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Polystyrene Cyclization Using Pyrene Excimer Formation. Effect of Geminate Pairs in Good Solvents

A. T. Reis e Sousa, E. M. S. Castanheira, A. Fedorov, and J. M. G. Martinho*

Centro de Química-Física Molecular, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex, Portugal

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The cyclization of polystyrene chains ($\bar{M}_n = 2600$, $\bar{M}_w/\bar{M}_n = 1.07$; $\bar{M}_n = 4500$, $\bar{M}_w/\bar{M}_n = 1.08$), both-ends labeled with 1-pyrenyl groups, was studied in the range of temperatures 25−90 °C, in two good solvents (toluene and 1,4-dioxane) and one poor solvent (methylcyclohexane). In methylcyclohexane a two-state Birks kinetics is followed, but in good solvents at high temperatures the contribution of geminate pairs recombination must be considered. Values of the standard enthalpies, $\Delta H°$, and entropies, $\Delta S°$, for excimer formation were determined from the van't Hoff plots. The $\Delta S°$ values are solvent and chain length dependent, while the $\Delta H°$ values are, within the experimental error, chain length independent.

Introduction

The cyclization of both short alkane and polymer chains has been studied by fluorescence,[1−4] using both-ends labeled chains with fluorophores able to form excimers. Upon electronic excitation of one fluorophore the chain can cyclize forming an intramolecular excimer. The rate coefficients for the cyclization and excimer dissociation (and ring opening) processes can be calculated from the decay curves of both the excited monomer and the excimer. For short chains, the lifetime of the fluorophore is not relevant since the reciprocal of the cyclization rate coefficient is generally larger than the fluorophore intrinsic lifetime. However, for polymer chains the rate of the cyclization process can be orders of magnitude lower, and consequently, to obtain reliable values of the rate coefficients, long-lived fluorophores should be used.

For long alkane chains[5] and polymers[1,6−11] labeled with 1-pyrenyl groups, it was observed experimentally that a two-state Birks kinetic scheme[12] describes well the fluorescence decay curves. This is not the case for short alkane chains, namely for 1,3-bis(1-pyrenyl)propane, as was fully discussed by Zachariasse et al.[5,13]

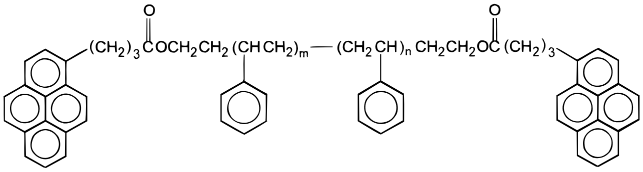
The cyclization rate coefficient contains relevant information on the conformation and dynamics of the chain in a given medium. In the case of polymer chains, it was shown that cyclization is dependent on chain length,[1,6−10] solvent quality,[1,8,9,11] temperature,[10,11] and hydrostatic pressure.[14,15]

The theory of polymer cyclization in dilute solutions was first addressed by Wilemsky and Fixman,[16] using the "closure approximation" and considering both the harmonic spring and the Rouse models for flexible chains. This work was further developed by Doi et al.[17] and Cuniberti and Perico,[18] who calculated theoretically the cyclization rate constant, considering the influence of capture radius, chain length, flexibility, and hydrodynamic interactions.

The introduction of excluded volume effects (relevant in good solvents), without preaverage hydrodynamics interactions, was done by Friedman and O'Shaughnessy.[19] These authors showed that in good solvents the rate constant scales as the equilibrium probability of the chain ends being in contact, while in Θ-solvents it scales with the longest relaxation time of the chain. The behavior in good solvents results from correlation effects that cause a "hole" in the probability density distribution of the end-to-end separation for chain ends in close proximity.

The effect of ring opening after cyclization of Gaussian chains was considered in a statistical approach developed by Liu and Guillet.[20a] Using an appropriate potential to describe the excimer, Liu[20b,c] calculated the monomer and excimer decay curves for both-ends labeled polymer chains. The simulated decays for pyrene-labeled chains, when fitted with Birks' kinetics, gave cyclization rate constants in agreement with theoretical and experimental values, but the excimer dissociation rate constant shows unexpected dependence on the intrinsic lifetimes of monomer and excimer.

This paper presents fluorescence results for the cyclization of two polystyrene chains, both ends labeled with 1-pyrenyl groups (structure **I**).



