were analyzed quantitatively in the homodyne limit. The computed formal retardation spectrum and the Arrhenius activation energy agree very well with dynamic mechanical, dielectric, and NMR data associated with the chair-chair inversion of the cyclohexyl ring.

Above $T_g$ the major part ($\sim$60%) of the total light-scattering intensity is due to the slow density fluctuations, and the experimental relaxation functions are dominated by the primary glass-rubber relaxation. The retardation spectrum shows a single-peak structure and displays a strong temperature dependence representated by the VFTH free volume equation.

We may finally note that the use of a carefully prepared polymer sample which displays only intrinsic scattering is a crucial point.

**Acknowledgment.** Thanks are due to Dr. W. Wunderlich, Röhm, Darmstadt, for his kindness in supplying the amorphous PCHMA sample and to J. Kanetakis for his assistance in computation. The work was supported by the Research Center of Crete.

**Registry No.** PCHMA, 25768-50-7.

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# End-to-End Cyclization of a Pyrene End-Capped Poly(bisphenol A-diethylene glycol carbonate)[1a]

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ABSTRACT: The cyclization dynamics of pyrene end-capped bis(bisphenol A-diethylene glycol carbonate) in dilute solution was investigated through studies of intramolecular fluorescent excimer formation. Steady-state and fluorescence decay data were used to determine all the rate constants for the cyclization of three samples having different molecular weights. Measurements performed in acetone, acetonitrile, and toluene showed the influence of both viscosity and quality of the solvent. The behavior of this type of chain was found to be totally classical with respect to the results already known for polystyrene. However, a polycarbonate chain shows a greater extent of cyclization than a polystyrene chain having the same number of backbone bonds. This could be explained by the high flexibility of the diethylene glycol moiety and the angular structure of the bisphenol A unit.

End-to-end cyclization of polymer chains has been the focus of numerous investigations for many years.[3] These studies are prompted by new developments in the theory of diffusion-controlled reactions of polymers,[4] coupled with new photophysical tools[5] for measuring cyclization events. Particularly meaningful information can be obtained from fluorescence measurements on pyrene end-capped macromolecules where cyclization is detected by the formation of a fluorescent intramolecular excimer. Here one can combine steady-state and fluorescence decay measure-

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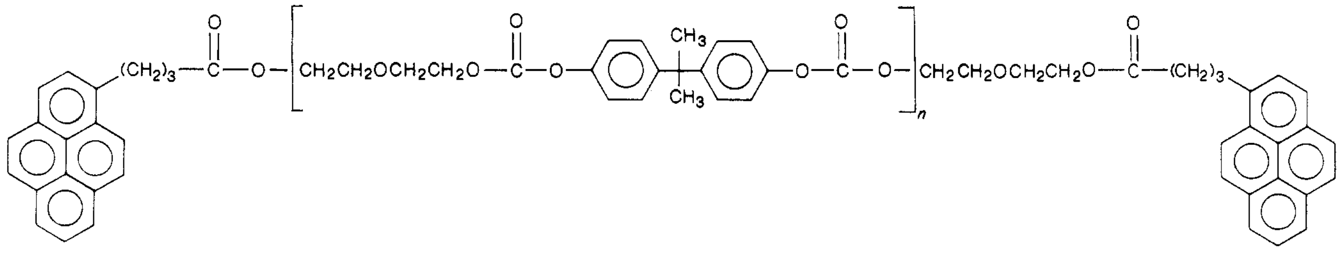

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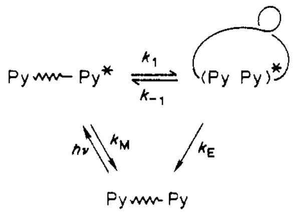
**Scheme I**



ments to obtain a detailed description of the reaction kinetics. In this way, the cyclization dynamics of polystyrene could be quite thoroughly investigated.[6] Poly(ethylene oxide)[5a,7] and poly(tetramethylene oxide)[8] have also been studied, as well as poly(dimethylsiloxane).[9]

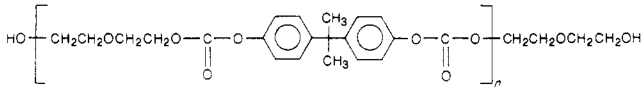
Cyclization is very sensitive to chain length. As a consequence, fluorescence measurements require polymers having a very narrow molecular weight distribution (typically $\bar{M}_w/\bar{M}_n = 1.1$) to yield meaningful data. This is quite difficult to achieve for polycondensates, and thus no quantitive measurements have been reported for these kinds of polymers. Recently we found that the use of the phase-transfer catalysis (PTC) technique in polycondensation leads to samples having much lower polydispersities than the polymers obtained by classical polycondensation.[10] Moreover, the nature of the chain ends is well-controlled and allows straightforward labeling of the polymer.

