Cyclization dynamics of polymers, 26

End-to-end cyclization of polystyrene in mixed solvents.
Effect of chain length

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SUMMARY:
Cyclization rate measurements were carried out on polystyrene chains of different molecular weights and labelled at both ends with 1-pyrenyl groups, using as solvents cyclopentane (a theta-solvent), acetone (a poor solvent), and their mixtures. These mixtures exhibit a cosolvency effect for polystyrene. The results show that the rate constants for cyclization and ring-opening are solvent- and chain-length-dependent. This was interpreted in terms of the influence of excluded volume effects on these processes. The results indicate that the solvent giving the largest excluded volume effect is an equimolar mixture of cyclopentane and acetone, which agrees with the light scattering and viscometry results for polystyrene in cyclohexane/acetone mixtures.

Introduction

Important information about the dynamics and conformation of polymer chains can be obtained from cyclization studies. The cyclization equilibrium constant, \( K_{cy} \), and the cyclization rate constant, \( k_{cy} \), depend on the quality of solvent for the polymer\(^{a)}\), and the properties of the polymer chain\(^{b)}\). These experiments are particularly useful for examining the consequences of excluded volume on polymer conformation and dynamics. The phenomenon of cosolvency sometimes offers special advantages in the study of polymer properties. Cosolvency describes the situation whereby certain mixtures of two poor solvents act as a good solvent for a polymer. By


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examining a chain property such as cyclization in binary solvent mixtures of different compositions, one can vary the strength of the excluded volume effect in a continuous way. These effects can be seen in a variety of experiments, including light scattering and viscometry.

In this paper we examine the kinetics of intramolecular excimer formation for polystyrene chains labelled at both ends with 1-pyrenyl groups (Py) (1). Experiments are carried out in dilute solution in two poor solvents for polystyrene, cyclopentane and acetone, and their mixtures. At the temperature of these experiments, cyclopentane is a theta-solvent, and acetone is a non-solvent, for very high molecular weight polystyrene. In a previous study, we reported cosolvency effects on polystyrene cyclization for two different molecular weights. Here we extend this study, to cover the molecular weight range of $\bar{M}_n = 3000$ to 39600.

The cyclization process leading to intramolecular excimer formation is described by Scheme 1. Upon excitation, cyclization leads to intramolecular excimer formation.

Scheme 1:

The rate constant $k_1$ describes the diffusion controlled cyclization step; $k_{-1}$ describes excimer dissociation and ring opening to reform the locally excited pyrenyl group, and $k_w$ and $k_E$ refer to the reciprocal lifetimes of the locally excited pyrene monomer and excimer, respectively.

The theory of polymer cyclization dynamics was treated initially by Wilemski and Fixman. In terms of the Rouse-Zimm model, their calculations predict a powerlaw dependence of the diffusion-controlled cyclization rate constant, $k_{cy}$, on chain length $N$, viz. $k_{cy} \sim N^{-\gamma}$. Excluded volume effects are neglected, and the magnitude of $\gamma$ depends upon the extent of hydrodynamic coupling associated with the polymer motion. For free draining chains, $\gamma = 2$, whereas the more realistic non-
draining description of polymers in dilute solution, $\gamma = 3/2$. Certain features of the
theory have been examined in detail by Doi. Perico and Cuniberti have extended
WF-theory to partially draining chains of finite length. Several recent publications
review both the theory and experiments associated with polymer cyclization.