I

We found deviations from the two-state Birks' kinetics at high temperatures in good solvents. This was attributed to the geminate pair generated by excimer dissociation, which recombines faster than chains that cyclize from their equilibrium conformation. This is a consequence of shorter average chain-end distances generated by excimer dissociation. A new kinetic scheme that considers two cyclization rate coefficients was used to analyze the fluorescence decays. This scheme predicts that both the excited monomer and excimer decay as a sum of three exponentials.

From the van't Hoff plots, values of the standard enthalpies, $\Delta H°$, and entropies, $\Delta S°$, for excimer formation were deter-

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* To whom correspondence should be addressed. Fax: 351-1-8464455/57. E-mail: jgmartinho@alfa.ist.utl.pt.

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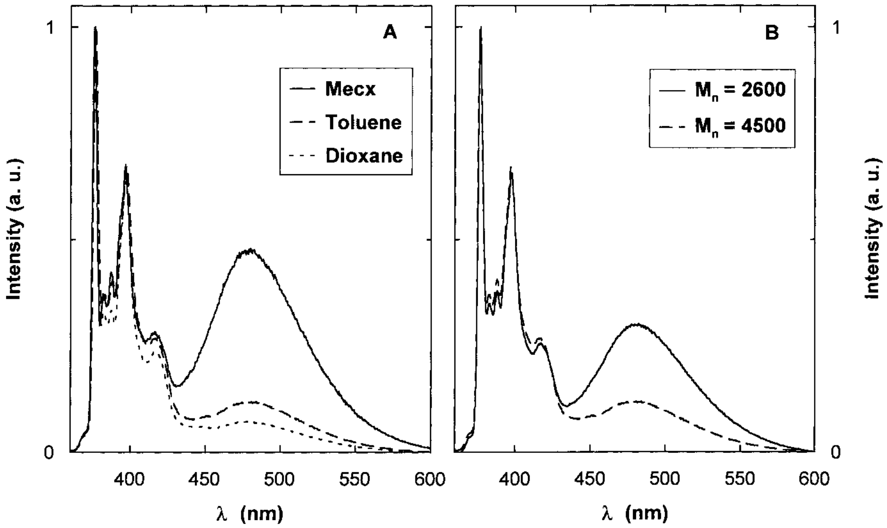


Figure 1. Fluorescence spectra for PyPSPy at 25 °C: (A) emission of PyPS4500Py in several solvents; (B) emission of PyPS(M_n)Py in toluene.

mined. The $\Delta H°$ values are similar for both chain lengths but solvent dependent, while the $\Delta S°$ values are solvent and chain length dependent, being more negative for the longer chain. The enthalpies for excimer dissociation, calculated from the Arrhenius plots of $k_{-1}\eta/T$, are close to the binding energy of the intermolecular pyrene excimer.

Experimental Section

The synthesis of polystyrene chains ($\bar{M}_n = 2600$, $\bar{M}_w/\bar{M}_n = 1.07$; $\bar{M}_n = 4500$, $\bar{M}_w/\bar{M}_n = 1.08$), both ends labeled with 1-pyrenyl groups, and their characterization have been reported elsewhere.[7] The solvents methylcyclohexane, toluene, and 1,4-dioxane, from Merck Uvasol, were of spectroscopic grade and were used as received. The absence of impurities was checked by UV–vis absorption and fluorescence. The viscosities of solvents at several temperatures were taken from the literature.[21,22]

Solutions of polymers ($C \approx 2 \times 10^{-6}$ M) were degassed using the freeze–pump–thaw technique and sealed under a vacuum better than 10^{-5} Torr. Fluorescence spectra at several temperatures were obtained in a Spex F112 spectrofluorometer.

Time-resolved picosecond fluorescence decays were obtained by the single-photon timing technique with laser excitation. The apparatus consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity-dumped Coherent 701-2 dye laser, delivering 3–4 ps pulses (with ≈40 nJ/pulse) at a frequency of 460 kHz. The excitation light ($\lambda = 330$ nm) was generated by frequency doubling the output of the Rhodamine 6G dye laser.

