Polystyrene fluorescence in cosolvent mixtures

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Fluorescence of atactic monodisperse and isotactic polystyrenes has been measured in liquid mixtures showing cosolvent behaviour, as a function of the solvent composition. Polymer intrinsic viscosities and solvent liquid viscosities have also been measured as a function of the solvent mixture composition. The ratio of excimer to monomer intensities changes slowly with solvent viscosity and is almost independent of the hydrodynamic volume of the coil. Three alternative mechanisms for intramolecular excimer formation were considered to explain the observed behaviour: (i) energy trapping by preformed dimers, the concentration of which is configuration-dependent; (ii) long-range excimer formation by chain recoiling, whose contribution depends on segment density; and (iii) segmental rotation to the sandwich conformation during the monomer excited-state lifetime, whose probability depends on solvent viscosity. It is concluded that, for atactic polystyrene, the largest contribution comes from the first mechanism, whilst for isotactic polystyrene, segmental rotation appears to be the predominant mechanism. Long-range excimers play a negligible role in the excimer formation process for either tactic form.

(Keywords: fluorescence; polystyrene; cosolvent mixtures; intrinsic viscosity; hydrodynamic volume)

INTRODUCTION

Polystyrene (PS) fluorescence has been extensively studied[1-7], but it is not yet completely understood. Of special interest is excimer emission, a red-shifted band with respect to monomer emission, which is originated by excited-state complexes called excimers. These are formed by two chromophores, one in the ground state and the other in the first singlet excited state (talking about fluorescence), when they are able to approach each other within a close distance (about 3 Å) with a relative orientation giving extensive overlap of their π electron clouds.

In the present work we deal with PS emission in several solvent mixtures. The influence of solvent quality[2], temperature[3,4], pressure[5], and polymer molecular weight[6,7] or tacticity[4] in PS excimer emission has already been studied. But the properties in different single solvents are difficult to correlate. The advantage of solvent mixtures is that each property of the liquid medium varies smoothly and monotonically with composition, and in this way it is easier to establish the dependence of emission on the properties of the system.

We have chosen solvent mixtures for PS which show the phenomenon of cosolvency. A cosolvent mixture[8] results by mixing two poor solvents or precipitants such that at intermediate compositions their mixture is a good solvent of the polymer. In this way, coil expansion can be varied in a broad range, from below theta conditions to large effective coil volume, just by changing solvent composition. The cosolvent mixture reported here for PS also has the advantage that the viscosities of the two pure liquids composing the mixture are very different and therefore the influence of the viscosity of the medium can also be studied.

EXPERIMENTAL

Polystyrene Monopol standards have been purchased from Polysciences. Two samples of 1.1×10^5 and 4.4×10^5 molecular weight and polydispersity less than 1.17 were employed. Residual monomer was eliminated by precipitation in benzene/diethyl ether as solvent/precipitant and subsequent freeze-drying.

Isotactic polystyrene ($M_v = 3 \times 10^5$) was provided by Dr M. R. Gómez-Antón (UNED) who synthesized it with a Ziegler–Natta catalyst[9]. ^{13}C n.m.r. spectra give practically 100% isotacticity. It was purified by the same procedure as the atactic samples.

Solvents used were from Carlo Erba of different quality, RS for fluorimetry and RPE for viscometry.

An Ubbelohde modified viscometer has been employed for solvent and polymer solution viscosity determinations. Temperature was kept at 20.00±0.05°C, and polymer concentration was below 0.8×10^{-2} g cm^{-3}. Intrinsic viscosity $[\eta]$ was obtained from the Huggins and Kraemer extrapolations.