**Experimental part**

The synthesis of the polymers and their characterization have been reported previously. Six
different polymer samples of structure and number-average molecular weights, $M_n$, ranging
from 3000 to 39600 were characterized by gel permeation chromatography (GPC), using ethyl
acetate as a solvent. The GPC calibration curve was constructed using “monodisperse”
($M_w/M_n = 1,07$) polystyrene standards (from Pressure Chemical, Co.). The molecular weights
obtained and polydispersity of the samples are shown in Tab. 1. Another polystyrene sample of
molecular weight, $M_n = 5900 (M_w/M_n = 1,33)$, labelled at only one end, was used as a model

<table>
<thead>
<tr>
<th>Polymera</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Py-Ps3000-Py</td>
<td>3 000</td>
<td>1,07</td>
<td>61</td>
</tr>
<tr>
<td>Py-Ps3100-Py</td>
<td>3 100</td>
<td>1,07</td>
<td>63</td>
</tr>
<tr>
<td>Py-Ps4500-Py</td>
<td>4 500</td>
<td>1,08</td>
<td>89</td>
</tr>
<tr>
<td>Py-Ps11500-Py</td>
<td>11 500</td>
<td>1,10</td>
<td>224</td>
</tr>
<tr>
<td>Py-Ps29400-Py</td>
<td>29 400</td>
<td>1,20</td>
<td>568</td>
</tr>
<tr>
<td>Py-Ps39600-Py</td>
<td>39 600</td>
<td>1,09</td>
<td>764</td>
</tr>
</tbody>
</table>

a) $P$sx = polystyrene with $M_n = x$.

The GPC analysis with UV-Vis detection shows that low-molecular-weight impurities absorbing light at 345 nm are less than 0,001 mol-%. The acetone and cyclopentane solvents (from Caledon, Spectrograde) were used as received. Dilute solutions of the polymers (ca. $2,0 \cdot 10^{-6}$ mol-1) in the two pure solvents and in mixtures of different compositions were prepared. The samples were degassed using the freeze-pump-thaw technique, and sealed under a vacuum of better than $2 \cdot 10^{-5}$ mbar. Fluorescence spectra were measured on a Spex Fluorolog 2 Spectrofluorometer. Decay curves were obtained using the time correlated single-photon counting technique. The apparatus has been described. Decay curves were analysed using an iterative nonlinear least-squares analysis program. The samples were excited at 345 nm, the monomer fluorescence decay was measured at 376 nm; and the excimer fluorescence, at 500 nm. In order to eliminate the color shift effect of the photomultiplier, the delta pulse convolution technique was used. Reference decay curves of dilute solutions of 1,4-bis(5-phenyl-1,3-oxazol-2-yl)benzene (POPOP) in cyclohexane ($\tau = 1,10$ ns) and 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene (BBOT) in 95% ethanol ($\tau = 1,47$ ns) were used respectively, in the analysis of the monomer and the excimer decay curves.

**Data and data analysis**

The fluorescence spectra of dilute solutions of 1 shows two different bands: a structured emission corresponding to the fluorescence of locally excited 1-pyrenyl
groups and a broad emission at lower energies attributed to the excimer emission of cyclized chains. According to Scheme I the ratio of the excimer ($I_E$) and monomer ($I_M$) emissions is given by\textsuperscript{14,15}

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

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

Fig. 1 shows the fluorescence spectra of three polystyrene samples of structure 1 ($\bar{M}_n = 4500$, $\bar{M}_n = 11500$, $\bar{M}_n = 39600$) in acetone. We observe a large decrease of

![Fluorescence spectra of different polystyrene chains with structure 1 in acetone.](image1)

Fig. 1. Fluorescence spectra of different polystyrene chains with structure 1 in acetone. (---): $\bar{M}_n = 4500$; (---): $\bar{M}_n = 11500$; (---): $\bar{M}_n = 39600$

![Fluorescence spectra of Py-Ps4500-Py chain in different solvents.](image2)

Fig. 2. Fluorescence spectra of Py-Ps4500-Py chain in different solvents. (---): Acetone, (---): cyclopentane, (---): acetone/cyclopentane (50 vol.-%) mixture
the $I_E/I_M$ ratio with increasing chain length, which essentially reflects the decrease of $k_1$.

Fig. 2 shows the influence of solvent composition on the $I_E/I_M$ ratio for a polymer of $\bar{M}_n = 4500$. We observe that the equimolar mixture has a lower ratio than either of the pure solvents.