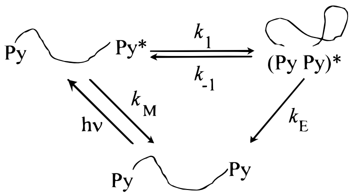
The monomer ($\lambda = 376$ nm) and excimer ($\lambda = 520$ nm) fluorescence was selected by a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm. The detector used was a Hamamatsu 2809U-01 microchannel plate photomultiplier.

Decay curves were analyzed using an iterative reconvolution method based on the algorithm of Marquardt.[23]

Data and Data Analysis

Cyclization of polystyrene chains, both ends labeled with 1-pyrenyl groups, has been described through the classical Birks' scheme (Scheme 1),[12] where k_1 describes the diffusion-controlled cyclization step, k_{-1} describes the excimer dissociation and ring-opening process, and k_M and k_E are the reciprocal lifetimes of the excited pyrene monomer and excimer, respectively.

SCHEME 1



The ratio of excimer to monomer fluorescence intensities is, according to Scheme 1, given by[12]

$$\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \frac{k_1}{k_{-1} + k_E} \tag{1}$$

where k_{FM} and k_{FE} are the monomer and excimer radiative rate constants, respectively.

For pyrene at room temperature $k_{-1} \ll k_E$, the ratio k_{FE}/k_{FM} and k_E being almost solvent independent.[12,24] Therefore, the fluorescence intensities ratio reflects mainly the variation of the cyclization rate constant, k_1.

Fluorescence spectra at room temperature for PyPSPy in Figure 1 show the influence of solvent (Figure 1A) and chain length (Figure 1B) on excimer formation.

The ratio I_E/I_M (and k_1) decrease with increasing chain length (Figure 1B), as theoretically predicted[16,18] and fully experimentally documented by Winnik and co-workers.[1,6–10] Cyclization is also dependent on viscosity and on the quality of solvent for the polymer. In a good solvent, excluded volume effects strongly diminish the probability of conformations with chain ends in close proximity.[9,19,25] This explains a smaller ratio I_E/I_M for toluene and dioxane (good solvents for polystyrene) than for methylcyclohexane (poor solvent, Figure 1A).

Scheme 1 predicts that after a δ-pulse of excitation light the monomer decays as a sum of two exponentials and the excimer as a difference of two exponentials,

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \tag{2}$$

$$I_E(t) = a_3 \exp(-\lambda_1 t) - a_4 \exp(-\lambda_2 t) \tag{3}$$

where the decay constants λ_1 and λ_2 are given by

$$2\lambda_{1,2} = (A_x + A_y) \mp \sqrt{(A_x - A_y)^2 + 4k_1k_{-1}} \tag{4}$$

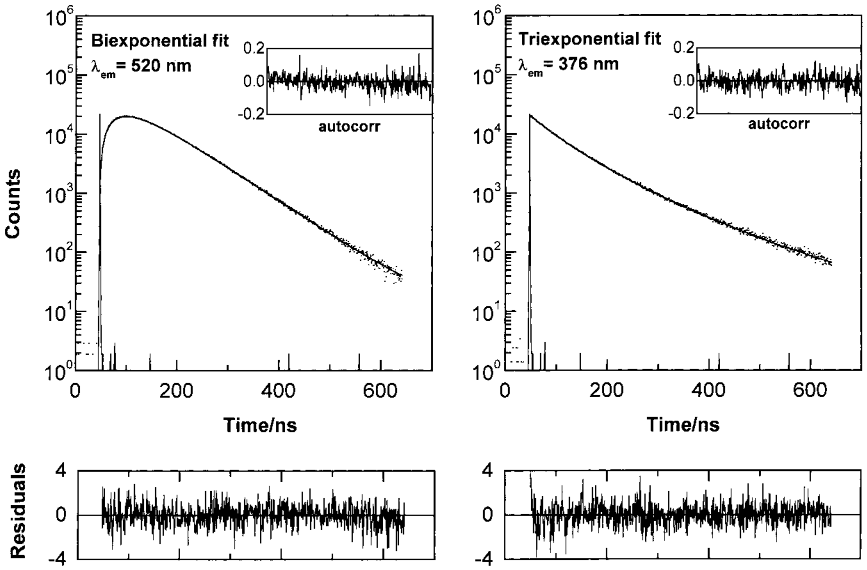


Figure 2. Fluorescence decay curves at 520 nm (excimer) and 376 nm (monomer) for PyPS2600Py in toluene at 30 °C. Fitting results: excimer, $a_1 = 0.375$, $\tau_1 = 75.80$ ns, $a_2 = -0.374$, $\tau_2 = 37.22$ ns, $\chi^2 = 1.02$; monomer, $a_1 = 0.0591$, $\tau_1 = 75.80$ ns, $a_2 = 0.0306$, $\tau_2 = 37.22$ ns, $a_3 = 0.0041$, $\tau_3 = 195.88$ ns, $\chi^2 = 1.09$.

