dilute solution that solvent effects on k_1 are larger than corresponding effects on R_G^2. In addition, we noted that k_{-1} is larger in good solvents than in poor solvents.[14] These correlation effects make important contributions to cyclization phenomena.

Figure 4 shows the polymer concentration dependence of I_E/I_M for the labeled chain 3 in toluene and in 2-butanone, a moderate solvent for polystyrene. In toluene, a large increase in PS concentration is accompanied by very little change in I_E/I_M. Only at weight fractions of PS above 20% do the I_E/I_M values decrease. Such modest changes are surprising, particularly in light of the enormous changes in solution viscosity.

In 2-butanone, the concentration dependence of I_E/I_M is intermediate between that in a good solvent and that in a Θ-solvent. At weight fractions above 40%, the behavior in ethyl acetate is very similar to that in toluene. We note that there is a concentration range where I_E/I_M, and therefore k_1, is even smaller in cyclopentane than in toluene or 2-butanone.

k_1 describes cyclization processes between pairs of interior sites on the chain. The rates of these processes depend upon the dynamic relaxation times of the chain. The appropriate relaxation times are those for motions of amplitudes comparable to the separation between chromophores. The cyclization rate also depends upon the distribution function of those distances. Addition of unlabeled polymer to a labeled chain in a good solvent screens the excluded volume effects which lead to chain expansion. It also screens the pair correlation effects which suppress the probability of nearby excimer-forming sites. Both phenomena should enhance cyclization at elevated polymer concentration in good solvents.

On the other hand, increasing polymer concentration increases the microscopic friction coefficient. It also screens the hydrodynamic coupling of motions within a polymer chain.[16] While the magnitude of these effects might be different in good solvents and in poor solvents for the polymer, the net effect will be to retard polymer motion. Large-amplitude motion will be affected more than local motion in the chain.[17]

In good solvents the factors of hydrodynamic screening and excluded volume screening largely offset one another. Cyclization rates are much less sensitive to polymer concentration in good solvents than in poor solvents.

We have neglected the possibility that entanglements play a role in the chain dynamics we observe at elevated polymer concentrations. The critical entanglement molecular weight for neat polystyrene in the melt is $M_c \approx 25\,000$.[18] In the presence of solvent, M_c should increase. Both our labeled chains and the matrix chains have $\bar{M}_w < M_c$, so that entanglement effects, if any, would be expected to be minor.

One further point needs to be raised. In the framework of modern treatment of the viscoelastic behavior of polymers,[19] one treats the slowest internal relaxation times observed experimentally as single-molecule relaxation times. These increase with increasing polymer concentration, and the extent of increase is nearly as large as that of the bulk viscosity. On the other hand, one has known for many years that localized segmental diffusion times are much less sensitive to polymer concentration than the zero-shear viscosity. Excimer formation in our experiments probes the relaxation of single molecules. Because of the contour separation of the pyrene groups, the experiment does not probe local segment mobility. Rather, it probes large-amplitude motion involving approximately one-fourth of the contour length of the chain.

Whereas the slowest relaxation times obtained from cyclization–fluorescence–excimer experiments (ca. k_1^{-1}) are in reasonable agreement with those obtained from viscoelastic measurements at very low polymer concentration, they differ by orders of magnitude at high concentrations of polymer. The two experiments seem to be sensitive to different aspects of polymer motion. This raises an interesting possibility. Perhaps the single-molecule interpretation of viscoelastic relaxation times may be only a conceptual simplification, and not a fundamental feature, of the model which has been so successful at describing a broad spectrum of bulk relaxation phenomena in polymers.

In order to test this idea, one needs quantitative measurements, based upon labeled-chain experiments, of large-amplitude single-chain relaxation times. A quantitative description of the phenomena we have described here will require fluorescence decay experiments of sufficient precision that the distribution of relaxation times contributing to excimer formation can be assessed. In addition, one needs theoretical models of sufficient sophistication that the appropriate form of the fluorescence decay curves can be predicted. It is not clear whether such experiments are possible with current technology and without a deeper understanding of the cyclization process.

Summary

Steady-state fluorescence measurements of excimer formation in a polystyrene sample containing evenly spaced pyrene pendant groups have been carried out as a function of the concentration of unlabeled polymer. In cyclopentane, a Θ-solvent, hydrodynamic screening causes a decrease in the rate of excimer formation at elevated polymer concentration. In toluene, a good solvent, hydrodynamic screening effects are offset by excluded volume screening so that intramolecular excimer formation is much less affected than in cyclopentane. An important observation is that the changes in cyclization rates induced by increased polymer concentration are orders of magnitude *smaller* than the corresponding increases in shear viscosity of the solution.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

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