Macromolecules **1986,** *19,* 2281-2284

Excluded Volume Effects on the End-to-End Cyclization of Polystyrene in Mixed Solvents[1]

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ABSTRACT: Samples of polystyrene ($\bar{M}_n$ = 4500 and 25 000), labeled with pyrene groups at both chain ends, were studied by fluorescence spectroscopy in dilute solution. Measurements were made of the rates of intramolecular excimer formation as a function of solvent composition for samples dissolved in cyclopentane, in acetone, and in their mixtures. Cyclopentane is a Θ solvent and acetone is a nonsolvent for high molecular weight polystyrene. Their mixtures form a good solvent for polystyrene; in these mixtures, the rate of ring closure is retarded, and the rate of ring opening is accelerated. Consequently the cyclization equilibrium constant is diminished significantly by excluded volume interactions.

One of the many fascinating phenomena in polymer chemistry is the observation that a mixture of two poor solvents, or nonsolvents, for a polymer can provide a medium that acts as a good solvent for the polymer.[3] These mixtures, called cosolvents, have been the object of many studies by light scattering[4] and by viscometry.[5,6] From these have developed a rather good appreciation of how the second virial coefficient A_2 and the intrinsic viscosity evolve with changing solvent composition: They pass through a maximum at a certain solvent composition where the polymer behaves as though it were dissolved in a good solvent.

Various cosolvent systems have been described for polystyrene (PS). Many contain acetone, a nonsolvent for high molecular weight PS, as a component. These include methycyclohexane–acetone,[3a] nitrobenzene–acetone,[7] heptane–acetone,[7] cyclohexane–acetone,[5,6] and diethyl ether–acetone.[8] Another curious cosolvent mixture is cyclohexane–*trans*–decalin.[9] The cyclohexane–acetone system in particular has been extensively studied by viscometry. It forms the basis for comparison for the studies of end-to-end cyclization of polystyrene which we report here. These represent the first description of polymer cyclization in mixed solvents and provide novel and unique insight into the nature of polymer excluded volume interactions in cosolvent media.

Our motivation in carrying out these experiments was to examine the way in which polymer cyclization[10] depends upon excluded volume. The older theories,[11] which trace their origins back to the pioneering work of Kuhn,[12] relate the cyclization equilibrium constant to the mean-squared end-to-end length $\langle r^2 \rangle$. They suggest that as the mean dimensions of a polymer increase from the unperturbed dimensions upon inclusion of excluded volume, the cyclization probability $W(0)$ should decrease.[13] Taking as a starting point the well-known result for Gaussian chains that

$$W_0(0) \sim \langle r^2 \rangle_0^{-3/2} \qquad (1)$$

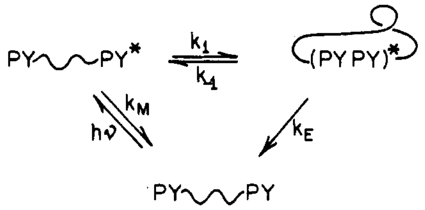
one argues that cyclization probability should decrease with chain expansion as

$$W(0) = W_0(0)[\langle r^2 \rangle_0 / \langle r^2 \rangle]^{3/2} \doteq \alpha^{-3/2} W_0(0) \qquad (2)$$

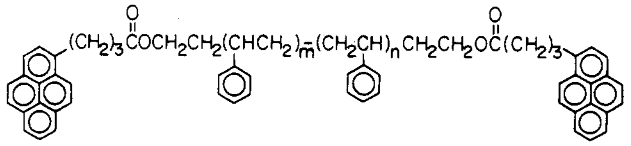
where the subscript zero refers to unperturbed dimensions and $\alpha = \langle r^2 \rangle / \langle r^2 \rangle_0$ is the expansion factor for the end-to-end distance. This argument is tantamont to assuming that only a single scaling length enters into the description of $W(0)$.[13]

More recent theory describes a second effect of excluded volume on polymer chains.[14,15] Correlation effects lead to changes in the shape of the distribution function $W(r)$ describing the chain end separation $\mathbf{r}$.[15] The most pronounced effects occur at small volumes of $\mathbf{r}$. These changes are depicted in Figure 1 and lead to the conclusion that cyclization probability would be more strongly affected by excluded volume than expansion of the mean chain dimensions.