$$A_x = k_M + k_1 \qquad A_y = k_E + k_{-1} \tag{5}$$

$$\frac{a_2}{a_1} = \frac{A_x - \lambda_1}{\lambda_2 - A_x} \qquad \frac{a_4}{a_3} = 1 \tag{6}$$

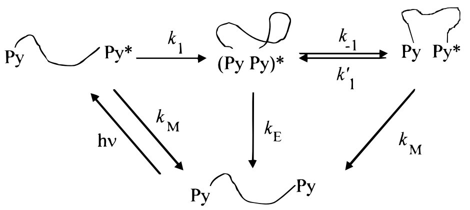
From the values of the decay parameters, λ_1 and λ_2, and the ratio a_2/a_1, all the relevant kinetic parameters can be calculated, once the monomer lifetime, $\tau_M = 1/k_M$, is known. The τ_M values are obtained from the monoexponential decay curves of dilute solutions ($C \approx 2 \times 10^{-6}$ M) of a polystyrene chain containing a 1-pyrenyl group at only one end ($\bar{M}_n = 5900$, $\bar{M}_w/\bar{M}_n = 1.33$), in the three solvents at each temperature.

The excimer decay curves of solutions of chain **I** in methylcyclohexane, toluene, and dioxane at room temperature can be fitted with a difference of two exponentials, with a ratio of preexponential factors very close to −1.0. This indicates that the presence of preassociated pyrene dimers is negligible. Figure 2 shows the biexponential fit of the excimer decay of a 2×10^{-6} M solution of PyPS2600Py in toluene at 30 °C.

The monomer decay curve can only be fitted with a sum of three exponentials, the long decay constant being close to the reciprocal lifetime of the model compound, k_M. This is attributed to some one-end 1-pyrenyl labeled polystyrene chains in solution. Nevertheless, the other two decay constants are close to the values obtained from the biexponential fit of the excimer decay curve.

The decay curves in methylcyclohexane at all temperatures and in toluene and dioxane below 70 and 60 °C, respectively, retain a similar behavior. However, at temperatures above 70 °C in toluene and 60 °C in dioxane, the excimer decay curves deviate from a biexponential fit. At these temperatures, three exponentials are needed to fit the excimer decay, while for the monomer one more exponential is needed to take into account the presence of one-end 1-pyrenyl labeled chains. Figure 3 shows the excimer and monomer decay curves of a 2×10^{-6} M solution of PyPS2600Py in toluene at 80 °C. Note that the sum of preexponential factors of the excimer decay is close to 0, showing that pyrene ground-state aggregation is negligible, as already observed at 30 °C. Upon cooling of the solutions in dioxane and toluene, the biexponential excimer decays are restored. The possibility of this effect being due to the time dependence of the rate coefficient is ruled out, since the solvent viscosity is low and the theory predicts for good solvents very small deviation of the cyclization rate constant from its value at infinite time.[19c]

SCHEME 2



These results lead us to consider the contribution to cyclization of the geminate pairs generated by pyrene excimer dissociation. Indeed, after excimer dissociation, the chain ends are in close proximity and can recyclize with a higher cyclization rate, before excimer intrinsic deactivation.

To take this effect into account, we consider two cyclization rate coefficients, one for the initially excited pyrene (k_1) and the other for the geminate pair (k'_1). Following this reasoning, we propose the kinetic Scheme 2. Scheme 2 predicts that the excited monomer and excimer decay as a sum of three exponentials

$$I_M(t) = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) + a_3 \exp(-\lambda_3 t) \tag{7}$$

$$I_E(t) = a_4 \exp(-\lambda_1 t) + a_5 \exp(-\lambda_2 t) + a_6 \exp(-\lambda_3 t) \tag{8}$$