Time resolved fluorescence measurements provide a more quantitative description of the cyclization kinetics. Scheme 1 predicts\textsuperscript{(14,15)} for $\delta$-pulse excitation that the excited monomer decays as a sum of two exponentials, and the excimer as a difference of two exponentials, namely

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

(2)

$$I_E(t) = a_3 [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]$$

(3)

where

$$2\lambda_{2,1} = (A_X + A_Y) \pm [(A_X - A_Y)^2 + 4k_1 k_{-1})]^{1/2}$$

(4)

with

$$A_X = k_M + k_1; \quad A_Y = k_E + k_{-1}$$

(5)

and

$$a_2/a_1 = (A_X - \lambda_1)/(\lambda_2 - A_X)$$

(6)

From the values of the decay parameters ($\lambda_1, \lambda_2$) and the ratio $a_2/a_1$, the kinetic rate constants can be calculated, once one knows the values of the inverse lifetime of the monomer emission, $k_M$. These values, at each solvent composition, were determined from the exponential decay curves of dilute solutions ($2.0 \cdot 10^{-6}$ mol·l$^{-1}$) of the model polymer, a labelled polystyrene chain ($\bar{M}_n = 5900, \bar{M}_w/\bar{M}_n = 1.33$) containing a 1-pyrenyl group at only one end (2). The $k_M$ values are insensitive to chain length in the range of chain lengths studied.

Figs. 3 and 4 show the excimer and excited monomer decay curves of a solution of polymer 1 ($\bar{M}_n = 3000, \bar{M}_w/\bar{M}_n = 1.07$) in cyclopentane. The excimer decay curve is well fitted as difference of two exponentials, with $\tau_1 = 1/\lambda_1 = 64.2$ ns, $\tau_2 = 1/\lambda_2 = 28.0$ ns and a ratio of the pre-exponential factors of 0.97. The monomer decay can only be fitted with a sum of three exponentials, with lifetimes $\tau_1 = 1/\lambda_1 = 52.3$ ns, $\tau_2 = 1/\lambda_2 = 24.8$ ns, $\tau_3 = 1/\lambda_3 = 249$ ns, and ratios of pre-exponential factor of $a_2/a_1 = 1.49$ and $a_3/a_1 = 0.13$. The two lifetimes $\tau_1$ and $\tau_2$ are close in magnitude to the ones recovered from the fitting of the excimer decay curve.

The long component of the decay makes a small contribution to the decay (ca. 2.5%) and its lifetime is close to that one obtained from the model polymer 2 in the same solvent ($\tau_M = 1/k_M = 251.4$ ns). We attribute this component to the presence of single-labelled chains in the polymer sample. Their presence is due to an inefficient process of labelling the chain ends with 1-pyrenyl groups. The labelling is done by
reaction of the HOCH₂CH₂-polystyrene-CH₂CH₂OH with 4-(1-pyrenyl)butyryl chloride in the presence of a tertiary amine. The fact that the labelling is not being completely efficient may be due to a yield of the esterification reaction lower than 100% and/or the presence of some polystyrene chains containing OH groups at only one end.
It is curious that the extent of end-labelling in the polymers examined here is significantly lower than that achieved by Redpath et al.\textsuperscript{2b,10} eight years ago. On the other hand, our fluorescence decay measurements are substantially more accurate, and the computer methods of data analysis are much more powerful than they were at that time. Re-analysis of Redpath's samples after all these years show that the decay times are essentially unchanged, and the amount of long component due to singly substituted chains in those samples is very small (ca. 2%). The major disadvantage of examining samples of containing significant amounts of singly labelled chains as an impurity is that it is no longer straightforward to use $I_E / I_M$ data to calculate relative values of $k_{cy}$\textsuperscript{16}.

