

End-to-End Cyclization of Polymer Chains

MITCHELL A. WINNIK

Lash Miller Laboratories, Department of Chemistry and Erindale College, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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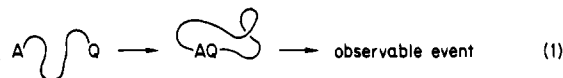
For many years I have been fascinated by the cyclization of flexible molecules. My own interests are best described as personal, a curiosity since my graduate-student days about the factors that induce or affect the tendency of a molecule to conjugate with its own tail. The subject of cyclization, of course, has its own history. First considered in the early days of this century by Freundlich^{1a} and by Ruggli,^{1b} it has attracted the interests of many of the most important contributors to the relatively young field of polymer chemistry and physics: Carothers,^{2a} Ziegler,^{2b} Ruzicka,^{2c} W. Kuhn,³ Flory,⁴ Stockmayer,⁵ and Wichterle,⁶ among others. Their interests were in part practical. Cyclized chains affect the properties of polymers such as nylon and silicone rubbers. In the perfume industry, musks were recognized as the first commercially important macrocyclic natural products. DNA cyclizes. The structure and function of circular DNA including the topology of supercoiling now defines an entire area of scientific interest.

A large aspect of their interest stemmed from the recognition that quantitative measurements of cyclization could convey detailed information about the shape and mobility of flexible polymers. The theoretical models developed to explore fundamental aspects of conformation and dynamics could be manipulated to yield predictions about that small fraction of chains with their ends in proximity. Testable predictions were generated. Techniques developed over the past 20 years have provided the methodology for carrying out many of the appropriate experiments.

These techniques fall into two categories, spectroscopic techniques and product isolation. In many ring-closure reactions, linear polymers are in equilibrium with their cyclic counterparts. These can frequently be separated and analyzed, yielding equilibrium constants for ring formation. The classic experiment was that of Brown and Slusarczuk⁸ in 1965, examining cyclization of poly(dimethylsiloxane). Subsequent investigation by Semlyen and co-workers have exploited these techniques.^{4a,8} Semlyen recently reviewed the entire area of ring-chain polymerization,^{7b} and his book on cyclization^{7c} will soon be published.

A more direct method involves the study of polymers end-substituted with groups which announce their proximity through some change in the spectroscopic properties of the system. One of the first examples, by Sisido's group⁹ in Japan, involved donor-acceptor complex formation between a dinitrobenzoate group at

one end of a poly(*N*-methylglycine) chain and a dimethylanilino derivative at the other end. Cyclized chains showed a new absorption in the UV-visible absorption spectrum. Analysis of the spectrum permitted the fraction of cyclized chains to be determined.



Other techniques, involving luminescence spectroscopy, have been applied to the study of cyclization phenomena. Fluorescence and phosphorescence quenching experiments have been carried out to examine the rate at which some quenching group Q at one end of the chain can influence the fluorescence or phosphorescence of a chromophore, A, at the other end of the chain. If A and Q are chosen appropriately, proximity of A* and Q can lead to a new emission in the fluorescence spectrum—broad structureless emission red-shifted from the normal fluorescence of A*. This emission from the (AQ)* complex is called exciplex fluorescence if A and Q are different and is called excimer fluorescence [from (AA)*] if Q and A are the same chromophore.¹⁰ We have focussed on these techniques.^{11,12} Horie and Mita¹³ in Tokyo have been exploring the kinetics of triplet-triplet [TT] annihilation between electronically excited anthracene at both ends of a polymer chain.

Contemporary Issues

The connectivity between the groups along a polymer chain serves to amplify the molecule's response to its

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Mitchell Winnik is Professor of Chemistry at the University of Toronto. He received his B.A. degree from Yale University and his Ph.D. degree from Columbia University, working with Ronald Breslow. After a postdoctoral year with George Hammond at Cal Tech, he undertook studies in organic photochemistry at Toronto. Thanks to a sabbatical year in France in 1977-1978 and the encouragement of several distinguished scientists in polymer field, he changed the direction of his research. His efforts now focus on photophysical and photochemical tools in polymer science.

surroundings. The groups along the chain act cooperatively. Effects involving energies of only a few calories per monomer unit, which would be imperceptible in systems of small molecules, become magnified. For example the entropy of mixing per unit volume of a polymer and a solvent is small and that of two polymers is miniscule. Consequently very small differences in mixing enthalpies can have large effects on polymer solubility, on polymer conformation in solution, and on polymer-polymer compatibility.

The starting point for a discussion of polymer conformation is the random-walk model.¹⁴ The polymer is seen as a connected series of N steps of length l . The dimensions are described in terms of the mean-squared end-to-end length, R_F^2 , and the mean-squared radius of gyration, R_G^2 . A more sophisticated version of this model, the rotational isomeric state [RIS] model, takes account of local geometry. All models that neglect the steric interactions between groups far removed along the chain contour (excluded volume) predict, for sufficiently long chains, that the distribution of end-to-end distances, $W(r)$, will be Gaussian. Thus R_F^2 and R_G^2 increase in proportion to Nl^2 . Real chains in good solvents have larger dimensions, because solvation induces swelling of the random coil, and the steric interactions associated with excluded volume prevent two chain atoms from occupying the same space. Here $W(r)$ is not Gaussian, and R_F^2 and R_G^2 increase faster than Nl^2 .