where the decay constants λ_1, λ_2, and λ_3 are given by

$$\lambda_1 = k_1 + k_M \tag{9}$$

$$2\lambda_{2,3} = (A_x + A_y) \mp \sqrt{(A_x + A_y)^2 + 4(k'_1 k_{-1} - A_x A_y)} \tag{10}$$

$$A_x = k_M + k'_1 \qquad A_y = k_E + k_{-1} \tag{11}$$

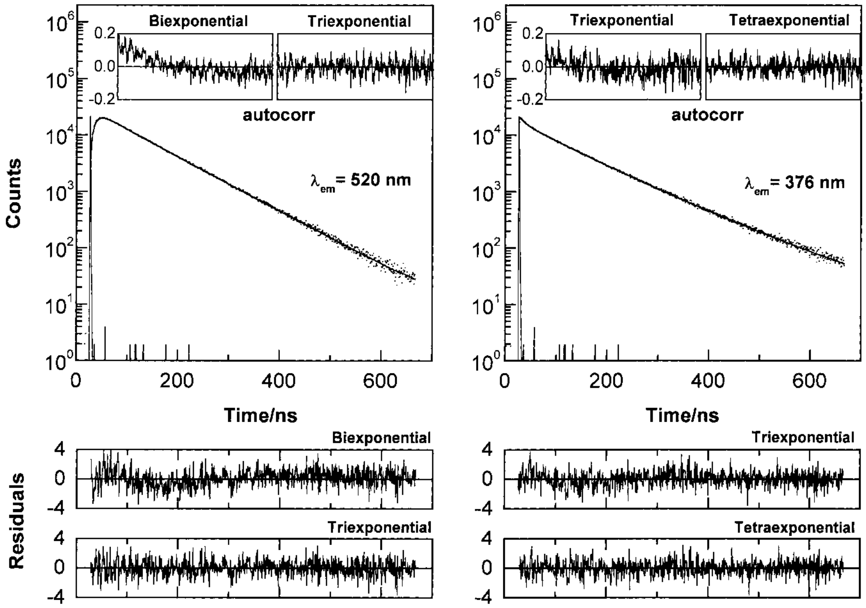


Figure 3. Fluorescence decay curves at 520 nm (excimer) and 376 nm (monomer) for PyPS2600Py in toluene at 80 °C. Fitting results: excimer, $a_1 = 0.0101$, $\tau_1 = 33.32$ ns, $a_2 = 0.0947$, $\tau_2 = 90.36$ ns, $a_3 = -0.103$, $\tau_3 = 10.08$ ns, $\chi^2 = 1.23$; monomer, $a_1 = 0.0043$, $\tau_1 = 33.32$ ns, $a_2 = 0.0454$, $\tau_2 = 90.36$ ns, $a_3 = 0.0156$, $\tau_3 = 10.08$ ns, $a_4 = 0.0048$, $\tau_4 = 183.77$ ns, $\chi^2 = 1.06$.

The preexponential factors ratios of the monomer decay are given by

$$\frac{a_2}{a_1} = \frac{(\lambda_3 - \lambda_1)}{(\lambda_2 - \lambda_3)} \frac{k_1 k_{-1}}{(A_y - \lambda_1)(A_x - \lambda_1) + k_{-1}(k_1 - k'_1)} \qquad (12)$$

$$\frac{a_3}{a_1} = \frac{(\lambda_1 - \lambda_2)}{(\lambda_2 - \lambda_3)} \frac{k_1 k_{-1}}{(A_y - \lambda_1)(A_x - \lambda_1) + k_{-1}(k_1 - k'_1)} \qquad (13)$$

For the excimer decay one obtains

$$\frac{a_5}{a_4} = \frac{(\lambda_3 - \lambda_1)}{(\lambda_2 - \lambda_3)} \frac{(A_x - \lambda_2)}{(A_x - \lambda_1)} \qquad (14)$$

$$\frac{a_6}{a_4} = \frac{(\lambda_1 - \lambda_2)}{(\lambda_2 - \lambda_3)} \frac{(A_x - \lambda_3)}{(A_x - \lambda_1)} \qquad (15)$$

$$\sum_{i=4}^{6} a_i = 0 \qquad (16)$$

as the ground-state aggregation of pyrene chromophores was not considered. When $k_1 = k'_1$, Scheme 2 reverts to the classical Birks' scheme (Scheme 1).

