

The influence of polymer concentration on the internal motion — intramolecular pyrene excimer formation — of a low molecular weight probe in solution

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Fluorescence decay measurements were used to study the kinetics of end-to-end cyclization of the molecule $\text{Py}-(\text{CH}_2)_5\text{Si}(\text{Me}_2)\text{OSi}(\text{Me}_2)(\text{CH}_2)_5\text{-Py}$ (**1**), where $\text{Py}=1$ -pyrenyl. Experiments were carried out in toluene at 22°C and in cyclohexane at 35°C, in the absence and in the presence of added polystyrene (PS). Addition of even small amounts (0.01 g/ml) of PS caused the cyclization rate of probe molecule **1** to decrease substantially in cyclohexane, whereas in toluene, a much milder retardation of cyclization rate with increasing PS was observed. These effects are interpreted in terms of a coupling between the chain dynamics and that of the probe molecule **1**, mediated by the solvent. These hydrodynamic screening interactions depend sensitively upon whether the polymer is in a good or a poor solvent.

Keywords End-to-end cyclization; polymer dynamics; hydrodynamic screening; pyrene; excimer

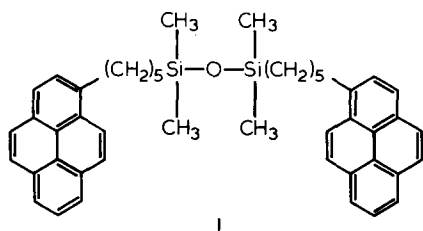
The diffusion of small molecules and the rates of conformational change of flexible small molecules¹ in solution are normally not found to be affected by the presence of polymer chains added to the solution. In very concentrated polymer solutions, and in bulk polymer, these motions are retarded². Access to free volume is a prerequisite to movement. These rates are limited by the corresponding rates of free volume fluctuations in the polymer².

Contemporary polymer theory takes a point of view in accord with these observations. It pictures the origin of effects of dilute solutions of polymer molecules on the motion of a test particle to depend upon chain overlap³. Chain overlap and interpenetration of polymer molecules become important at a critical polymer concentration c^* . At this concentration, the polymer coils, swollen with solvent, fill all the available space. Above this concentration, the chains are forced to interpenetrate one another. Above c^* , the mean separation between polymer chains is described by the distance ξ . The value of ξ decreases with increasing polymer concentration. The diffusion of a test particle is thought to be unimpeded by the presence of the polymer chains unless its diameter is comparable with, or larger than ξ . Similarly, the internal motion of a molecule ought not be affected by the matrix of added chains in solution unless its radius of gyration is comparable in size to ξ .

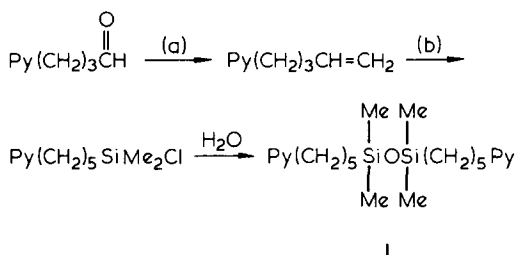
We have been studying the dynamics of end-to-end cyclization of polymer chains in solution, using for our experiments, polymers substituted on each end with appropriate fluorescent and fluorescence quenching groups^{4,5}. In most of our experiments we examined the

rates of intramolecular excimer formation between pyrenes covalently attached to the chain ends. Since the chains were labelled, we were able to examine them, in trace (10 ppm) concentration, in the presence of a vast excess of unlabelled chains⁶. For the case of polystyrene (PS) we observed that the rate constants for end-to-end cyclization $\langle k_1 \rangle$ depend to a large extent on the concentration of added, unlabelled PS, but that the form of the dependence was very different in a θ -solvent than in a good solvent.

In order to help us focus on certain microscopic features associated with the reaction, we decided to synthesize a small but very flexible molecule with pyrenes on both ends and to study its rate of intramolecular excimer formation. Although many studies have been reported on intramolecular excimer or exciplex interaction between groups separated by a 3-atom chain⁷, we wanted to insist that the chain be sufficiently long so that rotation about a limited number of bonds would not limit the conformational space accessible to the chain ends. In order to ensure rapid cyclization we envisaged two pyrenes connected by short chains and coupled by a 'universal joint'. For the universal joint we chose a Si-O-Si linkage which has both a low rotational potential about the Si-O bond angle⁸. This would permit the pyrenes to be well-separated, on the average, before excitation, but to have the chain impose the minimum impediments to their encounter after excitation. There was evidence from the work of Zachariasse that molecules with two pyrenes joined by polymethylene chains of 12 to 30 units gave substantial amounts of intramolecular excimer emission⁹.