Scheme I



This report describes the end-to-end cyclization behavior of polystyrene in cyclopentane, in acetone, and in their mixtures. We describe experiments carried out on PS samples of $\bar{M}_n$ = 4500 and 25 000 (with $\bar{M}_w/\bar{M}_n$ = 1.07 and 1.13, respectively). These polymers have structures I, with pyrene groups at the chain ends. They are referred to as Py-PS4500-Py and Py-PS25000-Py.



I

Upon excitation, cyclization leads to intramolecular excimer formation.[16] This process is summarized in Scheme I. The rate constant k_1 describes the diffusion-controlled cyclization step, k_{-1} describes the excimer dissociation and ring opening to re-form the locally excited pyrene group, and k_M and k_E refer to the reciprocal lifetimes of the locally excited pyrene "monomer" and excimer, respectively.

Experimental Section

The synthesis of I and its characterization have been reported previously.[17] An important part of the characterization is that low molecular weight impurities absorbing light at 345 nm as determined by GPC analysis with UV–visible analysis are less than 0.01 mol %. A more subtle feature of the characterization is that end-group analysis shows 2.0 pyrenes per chain with a precision of at best ±5%. The fluorescence decay data described below show an unusual features that is consistent with ca. 2% of the $\bar{M}_n$ = 4500 polymer containing only one Py group. Incorporating this into the data analysis leads to small changes but improved consistency in the values of the rate constants calculated from the data.

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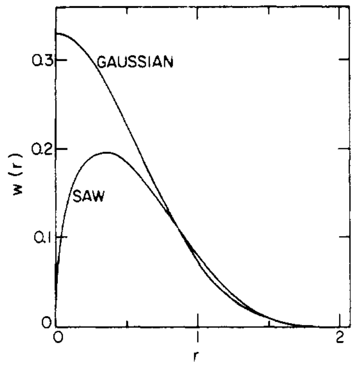

Figure 1. Plot of $W(r)$ vs. the normalized end separation $r = \mathbf{r}/\langle r^2\rangle^{1/2}$, following Oono and Freed,[15] for a Gaussian chain (no excluded volume) and a self-avoiding walk (hard-sphere excluded volume).

Fluorescence decay measurements were made by the time-correlated single-photon-counting technique.[18] Fluorescence spectra were measured on a SPEX Fluorolog II.

The solvents cyclopentane and acetone were spectro quality. Solutions of I were prepared so that the final polymer concentration was (1-2) × 10^{-6} M.

Data and Data Analysis

According to Scheme I, after sample excitation with a δ pulse, the pyrene fluorescence $I_M(t)$ should decay as a sum of two exponential terms, whereas the excimer emission $I_E(t)$ should grow in and decay as a difference of two exponential terms.

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \qquad (3)$$

$$I_E(t) = a_3 \exp(-\lambda_1 t) - a_4 \exp(-\lambda_2 t) \qquad (4)$$

Scheme I predicts that the fluorescence decay parameters obtained from the $I_M(t)$ and $I_E(t)$ measurements should be identical. For the two polymer samples studied here, the excimer data always fit eq 4 with $-a_3/a_4 = -1.0$. In the case of sample of $\bar{M}_n = 25\,000$, the $I_M(t)$ decay could be fit very cleanly to a single-exponential decay, suggesting that the amplitude a_2 of the short component was too small to be detected.