Much of the history of polymer physics has been concerned with Θ solvents. For each polymer there are unique sets of solvent and temperature combinations which compress the mean dimensions to that predicted by models which neglect excluded volume. Θ solvents are poor solvents for polymers.^{14b} Experimentally they represent the poorest solvent which will still dissolve an infinitely long polymer chain. One also predicts (and finds) that in a Θ solvent, the osmotic pressure increases linearly with polymer concentration. Visible light and (more recently) neutron scattering studies of polymers under Θ conditions are consistent with $W(r)$ being Gaussian and give the proper values of R_G^2 .

There has long been an important effort to appreciate the effects of excluded volume for polymers in good solvents. Light scattering¹⁵ and neutron scattering¹⁶ have been the most important experimental techniques. New developments in the theory of excluded volume effects have been particularly interesting.¹⁷ There have been important new insights, and the theory has provided the language with which this problem is discussed. Perhaps the most curious feature is that polymer dimensions decrease with increasing polymer concentration. In good solvents there is a reluctance for polymer coils to interpenetrate. When polymer concentration obliges polymer coil interpenetration,

polymer-polymer contacts replace polymer-solvent contacts. The dimensions shrink. Excluded volume is said to be "screened". At high polymer concentration, persisting to bulk polymer, the chains achieve the same dimensions as in a Θ solvent.

Polymer dynamics is a more complicated subject than equilibrium polymer dimensions.¹⁸ The models are less sophisticated. The phenomena are more subtle, and the experiments are more difficult to interpret. The most difficult issue involves the tendency of two groups, close in space, to have their motion coupled through the intervening solvent molecules: motion of the first group drags along solvent which in turn tugs at the second group. These hydrodynamic interactions fall off only as the reciprocal distance r_{ij}^{-1} between the groups and, thus, like coulombic interactions, persist to long range. One set of models of polymer dynamics treats the chains as "nondraining": they move as a coil with solvent trapped inside.

At elevated polymer concentrations, two new effects appear. First, with the onset of coil interpenetration, there will be interferences with the hydrodynamic coupling of motion between groups within one chain. The second polymer introduces additional frictional drag and "screens" these hydrodynamic interactions.¹⁹ A second effect appears for sufficiently long chains. Since two chains, like two strings, cannot pass through one another, lateral diffusion is inhibited. If the chains are so long that they cannot move out of each others way on the time scale of an experiment, entanglements prevent lateral diffusion entirely.^{17,20} Topological constraints require diffusion to occur by a snake-like motion called "reptation". The critical chain length for entanglements is usually inferred from melt viscosity experiments, as the point where η ceases to increase as $N^{1.0}$ and commences to increase as $N^{3.4}$.

These factors should influence both the probability and dynamics of polymer cyclization. Careful studies of these effects should aid in understanding the phenomena of excluded volume and provide new insights into polymer dynamics.

Concepts and Theory

Cyclization experiments can provide information either about cyclization probability or cyclization dynamics. If the reaction between $\sim A^*$ and $Q\sim$ occurs with unit efficiency, one says their reaction is "encounter controlled" or "diffusion controlled".^{7,21} In order to obtain information about chain dynamics, one must establish both that the reaction kinetics are dominated by the encounter of $\sim A^*$ and $Q\sim$ and that the dissociation of $(\sim A^*Q\sim)^*$ back to $A^*\sim$ and $Q\sim$ is kinetically unimportant. Such experiments give information about cyclization dynamics. There are two ways to determine cyclization probability. One can study a true equilibrium process, such as donor-acceptor complex formation, or ring-formation-ring-opening equilibria. Alternatively one can study the kinetics of a low efficiency reaction between $A^*\sim$ and $Q\sim$ such that a

(14) (a) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience: New York, 1969. (b) Even in a Θ solvent, the polymer coil is not very dense. Its size can be approximated by the intrinsic viscosity $[\eta]$. For polystyrene of $\bar{M}_w = 55\,000$ $[\eta]_0 = 20$ mL/g in cyclohexane at 34.8 °C, and $[\eta] = 32$ mL/g in toluene, a good solvent, at 22 °C. Data from: Berry, G. J. *Chem. Phys.* 1967, 46, 1338-1352.

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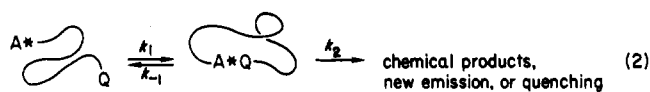
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preequilibrium precedes the rate-limiting step (eq 2).