Scheme 1

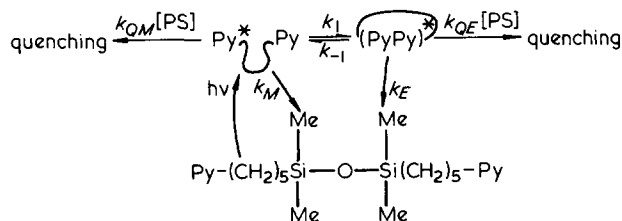


- (a) $\text{Ph}_3\text{P}=\text{CH}_2$, dimethoxyethane, 20°C .
 (b) Me_2SiHCl , H_2PtCl_6 , 150° , sealed tube.

The molecule **1**, which we have taken to call PySi_2 , satisfies these requirements. It was prepared by the route outlined in Scheme 1. After vigorous purification, we determined that end-to-end cyclization occurred in PySi_2 , after excitation in dilute solution, in less than 3 nanoseconds. Its fluorescence spectrum is shown in Figure 1. We denote the structured localized pyrene fluorescence intensity in **1** as I_M and that of its excimer, centred at 480 nm, as I_E .

The cyclization kinetics in PySi_2 are well described by the mechanism in Scheme 2, where k_1 describes the rate of excimer formation, k_{-1} its dissociation to locally excited pyrene, and k_E , its reciprocal lifetime in the absence of dissociation. The terms $k_{QM}[\text{PS}]$ and $k_{QE}[\text{PS}]$ describe the possibility of pyrene and excimer quenching by added PS. The values of k_M , the reciprocal monomer lifetime, and k_{QM} are determined from model studies using a molecule containing only one pyrene.

Scheme 2



Cyclization in **1*** is sufficiently fast that I_M is much weaker than I_E . This makes a proper analysis of $I_M(t)$ fluorescence decays difficult. The excimer emission, however, is easily resolved into a growing-in portion with rise time λ_1^{-1} and a decay time λ_2^{-1} . Although excimer dissociation makes a non-negligible contribution to I_M in steady-state fluorescence experiments, under the conditions of our fluorescence decay measurements we can assert that⁵

$$\lambda_1 \approx k_M + k_{QM}[\text{PS}] + k_1 \quad (1)$$

$$\lambda_2 \approx k_E + k_{QE}[\text{PS}] + k_{-1} \quad (2)$$

Since k_M and $k_{QM}[\text{PS}]$ are known from independent measurements, k_1 can be calculated from equation (1). In addition, since measured λ_2 values do not vary significantly with added PS, we can infer that excimer quenching by PS is negligible.

Steady-state spectra provide independent relative values of k_1 . Using the superscript ⁰ to denote the absence of added polymer, we can write

$$\frac{(I_E/I_M)}{(I_E/I_M)^0} = \frac{k_1}{k_1^0} \left[1 + \frac{k_{QE}[\text{PS}]}{k_E + k_{-1}} \right] \quad (3)$$

The second term on the right hand side of equation (3) can be neglected since $k_E \gg k_{QE}[\text{PS}]$ ⁵.

Values of k_1 calculated from equations (1) and (3) are plotted in Figure 2 versus the weight fraction of added PS. In toluene, a good solvent for PS, k_1 decreases essentially linearly with $[\text{PS}]$. This result is unexpected. Not only is there perceptible decrease of k_1 for PS concentrations well below c^* for the added polymer, and not only is k_1 independent of the chain length of the added PS, but the linear decrease of k_1 with $[\text{PS}]$ is strange.

