

# Polarity effects of solvent mixtures in exciplexes formed on cyclization of polystyrene chains

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The spectral shifts of the exciplex of methyl 4-(1-pyrene)butyrate with dimethyltoluidine, in mixtures of acetone and cyclopentane, were compared with the shifts of an intramolecular analogue, the exciplex formed on cyclization of both end-labelled polystyrene chains. The shifts are not linear with the mole fraction of the polar solvent. The deviations are due to a 'dielectric enrichment' of the solvent shell of the exciplex. The results were interpreted on the basis of a competition between the phenyl groups of the polymer and acetone to the 'dielectric enrichment', which depends on the length of the polymer chain.

(Keywords: pyrene; fluorescence; cosolvency; polymer cyclization)

## INTRODUCTION

One of the interesting features of a dilute polymer solution is that the individual polymer molecules represent domains of modest polymer segment concentration in an otherwise empty sea of solvent molecules. What this means is that the environment in the coil interior (i.e. polarity, viscosity) is different from that in the bulk solution, and this environment changes as the local segment density fluctuates. The situation becomes even more complicated for polymers in mixed solvents. Here an equilibrium is established, where the time-averaged solvent composition inside the conformationally averaged coil dimensions is commonly different from that present in the bulk liquid.

There are various approaches that one might take to study the solvent environment inside the coil. Light scattering, for example, is sensitive to the refractive-index gradient. From our point of view, a more direct method would be to attach a molecular sensor to the polymer. This could be a spin-label sensitive to local motion inside the coil or a fluorescent dye chosen for the sensitivity of its emission to the polarity of its environment. These methods all provide information about the polymer, which is averaged over all conformations of the chain. If one were interested in only a subset of this conformation population, such as largely elongated chains or cyclized chains, this simple single sensor approach would fail unless one could use an external stress (e.g. flow) to distort the conformation distribution.

For cyclized chains, a unique approach is possible based upon the spectroscopy of exciplexes. Exciplexes are electronically excited binary complexes characterized by a large dipole moment. If exciplex-forming groups are placed at the ends of a polymer chain, exciplex fluorescence from dilute solutions would report exclusively on

cyclized chains. Since the exciplex emission is exceedingly sensitive to solvent polarity<sup>1,2</sup>, undergoing a red-shift and an intensity decrease in a more polar environment<sup>2</sup>, such polymers provide the opportunity to examine the environment of the end-groups in cyclized conformations of the chain.

The specific polymers we examine have the structure I, shown below, with pyrene (Py) and dimethyltoluidinyl (DMT) end-groups being the partners in exciplex formation. We will be particularly concerned with polystyrene samples dissolved in mixtures of cyclopentane and acetone. These solvents show a cosolvency effect towards polystyrene<sup>3,4</sup> in that their mixtures act as a better quality solvent for the polymer than either pure solvent.

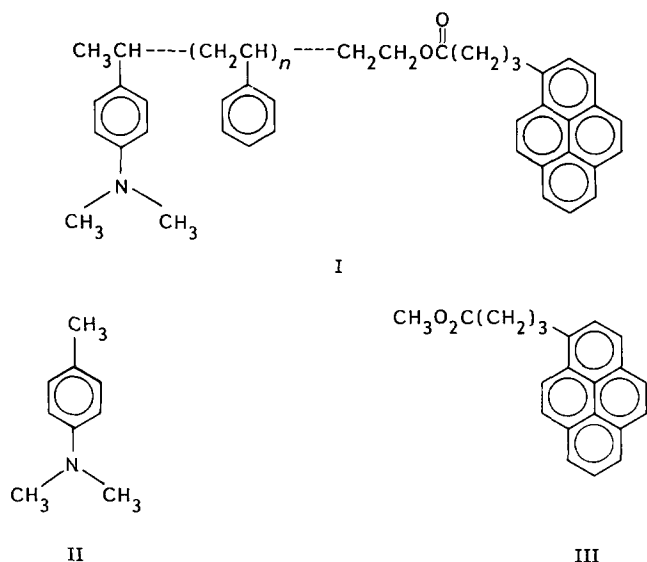
In the model system studied for comparison purposes, we examine exciplex formation from 4-*N,N*-dimethyltoluidine (II) plus methyl 4-(1-pyrene)butyrate (III). The features of interest are the spectral shifts of the maximum exciplex emission intensity, which occur as the solvent composition changes.