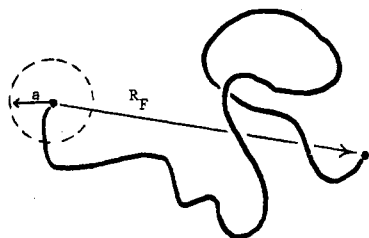
In the classic terms of simple kinetics, the experimental value, $k_{\text{obsd}} = k_1 k_2 / (k_2 + k_{-1})$, measures cyclization dynamics if k_1 is encounter controlled and $k_2 \gg k_{-1}$. It measures $k_1 k_2 / k_{-1}$, proportional to cyclization probability if $k_{-1} \gg k_2$.

Unfortunately, diffusion-controlled processes are complicated by transient phenomena.²¹ The bimolecular rate "constant" k_{diff} in three dimensions decreases as a function of time, ultimately attaining its (constant) steady-state value. The transient terms come about because A^*/Q pairs in proximity react faster than those far apart. Ultimately all A^* species which have nearby Q groups at $t = 0$ react, leaving only those A^* groups which have no nearby Q groups. The concentration of Q is no longer uniform in solution. A flux of the Q species diffusing toward A^* is set up. This flux is driven by Brownian motion and opposed by frictional (viscosity) effects. The rate of diffusion becomes the rate-limiting step in the reaction process.

Whether k_{diff} is a meaningful rate constant or not depends upon the theory of diffusion-controlled processes. In three dimensions, the diffusion equations yield a steady state solution, and k_{diff} is well-defined. In two dimensions, no steady-state solution exists.^{21,22} Interpretation of "experimental k_{diff} " values is fraught with difficulties.

For polymers, it is not obvious whether the dynamics of cyclization are well-defined by a unique rate constant, k_{cy} . One needs a theory which solves the diffusion equation in terms of some model of chain dynamics. The seminal papers were those of Wilemski and Fixman [WF],²³ which examined cyclization in terms of two models of flexible polymer chains: the harmonic spring model (two beads connected by a harmonic spring) and the more realistic Rouse-Zimm [RZ] model.

The RZ model treats the polymer chain as a series of beads which carry the mass and act as friction centers, each connected by harmonic springs. It provides a normal mode picture of chain motion, each with its own characteristic relaxation time. The slowest relaxation time τ_1 characterizes polymer motion delocalized over the entire chain with a node at the center-of-mass. This model has provided useful descriptions of the intrinsic viscosity $[\eta]$ of polymer solutions and the translational diffusion coefficient.

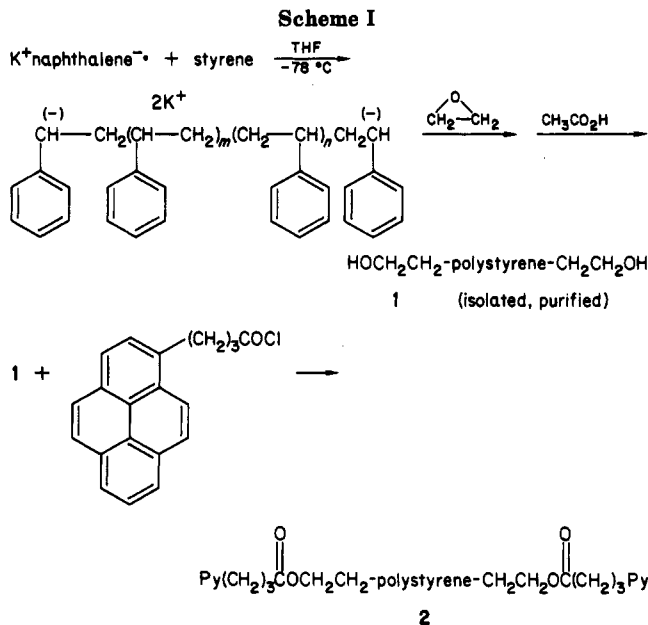


Certain features of the WF treatment attracted the attention of other theoreticians, notably Doi,²⁴ Perico,²⁵

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and Cuniberti.²⁶ The issues were the details of the capture process (different models suggested various dependences on a/R_F) and the factors affecting the molecular weight or chain length (N) dependence of k_{cy} . In each instance $k_{\text{cy}} \sim N^{-\gamma}$. For the RZ model, $\gamma = 2$ for the free draining Rouse model and $\gamma = 3/2$ for the nondraining Zimm model, and $k_{\text{cy}} \approx [\tau_1]^{-1}$. Perico and Cuniberti showed that for finite chains in the limit of $a/R_F \ll 1$

$$k_{\text{cy}} = 0.33D/R_G^2 \quad (3)$$

Strictly speaking eq 3 applies only to Θ solvents, where $\gamma = 3/2$. For shorter chains, the capture radius cannot be neglected. Since a/R_F changes with N , the experimental value of γ is affected; but for Θ solvents, it is always close to $3/2$.