The kinetic Scheme 1 is reasonably well obeyed in this case: The ratio of the pre-exponential factors of the excimer decay curve is close to 1,0, and the lifetimes recovered from the fitting of the monomer and the excimer decays are similar. This is expected if the cyclization rate constant is time-independent. Wilemski and Fixman\textsuperscript{19} showed that for sufficiently long chains the transient contribution to $k_1$ is very small. In order to extract the rate constants, we constrain the monomer fitting process, fixing two lifetimes to the values obtained from the excimer decay. The rate constants calculated using the free and constrained fitting procedures are very close. Differences appear only in the value of the rate constant for ring-opening, $k_{-1}$, which is very difficult to obtain accurately when the extent of excimer dissociation is small. For longer chains ($M_\eta > 25000$) the monomer decay is well fitted with a single exponential decay function. This is expected when $4k_1k_{-1} \ll (A_X - A_Y)^2$, which is verified for long chains where $k_1$ becomes very small. Under these circumstances, we use the values of $\lambda_1$ obtained from the fitting of the monomer decay curve to obtain $k_1$:

$$\lambda_1 = k_M + k_1$$

Discussion

The values of $k_{cy}$ recovered, using the procedure described above, are presented in Tab. 2 for all the polymer chains in the pure solvents and their mixtures. We observe for each composition a decrease on the cyclization rate constant with chain length, and for each chain length a minimum of $k_1$ at close to the equimolar solvent composition.

Fig. 5 shows the plot of the values of $k_{cy}$, corrected for solvent viscosity effects, as a function of solvent composition. Excluded volume effects should decrease the rate of polymer cyclization. We observe that the minimum occurs at close to the equimolar solvent composition. A maximum at close to this composition was also observed in the variation of the intrinsic viscosity [$\eta$] of solutions of polystyrene in mixtures of cyclohexane and acetone\textsuperscript{4}.

These results clearly show that a mixture of a theta-solvent and a poor solvent for a chain can be a better solvent than the pure solvents. Similar conclusions were extracted from studies of the intrinsic viscosity of polymers\textsuperscript{4} and light scattering measurements\textsuperscript{3} in mixtures of different pairs of poor solvents.
Tab. 2. Cyclization rate constants, \( k_{cy} \), for polystyrene solutions in acetone, cyclopentane and their mixtures.

\[
\begin{array}{cccccccc}
\bar{M}_n & 10^{-6} \cdot k_{cy} / \text{s}^{-1} \\
\text{for mixture compositions (in mol-\% acetone)} & 100 & 83.7 & 74.9 & 56.1 & 35.4 & 24.2 & 0 \\
3000 & 23.2 & 20.4 & 19.7 & 19.0 & 19.1 & 21.0 & 26.8 \\
3100 & 20.6 & 18.2 & 16.3 & 15.0 & 17.1 & 16.7 & 22.7 \\
4500 & 13.2 & 10.9 & 10.6 & 9.8 & 9.7 & 11.6 & 13.9 \\
11500 & 3.5 & 2.5 & 2.7 & 2.4 & 2.3 & 2.8 & 3.5 \\
29400 & 0.9 & 0.6 & 0.6 & 0.4 & 0.4 & 0.5 & 0.5 \\
39600 & 0.6 & 0.3 & 0.3 & 0.2 & 0.2 & 0.2 & 0.3 \\
\end{array}
\]

Fig. 5. Cyclization rate constants corrected for solvent viscosity effects for different polymers versus the solvent composition.
- [■]: Py-Ps3000-Py;
- [○]: Py-Ps3100-Py;
- [●]: Py-Ps4500-Py;
- [▲]: Py-Ps11500-Py;
- [▼]: Py-Ps29400-Py;
- [★]: Py-Ps39600-Py

The quality of the solvent influences the chain dimensions through the magnitude of the excluded volume effect. Excluded volume perturbs chain conformation in two quite different ways. First, it leads to an expansion of the coil dimensions, as described for example by the mean squared radius of gyration, \( R_g^2 \), and end-to-end distance, \( R_e^2 \). In addition, there is a strong decrease in the probability density distribution of end-to-end separations, \( W(r) \), for chain ends in close proximity (small \( r \)). This behavior has its origin in pair-correlation effects which are suppressed at the theta-point. Since the correlation hole in \( W(r) \) affects only a small fraction of the total number of polymer conformations, the second factor has no significant influence on chain properties such as \( R_g^2 \) and \([\eta]\), as determined for example by light scattering and viscometry. Cyclization experiments are unique in that they exhibit this dual sensitivity to excluded volume. The polymer chain lengths we examine here are...
rather short. As a consequence, excluded-volume effects on coil expansion are small. The sensitivity of these experiments to changes in solvency, are due primarily to changes in the magnitude of pair correlation effects associated with excluded volume.

