

## Tacticity dependence of excimer formation in polystyrene solutions

Dominique Sarazin\*, Joseph (Y.S.) Gan, and Jeanne François

Institut Charles Sadron, Centre de Recherches sur les Macromolécules, 6 rue Boussingault, F-67083 Strasbourg Cédex, France

### SUMMARY

This work deals with the excimer formation in dilute solution for a series of polystyrenes of various tacticity prepared by epimerization of an initial isotactic sample. The main result is that the relative excimer yield remains equal to that obtained for iPS if the percentage of isotactic dyads is higher than 65%. The range of energy migration could be roughly approximated to 6 chromophores.

### INTRODUCTION

The intramolecular excimer formation for polystyrene in bulk or in solution has been extensively studied<sup>(1)</sup>. It has been shown that the quantum yield of excimer emission for isotactic polystyrene (iPS) is much higher than that obtained with atactic polystyrene (aPS)<sup>(2,3)</sup> and this fact was puzzling since the distance between two chromophores in the isotactic structure seemed to be too high to allow excimer formation. Klöpffer<sup>(4)</sup> has suggested that the excimer sampling involves an initial excitation of a chromophore group followed by singlet exciton migration along the chain until a site geometrically suitable to excimer formation. The fraction of excimer forming sites depend on the difference of energy,  $\Delta E$ , between the excimer site and the ground state conformations<sup>(5)</sup>. From the calculations of Flory<sup>(6)</sup>, it can be concluded that  $\Delta E$  is smaller in the isotactic case and this explains that isotacticity favours excimer formation<sup>(3)</sup>. Nevertheless as already pointed out by Semerak and Frank<sup>(1)</sup> it should not be possible to predict the fluorescence behavior by simply averaging over the triad population without taking into account energy migration. Numerous studies on copolymers of vinyl monomers with

\* To whom offprint requests should be sent

spectroscopically inert monomers suggest that energy migration has sufficient range to "jump" over short sequences of the inert monomers<sup>(1,7-8)</sup>.

No systematical investigation of excimer formation in polystyrene of tacticity ranging between that of iPS (100% iso dyads) and that of aPS (around 45% of iso dyads whatever the method of polymerization) has been already made, at least at our knowledge. Starting from an iPS sample and modifying it by an epimerization reaction, as described by Shepherd et al.<sup>(9)</sup>, it is possible to obtain a series of PS of various tacticity. We have prepared, characterized such samples and studied their capability to form physical gels, in a previous work<sup>(10)</sup>. We give in the present paper results dealing with the excimer formation and which could be of some interest in the understanding of the phenomenon of energy migration

## EXPERIMENTAL

The iPS sample was prepared by the classical Natta method and the aPS sample was obtained by anionic synthesis.

The synthesis<sup>(9)</sup> of epimerized polystyrene samples (ePS) and their fractionation, characterization by light scattering, gel chromatography, viscosimetry, <sup>1</sup>H NMR have been already described<sup>(10)</sup>. Among the different fractions of ePS, we have selected those of weight average molecular weight ranging between  $1.68 \cdot 10^5$  and  $1.84 \cdot 10^5$  and of polydispersity indices ranging between 1.2 and 1.4.

In table 1 are reported the molecular characteristics of the samples used in this work and some of their statistical data. By starting from the Monte-Carlo method suggested by Shepherd et al.<sup>(9)</sup>, we have determined the average lengths of the iso and syndio sequences ( $n_m$  and  $n_r$  respectively)<sup>(10)</sup>. It must be pointed out that the epimerization at low reaction yield favours the even syndio sequences with respect to a bernoullian distribution calculated from the same values of dyad fractions. This explains that  $n_r$  is never lower than 2. Nevertheless, at high reaction yield, the distribution joins again that obtained from a bernoullian statistics which corresponds to the case of "atactic" polystyrene prepared by a classical polymerization method (anionic or radical)

Fluorescence spectra were recorded with a RF 540 Shimadzu spectrofluorometer coupled with a Data recorder DR-3. Fluorescence measurements were conducted at an excitation frequency of 255 nm with an emission slit width of 5nm and an excitation slit width of 10nm. The solutions in 1-2 dichloroethane were not desaturated and the polymer concentration was 30 mmole.l<sup>-1</sup> (chromophore units).

