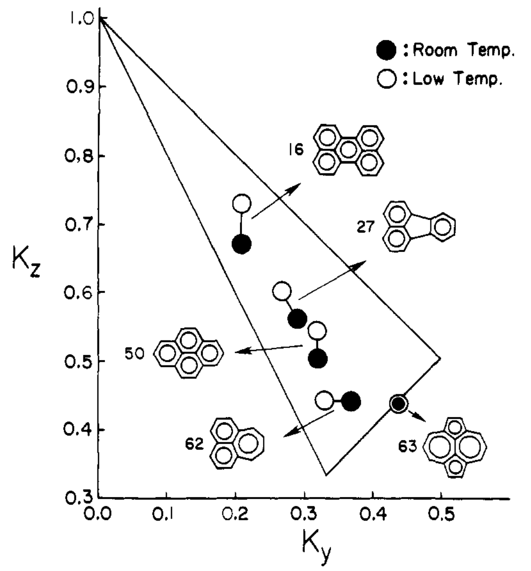

Figure 9. Orientation factors of selected hydrocarbons at room and at low temperatures (see text).

has not been possible from the observed spectra.

The main advantage of the method is its extreme simplicity, which now makes the determination of absolute polarization directions of electronic and vibrational transitions in most aromatic molecules a trivial task. The main shortcoming of the method is its purely empirical nature. The detailed mechanism of the orientation effect of stretched polyethylene can only be established through additional work, but the data base presented here can serve as a useful set of test cases against which more detailed models of orientation can be evaluated.

Acknowledgment. This work was supported by the U.S. Public Health Service (GM-19450), the U.S. Army Research Office (DAAG29-82-K-0024), and the Danish Natural Science Research Council. Technical assistance of Ludmila Jonas is gratefully acknowledged.

Registry No. 1, 28820-47-5; **2**, 92-94-4; **3**, 135-48-8; **4**, 15254-25-8; **5**, 213-46-7; **6**, 613-06-9; **7**, 782-23-0; **8**, 92-24-0; **9**, 189-55-9; **10**, 525-18-8; **11**, 886-66-8; **12**, 207-08-9; **13**, 224-41-9; **14**, 23913-06-6; **15**, 193-43-1; **16**, 198-55-0; **17**, 120-12-7; **18**, 13214-70-5; **19**, 501-65-5; **20**, 624-38-4; **21**, 581-40-8; **22**, 86-73-7; **23**, 132-65-0; **24**, 207-11-4; **25**, 92-82-0; **26**, 1012-72-2; **27**, 206-44-0; **28**, 529-85-1; **29**, 259-79-0; **30**, 117-80-6; **31**, 203-12-3; **32**, 215-58-7; **33**, 484-11-7; **34**, 6333-43-3; **35**, 230-17-1; **36**, 132-64-9; **37**, 260-94-6; **38**, 86-74-8; **39**, 85-01-8; **40**, 106-37-6; **41**, 2379-55-7; **42**, 195-19-7; **43**, 24300-95-6; **44**, 523-27-3; **45**, 1564-64-3; **46**, 781-92-0; **47**, 779-02-2; **48**, 10103-06-7; **49**, 191-24-2; **50**, 129-00-0; **51**, 771-97-1; **52**, 4145-24-8; **53**, 150-78-7; **54**, 779-03-3; **55**, 605-48-1; **56**, 3674-69-9; **57**, 95-94-3; **58**, 1079-71-6; **59**, 781-43-1; **60**, 24300-91-2; **61**, 28172-99-8; **62**, 208-20-8; **63**, 193-85-1; **64**, 3141-27-3; **65**, 81626-25-7; **66**, 191-68-4; **67**, 191-07-1; **68**, 253-52-1; **69**, 13638-84-1; **70**, 274-09-9; **71**, 3002-81-1; **72**, 91-20-3; **73**, 217-59-4; **74**, 95-50-1; **75**, 83-32-9; **76**, 5325-97-3; **77**, 625-84-3; **78**, 638-02-8; **79**, 612-71-5; **80**, 16458-17-6; **81**, 87-85-4; **82**, 891-22-5; **83**, 6830-78-0; **84**, 20343-16-2; **85**, 82823-46-9; **86**, 340-99-8; **87**, 17597-70-5; **88**, 54100-60-6; **89**, 20672-23-5; **90**, 27884-38-4; **91**, 82823-47-0; **92**, 209-42-7; **93**, 6580-41-2; **94**, 23062-31-9; **95**, 934-36-1; **96**, 2164-87-6; **97**, 27884-37-3; **98**, 4039-37-6; **99**, 15881-33-1; **100**, 82823-48-1; **101**, 13019-33-5; **102**, 210-80-0; **103**, 194-00-3; **104**, 40237-01-2; **105**, 211-53-0; **106**, 181-82-8; **107**, 275-51-4; **108**, 32495-80-0; **109**, 930-35-8; **110**, 27884-36-2; **111**, 208-96-8; **112**, 50356-52-0; polyethylene, 9002-88-4.