An unexpected result is observed for short chains. The cyclization rate constant corrected for viscosity effects should be highest in the poorest solvent. We find a higher value of \( k_{cy} \) in cyclopentane than in acetone for the small chains, and this result is confirmed by the \( J_E/J_M \) ratios (see Tab. 2 and Fig. 2). To explain this observation we assume that there is some specific interaction of acetone with the end groups on the polymer which affects the cyclization rate constant.

In Fig. 6 the values of the rate constant for the excimer dissociation, \( k_{-1} \), and the reciprocal of molecular excimer lifetime, \( k_E \), are plotted for samples of different chain lengths as a function of solvent composition. We observe that \( k_E \) is insensitive to chain length and solvent composition, as expected from similar results obtained for intermolecular pyrene excimer formation in different solvents\(^{15}\). With \( k_{-1} \) a curious feature is observed. The rate constant for excimer dissociation (the ring-opening process) is insensitive to chain length, but it depends sensitively on solvent composition. The variation of \( k_{-1} \) with solvent composition has a maximum at the solvent composition where \( k_1 \) has a minimum. We attribute this peculiar effect to the influence of the excluded volume effect on the shape of the distribution function of chain end distances, \( W(r) \). For theta-solvents the polymer coil has unperturbed dimensions and the distribution function is Gaussian. In good solvents, correlation effects between the chain ends creates a "hole" in \( W(r) \), for small chain end distan-
Fig. 7. Cyclization equilibrium constant, $K_{cy}$, versus the solvent composition for different polymer samples. (■): Py-Ps 3000-Py; (○): Py-Ps 3100-Py; (▲): Py-Ps 4500-Py; (●): Py-Ps 11 500-Py

ces\(^{17}\). The presence of this "hole" in the distribution function creates an entropic force that facilitates the separation of chain ends from this region, increasing $k_{-1}$.

The plot of $K_{cy} = k_1/k_{-1}$ versus solvent composition for chains of different lengths (Fig. 7) shows an accentuated minimum (the maximum and minimum values vary by almost a factor of 2) for the equimolar solvent composition. This reflects the opposing effects of excluded volume on $k_1$ and $k_{-1}$. If only coil expansions were important in cyclization, the equilibrium constant $K_{cy}$ and $[\eta]$ would be inversely proportional. The comparison of how these parameters vary with solvent composition shows\(^{18}\) that the changes in $K_{cy}$ are more pronounced that the ones observed in $[\eta]$. This demonstrates the importance of the correlation effects in $W(r)$ on the cyclization process.

Perico and Cuniberti\(^{7,8}\) have developed expressions which extend WF-theory to partially draining finite chains in the absence of excluded volume. These expressions can be parameterized for specific polymers using data available from diffusion coefficient ($D$) and intrinsic viscosity measurements ($[\eta]$). When these expressions are evaluated for polystyrene chains in the molecular weight range 30000 to 500000, a plot of $\log k_{cy}$ (calc.) vs. $\log M$ yields a linear plot with a slope $[-\gamma]$ equal to $-1.43$. These authors also point out a prediction of WF-theory, that in the limit of very long non-draining chains,

$$k_{cy} = 1.98 \frac{D}{R_T^2}$$

For polystyrene in cyclohexane at 34.5°C (the theta temperature), $D = 1.21 \times 10^{-4}$ $M^{-0.49}$ (cm\(^2\)·s\(^{-1}\)) and $R_T^2 = 4.9 \times 10^{-17} M$ (cm\(^2\))\(^{19}\). Eq. (8) thus predicts a powerlaw variation of $k_{cy}$ with $N$ with $(-\gamma) = -1.49$.