A preliminary study[11] using a pyrene end-capped polycarbonate of modest but still significant polydispersity showed classical cyclization behavior in dilute solution. However, the polydispersity of the sample ($\bar{M}_w/\bar{M}_n = 1.35$) prevented us from determining accurate kinetic parameters for its cyclization. All attempts to fit the data to the model shown in Scheme I were unsuccessful. Fits were especially poor for monomer fluorescence intensity decays in samples in which the extent of cyclization was large. Here we wish to report our results with the same polymer chain but free of polydispersity effects. Several samples of polymer 1, having different molecular weights, were examined in three different solvents.

Cyclization rate constants were then determined according to Birks' classical kinetic scheme[10] as adapted to intramolecular reactions (Scheme I). $\langle k_1 \rangle$ describes the rate of excimer formation and $k_{-1}$ its dissociation, whereas $k_M$ and $k_E$ measure the rates of deactivation of the excited species ("monomer" and excimer). The brackets for $\langle k_1 \rangle$ are there to remind us that this rate constant is very sensitive to chain length and that its value is in fact an average over the molecular weight distribution, even when the latter is very narrow. A comparison between the values found in our case and those known for polystyrene could then be made.

## Experimental Section

**Synthesis and Labeling.** Polymer 1 was synthesized using the PTC technique previously described,[10,11] starting from the disodium salt of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, BPA) in aqueous sodium hydroxide (3 N) and a solution of diethylene glycol bischloroformate in 1,2-dichlorobenzene. Tetrabutylammonium hydrogen sulfate was used as the phase-transfer agent. The mixture was stirred mechanically under nitrogen for 3 h at 20 °C. After an aqueous work up, the organic layer was poured into methanol. The polymer was filtered and dried under high vacuum. IR and $^1$H NMR spectroscopy were consistent with the hydroxy-terminated structure 2 for this sample. It was labeled by the standard procedure[6,11] using 4-(1-pyrenyl)butyroyl chloride. Polymer 2 (225 mg) was dissolved in a 10/1 mixture of dry toluene and dry dichloromethane (5 mL). After the addition of the acid chloride (0.43 mmol) and of dry triethylamine (0.86 mmol), the flask was flushed with nitrogen, and the mixture was stirred in the dark for 4 days. The polymer was then recovered by precipitation into methanol and purified by four reprecipitations from dichloromethane solution into methanol to remove all unattached chromophore.



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**Molecular Weight Analysis and Fractionation.** Molecular weights were examined by gel permeation chromatography (GPC) performed in tetrahydrofuran on a Waters 150C liquid chromatograph coupled with a home-built continuous capillary viscometer and a differential refractive index detector at the ESPCI.[13] The apparatus was equipped with four microstyragel columns ($10^6$, $10^5$, $10^4$, $10^3$ Å). Two different types of calibration were available: the classical calibration according to polystyrene (PS) standards and the universal calibration. In fact, neither of these is really well-adapted to our polymer. The structure of the polystyrene chain is indeed so different from ours that this type of calibration always leads to too high molecular weights. But on the other hand, the assumptions made to establish the universal calibrations are valid only for high enough molecular weights and might not be appropriate in our case. Thus the two calibrations gave systematically different values, and one suspects that the true molecular weights fall between. We take advantage of the information available from careful analysis of fluorescence decay curves of end-labeled polymers of narrow molecular weight distribution (see below). Here true values of $\bar{M}_n$ could be calculated from a combination of UV and fluorescence decay data.

After it was labeled, polymer 1 was fractionated on a preparative column in the same laboratory.[13] The experiment was run in dichloromethane. The solvent was then evaporated from the three central fractions and the polymers were dried under high vacuum.

The values found by GPC for the starting unlabled polymer 2 were $\bar{M}_n = 4650$, $I_p = 1.48$ and $\bar{M}_n = 2200$, $I_p = 1.77$ according to the universal calibration, where $I_p \equiv \bar{M}_w/\bar{M}_n$. For pyrene end-capped samples, we found the following values: polymer 1 before fractionation $\bar{M}_n(\mathrm{PS}) = 5100$, $I_p = 1.36$ and $\bar{M}_n(\mathrm{univ}) = 3200$, $I_p = 1.53$; fraction (a) $\bar{M}_n(\mathrm{PS}) = 9400$, $I_p = 1.09$ and $\bar{M}_n(\mathrm{univ}) = 6000$, $I_p = 1.13$; fraction (b) $\bar{M}_n(\mathrm{PS}) = 5100$, $I_p = 1.14$ and $\bar{M}_n(\mathrm{univ}) = 3000$, $I_p = 1.24$; fraction (c) $\bar{M}_n(\mathrm{PS}) = 3400$, $I_p = 1.21$ and $\bar{M}_n(\mathrm{univ}) = 1700$, $I_p = 1.24$.