Intramolecular Excimer Formation

Since k_{cy} is predicted to be so sensitive to chain length, experiments must be carried out on polymers of very narrow molecular weight distribution. In addition, the polymers must contain suitable end groups for attaching fluorescent chromophores. Taking guidance from the work of Zachariasse²⁷ and of Cuniberti and Perico,²⁸ we decided to examine intramolecular excimer formation between pyrene groups at the ends of a polymer chain. Polystyrene was chosen as the polymer, because the synthesis of HOCH_2CH_2 -polystyrene- $\text{CH}_2\text{CH}_2\text{OH}$ of narrow molecular weight distribution [MWD] is well documented (Scheme I). A wide variety of chain lengths could be produced. Attachment of the pyrene groups as esters of 4-(1-pyrene)butyric acid was straightforward.

The anionic polymerization of styrene initiated by naphthylpotassium produces a "living" dianion of narrow MWD. Its reaction with ethylene oxide is quantitative, as is the subsequent esterification of the α,ω -diol 1. Through very careful fractionation, polymer

(25) (a) Perico, A.; Cuniberti, C. *J. Polym. Sci., Polym. Phys. Ed.* 1977, 15, 1435-1450. (b) For an important recent review, see: Cuniberti, C.; Perico, A. *Prog. Polym. Sci.* 1984, 10, 271-316.

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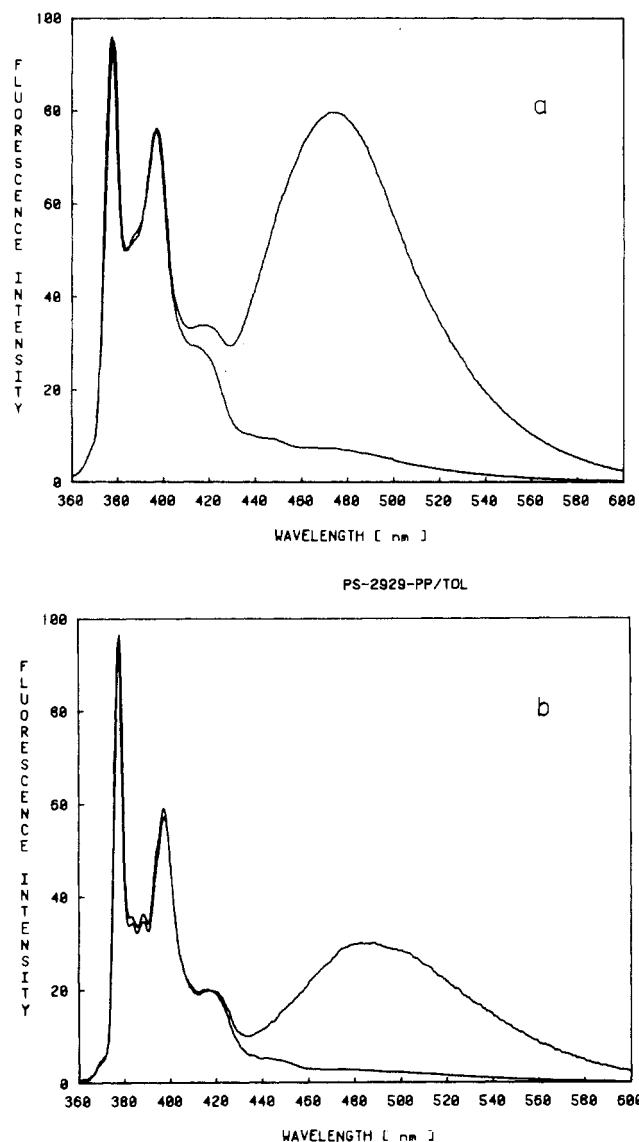


Figure 1. Fluorescence spectra at very low concentration (2 ppm by weight) of Py-polystyrene-Py of molecular weights $\bar{M}_n = 2900$ [upper curves] and $\bar{M}_n = 15500$ [lower curves]. Spectra were run in cyclohexane at 34.5 °C; spectra b were run in toluene at 22 °C.

samples of very narrow MWD were obtained. The final polymer **2** has seven atoms at each end separating the Py group from the PS. This introduces some ambiguity into the "degree of polymerization" of short polymer chains but overcomes steric effects of the bulky pendant phenyl groups that might interfere with excimer formation.

Kinetics and Experimental Methodology

The fluorescence spectra of pyrene and end-capped polymers show two distinct fluorescence bands (Figure 1). The structured blue emission (of intensity I_M) derives from locally excited pyrene groups, whereas the green excimer fluorescence (intensity I_E has its origin in chains which cyclize before photon emission from Py^* .