Temperature Dependence of Excimer Formation between Pyrenes at the Ends of a Polymer in a Good Solvent. Cyclization Dynamics of Polymers. 8[†]

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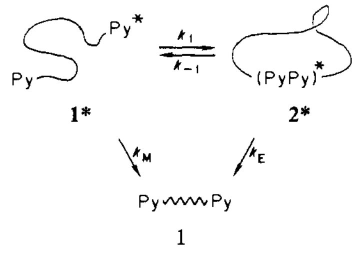
Contribution from the Lash Miller Laboratories, Department of Chemistry, and Erindale College, University of Toronto, Toronto, Ontario, Canada M5S 1A1. *Received February 4, 1982*

Abstract: The kinetics of intramolecular pyrene excimer formation have been studied in dilute toluene solution as a function of temperature for polystyrene molecules capped on both ends with pyrene groups. Three samples, of $\bar{M}_n$ 3900, 6600, and 9200, were examined. The cyclization rate constant $\langle k_1 \rangle$ was sensitive to chain length and had an E_a of 3.4 kcal/mol. Excimer dissociation back to locally excited pyrene (k_{-1}) was *insensitive* to chain length and had an E_a = 10.4 kcal/mol. Hence for these polymers, the $\Delta H°$ for pyrene excimer formation is 7 kcal/mol, very similar to that of pyrene itself.

Since the initial report in 1965 by Hirayama,[1] numerous reports have appeared describing intramolecular excimer formation in bichromophoric molecules and intramolecular exciplex formation between different groups at the ends of short-chain molecules.[2] These phenomena are of interest for a variety of reasons. With these molecules one can explore how the stereochemical constraints of the chain affect excimer and exciplex spectroscopy. In other instances, these kinds of molecules permit one to study interactions between pairs of chromophores at high dilution. Our interest is in the shape and motion of polymer chains. When one studies intramolecular cyclization between groups at the ends of long polymer chains, one can in principle obtain information about chain conformation and chain dynamics. These inferences depend

Scheme I



[†] This paper is dedicated to Mr. Schuster of the Centre de Recherches sur les Macromolécules in Strasbourg, France, on the occasion of his retirement.

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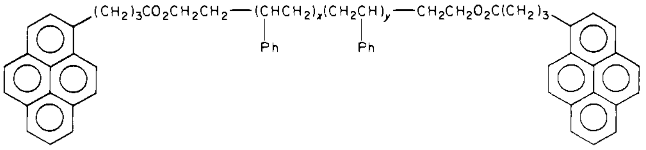
upon the validity of the mechanism one invokes to describe the reaction kinetics as well as the depth of one's knowledge of the spectroscopy of end-group interaction for intramolecular excimer or exciplex formation.

By analogy with bimolecular excimer kinetics,[3] one normally invokes the mechanism in Scheme I to describe intramolecular excimer and exciplex formation. This "two-state" mechanism, involving one locally excited state **1*** and one excimer state **2***, represents the simplest possible scheme to account for the possible reversibility of excimer formation. It assumes implicitly that the correlation function of the chain-end displacement in **1*** decays as a single exponential that can be described by a single rate constant (k_1).

