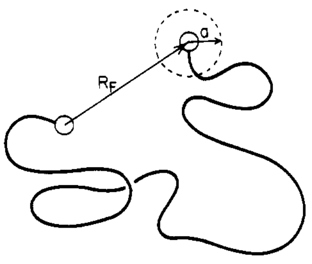
Cyclization Dynamics of Polymers. 17.[1] Probe Effects on Detection of Polymer End-to-End Cyclization

Polymer end-to-end cyclization is a topic which has interested both theoreticians and experimentalists in recent years. In the early 1970s Wilemski and Fixman[2] (WF) put forward a theory which described the dynamics of polymer end-to-end cyclization in terms of a Rouse–Zimm (RZ) bead-and-spring model. They defined the rate constant k_{cy} for diffusion-controlled cyclization of a polymer chain of length N and showed that $k_{cy} \sim N^{-3/2}$ in the absence of excluded volume. Various aspects of their model were examined in more detail by other theoretical groups, notably Doi and co-workers[3] in Japan and Perico and Cunniberti[4] in Italy. These theoretical papers[2-4] have had an important impact on the field of polymer dynamics. Further refinement of these theories is dependent on experimental measurement of cyclization rate constants in Θ solvents. The values of interest are the magnitude of k_{cy} and, more importantly, its dependence on polymer molecular weight, particularly in Θ solvents, which correspond to the neglect of excluded volume in the RZ model.

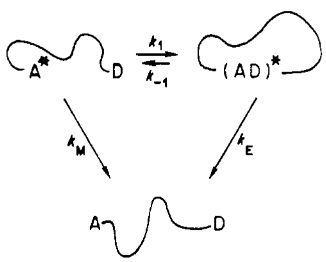
The theoretical contributions of the Italian group are of particular importance to experimentalists. They extended the WF theory to finite chains and to polymer–solvent hydrodynamic interactions that closely resemble the behavior of real polymers in dilute solution. For a given set of parameters approximating polystyrene and poly(dimethylsiloxane) in Θ solvents, they predict that k_{cy} would be slightly less dependent upon N: $k_{cy} \sim N^{-1.43}$. This decreased dependence comes about because of a peculiar dependence of k_{cy} on the ratio a/R_F of the capture radius a for the reaction to the root-mean-squared end-to-end distance R_F. This ratio, which decreases with increasing N, affects k_{cy} only when the chains are appropriately short ($\bar{M}_n = 10^4$ to 10^5 for polystyrene). For very long chains k_{cy} is no longer a function of a/R_F. A schematic representation of a polymer chain in solution is shown below.



An effective technique for obtaining intramolecular cyclization rate constants is to measure the rate at which a quencher on one chain end quenches the excited state of a chromophore at the other chain end. If the quenching reaction is diffusion controlled, the dynamics of the polymer will control the rate of approach of the two chain ends, and the experimental rate constant, $\langle k_1 \rangle$, will equal k_{cy}. The angle brackets around k_1 serve to emphasize that the experimental cyclization rate constant represents an average over a finite molecular weight distribution.

Horie and Mita[5] have used anthracene end-labeled polystyrene to probe cyclization. By exciting both anthracenes to their triplet state with a high-powered laser and observing triplet–triplet annihilation rates, they have inferred cyclization rates and examined the polymer moleculr weight dependence of cyclization. Winnik and Redpath[6] used pyrene end-labeled polystyrene to investigate cyclization rates. In this case one of the pyrenes was excited to its singlet excited state, and the rate of excimer formation was measured. Scheme I shows the kinetic model.

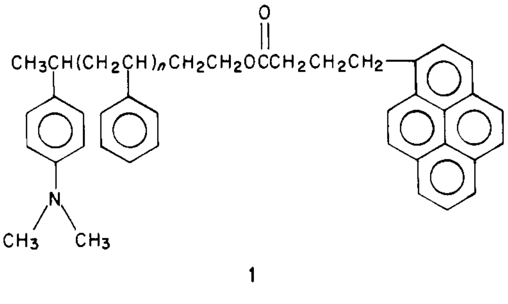
Scheme I



1, A = pyrene (Py)
D = *N,N*-dimethylaniline (DMA)
2, A = D = pyrene

In cyclohexane at 34.5 °C, a Θ solvent for polystyrene, the cyclization rate constants obtained by triplet–triplet (TT) annihilation are about 40 times slower than those obtained by pyrene excimer formation. The molecular weight dependences obtained were also somewhat different. One explanation of this would be that the differences in the rate are due to some aspect of the spectroscopy of the chromophore labels used, so that TT annihilation and excimer formation would occur at different end-group separations (a values). Another possibility is that the size of the end group, which should affect the rate of local motion of the chain end, might also affect k_{cy}.