By normal criteria, the $I_M(t)$ decays for the Py-PS4500-Py sample could be fit satisfactorily to a sum of two exponential decays. Nevertheless, small but consistent differences in λ values from the $I_M(t)$ and $I_E(t)$ decays ponted to the presence of a weak long-lived third component in the $I_M(t)$ decay. When the $I_M(t)$ decay was fit to a sum of three exponentials, with λ_1 and λ_2 constrained to values obtained from the $I_E(t)$ measurement, we recovered a value of λ_3 corresponding to that (λ_M) of a model polymer containing pyrene at one end only. This component represents approximately 4% of the total intensity of the monomer emission and correponds to the presence of some polymer ($\approx$2%) in the $\bar{M}_n = 4500$ sample containing only one pyrene.

For the Py-PS25000-Py samples, only values of k_1 could be obtained. These values were calculated from the expression

$$k_1 = \lambda_1 - \lambda_M \qquad (5)$$

For the $\bar{M}_n = 4500$ sample, values of k_1, k_{-1}, and k_E could be obtained from a full analysis[16,17] of the $I_M(t)$ and $I_E(t)$ data using the λ_1, λ_2, and a_2/a_1 data obtained as described above.

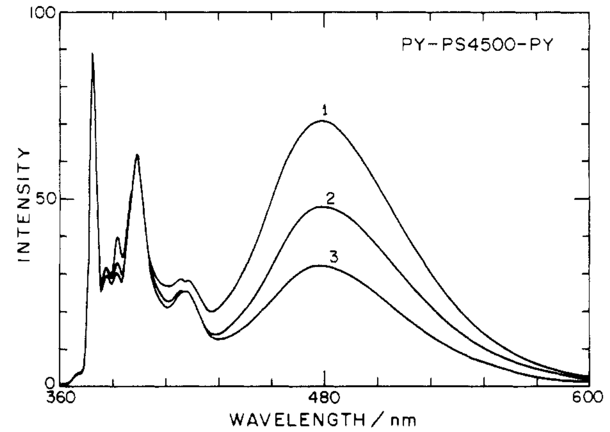

Figure 2. Fluorescence spectra of Py-PS4500-Py in (1) cyclopentane, (2) acetone, and (3) an acetone-cyclopentane mixture (56:44).

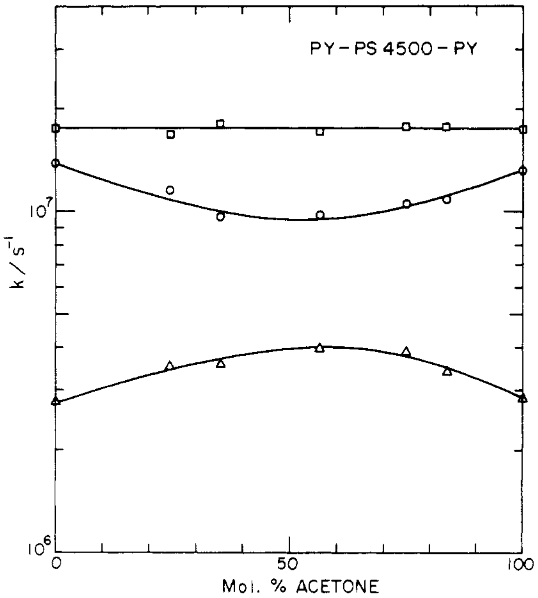

Figure 3. Plot of k_E (□), k_{-1} (△), and k_1 (○) as a function of solvent composition for Py-PS4500-Py.

Results and Discussion

In Figure 2 we show fluorescence spectra of Py-PS4500-Py in cyclopentane, in acetone, and in a mixture containing 56 mol % acetone. While it appears that there is less cyclization to form excimer in acetone than in cyclopentane, the most important observation is that there is even less excimer formed in the mixed solvent. Excimer formation is most pronounced in cyclopentane and least prominent in the mixed solvent. The pyrene excimer is remarkably insensitive to solvent polarity.[19] Our fluorescence decay data described below confirm this point. The explanation of the differences observed in Figure 2 must lie in the effect of solvent on the polymer chain.