We have presented in Scheme I the particular case of intramolecular pyrene [Py] excimer formation first studied by Zachariasse[4] and later extended to polymer chains by Cuniberti and Perico[5] and by ourselves.[6] The rate constant k_1 describes the diffusion-controlled excimer forming process and k_{-1} its dissociation to the ring-opened form with a locally excited pyrene. The rate constants k_M ($k_M = k_{fM} + k_{nM}$) and k_E ($k_E = k_{fE} + k_{nE}$) describe the sums of radiative and nonradiative decays of the pyrene and pyrene excimer, respectively. For a given chain length at sufficiently low temperature, the process described by k_{-1} becomes so slow that one can neglect it.

As in all diffusion-controlled processes, k_1 is a function of time. Its dependence upon time depends upon the distribution of end-to-end distances in **1*** and how this distribution function evolves in time. In this sense, the time dependence of k_1 resembles that of $k^{(2)}_{\text{diff}}$, the second-order rate constant for diffusion-controlled bimolecular reactions in solution. These points were first considered in the now classic papers of Wilemski and Fixman (WF)[7] and elaborated upon by Doi[8] and by Perico and Cuniberti.[9] The essential feature of these arguements is that Scheme I in its simplest form suffices to describe (the long time) cyclization dynamics only if a single mean relaxation time for the chain serves as the rate-limiting step for cyclization. Otherwise, one must consider explicitly the distribution of configurations of **1*** at $t = 0$ and the time dependence of k_1. For chains of 3, 4, or 5 atoms, the numbers of discrete configurations of **1** are small, and there are frequently several distinct pathways of comparable rate to interconvert **1*** to **1′***. Recent results from DeSchryver's laboratory[10] and Eisenthal's group[11] support this point of view.

This paper presents studies on pyrene-substituted polymers of the form Py-polystyrene-Py, **1**, for chains of 60–200 bonds. We show for polymers of sufficiently narrow molecular weight distribution that Scheme I is adequate to describe cyclization. We find that k_{-1} and k_E are independent of chain length, whereas k_1 is very sensitive to chain length, and that the activation energies associated with k_1 and k_{-1} are entirely consistent with cyclization being a diffusion- (encountered-) controlled process leading to a tightly bound pyrene excimer. We find that the binding energy ($\Delta H°$) for intramolecular excimer formation in **1** is very similar to that of the excimer formed bimolecularly from two pyrenes.



1, $x \approx y$

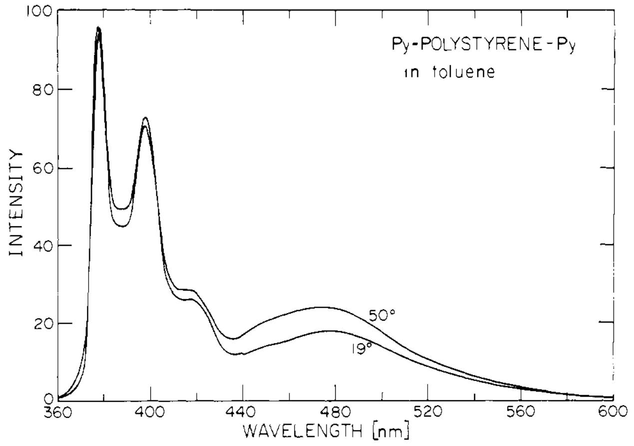


Figure 1. Fluorescence spectra of Py-PS3900-Py at 19 °C and at 50 °C, normalized at the (0,0) band of the pyrene fluorescence.

Experimental Section

The polymer samples were prepared as described previously.[6,12] Solutions of 2×10^{-6} M in purified toluene were degassed and sealed into Pyrex tubes under a vacuum better than 10^{-5} torr. Fluorescence decay times were measured by the time-correlated single-photon counting technique. Pyrene fluorescence decays $I_M(t)$ were measured at 380 nm. Pyrene excimer fluorescence decays were measured in the wavelength interval 515–550 nm. Steady-state emission spectra were run on an SLM Model 4000 fluorimeter and were not corrected. Fluorescence spectra of one of the polymer samples at two different temperatures are presented in Figure 1.