The spectral shifts (in energies) for  $S_0 \rightarrow S_1$  (absorption) and  $S_1 \rightarrow S_0$  (fluorescence) for a series of solvents of similar refractive indices and free of specific association are given by<sup>5</sup>:

$$\Delta E(S_0 \rightarrow S_1) = -\frac{\mu_g(\mu_e - \mu_g)}{a^3} \Delta f(D) \quad (1a)$$

$$\Delta E(S_1 \rightarrow S_0) = -\frac{\mu_e(\mu_g - \mu_e)}{a^3} \Delta f(D) \quad (1b)$$

where  $\mu_g$  and  $\mu_e$  are the solute dipole moments in  $S_0$  and  $S_1$  states, respectively,  $a$  is the radius of the cavity where the dipole is located and  $\Delta f(D)$  is the difference in reaction field factors. The reaction field factor can be evaluated



from Onsager's field model<sup>5,6</sup> as:

$$f = \frac{2(D-1)}{2D+1} \quad (2)$$

where  $D$  is the static dielectric constant of the solvent. Since  $\mu_g$  is known,  $\mu_e$  can be calculated from the spectral shifts  $\Delta E/\Delta f(D)$  of (1a) and (1b) or from the ratio method<sup>7,8</sup>, which does not require the value of the cavity radius,  $a$ .

For ideal mixtures of a polar solvent (P) with a non-polar solvent (N), the reaction field factor should be given by<sup>9</sup>:

$$f(D)_{\text{mix}} = \chi_P f(D_P) + \chi_N f(D_N) \quad (3)$$

where  $\chi_P$  and  $\chi_N$  are the mole fractions of the polar and non-polar solvent in the mixture, respectively. Some solvent mixtures show deviations from relation (3), which were attributed to specific solvent interactions or to aggregation effects<sup>9,10</sup>.

The spectral shift in an ideal mixture of a polar with a non-polar solvent should be a linear function of mole fraction of the polar solvent (see equations (1) and (3)). Nevertheless, the wavelength of the maximum in the absorption and fluorescence spectrum of polar molecules in both ideal and non-ideal mixtures does not obey the expected linear variation with mole fraction of the polar solvent<sup>9,10</sup>. The same phenomenon was observed<sup>10</sup> in intermolecular exciplexes formed in the encounter of an electron donor excited species with an electron acceptor. These deviations were attributed to an unspecific association between the polar solute molecule and the solvent of higher dielectric constant, creating a 'dielectric enrichment' of the solute solvation shell<sup>9,10</sup>. The spectral shifts of a solute molecule in mixtures of solvents give reliable information on its preferential solvation. Here we show how important is the competition between the phenyl groups of polystyrene and acetone to the 'dielectric enrichment' around the intramolecular exciplex formed when polystyrene chains of structure similar to I cyclize in acetone, cyclopentane and their mixtures.

## EXPERIMENTAL

Cyclopentane (CP) (Caledon, distilled in glass) and acetone (AC) (Caledon, spectroscopic grade) were used

as received. Dimethyltoluidine (II) from Caledon was freshly distilled under reduced pressure. Methyl 4-(1-pyrene)butyrate (III) was prepared by esterification of pyrenebutyric acid with methanol, purified by chromatography and recrystallized twice. The synthesis of the polystyrene chains of structure I was described previously<sup>11,12</sup>. The polymers were characterized by g.p.c., with  $M_n = 1970$ ,  $M_w/M_n = 1.06$  and  $M_n = 3400$ ,  $M_w/M_n = 1.06$ ; low-molecular-weight impurities are less than 0.01 mol%. Solutions of the polymers and of compounds II and III were prepared in cyclopentane, acetone and their mixtures. Polymer solutions have concentrations less than  $5.0 \times 10^{-6} \text{ mol l}^{-1}$  to eliminate intermolecular exciplex formation processes. The concentration of III in solutions of II with III was always lower than  $4.0 \times 10^{-6} \text{ mol l}^{-1}$  to prevent pyrene excimer formation. The solutions were degassed by the freeze-pump-thaw technique (five cycles), and sealed under a vacuum better than  $2 \times 10^{-5} \text{ Torr}$ . Polymer solutions were degassed in the dark to avoid photodegradation.

Fluorescence spectra were recorded on a Spex Fluorolog 2 and corrected for the spectral response of the fluorescence detecting system. Exciplex peak positions were determined by first subtracting from the spectra the pyrene emission, normalized at the (0,0) band. The exciplex band was then expanded in intensity, and the peak identified by eye, using the computer screen and the cursor.

