Cyclization dynamics of polymers: 7. Applications of the pyrene excimer technique to the internal dynamics of poly(dimethylsiloxane) chains

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Poly(dimethylsiloxane) (PDMS) polymers end-capped on both ends with pyrene chromophores have been synthesized. Rate constants for end-to-end cyclization $\langle k_1 \rangle$ have been determined for dilute solutions of these polymers in toluene solution using a combination of fluorescence decay and steady-state fluorescence measurements. While precise values of the critical exponent for the chain length ($\bar{N}$) dependence of $\langle k_1 \rangle$ are not yet available, these results are consistent with the $\bar{N}^{-3/2}$ dependence predicted by Wilemski–Fixman theory. PDMS chains cyclize somewhat more than two times faster than polystyrene chains of the same length in solvents of similar solvating power and viscosity. These results provide strong support for similar predictions made several years ago by Perico and Cuniberti, who used intrinsic viscosity data to parametrize the Rouse–Zimm model for analysis of polymer cyclization dynamics.

Keywords Polymer dynamics; polymer conformation; fluorescence; ring closure

INTRODUCTION

Contemporary theories of polymer dynamics are expressed in terms of models which ignore the details of chemical structure that distinguish one polymer from another. The Rouse–Zimm model[1] treats a polymer as a collection of point friction centres (beads) connected by harmonic springs. Two parameters suffice to describe the low-frequency dynamics of most polymer chains in terms of this model. One parameter describes the chain flexibility by an effective segment length between the beads. The other parameter measures the strength of the hydrodynamic interaction between the beads. These parameters are very useful to physical chemists, engineers and physicists who wish to have some means of relating quantitatively the differences of dynamic behaviour between different polymers. Nonetheless, they offer little help to the structural chemist who wishes to understand the origins of dynamic behaviour of polymer chains in terms of chemical structure, local rotational barriers and force constants for bond bending and torsional oscillations.

Simplified models will be succeeded by detailed models which include chemical structure only when there exists a large body of reliable data describing certain well defined classes of polymer motion for a variety of polymer chains. This is clearly a large task in which one must not only examine a wide variety of structures but also exercise careful choice in the classes of chain dynamics that one wishes to explore.

One important motion of polymer chains is its slowest internal relaxation time τ_1. This relaxation time can be obtained from viscoelastic measurements[2] on polymer solutions. For large polymers, one can in principle determine τ_1 from quasi-elastic light scattering measurements[3]. In these experiments, a superposition of low-frequency internal modes frequently contributes to the observed signal, sometimes introducing difficulties in the unambiguous determination of τ_1. An alternative approach is based upon intramolecular fluorescence quenching experiments[4], in which an efficient quencher Q at one chain end quenches fluorescence from a group A* attached to the other chain end. The theory of Wilemski and Fixman (WF)[5,6] relates in terms of the Rouse–Zimm model the rate constant for diffusion-controlled end-to-end cyclization k_{cy} in $A^* \sim\!\sim Q$ to τ_1. One of the attractive features of this experiment is that one can examine the labelled probe chain in trace concentrations in simple solutions or in the presence of excess unlabelled chains. Since only odd modes (τ_1, τ_3,...) affect the mean end-to-end displacement in polymer chains, this experiment ought to be only half as sensitive as other approaches to the contributions of higher-frequency motions which introduce ambiguities into the interpretation of the results. In practice, fluorescence decays are exponential[7]. Values of k_{cy} can be determined with precision; and cyclization rates are dominated by the slowest relaxation time of the chain.

EXPERIMENTAL

From an experimental point of view, the method of choice for measuring cyclization kinetics is the pyrene (Py)