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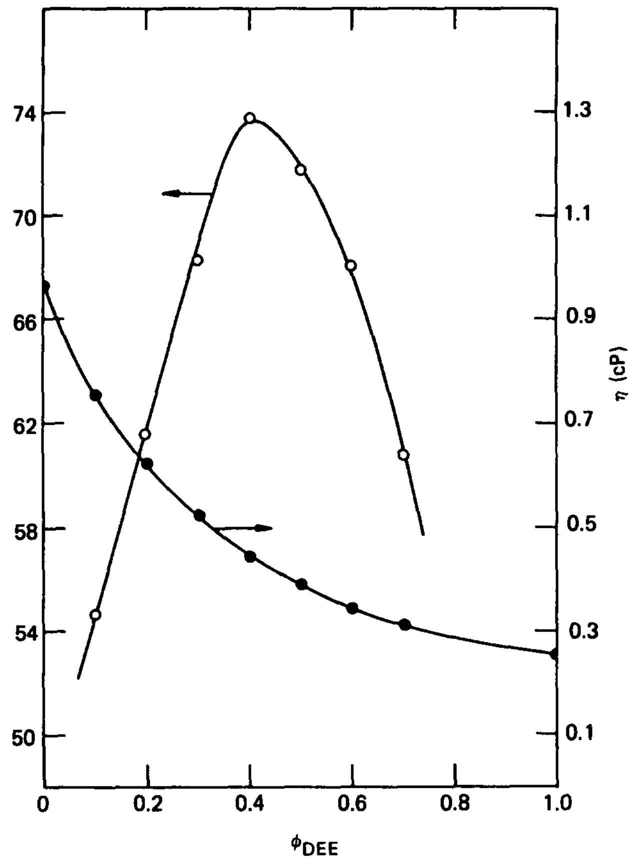


Figure 1 Intrinsic viscosity $[\eta]$ of at-PS and solvent viscosity η for the cosolvent mixture Ch–DEE as a function of the DEE volume fraction ϕ_{DEE} in the solvent

Emission spectra have been recorded in a Perkin-Elmer LS-3 fluorometer at 20.0°C, with 250 nm excitation wavelength and with a chromophore concentration of 1.6×10^{-3} M (optical density about 0.3) to avoid autoabsorption.

RESULTS

Cyclohexane (Ch) is a poor solvent for PS ($\theta = 34.5$°C for atactic PS)[10] and diethyl ether (DEE) is a precipitant of any tactic form of the same polymer. Mixtures of both solvents are good solvents for atactic PS (at-PS) at room temperature, but they do not dissolve our crystalline isotactic PS (it-PS).

Cosolvency is associated with large positive excess Gibbs energy of the solvent binary mixture[8,11]. This has prompted the explanation that the cosolvent action is due to the repulsive interactions between the molecules of the two solvent components, which favour the formation of polymer–solvent contacts in the ternary system. It seems that these repulsive interactions in the Ch–DEE pair are not enough to solubilize the isotactic crystalline PS ($\theta > 34.5$°C in Ch), although they give good solvent behaviour with the atactic sample.

Intrinsic viscosity ($[\eta]$) of at-PS and solvent viscosity (η) in the cosolvent Ch–DEE are shown in *Figure 1* as a function of DEE volume fraction in the solvent mixture (ϕ_{DEE}). Here $[\eta]$ shows the behaviour typical[12] of cosolvent systems, namely a pronounced maximum (at about $\phi_{DEE} = 0.5$) that corresponds to the best solvent quality. Adding less than 50% DEE to Ch, the solvent quality improves and, as a consequence, the coil expands. Above 50% DEE, polymer solubility decreases on adding more DEE and, therefore, the hydrodynamic volume decreases, the coil becoming more compact.

The solvent viscosity also suffers a large variation, decreasing as DEE is being added. Segmental diffusion of the polymer in solution is therefore favoured by adding DEE.

Figure 2 shows the same quantities for the same polymer in the mixture Dx–DEE (Dx = dioxane). Here $[\eta]$ again shows a maximum like the one of the cosolvent Ch–DEE because the Dx–DEE mixture also has a large positive excess Gibbs function. However, the mixture of DEE with Dx is not truly a cosolvent, because Dx is a good solvent of the polymer ($[\eta]$ in pure Dx is above $[\eta]_\theta$ instead of below as it is in pure Ch). Solvent viscosity is again a decreasing function of ϕ_{DEE}.