**Fluorescence Experiments.** Three different solvents were used: toluene was distilled over sodium under nitrogen. Spectrograde acetonitrile was distilled, while acetone was refluxed over potassium permanganate to eliminate all residual alcohols and then dried with potassium carbonate before being distilled.

4-Methyl(1-pyrenyl)butyrate (3) was used as a model compound for luminescence measurements. It was purified by silica gel

**Table I**
**Monomer and Excimer Decay Parameters**[a]

| $\bar{M}_n$ | solvent | $\tau_1^E$, ns | $\tau_2^E$, ns | $\chi_E^2$ | $a_4/a_3$ | $\tau_M$ model compd, ns | $\tau_M$ recovd, ns | $a_1$ | $a_2$ | $a_M$ | $\chi_M^2$ | $\alpha$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7400 | acetone | 116.6 | 44.8 | 1.29 | –0.97 | 214.5[b] | 209.2 | 0.122 | 0.016 | 0.012 | 1.01 | 84.7 |
| 4900 | | 88.0 | 40.1 | 1.36 | –0.97 | 214.5 | 200.8 | 0.149 | 0.067 | 0.024 | 1.00 | 81.6 |
| 3900 | | 75.8 | 33.4 | 1.29 | –0.99 | 214.5 | 201.5 | 0.117 | 0.111 | 0.018 | 1.03 | 86.7 |
| 7400 | acetonitrile | 89.6 | 43.5 | 1.20 | –0.95 | 198.1 | 185.5 | 0.143 | 0.032 | 0.026 | 1.21 | 77.3 |
| 4900 | | 68.3 | 34.1 | 1.02 | –0.97 | 198.1 | 186.5 | 0.161 | 0.147 | 0.024 | 1.14 | 86.6 |
| 3900 | | 60.6 | 26.8 | 1.16 | –0.97 | 198.1 | 192.7 | 0.050 | 0.108 | 0.010 | 1.01 | 88.6 |
| 4900 | toluene | 97.8 | 42.7 | 0.95 | –0.98 | 191.0[b] | 186.4 | 0.195 | 0.026 | 0.036 | 1.14 | 75.6 |
| 3900 | | 83.0 | 39.3 | 1.05 | –0.96 | 191.0 | 187.7 | 0.139 | 0.040 | 0.029 | 1.12 | 75.4 |

[a] Excimer, $\tau_1^E$ and $\tau_2^E$ (free fit); monomer, $\tau_1^M$ and $\tau_2^M$ fixed from the excimer decay. [b] Reference 16.

column chromatography in dichloromethane and recrystallization from hexane.

Dilute solutions of the samples (ca. $3 \times 10^{-6}$ mol L$^{-1}$ in pyrene to avoid the formation of intermolecular excimers) were prepared in 1-cm$^2$ Pyrex cells and carefully degassed by five pump–freeze–thaw cycles before being sealed off under high vacuum ($1 \times 10^{-5}$ Torr).

Fluorescence spectra were run on a SPEX Fluorolog II spectrometer at 22 °C. Decay curves were obtained by using the time-correlated single-photon counting technique.[14] The excitation wavelength was 345 nm; the monomer fluorescence was observed at 376 nm and the excimer fluorescence at 520 nm. The analysis of the excited monomer and excimer decay curves was performed by using the $\delta$-pulse convolution method.[15] Reference decay curves of degassed solutions of 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)thiophene (BBOT) in ethanol ($\tau$ = 1.47 ns) and 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP) in cyclohexane ($\tau$ = 1.1 ns) were used for analysis of the excimer and monomer decay curves, respectively.

## Data Analysis

Scheme I predicts that after a $\delta$-pulse excitation, the intensity of the resulting "monomer" fluorescence $I_M(t)$ should decrease as the sum of two exponential terms, whereas the intensity of the excimer $I_E(t)$ should increase and then decrease as the difference of two exponential terms, but with the same lifetimes ($\lambda_1 = 1/\tau_1$, $\lambda_2 = 1/\tau_2$):

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

$$I_E(t) = a_3 \exp(-\lambda_1 t) - a_4 \exp(-\lambda_2 t) \tag{1b}$$

with $a_3$ equal to $a_4$.