Spectra are shown in Figure 1 for PS of two different chain lengths, $\bar{M}_n = 2900$ and $\bar{M}_n = 15500$. In both cyclohexane at 35.4 °C (Figure 1a) and in toluene at 22 °C (Figure 1b) the shorter chain gives a more intense excimer emission than the longer chain. These results

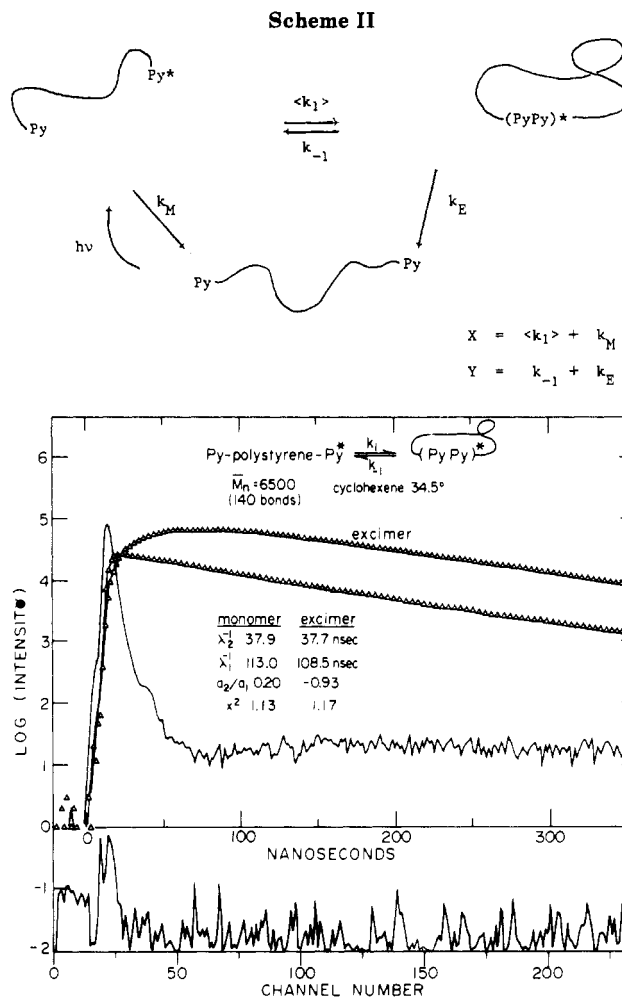


Figure 2. Plots of $\log I_E(t)$ vs. t [upper curve, labeled "excimer"] and $\log I_M(t)$ for Py-polystyrene-Py of $\bar{M}_n = 6500$ and $\bar{M}_w/\bar{M}_n = 1.06$.

are in accord with the WF theory, which predicts that cyclization rates decreases with increasing chain length. Comparing parts a and b of Figure 1, one also notices that there is significantly more excimer emission in cyclohexane at 34.5 °C, a θ solvent for polystyrene, than in toluene, a good solvent for PS. One sees that chain length and solvent quality are important parameters that affect polymer cyclization.

The simplest mechanism to describe this process is shown in Scheme II, where k_M and k_D represent the reciprocal pyrene and excimer lifetimes, respectively. $\langle k_1 \rangle$ is the (experimentally determined) rate constant for cyclization; k_{-1} describes the rate of ring opening via excimer dissociation. The brackets on $\langle k_1 \rangle$ serve as a reminder that all samples have a finite polydispersity. The magnitude of $\langle k_1 \rangle$ represents some average over that molecular weight distribution.

Scheme II predicts that the blue fluorescence will decay as the sum of two exponential terms and the excimer fluorescence, as the difference of two exponential terms, with the same decay constants ($\lambda_1 = \lambda_3$ and $\lambda_2 = \lambda_4$).

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \quad (4)$$

$$I_E(t) = a_3 [\exp(\lambda_3 t) - \exp(-\lambda_4 t)] \quad (5)$$

These are testable predictions. An example is shown in Figure 2, where plots are displayed of $\log I_M(t)$ and $\log I_E(t)$ vs. time. One sees that the λ_1 values are in

good agreement and that the λ_2 values are indistinguishable within experimental error. The ratio of preexponential factors in the $I_E(t)$ data should be -1.0 . We always observe values between -0.93 and -0.97 and do not consider these deviations to be serious.

It is explicitly assumed in Scheme II that a single rate constant suffices to describe the (diffusion-controlled) cyclization process. This is tantamount to assuming that cyclization is dominated by a single chain relaxation time. Deviations of the $I_M(t)$ and $I_E(t)$ curves from the forms predicted by eq 4 and 5, in combination with an appropriate theoretical model, may permit this question to be examined. This is a delicate matter since polydispersity also affects the λ values. What one observes is that in a few instances the λ values differ significantly from $I_E(t)$ to $I_M(t)$.

$$2\lambda_1, \lambda_2 = (k_M + \langle k_1 \rangle + k_{-1} + k_E) \pm \{[(k_{-1} + k_E) - (k_M + \langle k_1 \rangle)]^2 - 4\langle k_1 \rangle k_{-1}\}^{1/2} \quad (6)$$

$$\langle k_1 \rangle = (\lambda_1 + A\lambda_2)/(1 + A) - k_M \quad (7)$$

There are three unknown quantities in Scheme II. These are the rate constants $\langle k_1 \rangle$, k_{-1} , and k_E ; k_M is determined independently from measurements on a model polymer containing only one pyrene group. The three experimental values used to determine these rate constants are λ_1 , λ_2 , and $A = a_2/a_1$. The λ values are related to the rate constants through eq 6.