PS fluorescence spectra show the usual two bands corresponding to monomer (about 285 nm) and excimer (about 330 nm) emissions. The relative intensities of these two bands depend on solvent composition, as can be seen in *Figures 3* and *4*, for two of the systems here studied.

Corrections for band overlap are very small. We have used benzyl acetate as the model compound to correct for the influence of the monomer on the excimer band. At 330 nm, the model emission is 10% of its maximum intensity. This amounts to a correction of only $\simeq 2\%$ in the excimer band intensity read at 330 nm. Likewise, we have neglected the influence of excimer on the monomer band at 285 nm, since the excimer band extrapolates to zero intensity at such wavelengths.

Polymer concentrations (1.6×10^{-3} M) are below the critical concentration for coil overlap and the results for the Huggins constant (k_H) show no sign of polymer

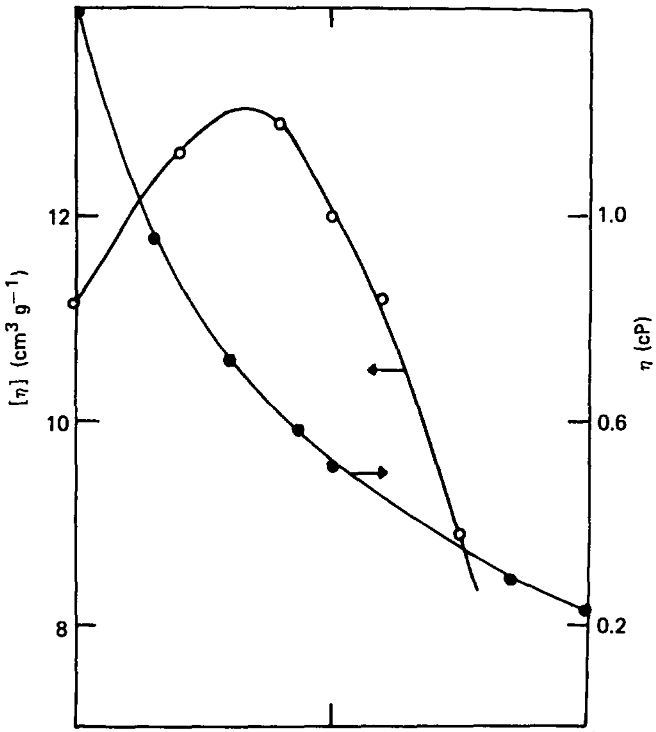


Figure 2 Intrinsic viscosity $[\eta]$ of at-PS and solvent viscosity η for the solvent mixture Dx–DEE as a function of the DEE volume fraction ϕ_{DEE}