In our case UV measurements recorded at different steps of the preparation of the samples suggested that part of the chains (roughly 15–20%) bore only one chromophore. In this case a third exponential term appears in the expression of $I_M(t)$, due to the presence of singly labeled polymer, which should have the same lifetime as the model compound:

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

Figure 1 shows typical monomer and excimer decays. It is easy to see the "tail" corresponding to the long component on the monomer curve. We were able to fit the excimer decays to eq 1b without any problem. In the case of monomer decays, the best results were obtained when fixing $\lambda_1$ and $\lambda_2$ from the corresponding excimer curve. The $\tau_M$ values obtained in this way, Table I, were always slightly smaller than those measured directly for the model compound in the same solvent. For samples in acetone and acetonitrile, these differences in $\tau_M$ values were always less than 7%; and for samples in toluene, the differences were less than 3%, i.e., within experimental error. This result suggests that there may be a small contribution to the $I_M(t)$ data of quenching of Py* by the polymer backbone. The extent of this quenching is too small to affect any quantitative analysis of the data presented here.

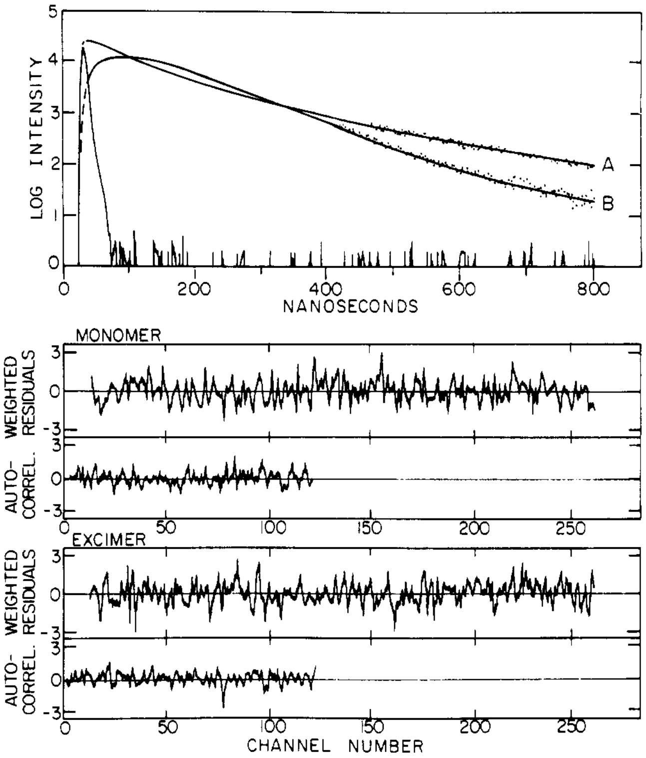

**Figure 1.** Fluorescence decay curves $I_M(t)$ (A) and $I_E(t)$ (B) of fraction c ($\bar{M}_n$ = 3900) in toluene at 22 °C ([Py] = $3 \times 10^{-6}$ M). Bottom parts: excitation lamp profile. Monomer: $\tau_1^M$ = 83.0 ns; $\tau_2^M$ = 39.3 ns (both fixed); $\tau_M$ = 187.7 ns; $\chi_M^2$ = 1.12. Excimer: $\tau_1^E$ = 83.0 ns; $\tau_2^E$ = 39.3 ns; $a_4/a_3$ = –0.961; $\chi_E^2$ = 1.05.

Knowing all the fitting parameters, it is then easy to estimate the fraction $\alpha$ of chains labeled on both ends, using the expression:

$$\alpha = \frac{[M_2]}{[M_1] + [M_2]} = \frac{a_1 + a_2}{a_1 + a_2 + 2a_M} \tag{3}$$

where $[M_1]$ and $[M_2]$ stand for the total amounts, respectively, of once-labeled and twice-labeled chains. Measurements in acetone and in acetonitrile gave an average value of 85% for $\alpha$, although values recovered in toluene were somewhat lower. Assuming $\alpha$ = 0.85, precise UV measurements on carefully weighed amounts of polymer allowed us to recalculate the following molecular weights for our samples: fraction a, $\bar{M}_n$ = 7400; fraction b, $\bar{M}_n$ = 4900; fraction c, $\bar{M}_n$ = 3900.

For the fluorescence decay curves, goodness of fit ($\chi^2$) was always close to 1.0 and $a_4$ almost equal to $a_3$. Free fits for monomer decays gave values of $\tau_1^M$ and $\tau_2^M$ very close to $\tau_1^E$ and $\tau_2^E$. All the data collected are displayed in Table I.