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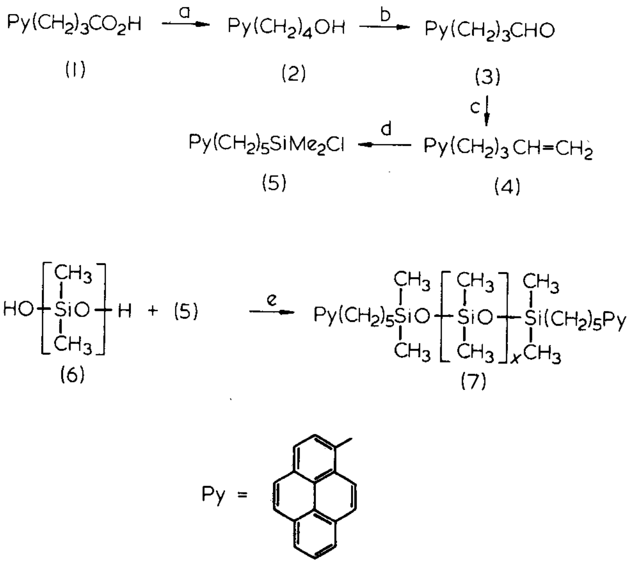
excimer technique[4,7,8]. In a polymer of the form Py–polymer–Py*, the locally excited pyrene fluoresces blue (with intensity I_M), whereas when Py* encounters Py a tightly bound excimer is formed which fluoresces green (with intensity I_E). For long chains the weak green excimer fluorescence permits one to measure cyclization events on a time scale up to 100 μs, even though the fluorescence lifetime of Py* is only 200 ns. We have devoted considerable effort to the study of cyclization dynamics in Py–polystyrene–Py, in a θ-solvent[7], in good solvents[7,8], at various temperatures[9], and as test chains in polystyrene solutions of high concentration[10]. In this paper, we turn our attention to poly(dimethylsiloxane), which is of special interest because of its low internal rotational potential and its elastomeric properties.

Synthesis of Py–PDMS–Py

Two considerations entered into the design of an appropriate reagent for attaching pyrenes to the ends of a dimethylsiloxane polymer. First, we recognized the importance of a C–Si bond to stabilize the end group against hydrolytic displacement from the chain. Secondly, in order to avoid the possibility of steric effects on pyrene excimer formation, we chose to separate the pyrene from the polymer by a small number of CH_2 groups.

Our method of choice is outlined in Scheme 1.

Scheme 1



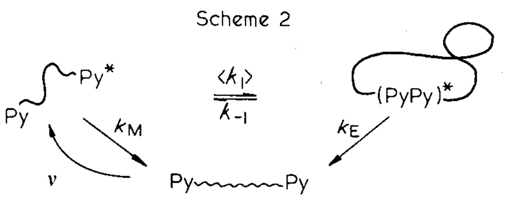
a: $LiAlH_4$/ether, reflux
b: Pyridine HCl + CrO_3/CH_2Cl_2, 35°C
c: $Ph_3P{=}CH_2$, dimethoxyethane, 0°C to 20°C then 1h reflux
d: $Me_2SiHCl + H_2PtCl_6$, 150°C
e: Excess (5), toluene-pyridine, 48h, 22°C

Samples of HO-terminated PDMS (6) were generous gifts from Dow–Corning Corp. These were carefully dried over CaH_2 under vacuum and fractionally precipitated from toluene solution with acetonitrile at 4°C. The most delicate step in the synthesis was the hydrosilylation of (4) to produce (5), a solid very sensitive to moisture. In this reaction, 100 mg (4) and 1 drop of 1 M H_2PtCl_6 solution in propan-2-ol were heated under argon for 1 h at 100°C in a Pyrex tube; 100 mg of Me_2SiHCl was added and the tube was sealed. It was heated in an autoclave for 6 h at 150°C to complete the reaction. After all the unreacted Me_2SiHCl was removed, 100 mg of the crude product (excess) was added to an equal weight of polymer in toluene solution in the presence of 0.1 ml pyridine. This reaction mixture was stirred for two days at room temperature. The final polymers (7) were repeatedly reprecipitated from toluene with acetonitrile. Samples for fluorescence analysis were further purified in 1–2 mg quantities by gel permeation chromatography (g.p.c.) using a series of three Microstyragel columns: 500 Å, 10^3 Å, 10^4 Å. These same columns were used to analyse the polymer molecular weights (solvent: toluene), along with polystyrene standards and literature values of the various polymer intrinsic viscosities.

Fluorescence measurements

Solutions of Py–PDMS–Py in toluene at 2×10^{-6} M were prepared, degassed to remove oxygen, and sealed in pyrex tubes. Steady-state fluorescence spectra were run to obtain the ratio I_E/I_M of excimer intensity to pyrene fluorescence intensity (*Figure 1*). The time-correlated single-photon counting technique[11] was used to determine $I_E(t)$ and $I_M(t)$. All measurements were carried out at 22°C. For polymers of $\bar{M}_n > 10\,000$, $I_M(t)$ was exponential over at least 99% of the fluorescence decay (with decay time λ), whereas for shorter chains, $I_M(t)$ was non-exponential and was fit to the sum of two exponential decays (see below). The excimer intensity $I_E(t)$ is initially zero. It grows in and then decays, with the decay portion having the same decay rate (λ_1) as that for $I_M(t)$. These results can be interpreted in terms of Scheme 2.