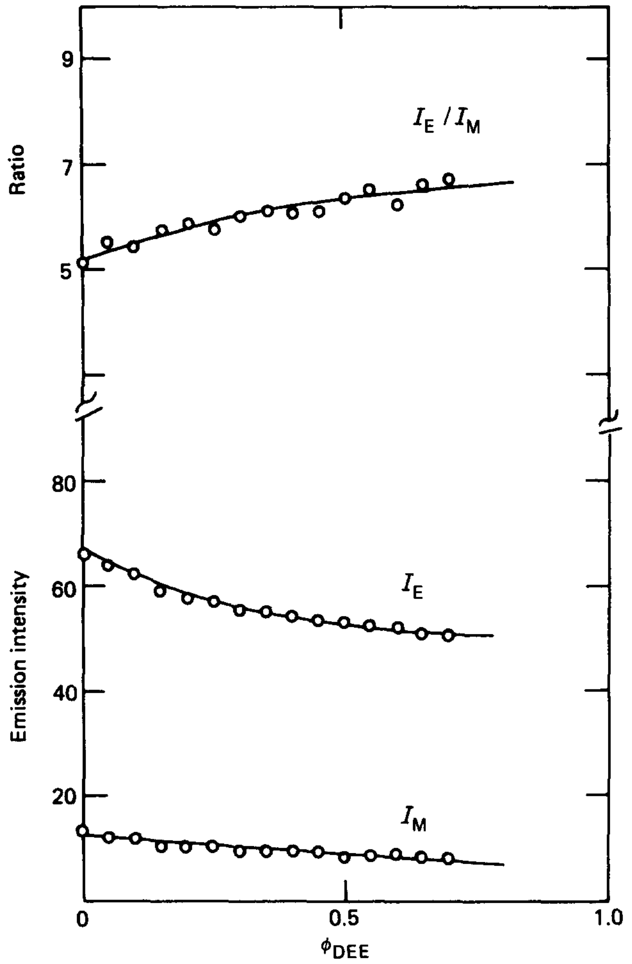


Figure 3 Variation of the excimer (I_E) and monomer (I_M) emission intensities and the ratio I_E/I_M as a function of DEE volume fraction in the solvent mixture for the system at-PS/Ch+DEE

aggregation; therefore we can conclude that the observed excimers are intramolecular.

DISCUSSION

Monomer (I_M) and excimer (I_E) emission intensities are frequently explained by the standard kinetic scheme of Birks[1], assuming stationary conditions

$$\frac{I_E}{I_M}=\frac{k_{FE}k_{EM}[M]}{k_{FM}(k_E+k_{ME})} \qquad (1)$$

where k_{FE} and k_{FM} are rate constants for excimer and monomer radiative decay, k_{ME} corresponds to excimer dissociation to excited monomer, k_{EM} corresponds to excimer formation, [M] represents the concentration of monomer units with conformation adequate for excimer formation, and k_E is the rate constant for excimer decay, both by radiative and non-radiative pathways.

We assume that the most important mechanisms for excimer formation in PS and polystyrene-like polymers are the three represented below.

(i) The first one corresponds to energy trapping or direct excitation of one of the chromophores of the preformed dimers in the ground state. Such dimers correspond to *tt* conformers in meso diads and to *tg* conformers in racemic diads. It can be assumed that their

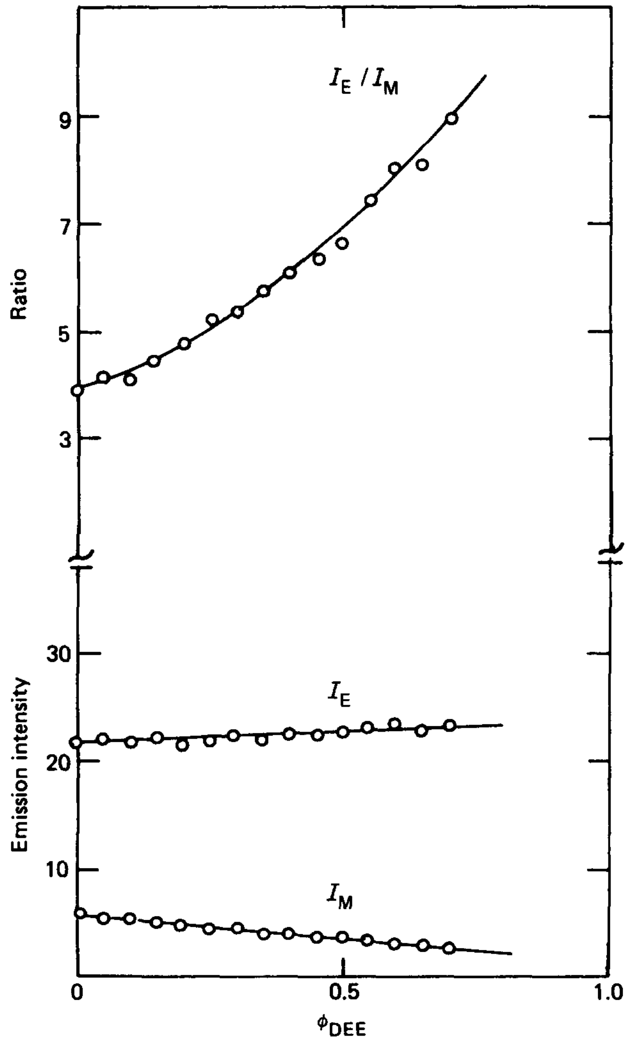
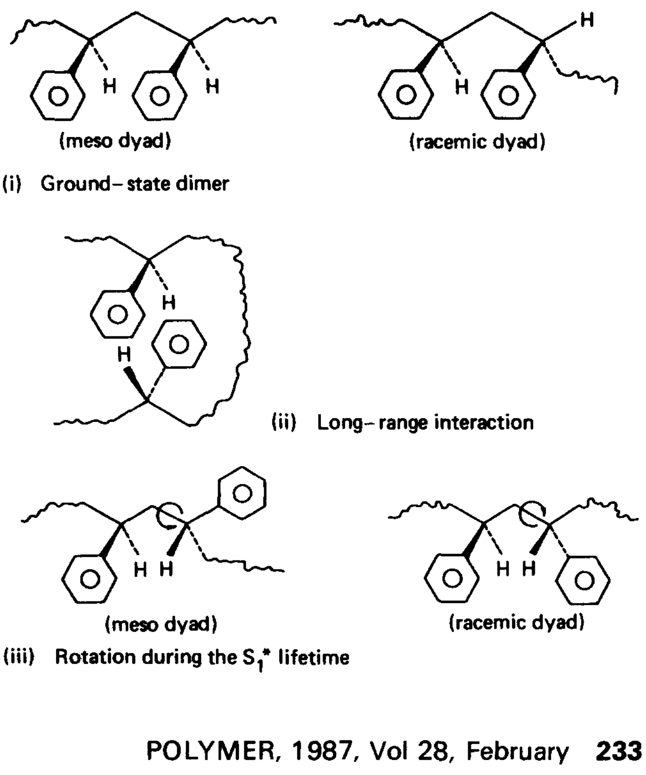