Earlier experiments in our laboratory\(^{10}\) gave results ($\gamma = 1.43$)\(^{20}\) in very good agreement with these predictions for polystyrene under theta-conditions. Those
experiments took advantage of the fact that the samples had nearly complete end group functionalization, so that steady-state fluorescence data and Eq. (1) could be used in conjunction with fluorescence decay measurements to obtain more reliable values of $k_{cy}$ for long chains.

Here, we observe a large deviation for large values of $N$ which is attributed to the lower accuracy of the values of $k_{cy}$ for long chains. Indeed for large $N$, using Eq. (7), the values of $k_{cy}$ are obtained as a difference of two similar numbers. Small errors in the values of $\lambda_1$ and/or $k_m$ gives large errors in $k_{cy}$. The values of $\lambda_1$ are also affected to some extent by the presence in the monomer decay of a long component due to mono-labelled chains, which decreases the experimental value of $\lambda_1$. Fig. 8 shows the variation of $k_{cy}$ with the number of bonds of the polymer chain, $N$, for three different solvent compositions. The values of $N$ were calculated with the expression

$$N = 2(M_e - 630)/104 + 15$$

which takes account of the contribution of the end groups. These data are collected in Tab. 1. The fitting according to a power law variation ($k_{cy} \propto N^{-\gamma}$) is reasonable.

Fig. 9 shows the variation of $\gamma$ with solvent composition. This value is solvent dependent and has a maximum close to the equimolar solvent composition. The theory of cyclization dynamics has not yet been developed to consider explicitly excluded volume effects. However, if we assume that Eq. (8) remains valid for good solvents, an increase in the exponent $\gamma$ is expected. This analysis neglects pair correlation effects on $k_1$. Indeed, for polystyrene in toluene (a good solvent) $D = 3.92 \cdot 10^{-4} M^{-0.574} (\text{cm}^2 \cdot \text{s}^{-1})$ and $R_k^2 = 9.36 \cdot 10^{-18} M^{1.19} (\text{cm}^2)$, which gives a value of $\gamma = 1.76$, in agreement with our earlier cyclization studies of polystyrene chains in toluene using either excimer formation or exciplex formation studies. Our results here give a value of $\gamma = 1.62$ for the 56 mol-% acetone solvent mixture (vol. ratio 1:1). This result is consistent with one's expectation of cyclization behavior in
solvents where the excluded volume effect is not fully expressed. This kind of results has been seen previously for polystyrene cyclization in a variety of different solvents\textsuperscript{23) and for PS cyclization in cyclopentane at a series of different temperatures\textsuperscript{24).}

6) M. Doi, Chem. Phys. 9, 455 (1975)
16) F. Méchin, S. Boileau, J. M. G. Martinho, M. A. Winnik, Macromolecules in press
In earlier publications from our laboratory, Redpath et al.\textsuperscript{10} reported a value of \((-\gamma) = -1.68\) for cyclization of I(Py-polystyrene-Py) in cyclohexane at the theta-temperature (34.5°C) and Winnik et al.\textsuperscript{25} reported a value of \(\gamma = 1.64\) for cyclization, studied by exciplex formation kinetics in III (DMT-polystyrene-Py), where DMT is the 4-dimethylaminophenyl group. When we looked closely at these data in the course of drafting this manuscript, we found that the slopes of the log-log plots had been calculated using an unweighted linear least squares analysis. Re-analyses of these data with a weighted (due to the logarithmic transformation) linear least squares (cf. R. de Levie, \textit{J. Chem. Ed.} 63, 10 (1986) algorithm gives a value of \(\gamma = 1.43\).

\textsuperscript{24} A. M. Sinclair, \textit{Ph. D. Thesis}, University of Toronto, 1986