Scheme 2



In Scheme 2, $\langle k_1 \rangle$ describes the mean rate of cyclization of a polymer of finite polydispersity. Since this reaction is diffusion-controlled, $k_1 = k_{cy}$. Excimer dissociation back

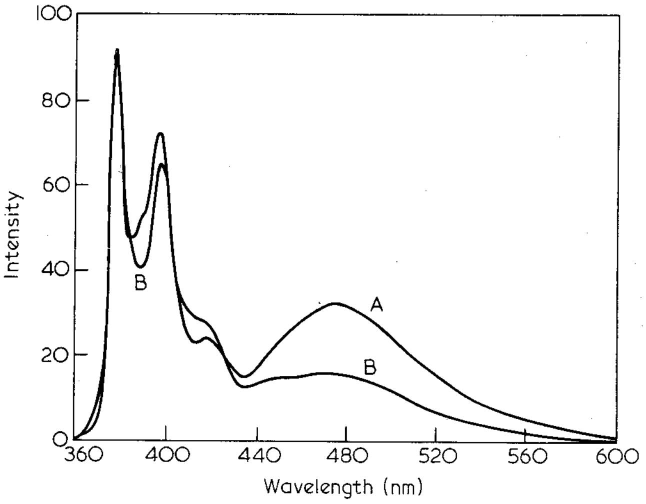


Figure 1 (a) Fluorescence spectrum of Py–(PDMS 6600)–Py in toluene (2 x 10^{-6} M) at 22°C. (b) Fluorescence spectrum of Py–(PS 9200)–Py in cyclohexane at 34.5°C. Both chains have their pyrene chromophores separated by $\bar{N}$ = 175 bonds. Note the solvent effect on the fine structure of the locally excited pyrene fluorescence

Table 1 Molecular weights and cyclization rates for Py—PDMS—Py in toluene at 22°C

$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	$\bar{N}$ [b]	Relative I_E/I_M	$10^{-6}\langle k_1\rangle$ [c] (s^{-1})
6640	1.06	175	2.22	8.6
9900	1.06	263	1.35	4.8
13 700	1.10	365	1.00	3.4
20 700	1.06	553	0.72	2.2
25 800	1.06	692	0.44	1.4

[a] From g.p.c. measurements and universal calibration curve
[b] Mean chain length from $[(\bar{M}_n-542)/37+12]=\bar{N}$
[c] The values reported are the averages of $\langle k_1\rangle$ values calculated from fluorescence decay and from (I_E/I_M) measurements. Measurements were made at 2×10^{-6} M polymer concentration

to locally excited pyrene is described by k_{-1}, and its decay (radiative plus non-radiative) is described by k_E. The corresponding pyrene decay k_M is determined by reference to a model compound containing only one pyrene. For these experiments we used the methyl ester of pyrenebutyric acid (8) as our model compound. We set its exponential decay rate $\lambda_{mod}=k_M$. Excimer dissociation becomes more important for short chains than long chains[12] since a large fraction of very short chains cyclize during the lifetime of Py*.

According to Scheme 2, $I_M(t)$ should be described by the sum of two exponentials for short chains, and by a single exponential for long chains, if *cyclization is by a single relaxation time of the polymer chain.* Our results are in accord with these predictions. For samples of $\bar{M}_n>10^4$, $\langle k_1\rangle$ values were determined from the exponential decay times (λ) from the equation

$$\lambda-\lambda_{mod}=\langle k_1\rangle \tag{1}$$

For the two shortest chains, $\langle k_1\rangle$ values were obtained from a full analysis of $I_M(t)$ and $I_E(t)$ decays. Relative values of $\langle k_1\rangle$ were obtained from I_E/I_M measurements, equation (2), using the $\langle k_1\rangle$ value for Py-(PDMS 13 700)-Py obtained from equation (1) as the reference.

$$\frac{(I_E/I_M)_1}{(I_E/I_M)_2}=\frac{\langle k_1\rangle_1}{\langle k_1\rangle_2} \tag{2}$$