Table II
Values of $I_E/I_M$ and Cyclization Rate Constants for Fractions a, b, and c in Acetone, Acetonitrile, and Toluene at 22 °C[a]

| $\bar{M}_n$ | solvent | $\eta_0$(20 °C), cP | $10^{-6}\langle k_1\rangle$, s$^{-1}$ | $10^{-6}k_{-1}$, s$^{-1}$ | $10^{-6}k_M$, s$^{-1}$ | $10^{-7}k_E$, s$^{-1}$ | $K_{cy}$ | $I_E/I_M$ (meas) | $I_E/I_M$ (corr) |
|---|---|---|---|---|---|---|---|---|---|
| 7400 | acetone | 0.32 | 5.4 | 3.6 | 4.8 | 1.7 | 1.5 | 0.67 | 0.78 |
| 4900 | | | 10.6 | 3.7 | 5.0 | 1.7 | 2.8 | 1.25 | 1.55 |
| 3900 | | | 16.4 | 4.3 | 5.0 | 1.8 | 3.8 | 1.77 | 2.34 |
| 7400 | acetonitrile | 0.37 | 7.9 | 2.6 | 5.4 | 1.8 | 3.0 | 0.95 | 1.14 |
| 4900 | | | 16.3 | 3.3 | 5.4 | 1.9 | 4.9 | 1.82 | 2.40 |
| 3900 | | | 25.5 | 3.7 | 5.2 | 1.9 | 6.9 | 2.59 | 3.76 |
| 7400 | toluene | 0.59 | | | | | | 0.14 | |
| 4900 | | | 6.4 | 2.8 | 5.4 | 1.9 | 2.3 | 0.79 | 0.93 |
| 3900 | | | 9.7 | 3.2 | 5.3 | 1.9 | 3.0 | 1.04 | 1.28 |

[a] Parameters could not be determined for fraction a ($\bar{M}_n$ = 7400) in toluene because of a too low excimer fluorescence intensity.

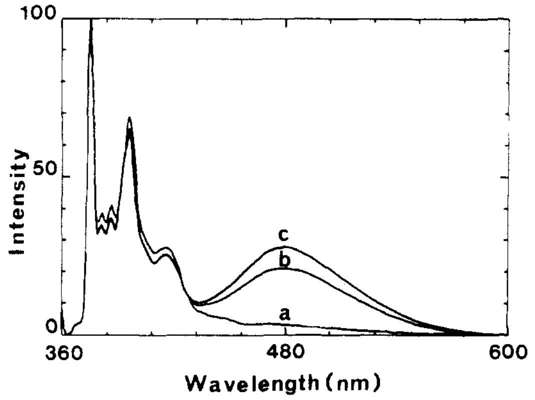

**Figure 2.** Fluorescence spectra of fractions a ($\bar{M}_n$ = 7400), b ($\bar{M}_n$ = 4900), and c ($\bar{M}_n$ = 3900) in toluene at 22 °C. Spectra were normalized at the (0,0) band of pyrene fluorescence at 375 nm.

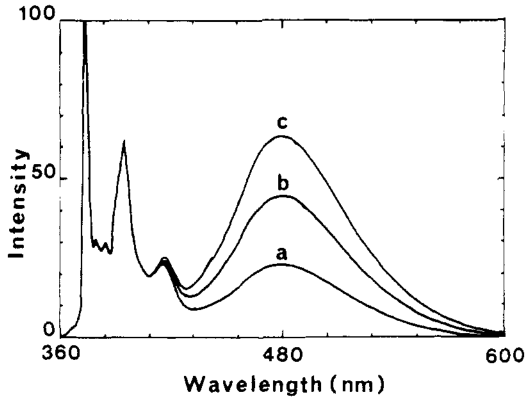

**Figure 3.** Fluorescence spectra of fractions a, b, and c in acetonitrile at 22 °C. The curves were normalized at the (0,0) band of pyrene fluorescence (374 nm).

## Results and Discussion

Examples of steady-state fluorescence spectra are shown in Figures 2 and 3. One sees clearly that the extent of cyclization becomes greater as the chain becomes shorter. This type of behavior is well-known for pyrene end-labeled polystyrene[6b] and is observed here in the three solvents we examined.

The solvent effect was more complex. Cyclization is more significant in acetone than in toluene, consistent with the difference in viscosities of these two solvents. But the relative amount of excimer was found to be even larger in acetonitrile than in acetone, in spite of the fact that acetonitrile is more viscous than acetone. We interpret this result to imply that acetonitrile is a poor solvent for the polymer. It facilitates cyclization with the suppression of excluded-volume effects which normally prevent the segments located at both ends of a polymer chain from coming too close to one another.