In the steady-state fluorescence spectra, the intensity rato I_E/I_M increases in proportion to k_1:

$$\frac{I_E}{I_M} = \frac{k_{fE}k_1}{k_{fM}(k_E + k_{-1})} \qquad (6)$$

Figure 3 indicates that k_E maintains a constant value throughout the range of solvent compositions. Both k_1 and k_{-1} should be proportional to solvent viscosity η, but since k_{-1} is nearly an order of magnitude smaller than k_E, its contribution to I_E/I_M can be neglected. Two factors, then, affect the shape of the fluorescence spectra in Figure 2. Solvent viscosity differences make a small contribution to the larger amount of excimer formed in cyclopentane than in acetone. Solvent quality and cosolvency alter chain dynamics, and these in turn affect the dynamics of end-to-end cyclization, described by k_1.

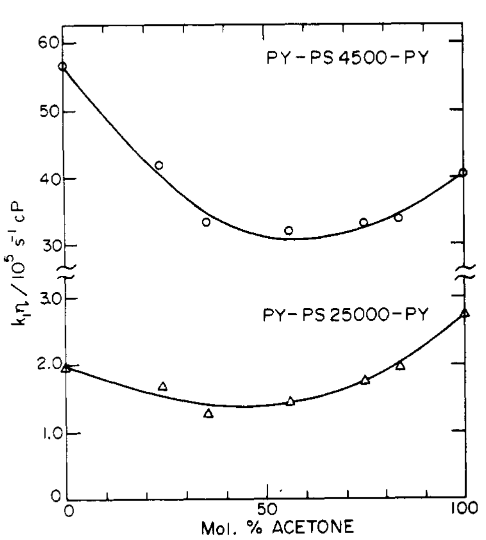

Figure 4. Plot of $k_1\eta$ vs. solvent composition for both polymers: (○) Py-PS4500-Py; (△) Py-PS25000-Py.

Rate Constants. Absolute values of the rate constants (Scheme I) for Py-PS4500-Py are plotted as a function of solvent compositions in Figure 3. k_1 decreases by as much as 30% over this range and passes through a minimum around 55 mol % acetone. An even more surprising result is the increase in k_{-1}. These mixed solvents lead to faster excimer dissociation than either pure solvent. Excimer dissociation rates for small molecules are normally unaffected by solvent properties other than viscosity, which changes monotonically for binary mixtures. It appears that excluded volume factors operate on even this short polymer to accelerate the rate of ring opening.

The product $k_1\eta$ should be independent of solvent viscosity. In Figure 4 we plot these values as a function of solvent composition for the low and higher molecular weight polymers. The shorter chain undergoes cyclization some 20 times faster than the longer chain. Both curves show a minimum in $k_1\eta$ values, with the minima occurring at ca. 50 mol % acetone. The minima reflect the change in solvent quality and the influence of excluded volume on the dynamics of cyclization. Most unusual, however, is the difference in the change in $k_1\eta$ in going to solvents rich in acetone. These solvents, particularly acetone itself, cause a large increase in $k_1\eta$ for Py-PS25000-Py but very little increase for the shorter chain.

The acetone effect, we believe, involves "specific" solvent interactions with the chain ends. The pyrenes are attached by means of ester groups. These in turn are more polar than the pendant groups of the polymer itself. Acetone is normally a very poor solvent for polystyrene. The polar end groups facilitate interactions with the polar solvent. In longer polymers, the relative contribution of this end-group interaction is less important. One can see in Figure 4 for Py-PS25000-Py the expected result that the viscosity-corrected cyclization rate is faster in acetone, the poorer solvent, than in cyclopentane.

Comparison with Intrinsic Viscosity Behavior. Intrinsic viscosity $[\eta]$ measurements for PS in cyclohexane–acetone mixtures have been reported by a number of groups. The most extensive data are those of Maillols, Bardet, and Gromb.[6] We have plotted their data for two PS samples in Figure 5. The scale for the lower molecular weight sample ($\bar{M}_w$ = 50 800) has been expanded to emphasize that the fractional change in $[\eta]$ is smaller than for the higher molecular weight sample ($\bar{M}_w$ = 870 000). For example, the cosolvent containing 0.853 mol % acetone is a Θ solvent for PS. Using this composition as a reference point we see that $[\eta]$ increases by 2.4 times for $\bar{M}_w$ = 870 000 in the 1:1 solvent mixture, whereas for $\bar{M}_w$ = 50 800, the increase is a factor of 1.5.