PDMS is more difficult than polystyrene to study by these techniques. Dealing with submilligram quantities of oils and gums poses problems that are not present when one can study solid samples, particularly when the groups on the chain ends are susceptible to photo-oxidation in solution. In spite of our precautions, the precision of the measurements reported here, as reflected in χ^2 values, are somewhat poorer than those we have previously obtained for polystyrene solutions. Values of $\langle k_1\rangle$ are collected in *Table 1.*

RESULTS

Chain dynamics

The results in *Table 1* indicate that $\langle k_1\rangle$ decreases from a value of 8.6×10^6 s^{-1} for Py-(PDMS 6600)-Py ($\bar{M}_n=6600$) to a value of 1.4×10^6 s^{-1} for Py-(PDMS 26 000)-Py, in toluene solution at 22°C. A factor of four increase in chain length causes the cyclization rate to decrease six-fold. WF theory predicts that for a polymer chain in dilute solution in a θ-solvent, k_{cy} decreases as $N^{-3/2}$. In good solvents one anticipates a more rapid decrease of k_{cy} with N due to the increase of chain dimensions, and hence the mean end-to-end separation, associated with the excluded volume effect.

In *Figure 2* we present a log-log plot of $\langle k_1\rangle$ vs. log $\bar{N}$, where $\bar{N}$ values are calculated from the polymer molecular weight $\bar{M}_n$ after subtracting the mass of the pyrene groups, and then adding 12 bonds to accommodate the contribution of the ten CH_2 groups: $\bar{N}=(1/37)(\bar{M}_n-542)+12$. Values of $\langle k_1\rangle$ calculated both from fluorescence decay and from I_E/I_M measurements are shown in the figure. The data are too limited at this time for a detailed analysis of the best slope which can be fitted to these points. We have chosen, instead, to draw a line of slope $-3/2$ through the data points to emphasize that our results are entirely consistent with the predictions of WF theory.

Since our intent is to examine the influence of chemical structure on cyclization dynamics, we compare in *Figure 2* values of $\langle k_1\rangle$ obtained here with those obtained previously for polystyrene chains of similar length. The PDMS chains cyclize more rapidly.

The factors which contribute to the rate of end-to-end cyclization of a polymer chain are (i) solvent viscosity (η_0), (ii) chain dimensions, and (iii) dynamic chain flexibility.

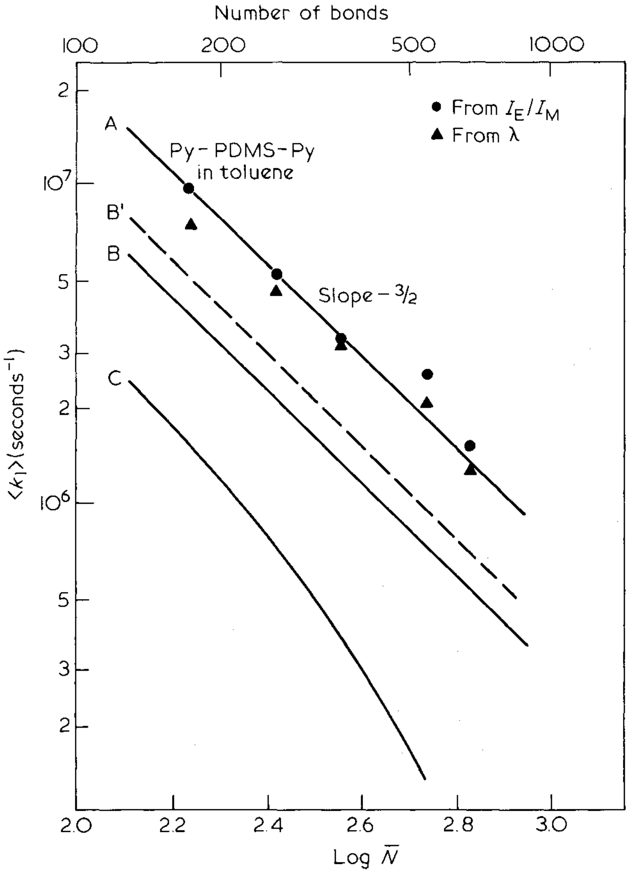


Figure 2 Log—log plot of the mean cyclization rate constant $\langle k_1\rangle$ vs. mean chain length $\bar{N}$. Curve A: data from these experiments for Py—PDMS—Py in toluene at 22°C (● from I_E/I_M; ▲ from fluorescence decay); the line drawn through the points has a slope of −3/2. Curve B: summary of previous results for Py—PS—Py in cyclohexane at 34.5°C; the experimental slope is −1.52. Curve B': data of curve B corrected (η_0/T) to 22°C and the viscosity of toluene. Curve C: summary of previous results for Py—PS—Py in toluene at 22°C