Figure 4 Variation of the excimer (I_E) and monomer (I_M) emission intensities and the ratio I_E/I_M as a function of DEE volume fraction in the solvent mixture for the system it-PS/Dx+DEE

Mechanisms of excimer formation in PS solutions



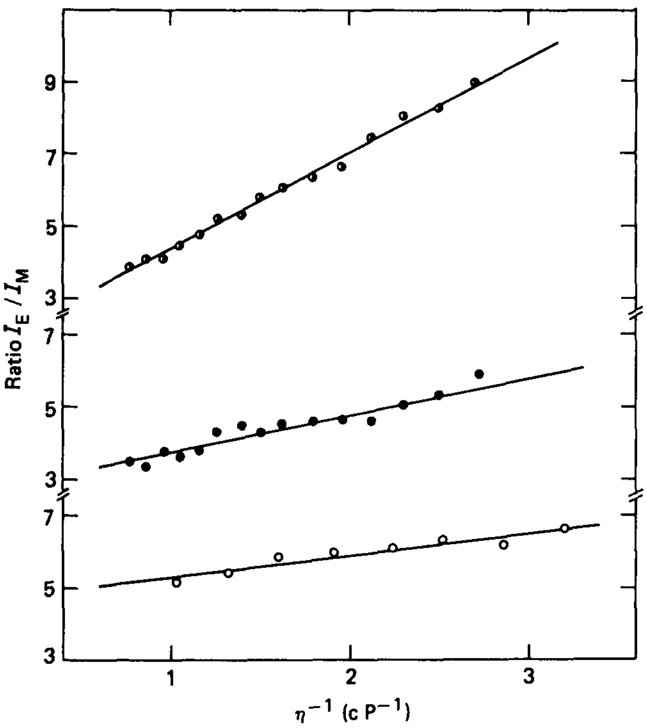


Figure 5 Excimer to monomer intensity ratio (I_E/I_M) as a function of the inverse of solvent viscosity (η^{-1}) for the three systems studied here: ○, at-PS/Ch+DEE; ●, at-PS/Dx+DEE; ◑, it-PS/Dx+DEE

probability of occurrence is dependent only on polymer tacticity.

(ii) The second proposed mechanism is the formation of excimers by chain recoiling. Two chromophores, which are separated by several monomeric units along the chain contour, come into contact in a suitable sandwich structure. This is thus a long-range interaction. It can be assumed that the contribution of this mechanism to the total excimer concentration is proportional to the segmental density inside the coil, that is to say, for a given molecular weight it is proportional to $[\eta]^{-1}$.