An important simplification occurs if $4\langle k_1 \rangle k_{-1}$ is much smaller than $[(k_{-1} + k_E) - (k_M + \langle k_1 \rangle)]^2$. Under these conditions the decay of $I_M(t)$ becomes exponential, and the measured $\lambda_1 = k_M + \langle k_1 \rangle$. Since k_M is known, $\langle k_1 \rangle$ can be obtained directly.

An alternative method permits relative values of $\langle k_1 \rangle$ to be obtained. The (I_E/I_M) values from samples of different chain lengths, but otherwise identical, are proportional to the $\langle k_1 \rangle$ values:

$$\frac{(I_E/I_M)_1}{(I_E/I_M)_2} = \frac{\langle k_1 \rangle_1}{\langle k_1 \rangle_2} \quad (8)$$

This approach is particularly useful for studying long chains, since under these circumstances $\lambda_1 \approx k_M$, and the $\langle k_1 \rangle$ values calculated from $I_M(t)$ measurement have poor precision.^{11,12} Cuniberti and Perico used steady-state I_E/I_M values for pyrene-end-capped poly(ethylene oxide) to infer relative cyclization rate constants in the first experimental study of polymer cyclization dynamics.²⁸

Cyclization in a θ Solvent

Cyclohexane at 34.5 °C is a θ solvent for polystyrene. Values of $\langle k_1 \rangle$ obtained in cyclohexane at this temperature are shown in Figure 3. The magnitude of $\langle k_1 \rangle$ decreases from a value of 2×10^7 s⁻¹ for chains of 60 bonds to 2×10^4 s⁻¹ for chains of 2000 bonds. The plot of $\log \langle k_1 \rangle$ vs. $\log N$ is linear, indicating that $\langle k_1 \rangle \approx N^{-\gamma}$. Thus one of the predictions of the WF theory²³⁻²⁵ is upheld.

After corrections are made for MW distribution differences in our samples, we obtain a value of $\gamma = 1.62 \pm 0.10$. This value is larger than that of -1.5 predicted for the nondraining Zimm chain or that of -1.41 predicted for finite partially draining chains.^{25b} The ex-

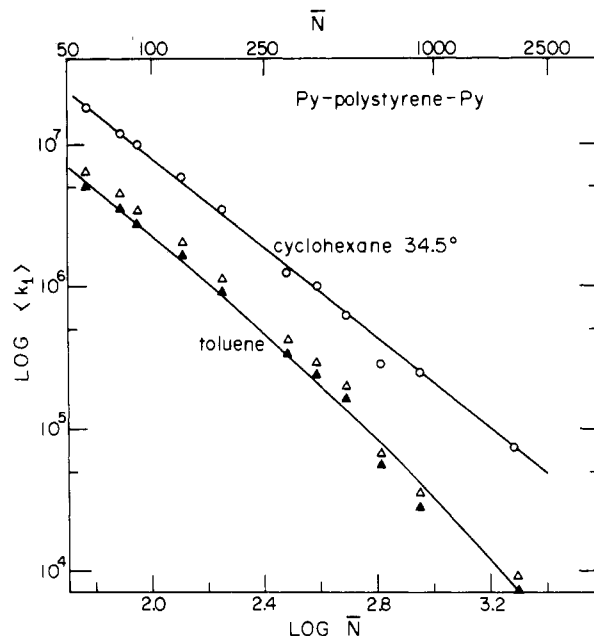


Figure 3. log-log plots of the rate constants for excimer formation $\langle k_1 \rangle$ vs. mean chain length \bar{N} : (O) cyclohexane at 34.5 °C; (Δ) toluene at 22 °C. The filled points (\blacktriangle) are the data for toluene corrected to the viscosity of cyclohexane and to 34.5 °C by the expression $\langle k_1 \rangle_2 = \langle k_1 \rangle_1 \eta_1 T_2 / \eta_2 T_1$. \bar{N} is calculated from \bar{M}_n as $[(\bar{M}_n - 450)/104 + 15]$ to account for the weight and bonds contributed by the terminal substituents.

perimental exponent is influenced by cyclization rates of the highest molecular weight samples where the error in $\langle k_1 \rangle$ is largest.