Fluorescence spectra provide steady-state values of $I_E/I_M$ for every sample. These "raw" data must be corrected for the amount of singly labeled chains which contribute to the intensity of $I_M$(meas):

$$I_M(\text{meas}) = k_{FM}\frac{Y}{k_M Y + \langle k_1\rangle k_E}[M_2^*]_0 + \frac{k_{FM}}{k_M}[M_1^*]_0 \quad (4)$$

where $[M_2^*]_0$ and $[M_1^*]_0$ are the initial concentrations of excited molecules respectively doubly and singly labeled with pyrene groups; $k_{FM}$ is the radiative rate constants for the "monomer" emission and

$$X = \langle k_1\rangle + k_M; \qquad Y = k_{-1} + k_E; \qquad k_M = 1/\tau_M$$

The excimer emission is due only to the doubly labeled chains

$$I_E = k_{FE}\frac{\langle k_1\rangle}{k_M Y + \langle k_1\rangle k_E}[M_2^*]_0 \quad (5)$$

where $k_{FE}$ is the excimer radiative rate constant. Dividing eq 4 and 5 we obtain

$$\frac{I_E}{I_M}(\text{corr}) = \frac{I_E}{I_M}(\text{meas})\left\{1 + \frac{1}{2}(\alpha^{-1} - 1)\left[1 + \frac{\langle k_1\rangle k_E}{k_M Y}\right]\right\} \quad (6)$$

where $\alpha$ is the fraction of doubly labeled chains and $I_E/I_M$(corr) stands for the value that should be observed if only doubly labeled chains were present in the sample. The correction term in eq 6 depends on the values of the rate constants in Scheme I, which can be evaluated by using the parameters ($\lambda_1$, $\lambda_2$, $a_1/a_2$) from the fluorescence decay measurements:

$$2\lambda_1,\lambda_2 = (X + Y) \mp [(Y - X)^2 + 4\langle k_1\rangle k_{-1}]^{1/2} \quad (7)$$

$$a_2/a_1 = \frac{X - \lambda_1}{\lambda_2 - X} \quad (8)$$

The values of these parameters are collected in Table I.

Sometimes a poor batch of solvent provides an opportunity to check the validity of a reaction mechanism used to fit experimental data. In one sample of acetone not dried over potassium carbonate before distillation, we found $\tau_M$ = 181 ns instead of 214.5 ns for the model compound 3. From measurements on fraction c ($\bar{M}_n$ = 3900) in this batch of solvent we calculate $\langle k_1\rangle = 16.7 \times 10^6$ s$^{-1}$, $k_{-1} = 4.4 \times 10^6$ s$^{-1}$, and $k_E = 1.9 \times 10^7$ s$^{-1}$. These values are very similar to those obtained in the repurified solvent, Table II, and provide additional support for the mechanism of Scheme I.

Steady-state and fluorescence data (Table II) were corrected by using eq 6 with $\alpha$ = 0.85. The kinetic Scheme I predicts

$$\frac{I_E}{I_M}(\text{corr}) = \frac{k_{FE}}{k_{FM}}\frac{\langle k_1\rangle}{(k_{-1} + k_E)} \quad (9)$$

**Table III**
**Values of $\langle k_1 \rangle$ Calculated from Fluorescence Decays and from Equation 3, Taking Fraction c ($\bar{M}_n$ = 3900) as a Reference**

| | $10^{-6}\langle k_1 \rangle$ from fluorescence decays, $s^{-1}$ | | | $10^{-6}\langle k_1 \rangle$ from eq 3, $s^{-1}$ | | |
|---|---|---|---|---|---|---|
| $\bar{M}_n$ | acetone | acetonitrile | toluene | acetone | acetonitrile | toluene |
| 3900 | 16.4 | 25.5 | 9.7 | 16.4 | 25.5 | 9.7 |
| 4900 | 10.6 | 16.3 | 6.4 | 10.8 | 16.0 | 7.1 |
| 7400 | 5.4 | 7.9 | | 5.3 | 7.5 | |

Moreover, it is known that the radiative rate constants only depend on the refractive index of the solvent, and we can see in Table II that $k_{-1}$ and $k_E$ seem to be molecular weight independent. Thus we find for any two polymers in a given solvent that

$$\frac{\langle k_1 \rangle_1}{\langle k_1 \rangle_2} = \frac{[I_E/I_M]_1}{[I_E/I_M]_2} \qquad (10)$$

If we chose the value of $\langle k_1 \rangle$ determined, for example, for fraction c ($\bar{M}_n$ = 3900) as a reference, eq 10 enables us to recalculate new values of $\langle k_1 \rangle$ for the other two samples. Values of $\langle k_1 \rangle$ calculated from eq 10 are in good agreement, Table III, with those obtained from fluorescence data.