Results and Discussion

Viability of Scheme I. Scheme I predicts that the blue pyrene fluorescence in **1** should decay as a sum of two exponential components, with decay constants λ_1 and λ_2. Under the same conditions, the excimer emission $I_E(t)$ should grow in and decay as the difference of two exponential terms ($a_3 = -a_4$) with the same decay constants.

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \tag{1}$$

$$I_E(t) = a_3 \exp(-\lambda_1 t) + a_4 \exp(-\lambda_2 t) \tag{2}$$

The $\lambda_{1,2}$ values are related to the rate constants in Scheme I by the expression

$$\lambda_1, \lambda_2 = \tfrac{1}{2}\{(X + Y) \mp [(Y - X)^2 + 4k_1k_{-1}]^{1/2}\} \tag{3}$$

$$\frac{a_2}{a_1} = \frac{\lambda_1 - X}{X - \lambda_2} \tag{4}$$

To obtain rate constants from the decay data, one needs not only values for $\lambda_{1,2}$ and a_2/a_1 but also an independent measure of k_M. A convenient way of solving this problem is to assume that the decay constant λ_{mod} of an appropriate model compound containing a single pyrene provides a measure of k_M. We chose as our model a polystyrene sample of $\bar{M}_n = 5900$ containing a pyrene at only one end. We assume for each temperature that $k_M = \lambda_{\text{mod}}$.

A simplification occurs if $4k_1k_{-1}$ is much smaller than $(Y - X)^2$. The $I_M(t)$ decays become exponential with a decay constant $\lambda_1 = X = k_1 + k_M$. The λ_2 values obtained from the rise time of the excimer equal $Y = k_{-1} + k_E$. Note that when k_1 is relatively small, this result might obtain even if k_{-1} is comparable in value to k_E.

We have found that at 22 °C in toluene, $I_M(t)$ decays can be fit to a single exponential, with χ^2 values close to 1.1, over two and a half decades of the emission decay for each of the three

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Table I. Decay Times and Rate Constants for Py-polystyrene Samples in Toluene at 71 °C

$\bar{M}_n$	$\bar{M}_w/M_n$	$\bar{N}^a$	$10^{-7}\langle k_1\rangle$, s^{-1}	$10^{-7}k_{-1}$, s^{-1}	$10^{-7}k_E$, s^{-1}	$\langle K_1\rangle^b$	λ_2^{-1}, ns	λ_1^{-1}, ns	χ^2	a_4/a_3; a_2/a_1
3900	1.08	80	1.37	3.35	2.35	0.41	15.0	104	1.23	−0.93
							18.2	112	1.20	0.204
6600	1.12	135	0.74	2.95	1.85	0.25	18.7	131	1.23	−0.94
							11.8	136	2.09	0.134
9200	1.13	185	0.50	3.07	1.86	0.16	18.9	143	0.97	−0.91
							15.1	150	1.33	0.086

[a] Mean chain length, calculated from $[(\bar{M}_n - 450)/52] + 15 = \bar{N}$ (bonds). [b] $\langle K_1\rangle = \langle k_1\rangle/k_{-1}$.

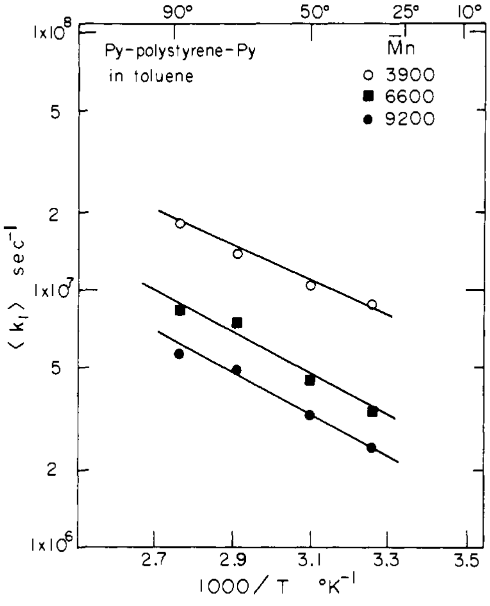

Figure 2. Arrhenius plot of log $\langle k_1\rangle$ vs. $1/T$ for Py-polystyrene-Py: (○) Py-PS3900-Py; (■) Py-PS6600-Py; (●) Py-PS9200-Py.