One might, for example, presume that the 'microscopic viscosity' of the solution (η_m) would increase linearly with solute concentration. Cyclization in **1*** is diffusion controlled, and $k_{\text{diff}} \sim \eta^{-1}$. Consequently this argument leads to the suggestion that $k_1 \sim [\text{PS}]^{-1}$. In cyclohexane at 35°C , a good solvent for **1** but a poor (θ -) solvent for PS, k_1 declines rapidly with the initial addition of PS. It is less sensitive to subsequent additions. This behaviour is consistent with $k_1 \sim [\text{PS}]^{-1}$, and a plot of k_1^{-1} vs. $[\text{PS}]$ is linear for about half the concentration range depicted in Figure 1.

While one cannot yet rule out completely the possibility that **1** in cyclohexane is somehow preferentially bound to a polymer-rich environment, another explanation is more likely. We envision the motion of **1** to be coupled to the added polymer chains through hydrodynamic interactions with solvent¹⁰. These hydrodynamic interactions must persist well beyond the mean radius of gyration of the polymer molecules. At elevated polymer concentrations, polymer motions are slowed through

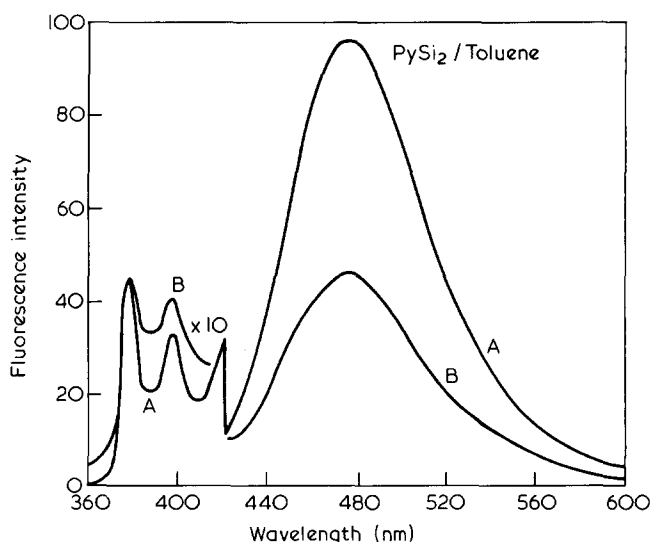


Figure 1 Plot of fluorescence intensity of PySi_2 at 2×10^{-6} M in toluene at 22°C in the absence (A) and presence (B) of 30% polystyrene by weight

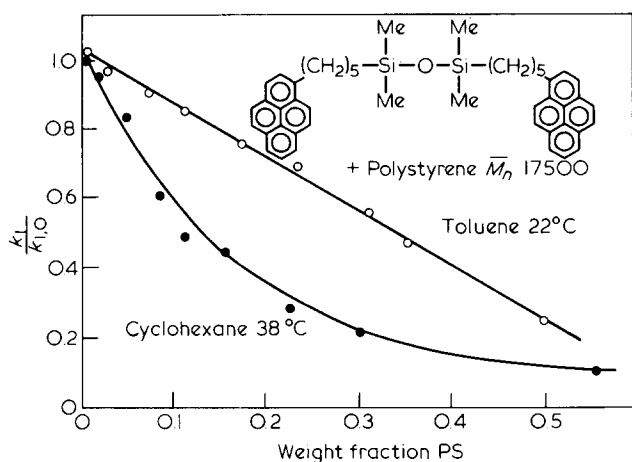


Figure 2 Plot of k_1 vs. polystyrene concentration for PySi₂ in toluene at 22°C and cyclohexane at 35°C

hydrodynamic screening interactions. This behaviour is predicted by the theory of Muthukumar and Freed¹¹, and our own experiments with pyrene-end-labelled polystyrene in a θ -solvent show the same dependence of k_1 on PS concentration as is seen in Figure 2 for PySi₂⁶.

For polystyrene in toluene, the hydrodynamic screening effects that retard polymer motion are accompanied by excluded volume screening which compresses the mean molecular dimensions. These tend to have offsetting effects, since the low frequency relaxation times of polymers decrease with a decrease in chain dimensions. The picture that emerges is that the motion of solvent molecules is coupled by hydrodynamic interactions with the motion of solute polymer chains. Even at low polymer concentration this acts to retard the low frequency motion in PySi₂ necessary to bring the large pyrene groups into proximity. The linear

dependence of k_1 on [PS] in toluene, while enticingly simple, may be the results of compensating effects on chain dynamics and chain dimensions for the added polymer which offset one another as the polymer concentration in a good solvent is raised.

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