With this model, rate constants for cyclization, excimer dissociation, and geminate pair recombination were calculated from λ_1, λ_2, and λ_3 and one of the ratios (eq 12 or 13) of preexponential factors of monomer decay. The value of preexponential factor of the new component (a_1) is very small ($a_1 \approx 0.1a_2$, a_3). This fact limitates the accuracy of the rate coefficients evaluation. The use of excimer and monomer global analysis did not improve the rate constants evaluation.

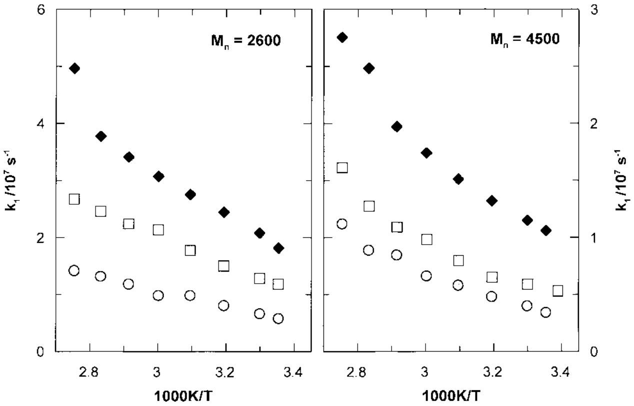


Figure 4. Cyclization rate constant, k_1, for PyPSPy as a function of temperature, in dioxane (○), toluene (□), and methylcyclohexane (◆).

TABLE 1: Ratio of Pair Recombination and Cyclization Rate Coefficients, k'_1/k_1, for Good Solvents at High Temperatures

solvent	temp (°C)	$\bar{M}_n = 2600$	$\bar{M}_n = 4500$
toluene	70	1.13	1.13
	80	1.34	1.31
	90	1.41	1.57
dioxane	60	1.49	1.22
	70	1.64	1.15
	80	1.80	1.22
	90	1.97	1.14

Results and Discussion

Cyclization rate constants, k_1, at several temperatures are plotted in Figure 4 for two polystyrene chains in the three solvents. The increase of k_1 with temperature for both chains is similar, although the values are always lower for the longer chain.

The influence of solvent on k_1 comes from the variation of viscosity and the quality of solvent for polystyrene. k_1 is higher in the poor solvent (methylcyclohexane) than in good solvents, due to excluded volume effects.[8,9,19,25] The difference between k_1 in toluene and dioxane is mainly due to the higher viscosity of dioxane ($\eta_{\text{dioxane}} \approx 2\eta_{\text{toluene}}$).

Table 1 shows that the rate coefficient for pair recombination, k'_1, is higher than the cyclization rate constant, k_1. The k'_1/k_1 ratios are different for dioxane and toluene, and for dioxane a clear dependence on chain length is also detected.

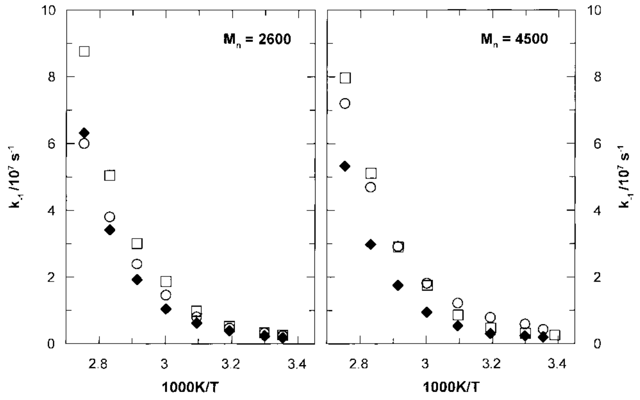


Figure 5. Excimer dissociation rate constant, k_{-1}, for PyPSPy as a function of temperature, in dioxane (○), toluene (□), and methylcyclohexane (◆).