polystyrene samples. For the emission decay to the exponential, WF theory requires a corresponding exponential decay for the mean correlation function $\rho(t) = \langle G(r,t)G(r,t+\tau)\rangle$ of the chain end displacement. Consequently, end-to-end cyclization is dominated by a single mode of the chain motion, which we assign to τ_1, the slowest internal relaxation time of the chain.

At temperatures above 30 °C, the decay of $I_M(t)$ is no longer exponential. If these deviations from exponentially have their origin in the growing importance of the k_{-1} process at elevated temperatures, the $I_M(t)$ and $I_E(t)$ data should satisfy both eq 1 and 2. This is found to be the case. λ_1 and λ_2 values from the two experiments are similar; $-a_3/a_4$ values are essentially unity; and the χ^2 for the data are acceptable. The data in Table I are typical. They have been chosen to emphasize that there are differences in the $\lambda_{1,2}$ values from the two experiments, with the poorest result for all our experiments shown for λ_2 ($\bar{M}_n$ = 6600). λ_1 values from $I_M(t)$ decays are consistently 4–8% larger than those from $I_E(t)$ decays, and a_3/a_4 is always in the range −0.93 to −0.97. These deviations may arise from the finite dispersity of chain lengths in our polymer samples and from the possible presence of 1% or less of polymers in our sample containing only one pyrene. We take the overall agreement as further support of the validity and applicability of Scheme I.

Rate constants calculated from the data for the three Py-polystyrene-Py samples at 71 °C in toluene are also reported in Table I. From the table, it may be seen that k_{-1} and k_E values are not sensitive to chain length, whereas k_1 and K_1 (= k_1/k_{-1}, the equilibrium constant for end-to-end cyclization) decrease substantially with an increase in chain length. Results at other temperatures support these observations. Since k_1 and K_1 are so sensitively dependent upon chain length, we emphasize by angle brackets, ⟨ ⟩, in the discussion that follows that $\langle k_1\rangle$ and $\langle K_1\rangle$, calculated from our data, describe values averaged over the small but finite polydispersity of molecular weights in each of our polymer samples.

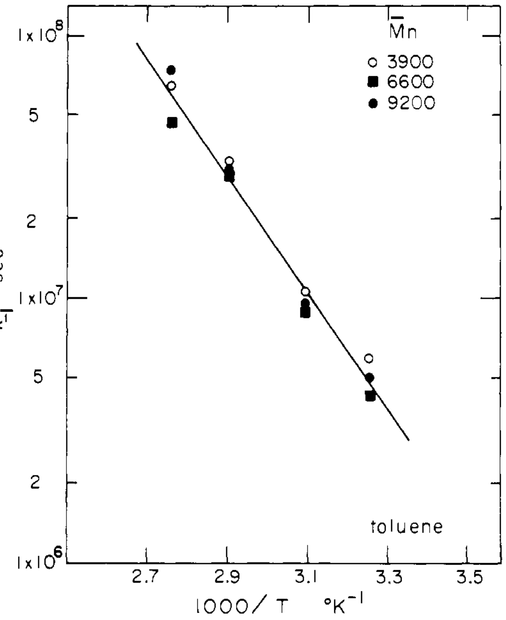

Figure 3. Arrhenius plots of log k_{-1} vs. $1/T$: (○), Py-PS3900-Py; (■) Py-PS6600-Py; (●) Py-PS9200-Py.