To address these concerns we decided to prepare polystyrene polymers in which a pyrene (Py) excited state on one end could be quenched by a different and smaller quencher on the other end. *N,N*-Dimethylaniline (DMA) was chosen since it quenches pyrene fluorescence at the diffusion-controlled rate to yield an emissive (Py/DMA)* exciplex.[7] Its spectroscopy is reasonably well understood. We considered various approaches to synthesize the required polymer DMA–polystyrene–Py (1). Treatment of 1-ethoxy-1-[4-(dimethylamino)phenyl]ethane with potassium in THF produced a carbanion which was effective at initiating anionic polymerization of styrene. The living polymers produced were terminated with ethylene oxide to yield samples of DMA–polystyrene–OH. Subsequent esterification with the acid chloride of 4-(1-pyrenyl)butyric acid[6] yielded the desired polymers 1. A series of eight molecular weights from 3000 to 28 000 with $\bar{M}_w\bar{M}_n < 1.2$ were synthesized.[8,9]



1

The fluorescence spectra of 1 at 2-ppm concentration in cyclohexane solution showed monomer and exciplex bands at 400 and 480 nm, respectively. The exciplex band intensity (I_E) was red shifted and considerably weaker in more polar solvents for a given molecular weight. This is in contrast to pyrene excimer (PyPy)* spectroscopy, where the excimer emission maximum and intensity are both insensitive to solvent.[10]

Cyclization rate constants $\langle k_1 \rangle$ in cyclohexane at 34.5 °C (Θ conditions for polystyrene) were determined by both fluorescence decay $I(t)$ measurements and steady-state determinations of the exciplex-to-pyrene "monomer"

0024-9297/85/2218-1517$01.50/0 © 1985 American Chemical Society

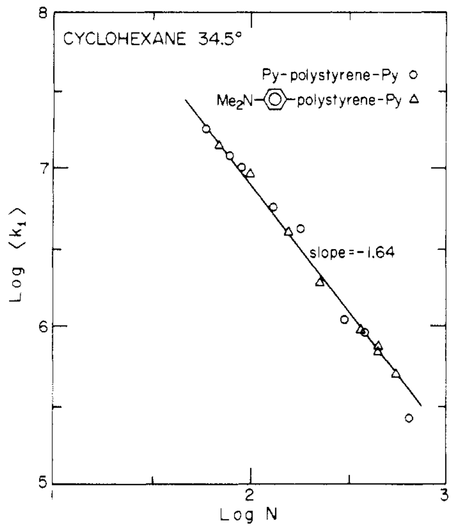


Figure 1. Plot log $\langle k_1 \rangle$ vs. log N (number of bonds) for DMA–polystyrene–Py and Py–polystyrene–Py in cyclohexane at 34.5 °C. The slope of the best fit line is −1.64 ± 0.04.

fluorescence intensities (I_E/I_M). For polymers 1 of $\bar{M}_n <$ 11 000, $I_M(t)$ was fit to a sum of two exponential terms, and $\langle k_1 \rangle$ was calculated from a detailed analysis of the decay parameters.[6] For longer chains the decay of $I_M(t)$ was exponential, with a decay constant λ_1. Rate constants $\langle k_1 \rangle$ could be calculated from

$$\langle k_1 \rangle = \lambda_1 - k_M \qquad (1)$$

where k_M was taken as the value of λ for a polymer Py–polystyrene without a quencher on the other end. For all polymer chain lengths, with constant solvent and temperature, the relative values of $\langle k_1 \rangle$ can be obtained from analysis of the steady state spectra using

$$(I_E/I_M)_1/(I_E/I_M)_2 = \langle k_1 \rangle_1/\langle k_1 \rangle_2 \qquad (2)$$

where the subscripts 1 and 2 refer to samples of two different chain lengths.