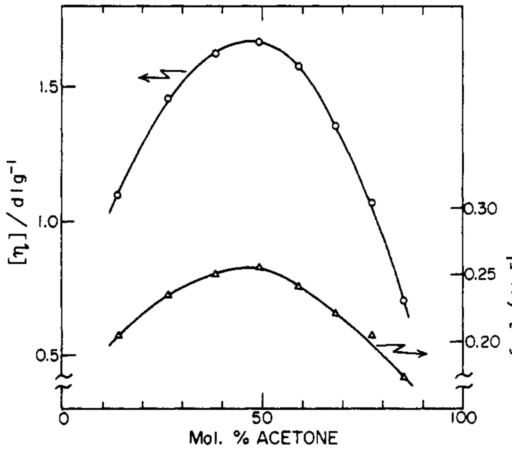

Figure 5. Variation of the intrinsic viscosity for two PS samples as a function of solvent composition in cyclohexane–acetone mixtures: (○) $\bar{M}_w$ = 870 000; (△) $\bar{M}_w$ = 50 800. Data from ref 16.

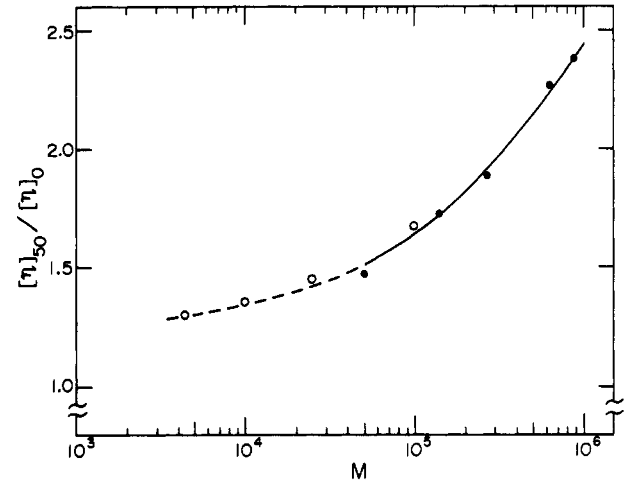

Figure 6. Fractional increase in intrinsic viscosity induced by cosolvency as a function of PS molecular weight. $[\eta]_0$ refers to 85.3 mol % acetone–cyclohexane at 25 °C, a Θ solvent. $[\eta]_{50}$ refers to 49.1 mol % acetone as solvent. (●) From experimental data in ref 6; (○) calculated from eq 7 using parameters of K_Θ and B given in ref 6.

Maillols et al.[6] interpreted their data in terms of the Stockmayer–Fixman–Yamakawa equation[20] in order to obtain values of K_Θ (from which $\langle r^2 \rangle_0$ can be calculated) and B, an interaction parameter that measures the strength of the excluded volume interaction. We can rewrite this equation as

$$[\eta] = K_\Theta M^{1/2} + 0.346\Phi_0 BM \qquad (7)$$

where Φ_0 takes the value 2.5×10^{21} dL·cm^{-3}·mol^{-1}, and use the data of Maillols et al.[6] to estimate the changes in $[\eta]$ which occur for other molecular weights. For example, this analysis predicts that for PS (M = 25 000), $[\eta]$ increases from 0.12 dL·g^{-1} to 0.17 dL·g^{-1}, or by 45%, when transferred from the cosolvent containing 85.3 mol % acetone to that containing 49.1 mol %. In the former cosolvent, B = 0.00: this mixture is a Θ solvent for polystyrene.