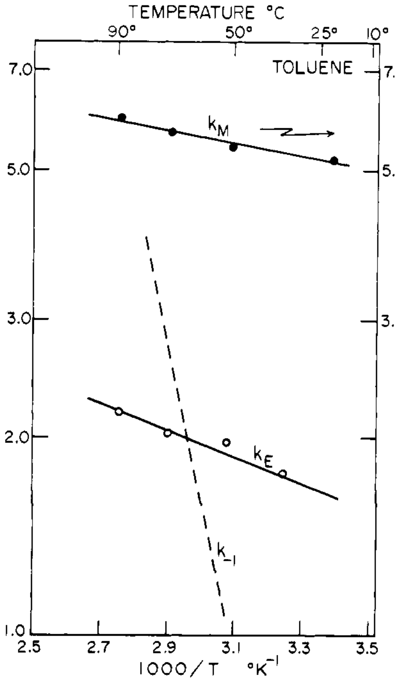

Figure 4. Arrhenius plots of log k_E (○) and log k_M (●) vs. $1/T$. The k_E data represent averaged values from the polymer samples at each temperature. Also shown is a portion of the best-fit straight line of the k_{-1} plot from Figure 3.

Temperature Dependence of the Rate Constants. A plot of log $\langle k_1\rangle$ vs. $1/T$ is shown in Figure 2, log k_{-1} vs. $1/T$ in Figure 3, and plots of log k_M and log k_E vs. $1/T$ in Figure 4. Good Arrhenius behavior is observed for each of the rate constants. The

Table II. Activation Energies[a] and Preexponential Factors for Excimer Formation in Py-polystyrene-Py in Toluene

k	$\overline{M}_n$	$A \exp(-E_a/RT)$, s^{-1}
$\langle k_1 \rangle$[b]	3900	$1.00 \times 10^9 \exp(-2.9/RT)$
	6600	$1.65 \times 10^9 \exp(-3.8/RT)$
	9200	$8.05 \times 10^8 \exp(-3.5/RT)$
k_{-1}[c]		$1.17 \times 10^{14} \exp(-10.4/RT)$
k_E[c]		$6.63 \times 10^7 \exp(-0.80/RT)$
k_M		$1.33 \times 10^7 \exp(-0.41/RT)$

[a] E_a in kcal/mol. [b] The average value $\bar{E}_a(\langle k_1 \rangle)$ for the three samples is 3.41 kcal/mol. [c] From the combined data for all three samples.

activation energies for $\langle k_1 \rangle$ for each of the polymer samples are similar and probably identical within experimental error. The excimer dissociation process described by k_{-1} is independent of chain length at all temperatures and is by far the process most sensitive to temperature. The temperature sensitivity of k_{-1} is typical of that of all tightly bound excimers and exciplexes of bimolecular origin.[13] Note that k_M and k_E are relatively insensitive to temperature. Activation energies for these processes and their respective preexponential A factors are collected in Table II.

The binding energy of the excimer could be calculated from $\bar{E}_a(\langle k_1 \rangle) - \bar{E}_a(k_{-1}) = \Delta H°$ by using the averaged values of the activation energies from the three polymer samples. The value of $\Delta H° = -7.0$ kcal/mol is typical of pyrene excimers. For example, pyrene itself in cyclohexane forms an excimer with $\Delta H° = -8.0$ kcal/mol.[14]

The activation energy $\bar{E}_a(\langle k_1 \rangle)$ for the cyclization step, 3.4 kcal/mol, is of particular interest in the area of polymer dynamics. Its meaning depends upon the model one invokes to interpret this value. In the Rouse and Zimm models,[7,9] the motion associated with $\langle k_1 \rangle$ is delocalized over the entire chain, with a node at the center of mass. The activation energy for $\langle k_1 \rangle$ should be that of a typical diffusion process, where E_{diff} can be obtained from an Arrhenius plot of T/η_0, where η_0 is the solvent viscosity. For example, Perico and Cuniberti[9] have argued that