For polymer samples of molecular weight 3000 to 10000, $I_M(t)$ decays are sums of two exponential terms. The λ values from the $I_M(t)$ and $I_E(t)$ decays are in reasonable agreement (Figure 2). Consequently good values can be obtained for k_{-1} and k_E . At 34.5 °C these values are 3.5×10^6 s⁻¹ and 1.8×10^7 s⁻¹, respectively. They are independent of chain length, within experimental error. The former is very sensitive to temperature ($E_a = 11$ kcal/mol) whereas k_E depends only weakly upon temperature ($E_a = 1.5$ kcal/mol). From these data, an apparent binding energy of $-\Delta H_0 = 8$ kcal/mol can be calculated for the intramolecular pyrene excimer. This compares to a value of 8 kcal/mol reported by Birks for bimolecular excimer formation from pyrene itself in cyclohexane.²⁹

The interpretation of the $\Delta H_0 = -8$ kcal/mol value is delicate. The quality of cyclohexane as a solvent changes very sensitively with temperature near the θ point. Above 34.5 °C, it becomes an increasingly better solvent for PS, which would promote swelling of the chain. If these factors retard cyclization at high temperatures (see below), the excimer binding energy would be greater than that calculated from the experimental data.

Cyclization in Toluene

Toluene is a good solvent for polystyrene. One anticipates that the chains will be swollen with solvent and their dimensions increased over those in cyclohexane. Since the ends of the chain will on the average be further apart, cyclization should be slower. Excluded volume effects should be important. These effects are

(28) (a) Cuniberti, C.; Perico, A. *Eur. Polym. J.* 1980, 16, 887-893; (b) *Ibid.* 1977, 13, 369-374. (c) *Ann. N.Y. Acad. Sci.* 1981, 366, 35-43.

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seen in Figure 3, where we plot $\log \langle k_1 \rangle$ vs. $\log N$ for experiments carried out in toluene at 22 °C.

The important features in Figure 3 are that the cyclization rates in toluene are significantly slower than in cyclohexane, and that the $\log \langle k_1 \rangle$ vs. $\log N$ plot has a downward curvature. If one corrects for the viscosity and temperature differences between the two sets of experiments (filled points in Figure 3), the rate differences between toluene and the θ solvent are accentuated. TT annihilation studies of anthracene terminated polymers by Horie and Mita¹³ gave results different from ours. Their k_1 values in cyclohexane were much smaller (40 times), although in benzene (after a viscosity correction) their values and ours in toluene are close. For both sets of experiments, their values of γ were closer to 1 than to 1.5. We do not understand this discrepancy.

An Arrhenius study of three of our polymer samples of $\bar{M}_n = 3400$ – 9200 provides further interesting insights into the cyclization process.³⁰ Ring opening is very sensitive to temperature ($E_a = 11$ kcal/mol) but within experimental error is independent of chain length. The exciplex binding energy is $-\Delta H_0 = 8$ kcal/mol. This value should be free from ambiguity because the quality of toluene as a solvent for PS changes little over the temperature range of the experiments.

Correlation Holes

A correlation hole is a minimum in a probability distribution function.¹⁷ In the cyclization process, the presence of one chain excludes volume from other elements of the chain and depresses the probability of the other end being in its vicinity. While the steric effect remains even in a θ solvent, the correlation hole should disappear because the net attraction between polymer elements exactly cancels the excluded volume effect in the space surrounding the end group.^{17,31}

In order to examine this possibility, we had to choose between long chains where excluded volume is most important and very short chains where the magnitude of the $4 \langle k_1 \rangle k_{-1}$ term in eq 6 makes determination of k_{-1} at room temperature possible. We made the latter choice and examined a Py-PS2900-Py sample in six solvents including good solvents (toluene, THF), modest solvents (2-butanone, ethyl acetate), and poor solvents (cyclopentane, acetone) for PS. We found that $\langle k_1 \rangle$ values were significantly faster in the poor solvents than the good solvents. The exact factor varied from 3 to 4 times depending upon the data analyzed since λ_1, λ_2 values from $I_M(t)$ differed by as much as 20% from $I_E(t)$ measurements. No matter how the data are treated, the pattern of the results is consistent. Cyclization is retarded in good solvents, and surprisingly, *ring opening is accelerated*. These combine to accentuate the sensitivity $\langle K_{cy} \rangle = \langle k_1 \rangle / k_{-1}$ to solvent quality. For example, between cyclopentane and THF, where R_G^2 changes by less than 20%, $\langle K_{cy} \rangle$ changes by more than a factor of 10. Since the binding energy of the pyrene excimer shows little if any sensitivity to solvent changes, these effects are due to solvent-polymer interactions. They are a manifestation of the correlation hole in $W(r)$