(iii) The last mechanism considered here is the rotation of one skeleton bond during the lifetime of one chromophore in the excited state, thus placing it together in a suitable position with another one in the ground state. For a given polymer–solvent system, it can be assumed that the segmental rotation probability is inversely proportional to the solvent viscosity.

Finally, assuming that the three mechanisms are independent, the rate constant for excimer formation can be expressed as

$$k_{EM}[M]=k_1[D]+k_2[\eta]^{-1}+k_3\eta^{-1} \qquad (2)$$

where k_1, k_2 and k_3 are the rate constants for the respective mechanisms and [D] is the concentration of preformed dimers.

At zero segmental density and infinite solvent viscosity (solid state), only the first mechanism is operative and then

$$\lim_{[\eta]^{-1},\eta^{-1}\to 0} k_{EM}[M]=k_1[D] \qquad (3)$$

The relative contribution of mechanism (i) to the total excimer emission is therefore

$$\frac{k_1[D]}{k_{EM}[M]}=\frac{(I_E/I_M)^0}{(I_E/I_M)} \qquad (4)$$

where $(I_E/I_M)^0$ is the extrapolated value at $\eta^{-1}=[\eta]^{-1}=0$.

In our model, the influence of energy migration in excimer formation is included in rate constant k_{EM}.

The relative contribution of mechanism (ii) (long-range excimers) can be neglected for the systems studied here. The dependence of $[\eta]$ on solvent composition (*Figures 1* and *2*) passes in all cases through a maximum, whereas I_E, I_M and I_E/I_M change monotonically with the solvent mixture composition (*Figures 3* and *4*). Besides, the ratio I_E/I_M shows a linear dependence on η^{-1} (*Figure 5*) that is destroyed when $\eta^{-1}+a[\eta]^{-1}$ is used instead of η^{-1} for any value of the coefficient a. This result is in accordance with previous reports[2,7,13–17]. However, this final conclusion has been rather controversial and there are also a few other reports supporting the opposite conclusion, that long-range excimers can be an important contribution for PS and styrene copolymers[18].

The linearity of I_E/I_M *versus* η^{-1}, as shown in *Figure 5*, extends over a wide range of η^{-1} values and allows for a reasonable extrapolation to $\eta^{-1}\to 0$, thanks to the very different viscosities of the solvents chosen in this study.

Table 1 summarizes the relative contribution of the preformed dimer mechanism for iso- and at-PS. It seems that in it-PS excimers are predominantly formed by mechanism (iii), that is to say, by rotation of the backbone to get an adequate face-to-face conformation of two neighbouring rings. In contrast, in at-PS the predominant mechanism is controlled by the number of preformed dimers and only about one-third of the excimers are formed by segmental rotation. This is in accordance with the larger dynamic flexibility of it-PS with respect to at-PS. Conformational analysis of model systems formed by two joined monomeric units reveals too that the rotational barrier between *tt* and *tg* conformers for the racemic isomer is larger than that corresponding to *tg*→*tt* conformers for the meso compound[19,20].

CONCLUSIONS

Recoiling of long PS chains does not put together pairs of aromatic rings from non-neighbouring monomer units long enough to form excimers.

Therefore, the only mechanisms that contribute to the formation of intramolecular excimers are: excitation of one of the chromophores in a preformed ground-state dimer by direct absorption of light or by trapping a photon from energy migration; and segmental rotation to get two neighbouring rings in a suitable position during the lifetime of the first singlet excited state of one of them.

In it-PS the largest contribution comes from the second mechanism but in at-PS is the opposite, in accordance

Table 1 Contribution of the preformed dimer mechanism to the total excimer formation as given by equation (4) in different systems

Polymer	Solvent	$\frac{(I_E/I_M)^0}{(I_E/I_M)}$
at-PS	Dx–DEE	0.63
at-PS	Ch–DEE	0.78
it-PS	Dx–DEE	0.29

with the larger segmental mobility of it-PS. Quantification of these mechanisms is given in *Table 1*.

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