In order to get an overview of the magntiude of this change, we have plotted this ratio as a function of molecular weight in Figure 6, using eq 7 to calculate values of $[\eta]$ for values of M lower than those studied by Maillols et al.[6] The derivation of eq 7 presumes nondraining polymer coils. This assumption breaks down for shorter chains. Arguments based upon eq 7, applied to a sample

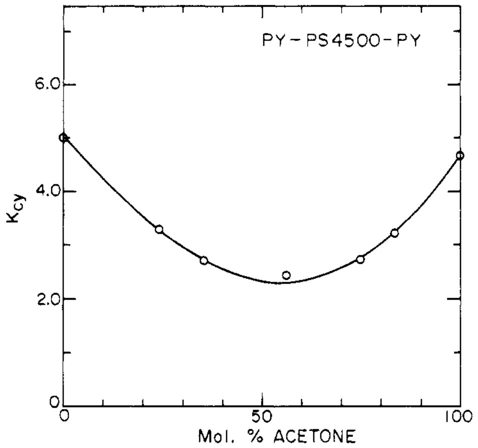

Figure 7. Plot of $K_{cy} = k_1/k_{-1}$ as a function of solvent composition for Py-PS4500-Py.

of $M = 4500$, corresponding to our lower M sample, must be considered qualitative or at best semiquantitative. Nevertheless, Figure 6 suggests that such a change in solvent would lead to a 45% increase in $[\eta]$ for our sample of $\bar{M}_n = 25\,000$ and perhaps a 20–30% increase in $[\eta]$ for our sample of $\bar{M}_n = 4500$. Since both $[\eta]$ and $[W(0)]^{-1}$ vary as $\langle r^2 \rangle^{3/2}$, we anticipate that cyclization equilibria for these polymers will also change by 20–50%.

Cyclization Equilibria. Values of the cyclization equilibrium constant $K_{cy} = k_1/k_{-1}$ can be calculated from our data on the PS sample of $\bar{M}_n = 4500$. These values are plotted in Figure 7 as a function of solvent composition. The changes in K_{cy} are substantial. The maximum and minimum values vary by almost a factor of 2.

If only coil expansion were important in affecting the magnitude of cyclization probability, we would expect changes in K_{cy} and $[\eta]$ to be inversely proportional. Arguments presented in the preceding section suggested that a change of 20–30% might reasonably be expected for this low molecular weight polymer sample between the good-solvent and Θ-solvent values of $[\eta]$. Our experiments involve cyclopentane–acetone mixtures at 22 °C whereas Maillols et al.[6] employ cyclohexane–acetone mixtures at 25 °C. Some small differences in behavior might be expected because of solvency differences between cyclohexane and cyclopentane for PS. Even if all the uncertainties are added, however, it is still not possible to explain the large changes in K_{cy} in terms of solvent effects on $\langle r^2 \rangle$ alone.

We conclude, therefore, that some other factor is responsible for the strong sensitivity of the cyclization equilibrium to cosolvency power. This second factor can be identified as the influence of excluded volume on the shape of the end distance distribution function. Because of pair correlation effects, $W(r)$ is suppressed for short end-to-end separations (cf. Figure 1). In good solvents, where excluded volume is important, this factor lowers the equilibrium constant for end-to-end cyclization.

Our kinetics experiments indicate that these correlation effects operate in two ways. They diminish the dynamics of end-group encounter. In addition, they operate to accelerate the separation rate of two chain ends in proximity. These experiments emphasize the latter effect. The excimer potential energy well is steep and quite narrow.[19] With a depth of 8 kcal/mol,[19,21] it serves to maintain a large proportion of the polymer chains in a cyclized conformation. It can be seen from the magnitude of K_{cy} in Figure 7 that the vast majority of photoexcited chains are the cyclized conformation.

The equilibrium is dynamic. Those chains whose trajectories cause the pyrene groups to separate (to form Py*$\sim\sim\sim$Py) act under the influence of an entropic force which is decidedly more severe when excluded volume is important.

Acknowledgment. We thank NSERC Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. The manuscript was written when M.A.W. was a visiting scientist at the Tokyo Institute of Technology. M.A.W. expresses his gratitude to Professor S. Tazuke for his hospitality and to the JSPS for a fellowship.

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