There are two features of the data that are particularly important. The first is the actual magnitude of $\langle k_1 \rangle$ and its comparison with values obtained from studies of Py–polystyrene–Py (**2**). The second is the value of the critical exponent in the scaling relationship of $\langle k_1 \rangle$ with N. A plot of log $\langle k_1 \rangle$ vs. log N is shown in Figure 1 for the eight samples of 1. Also shown are data from Redpath and Winnik for cyclization rates of 2. The cyclization rates are identical within experimental error, estimated to be ±10%. The $\langle k_1 \rangle$ values shown are calculated from fluorescence decay measurements on 1. Values obtained from steady-state measurments are virtually identical. We find these results satisfying because they demonstrate the precision of the method and because they indicate that replacing a pyrene group by the smaller dimethylanilino moiety has no noticeable affect on the cyclization rate.

The slope obtained for a best fit to all of the data is −1.64 ± 0.04. The slopes of the two individual sets of data are also both −1.64.[11] Inclusion of the steady-state data does not alter the result. These values are consistently larger than the slope of −1.50 predicted by WF theory[2] and the value of −1.43 predicted for finite polystyrene chains in Θ solvent.[4] We note that some of the samples we have examined have chain lengths even shorter than those accommodated into the treatment of finite polystyrene chains, yet we see no obvious source of differences between theory and experiment.

Acknowledgment. We thank NSERC (Canada) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. A.M.S. thanks the University of Toronto for an Open Fellowship.

References and Notes

(1) For Part 16, see: Winnik, M. A. In "Cyclic Polymers"; Semlyen, A., Ed.; Applied Science Publishers: London, 1985.
(2) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1974**, *60*, 866–877, 878–890.
(3) Doi, M. *Chem. Phys.* **1975**, *9*, 455–466; **11**, 107^{-}113, 115^{-1}21.
(4) Cunniberti, C.; Perico, A. *Prog. Polym. Sci. 10*, 271–316, Perico, A.; Cunniberti, C. *Eur. Polym. J.* **1977**, *13*, 369–374.
(5) Horie, K.; Schnabel, W.; Mita, I.; Ushiki, H. *Macromolecules* **1981**, *14*, 1422–1428, Ushiki, H.; Horie, K.; Okamoto, A.; Mita, I. *Polym. J.* **1980**, *12*, 35–41.
(6) Winnik, M. A.; Redpath, A. E. C.; Paton, K.; Danhelka, J. *Polymer* **1984**, *25*, 91–99 and earlier references cited therein.
(7) (a) Weller, A. In "The Exciplex"; Gordon, M., Ware, W., Eds.; Academic Press: New York, 1975. (b) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1976**, *101*, 371–390; **1982**, *130*, 129–138; **1982**, *133*, 93–98. (c) Knibbe, H. Ph.D. Thesis, University of Amsterdam, The Netherlands, 1969.
(8) The synthesis and characterization of 1 will be described in detail elsewhere. End-group analysis of DMA–polystyrene–OH by UV spectroscopy indicated 1.0 DMA groups per chain. Similar analysis of 1 indicated slightly less than one pyrene per chain. The eight samples have $\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$) values of 3200 (1.22), 4770 (1.12), 7700 (1.19), 11 400 (1.08), 18 600 (1.07), 22 800 (1.05), 22 800 (1.05), and 28 300 (1.13). Note: two different samples synthesized happened to yield the same $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$.
(9) Winnik, M. A.; Sinclair, A. M.; Beinert, G. *Can. J. Chem.*, in press.
(10) (a) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1971. (b) Birks, J. B. *Rep. Prog. Phys.* **1975**, *38*, 903–974.
(11) One of the reviewers pointed out that in ref 6 we drew a line of slope −1.52 through the data points for pyrene excimer probed cyclization. This line included data for higher molecular weight samples, which had larger polydispersities and for which the cyclization rate constants have a higher uncertainty. Here we compare data for polymers of similar molecular weights.
(12) A plot of log (I_E/I_M) vs. log N gives a slope of −1.61 ± 0.05.

Mitchell A. Winnik* and Andrew M. Sinclair
Lash Miller Laboratories, Department of Chemistry and
Erindale College, University of Toronto
Toronto, Ontario, Canada M5S 1A1

Gerard Beinert
Centre de Recherches sur les Macromolécules
67083 Strasbourg, France

Received March 15, 1985