## RESULTS AND DISCUSSION

Figure 1 shows the fluorescence spectra of solutions of II ( $c = 3.9 \times 10^{-4} \text{ M}$ ) with III ( $c = 1.5 \times 10^{-6} \text{ M}$ ) and of polymer I,  $M_n = 3400$  ( $c = 3.4 \times 10^{-6} \text{ M}$ ), in a mixture of cyclopentane and acetone (CP:AC = 2:1 vol%). Both spectra are composed of a structured emission at lower wavelengths attributed to the local excited pyrene derivative and a broad one at longer wavelengths due to the exciplex emission. The polymer has essentially no effect on emission from the locally excited pyrene ('monomer' emission). On the other hand, the exciplex emission is blue-shifted compared to the model involving the small molecules II + III. This kind of polarity effect is due to the large dipole moment of the Py-DMT exciplex ( $\sim 15 \text{ D}$ ). Indeed, only molecules with large

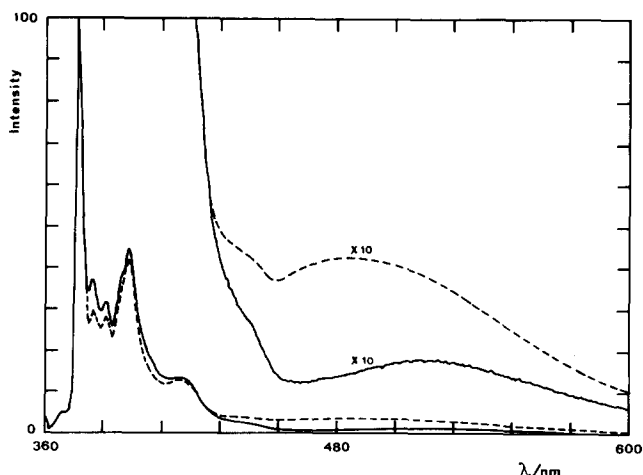


Figure 1 Fluorescence spectra of solutions of II with III (—) and of polymer I,  $M_n = 3400$  (---) in a mixture of cyclopentane and acetone (CP:AC = 2:1 vol%)

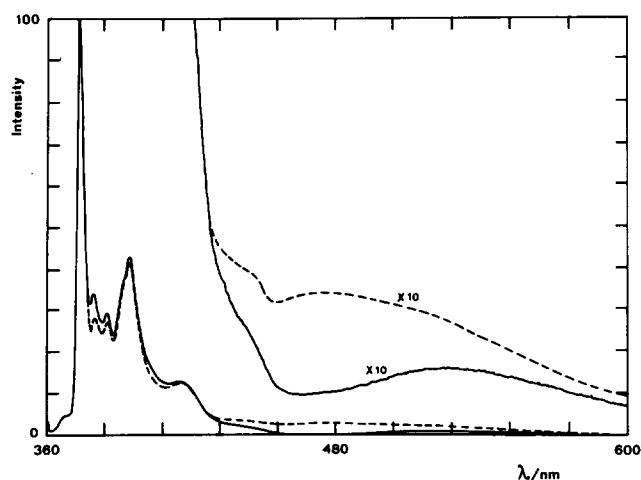


Figure 2 Fluorescence spectra of solutions of II with III (—) and of polymer I,  $M_n = 3400$  (---) in a mixture of cyclopentane and acetone (CP:AC = 1:1 vol%)

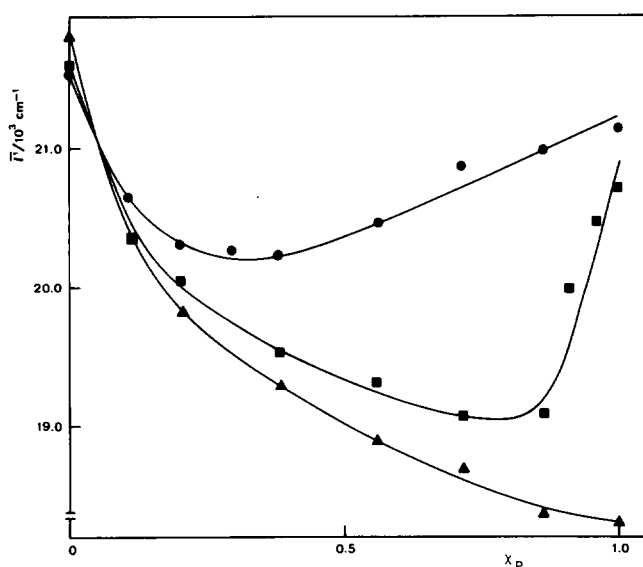


Figure 3 Maximum of the exciplex emission versus mole fraction of acetone ( $\chi_p$ ): (▲) model exciplex; (■) intramolecular exciplex of polystyrene chain of structure I and  $M_n = 1970$ ; (●) intramolecular exciplex of polystyrene chain of structure I and  $M_n = 3400$

dipole moments have significant spectral shifts with changes in the polarity of solvent (see equation (1)).