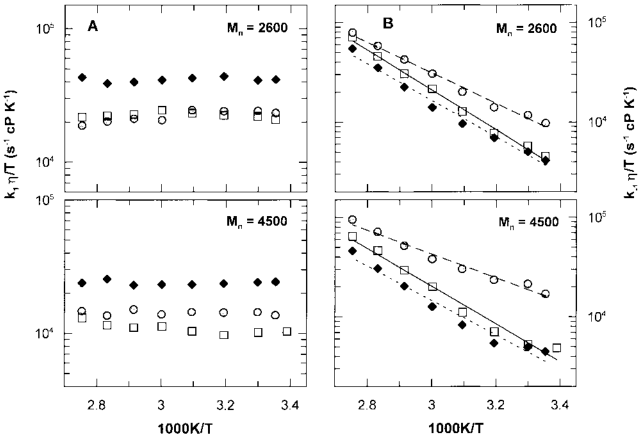


Figure 6. (A) Variation with temperature of $k_1\eta/T$ for PyPSPy, in dioxane (○), toluene (□), and methylcyclohexane (◆). (B) Arrhenius plot of $k_{-1}\eta/T$ for PyPSPy, in dioxane (○), toluene (□), and methylcyclohexane (◆).

In the absence of the correlation hole at short end-to-end distances, the k'_1/k_1 ratio should increase with chain length and solvent viscosity. This is a consequence of the differences in chain-ends distance distribution functions for the initial excited chains (equilibrium distribution) and the geminate pair. However, the presence of the correlation hole for short end-to-end distances disturbs this reasoning. The correlation hole is dependent on the solvent quality and temperature.[26] In toluene it was observed that the influence of chain length is negligible, increasing the ratio k'_1/k_1 with temperature increase. The same trend is observed for the smaller chain in dioxane, but not for the longer one. The interpretation of this effect is not straightforward, since the effects of chain length and solvent on the correlation hole are not completely understood.[19]

Due to the decrease of solvent viscosity with temperature, it would be expected that geminate pair recombination effect is more important at low temperatures. However, excimer dissociation strongly decreases with temperature decrease, and consequently, the concentration of geminate pairs is very low. This leads to undetectable deviations from the two-state Birks' kinetics, which prevents the determination of k'_1 at low temperatures.

For methylcylohexane (poor solvent) the initial equilibrium distribution of chain ends separation and the one generated by excimer dissociation should be similar, and therefore, $k_1 = k'_1$. This may not be the case for longer polymer chains.

The excimer dissociation rate constant, k_{-1}, is pratically independent of chain length and solvent and is much more sensitive to temperature than k_1 (Figure 5). This behavior is well-known for stable bimolecular excimers and exciplexes[12,27] and is explained by the high activation energy for excimer (exciplex) dissociation.

The variation of k_1 and k_{-1} with temperature is more clearly studied if the influence of viscosity is removed by multiplying the rate constants by η/T (Figure 6). In the range of temperatures studied, no significant changes in the quality of solvents for polystyrene are anticipated.[11] $k_1\eta/T$ is essentially constant over the range of temperatures studied (Figure 6A).

The activation energy for cyclization, E_a, should be similar to the activation energy for the solvent viscosity, E_η, calculated from the Arrhenius plot of viscosity,

$$\eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \tag{17}$$

In Table 2, the similarity between values of E_a, obtained from the Arrhenius plot of k_1/T, and E_η for the three solvents studied can be seen. This fact supports that cyclization is a diffusion influenced process, in both poor and good solvents. The increase of $k_1\eta/T$ at high temperatures observed previously in toluene[11] has to be attributed to the geminate pair recombination.

Assuming that the excimer dissociation process is diffusive, the excimer dissociation enthalpy, ΔH, can be estimated from[28]

$$k_{-1} \propto \left(\frac{3D_e}{{R_e}^2}\right) \exp\left(\frac{-\Delta H}{RT}\right) \tag{18}$$

where R_e is the encounter radius and D_e is the diffusion coefficient for excimer dissociation. This equation is derived by assuming that the encounter finishes at an arbitrary distance of $1.7R_e$. Figure 6B shows the Arrhenius plots of $k_{-1}\eta/T$ for the two chains and in the three solvents.

The ΔH values for both chains in methylcyclohexane and toluene (Table 2) are very close to reported values for intermolecular pyrene excimer (9−10 kcal mol^{-1}).[12,27,29] In dioxane, the ΔH values are smaller by ≈2 kcal mol^{-1}. This is consistent with the ΔH value for intermolecular pyrene excimer measured in dioxane, $\Delta H = 8.3 \pm 0.3$ kcal mol^{-1}.