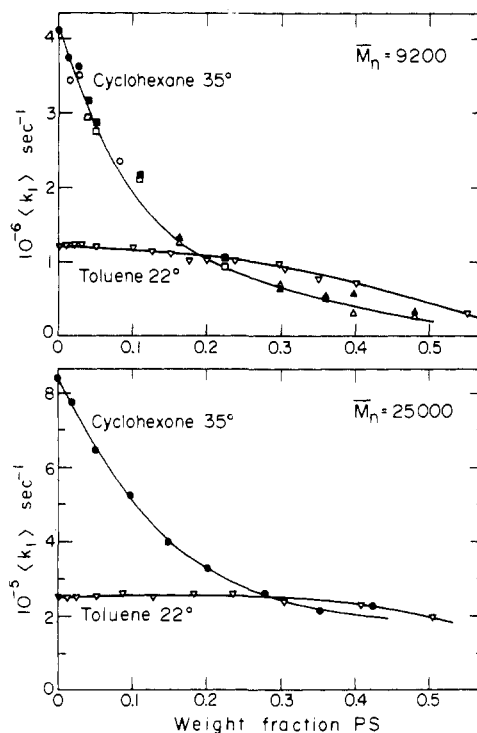


Figure 4. Plots of $\langle k_1 \rangle$ vs. weight fraction unlabeled polystyrene in toluene at 22 °C and cyclohexane at 35 °C. The upper graph describes data with Py-polystyrene-Py, $\bar{M}_n = 9200$ at 2 ppm. Unlabeled PS of various molecular weights from 9000 to 360 000 were used. The upper curve describes a labeled chain of $\bar{M}_n = 25000$ at 2 ppm. The unlabeled polymer had $\bar{M}_n = 17500$, $\bar{M}_w/\bar{M}_n = 1.06$.

and its sensitivity to the strength of the excluded volume interactions.

Concentrated Polymer Solutions

It is a straightforward matter to prepare solutions containing trace amounts of pyrene-end-labeled polymer 2 and a large excess of unlabeled polystyrene. The fluorescence experiment observes only the labeled chain. One can assess the influence of total polymer concentration c on the cyclization dynamics of 2. We have been able to carry out these experiments on samples containing upward of 65% PS by weight.³² These solutions are rubbery solids that do not flow at room temperature on the time scale of months.

There are two possible problems that can complicate determination of $\langle k_1 \rangle$ in the presence of unlabeled PS. The PS could quench locally excited pyrene (rate = $k_{qM}[\text{PS}]$), and it might quench the pyrene excimer (rate = $k_{qE}[\text{PS}]$). The former effect is small but important.³³ Careful control experiments were necessary to determine the fluorescence decay time of polystyrene- $\text{CH}_2\text{CH}_2\text{OC}(=\text{O})(\text{CH}_2)_3\text{Py}$ as a function of $[\text{PS}]$ in each solvent we examined. Fortunately for us the $k_{qE}[\text{PS}]$ term turned out to be negligible.

Rate constants could be calculated directly from the fluorescence decay data or, especially for longer chain polymers, from fluorescence intensity measurements.

$$\frac{I_E}{I_M} \propto \frac{\langle k_1 \rangle}{k_{-1} + k_E + k_{qE}[\text{PS}]} \quad (9)$$

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Relative values of $\langle k_1 \rangle$ could be obtained as a function of [PS] from I_E/I_M values (eq 9). Increases in [PS] cause the rate of ring opening to decrease.³² Since even at 35 °C, k_{-1} is at most 20% of k_E , this correction is small. Fluorescence decay data from the $\bar{M}_n = 9200$ sample can be used to make a first-order correction to the I_E/I_M values for the $\bar{M}_n = 25\,000$ sample.

The data for the PS concentration dependence of $\langle k_1 \rangle$ are shown in Figure 4. The most striking feature of the data is the difference of behavior in toluene and in cyclohexane. In the Θ solvent, addition of small amounts of PS cause a marked decrease in $\langle k_1 \rangle$, whereas in the good solvent, values of $\langle k_1 \rangle$ are hardly affected. The second feature of the data is that the changes in $\langle k_1 \rangle$, even in the Θ solvent, are quite modest. Under conditions where the bulk solution viscosity varies by several orders of magnitude, $\langle k_1 \rangle$ in cyclohexane decreases by less than a factor of 8. The third interesting observation is that $\langle k_1 \rangle$ is insensitive to the molecular weight of the added PS.

The explanation of this behavior starts with the recognition that R_F^2 should be independent of c in a Θ solvent. The decrease in $\langle k_1 \rangle$ occurs because of in-

creased screening of the hydrodynamic interaction within the labeled chain as unlabeled polymer is added to the solution.^{35,38} In toluene, several factors operate. As in a Θ solvent, hydrodynamic screening increases the frictional forces, which should lead to a decrease in $\langle k_1 \rangle$. Opposing this is the screening of excluded volume interactions. Not only does R_F^2 decrease with an increase in c as the solution approaches Θ conditions. The correlation hole in $W(r)$ disappears, with the consequence that cyclization probability also decreases.

While I am the one who has written this paper, my students and postdoctoral associates, cited in the references, carried out all of the experiments. It is only through their talent and dedication that these experiments have succeeded. A. E. C. Redpath and X. B. Li deserve special commendation for their efforts. Among those whose comments and insights were particularly valuable to me as this work developed are Professors H. Morawetz, W. H. Stockmayer, K. F. Freed, and F. C. DeSchryver, as well as Dr. K. Zachariasse.

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