Figure 2 shows the same kind of spectra, but now in a mixture richer in acetone (CP:AC = 1:1 vol%). Comparison of these spectra with those in Figure 1 shows that the intermolecular exciplex (model) shifts to the red and the intramolecular one to the blue with increasing acetone content in the mixture.

The wave number  $\bar{\nu}$  corresponding to the maximum of the emission of the intramolecular exciplexes of two molecular-weight polystyrene chains ( $M_n = 1970, 3400$ ) of structure I and of the model exciplex are plotted in Figure 3 versus the mole fraction of acetone  $\chi_p$ .

Large deviations from linearity were observed for both the model and the intramolecular exciplexes. The same behaviour was observed by Suppan<sup>10</sup> in the intermolecular exciplex of pyrene-dimethylaniline in different mixtures of polar with apolar solvents. This cannot be explained by the deviations from linearity of the reaction field factor  $f(D)$  of the mixture with  $\chi_p$ , which are usually

rather small. A 'dielectric enrichment' of the solute shell caused by an unspecific association of the solute with the polar solvent, proposed by Suppan<sup>9,10</sup>, satisfactorily explains the results. The steady-state 'dielectric enrichment' is attained in some nanoseconds<sup>10</sup>, prior to exciplex emission, which has a lifetime of  $\sim 100$  ns<sup>13</sup>. The spectral shifts for the intramolecular exciplexes with solvent polarity are rather curious and reflect the influence of the polymer chain. The wave number  $\bar{\nu}$  of the intramolecular exciplexes is shifted to the blue relative to that of the model exciplex. It has a minimum value with solvent polarity that depends on the polymer chain length. Acetone is a poor solvent for polystyrene at 22°C and cyclopentane is a theta solvent. Since the mixed solvent is a better solvent for the polymer chain than either pure solvent<sup>3,14</sup>, we anticipate somewhat enhanced coil dimensions for the polymer in the mixed solvents. From previous studies, one expects the best solvent for the polymer to be the 1:1 mixture of acetone and cyclopentane<sup>3,14</sup>. Nevertheless, because the molecular weights of the polymers examined here are so low, the changes in the mean dimensions of the polymer coil caused by altering the solvent composition are undoubtedly small.

What we observe in Figure 3 is probably a competition between solvation of the exciplex by acetone and by the phenyl substituents of the polymer. In the model system no polymer is present, and the lowermost curve is obtained. The exciplex maxima for both polymer samples in cyclopentane exhibit a small red-shift compared to the model compound. The shift is somewhat larger for the longer polymer. These observations point to a preferential solvation of the exciplex by the phenyl groups on the polystyrene. This effect is far more pronounced for the polymer samples in acetone. Here, too, the exciplex maxima appear in the region of  $21000$   $\text{cm}^{-1}$ , now strongly blue-shifted from that of the model compound. There is strong preferential solvation of the exciplex by the polymer, and the long-chain polymer is more effective. As the 'dielectric enrichment' occurs after exciplex formation, the chain conformation changes until the equilibrium is attained. For the short chains examined here, the Rouse relaxation time is of the order of some tens of nanoseconds and relaxation to equilibrium must occur during exciplex emission.

The behaviour of the system in the solvent mixtures is more complex. Addition of acetone to the polymer solutions in cyclopentane, or of cyclopentane to the polymer solutions in acetone, both provoke a strong red-shift in the maxima of the exciplex emission. This strange behaviour reflects a competition between conflicting demands on the system. Mixtures of cyclopentane and acetone are better solvents for the polymer than either individual solvent. The way this operates at a molecular level is not well understood, but the excluded-volume effects of cosolvency have a particularly large effect on cyclization probability<sup>3</sup>. This cosolvency effect competes with the solvation preferences of the exciplex, which seems to prefer solvation by phenyl groups. Excluded volume suppresses the more compact polymer conformations that provide this solvation. Chain stiffness may also play a role, since in the sample of  $M_n = 1970$ , an oligomer containing  $\sim 20$  styrene units, the chain competes much less effectively with solvent than in the sample of  $M_n = 3400$ .

It will be interesting to extend these experiments to

samples of longer chain length. Here the experiments become progressively more difficult because the amount of exciplex formed decreases so strongly with increasing polymer molecular weight. We hope to explore in the future the extent to which such experiments are feasible.

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