The cyclization equilibrium constant, K_{eq}, allows the evaluation of the standard enthalpy, $\Delta H°$, and entropy, $\Delta S°$, for excimer formation, through the equation:

$$K_{eq} = \exp\left(\frac{\Delta S°}{R}\right) \exp\left(\frac{-\Delta H°}{RT}\right) \tag{19}$$

Figure 7 shows very reasonable linear plots of log K_{eq} vs $1/T$, when the value of k'_1 is used at high temperatures in toluene and dioxane (in this case, $K_{eq} = k'_1/k_{-1}$). The values of $\Delta H°$ and $\Delta S°$ are presented in Table 2. The difference between

TABLE 2: Activation Energies, Standard Enthalpies, and Standard Entropies for Polystyrene Cyclization

param	symbol	methylcyclohexane		toluene		1,4-dioxane	
activation energy for solvent viscosity	E_η (kcal mol^{-1})	2.46		2.10		3.02	
molecular wt of the chain	$\bar{M}_n$	2600	4500	2600	4500	2600	4500
activation energy for cyclization	E_a (kcal mol^{-1})	2.4 ± 0.2	2.6 ± 0.2	2.2 ± 0.2	2.8 ± 0.2	2.4 ± 0.3	3.1 ± 0.2
excimer dissociation enthalpy	ΔH (kcal mol^{-1})	10.3 ± 0.4	9.8 ± 0.4	10.3 ± 0.4	9.6 ± 0.3	7.6 ± 0.2	6.9 ± 0.3
std formation enthalpy	$-\Delta H°$ (kcal mol^{-1})	8.8 ± 0.4	9.2 ± 0.2	7.4 ± 0.3	7.5 ± 0.3	5.0 ± 0.2	5.0 ± 0.5
std formation entropy	$\Delta S°$ (cal mol^{-1} K^{-1})	−24 ± 1	−27 ± 1	−21 ± 1	−23 ± 1	−15 ± 1	−17 ± 1

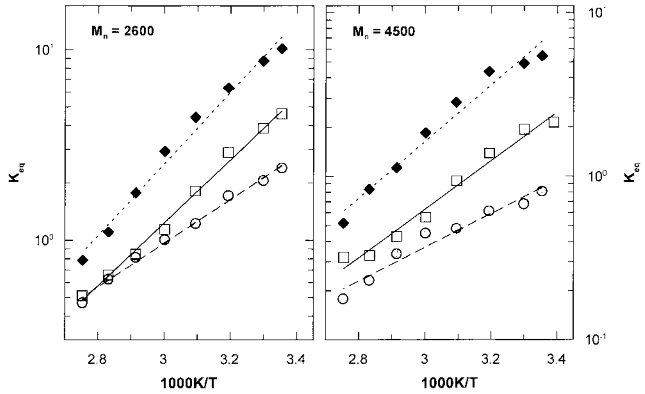


Figure 7. Van't Hoff plot of the equilibrium constant, K_{eq}, for PyPSPy, in dioxane (○), toluene (□), and methylcyclohexane (◆).

$-\Delta H°$ and ΔH is greater in good solvents than in the poor solvent. This is contrary to what was observed for intermolecular pyrene excimer, where $-\Delta H° \approx \Delta H$ in the three solvents studied. We must point out that some chain conformation changes are required for the cyclization process, giving a positive contribution to the value of $\Delta H°$. Conformational changes are greater in good solvents than in a poor solvent. Nevertheless, these conformational changes do not contribute to the excimer dissociation enthalpy, where only the process of separation of the two pyrenyl groups is accounted for.

The standard formation entropy, $\Delta S°$, is negative as expected for a process with a decrease in the degrees of freedom. The $\Delta S°$ values are solvent and chain length dependent, being more negative for the longer chain, where more restrictions occur upon excimer formation.

Conclusions

The cyclization of two polystyrene chains, both ends labeled with 1-pyrenyl groups, was studied as a function of temperature, in good and poor solvents. In poor solvents, Birks' kinetics is obeyed at all temperatures studied, but in good solvents at high temperatures the kinetic scheme must consider the contribution of the recombination of geminate pairs originated from excimer dissociation. For the two chain lengths studied the standard enthalpy for excimer formation seems to be independent of chain length, while the values of the standard formation entropy clearly depend on chain length and solvent. Enthalpies for excimer dissociation are in good agreement with published values of the binding energy of intermolecular pyrene excimer.

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