The theory of diffusion-controlled reactions predicts that $k_1$ should vary as $T/\eta_0$, where $\eta_0$ is the solvent viscosity, and $T$, the absolute temperature. This prediction is followed for the samples of 1 in toluene and acetone. We find, for example, $\langle k_1 \rangle(\text{acetone})/\langle k_1 \rangle(\text{toluene}) = 1.70$ and $[\eta_0(\text{acetone})/\eta_0(\text{toluene})]^{-1} = 1.84$. Toluene and acetone were two of the solvents shown to be of comparable quality for 1 in our preliminary study.[11] Values of $\langle k_1 \rangle$ for samples in acetonitrile are larger than those predicted from changes in solvent viscosity. This enhancement of $\langle k_1 \rangle$ values is typical of the behavior of polymer in a poor solvent, where suppression of excluded-volume effects leads to a large enhancement in the extent of cyclization.[6c]

Wilemski–Fixman theory[4a] predicts that $\langle k_1 \rangle \sim N^{-\gamma}$, where $N$ is the chain length and the magnitude of $\gamma$ depends upon the strength of the excluded-volume interaction. We anticipate, therefore, a linear dependence of log $\langle k_1 \rangle$ on $\bar{N}$. For chains of sufficient length we could simply let $\bar{N}$ be proportional to the degree of polymerization ($n$) of the polymer and ignore the contribution of the butyl ester groups to the chain length.

Considering structure 1 and the fact that the molecular weights are rather low, the contribution of the end groups must be taken into account. We do this in a somewhat arbitrary way, assigning one "bond" to the $-O-C_6H_4-$ group and count 12 bonds per repeat unit of the chain and 16 bonds for the end groups, i.e., ($N = 12n + 16$), since $M_n = 646 + 386n$, we calculate $N$ from the expression

$$N = 12[(M_n - 646)/386] + 16 \qquad (11)$$

The proper $\bar{M}_n$ values to use in this expression are those obtained by end-group analysis as described above.

In Figure 4 we plot log $[(I_E/I_M)_{\text{corr}}]$ vs log $\bar{N}$ and in Figure 5 we plot log $\langle k_1 \rangle$ vs log $\bar{N}$. Linear plots are obtained for the samples in all three solvents in Figure 4 and, in Figure 5, for the samples in acetone and acetonitrile. For the $\bar{M}_n$ = 7400 sample in toluene, the excimer intensity was so weak that meaningful $I_E(t)$ measurements were not possible. Apparent slopes ($-\gamma$ values) are $-1.9$ for acetonitrile and $-1.7$ for acetone. Considering the approximations made in calculating $\bar{N}$ and the fact that we have only three different chain lengths, we take these data to indicate a steep dependence of $\langle k_1 \rangle$ on chain length. It is premature and probably unwarranted to ascribe any deeper significance to $\gamma$ values obtained from such limited data.

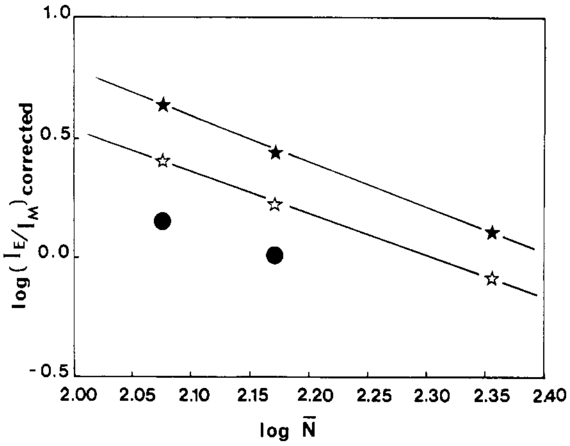

**Figure 4.** Plot of log $(I_E/I_M)_{\text{corr}}$ versus log $\bar{N}$: $\bar{N}$ = average number of bonds; (★) acetonitrile; (☆) acetone; (●) toluene.

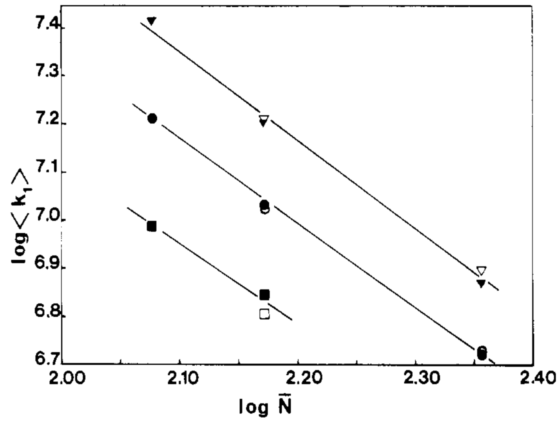

**Figure 5.** Plot of log $\langle k_1 \rangle$ versus log $\bar{N}$: (open symbols) $\langle k_1 \rangle$ from fluorescence decays; (filled symbols) $\langle k_1 \rangle$ from eq 10; (□) toluene; (○) acetone; (▽) acetonitrile.