Solvent viscosity effects are effectively described by the η_0/T dependence of diffusion-controlled rate processes. This dependence has been confirmed experimentally[4b,9b]. The important dimensional parameter is the distribution function of the end-to-end distances of the chain. This function describes the average distance over which chain ends must diffuse in order to cyclize. It is a useful simplification to focus instead on the mean-squared end-to-end distance R_F^2 or mean-squared radius of gyration R_G^2 of the polymer, since factors which cause chain expansion also increase R_F^2 and R_G^2. At the monomer level, dynamic factors derive from local rotational barriers and force constants for bond bending and torsional motions. In terms of the bead-and-spring model, these dynamic factors are described in terms of two parameters: b, an effective dynamic segment length between beads, and r/b, which measures the strength of the hydrodynamic interaction between beads.

From the data in *Figure 2*, it is clear that Py–PDMS–Py chains cyclize significantly faster than Py–PS–Py chains of the same length. One also notices that the PS chains cyclize faster in cyclohexane at the θ-temperature (34.5°C, curve B), then they do in toluene (22°C, curve C), a good solvent for PS. When the cyclohexane data are corrected to the same solvent viscosity as toluene at 22°C, cyclization rates are predicted to increase (curve B′). The slower rate of cyclization in toluene and the pronounced downward curvature in the log $\langle k_1 \rangle$ vs. log $\bar{N}$ plots arise from the excluded volume effect accompanying chain expansion in a good solvent. The absence of curvature in the PDMS data suggests that toluene is not as good a solvent for PDMS as it is for PS. This point of view is supported by literature values of Mark–Houwink exponents for the two polymers in toluene solution[13].

From the somewhat limited data in *Figure 2* one sees that PDMS chains of a degree of polymerization 100 to 400 cyclize 1.9 times faster than PS chains of corresponding length in cyclohexane, after correcting for viscosity and temperature differences. These PDMS chains cyclize 14 to 20 times faster than corresponding PS chains in toluene. Since toluene is a better solvent for PS than it is for PDMS, and since cyclohexane is a poorer solvent for PS than toluene is for PDMS, the enhancement factors given above represent upper and lower limits for the enhanced cyclization of PDMS over PS in dilute solution.

In θ-solvents, (R_F^2/M) for PS is larger than (R_F^2/M) for PDMS. Perico and Cuniberti[14] report values of 0.480×10^{-16} cm^2 and 0.413×10^{-16} cm^2, respectively, on the basis of their critical evaluation of light scattering data in the literature. When corrected for the different molecular weight per monomer, these values indicate that R_F^2 for PDMS should be some 20% larger than R_F^2 for a PS chain of the same length. Consequently one anticipates somewhat smaller $\langle k_1 \rangle$ values for PDMS solely on the basis of its end-to-end separation, quite apart from dynamic considerations. In order to appreciate the contributions of chain conformation and chain dynamics to the cyclization dynamics of real polymer chains, Perico and Cuniberti' have extended WF theory to partially draining finite chains in terms of their solution to the hydrodynamic equation for the bead-and-spring model[14]. The eigenvalues from their mathematical treatment were introduced into the bead–spring model expression for the intrinsic viscosity. By comparing this expression with literature intrinsic viscosity data, they were able to obtain best-fit values for the parameters b and r/b for both PS and PDMS.[15] For example, they found b(PS) = 60 Å (144 bonds per subchain) and b(PDMS) = 20 Å (26 bonds per subchain). The best-fit values of r/b(PS) = 0.23 and r/b(PDMS) = 0.30 are both close to values appropriate for non-draining conditions. When these parameters, in conjunction with the R_F^2/M values, are inserted into the appropriate bead–spring model expressions for k_{cy}, these authors predict PDMS to cyclize twice as fast as PS chains in θ-solvents at the same solvent viscosity. Our results suggest that $\langle k_1 \rangle_\theta^{PDMS}$ are somewhat larger than $2\langle k_1 \rangle_\theta^{PS}$. Nonetheless one should emphasize that the predictions of Perico and Cuniberti are remarkably accurate. They emphasize that the bead–spring model is quite successful at relating the rates of end-to-end cyclization to other low-frequency dynamic processes of polymer chains.

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