$$k_1 = B(D_{\text{tr}}/R_G^2) \tag{5}$$

where D_{tr} is the translational diffusion constant of the polymer, R_G^2 is its mean-squared radius of gyration, and B is a proportionality constant whose value is model dependent. Since for polystyrene in a good solvent R_G^2 changes very little with temperature,[15] the Arrhenius behavior of k_1 must reflect that of D_{tr}. E_{diff} for toluene is 2.31 kcal/mol,[16] about 1 kcal/mol smaller than $\bar{E}_a(\langle k_1 \rangle)$. We believe this difference to be outside of current experimental error, which suggests that certain details of the model above may need to be reconsidered. On the other hand, $E_a(\langle k_1 \rangle)$ is significantly smaller than the barrier for internal backbone rotation, estimated at greater than 5 kcal/mol for polystyrene.[17]

Kramers's theory[17,18] provides a different basis for interpreting activation energies for dynamic processes in polymers. Under the conditions of high viscous damping, E_a can be written as the sum of the activation energy for the solvent viscosity (E_η) and the height of the internal potential barrier (E*).

$$E_a(\langle k_1 \rangle) = E_\eta + E^*(\langle k_1 \rangle) \tag{6}$$

Since the value of E_η for toluene is 2.08 kcal/mol,[16] this identifies end-to-end cyclization with a process with an internal potential barrier of 1.3 kcal/mol.

Table III. Cyclization Probabilities and Entropies for Py-polystyrene-Py in Toluene

$\overline{M}_n$	ΔS_{cy}, cal deg^{-1} mol^{-1}	$W(0)$[a]
3900	-21.9[b]	1.61×10^{-5}
6600	-23.1[b]	9.18×10^{-6}
9200	-24.0[b]	5.56×10^{-6}

[a] From $W(0) = \exp(\Delta S_{\text{cy}}/R)$. [b] ΔS values were obtained from $\langle K_1 \rangle$ values at each temperature, using $\Delta H = -7.0$ kcal/mol, and averaged.

Chain Conformation and Dynamics. According to WF theory,[7] $k_1 \sim N^{-3/2}$ for a polymer in a θ solvent, where the distribution function of the end-to-end displacement is Gaussian in form and N is the chain length. In good solvents, where the chains are swollen, $k_1 \sim N^{-9/5}$ in the limit of long chain length. These predictions follow also from eq 5: in a θ solvent, $D \sim N^{-1/2}$, $R_G^2 \sim N$; whereas in a good solvent, $R_G^2 \sim N^{2\nu}$ with $\nu = {}^3/_5$, and in the limit of long chain length, $D \sim N^{-\nu}$.[19] Our previous experiments, in toluene at 22 °C and in cyclohexane at 34.5 °C, the θ temperature, have been in accord with these observations.

One issue of current concern in polymer science is whether dynamic processes of polymers scale according to the same critical exponents as thermodynamic properties.[15,19] This matter is less controversial in θ solvents than in good solvents where excluded volume considerations become important. Our results permit us to comment on one aspect of this problem. From Table I and Figure 3, we find that k_{-1} is not sensitive to chain length. Since the equilibrium constant $\langle K_1 \rangle$ for end-to-end cyclization is equal to $\langle k_1 \rangle / k_{-1}$, we conclude that $\langle k_1 \rangle$ and $\langle K_1 \rangle$ must show identical dependencies on chain length. This confirms an observation first made for cyclohexane solutions of Py-polystyrene-Py at the θ temperature.[20]

Our data provide one other piece of information relevant to the study of chain conformation. The entropy of cyclization ΔS_{cy} can be calculated for each chain length, and from these values, we can estimate the cyclization probabilities $W(0)$:

$$W(0) = e^{\Delta S_{\text{cy}}/R}$$

These values are collected in Table III. $W(0)$ varies from 1.6×10^{-5} for the polymer of mean chain length $\bar{N} = 80$ bonds to $W(0) = 5.6 \times 10^{-6}$ for the sample with $\bar{N} = 185$ bonds. These results emphasize how sensitive cyclization probability is to the length of the chain separating the chromophores on the chain ends.

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