It is more reasonable and quite interesting to compare $\langle k_1 \rangle$ values of the polycarbonate [PC] 1 to that of polystyrene [PS] of similar chain length. For example, for fraction a of 1 ($\bar{M}_n$ = 7400), we calculate $\bar{N}$ = 227. This corresponds to Py–polystyrene–Py (4) of $\bar{M}_n$ = 11 600. Martinho[16] has examined the kinetics of intramolecular excimer formation of 4 in acetone for a sample of $\bar{M}_n$ = 11 500. The comparison for the two samples in acetone are as follows: $\langle k_1 \rangle(\text{PS}) = 3.5 \times 10^6\ s^{-1}$; $\langle k_1 \rangle(\text{PC}) = 5.4 \times 10^6\ s^{-1}$; $k_E(\text{PS}) = 1.8 \times 10^7\ s^{-1}$; $k_E(\text{PC}) = 1.7 \times 10^7\ s^{-1}$. The polycarbonate cyclizes more quickly. Every assumption made in this comparison operates to enhance the cyclization rate of PS. For example, the calculation for $\bar{N}$ for 1 may underestimate the effective chain length of the polycarbonate. Comparison with a longer chain PS would imply comparison of the $\langle k_1 \rangle$(PC) value with an even smaller $\langle k_1 \rangle$(PS) value. Acetone is a good solvent for PC but a very poor solvent for PS. Cyclization of PS in acetone is much faster than for PS in toluene, even after correction for the solvent viscosity differences. We conclude that some feature of the PC structure leads to faster cyclization than that of PS of comparable chain length.

Two features might lead to faster cyclization of the PC structure. The first could be the flexibility of the diethylene glycol moiety and the carbonate group. Polystyrene has a higher glass transition temperature ($T_g$ = 104 °C) than 1 ($T_g$ = 67 °C). It is noteworthy that the more flexible polymer (which has the lower $T_g$) gives the higher extent of cyclization.[8] The second feature could be the helical nature of the polycarbonate chain, which might act to decrease the mean separation between the polymer chain ends.[17]

It is also interesting to note that 1 and 4 give nearly identical $k_E$ values. This term should be sensitive only to the local interactions within the pyrene excimer. Its value might vary from solvent to solvent. It is reassuring that this value is not sensitive to the structure of the intervening chain.

We can conclude that the poly(bisphenol A–diethylene glycol carbonate) exhibits a classical behavior for its cyclization in dilute solution. Intramolecular excimer formation proved to be a very well-adapted and powerful technique for this study. We can thus expect that similar studies on closely related polymers could lead to a better understanding of the relationship between structure and chain dynamics.

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# Dielectric Relaxation Studies of Ion Motions in Electrolyte-Containing Perfluorosulfonate Ionomers. 3. $ZnSO_4$ and $CaCl_2$ Systems

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ABSTRACT: The dielectric relaxation spectra of Nafion perfluorosulfonate membranes that were equilibrated in aqueous $ZnSO_4$ and $CaCl_2$ solutions were obtained as a function of electrolyte concentration and temperature over the frequency range 5 Hz to 13 MHz. A low-frequency conductivity peak, dormant at ambient temperature but activated slightly above, was observed for both incorporated electrolytes and attributed to a superposition of the enhancing effect of long-range ion migration throughout the membrane and the current-limiting effect of ionic space-charge capacitance in the near-electrode region. A single high-frequency peak, seen at all temperatures for all samples, was suggested to arise from a relaxation of interfacial polarization due to the diffusion-controlled accumulation and dissipation of mobile ionic charge at the hydrophilic cluster boundaries. The overall impedance behavior observed with increasing electrolyte concentration was rationalized in terms of a shifting equilibrium between dissociated ions and multipolar associations that acts to control ionic mobility. Finally, we have attempted to consolidate and refine our concepts of "interfacial polarization" and "dc conductivity" within the framework of the unique hydrophilic/hydrophobic phase separation presented by Nafion perfluorosulfonate materials.

## Introduction

In recent correspondence Mauritz, Fu, and Yun have presented dielectric relaxation analyses of Nafion perfluorosulfonate membranes[1] that were equilibrated in aqueous NaOH and NaCl (referred to as part 1)[2] and $CH_3COONa$, KCl, and KI (referred to as part 2)[3] solutions at various temperatures over the frequency range 5 Hz to 13 MHz as a function of external solution concentration. In all cases, a temperature-activated absorption process was identified and suggested to arise from the relaxation of an interfacial polarization consisting of the diffusion-

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