TABLE 1

| sample | $M_w * 10^{-5}$ | I    | m    | $n_m$ | $n_r$ | $n_{rmax}$ |
|--------|-----------------|------|------|-------|-------|------------|
| IPS    | 3.4             | 2.8  | 1.00 |       |       |            |
| E40    | 1.7             | 1.20 | 0.93 | 12.7  | 2.00  | 2          |
| E85    | 1.7             | 1.25 | 0.84 | 9.1   | 2.09  | 4          |
| E150   | 1.6             | 1.44 | 0.76 | 5.4   | 2.19  | 6          |
| E300   | 1.8             | 1.37 | 0.64 | 3.3   | 2.26  | 8          |
| E400   | 1.6             | 1.40 | 0.55 | 2.4   | 2.30  | 10         |
| aPS    | 1.0             | 1.10 | 0.45 | 1.9   | 2.38  | 14         |

$M_w$  : Weight average molecular weight measured by LS

I : polydispersity index obtained by GPC

m : fraction of isotactic dyads from <sup>1</sup>H NMR experiments

$n_m$  and  $n_r$  : average length of iso and syndiotactic sequences respectively and  $n_{rmax}$  : maximum length of syndiotactic sequences (probability of longer sequences lower than 1/1000) obtained by statistical calculations from values of m and assumptions about epimerization mechanisms<sup>(9,10)</sup>

## RESULTS AND DISCUSSION

The fluorescence emission spectra of isotactic and atactic polystyrene and those of epimerization products E300 and E400 are shown in Fig.1 as typical cases. Each of them consists of two main bands : one is assigned to the monomer emission and the other to the excimer

emission. Their maximum are about  $3.54 \times 10^{-4}$  and  $3.01 \times 10^{-4} \text{ cm}^{-1}$  respectively, in good agreement with the literature data<sup>(2-3)</sup>.

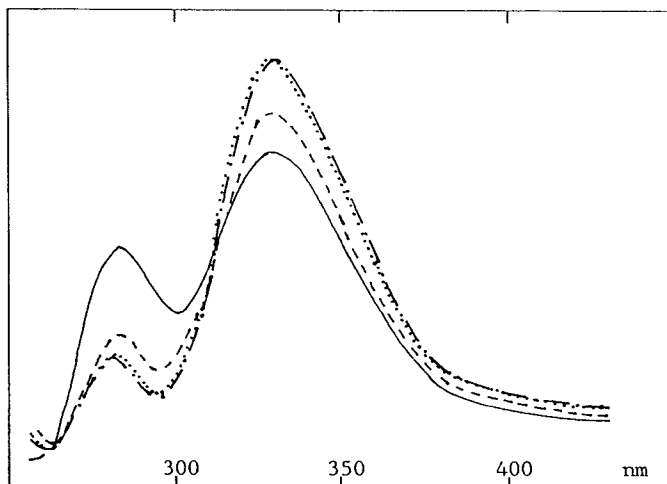
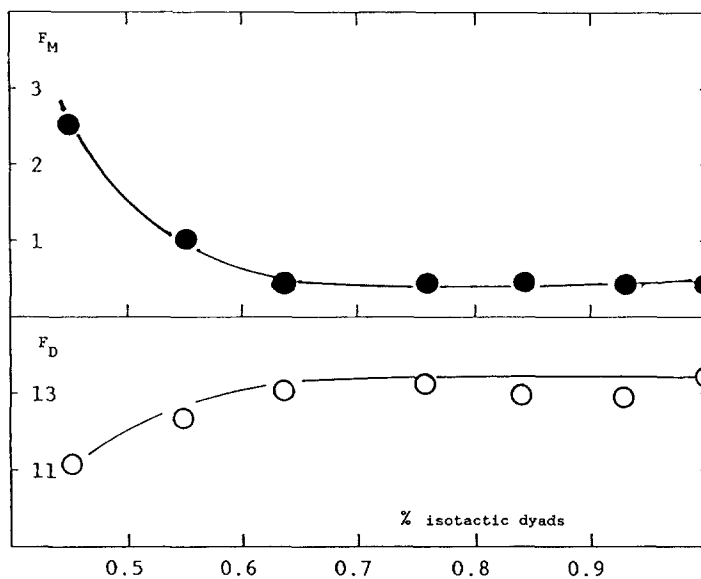
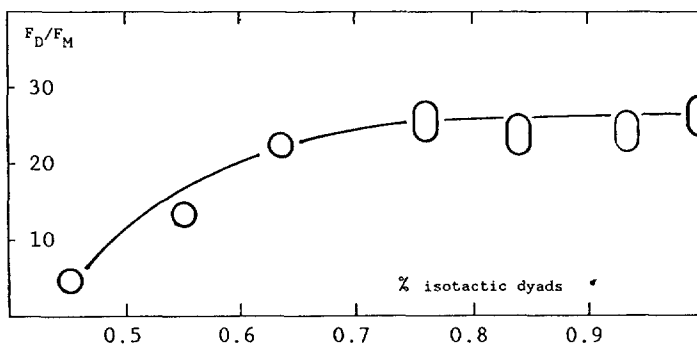


Fig. 1 : Fluorescence spectra of aPS (—) , E400 (- - -) , E300 (.....) and iPS (- · -)

The tacticity dependence of the relative quantum yield of monomer ( $F_M$ ) and excimer ( $F_D$ ) bands is shown in fig. 2A. With increasing isotactic dyad fraction the relative quantum yields of the monomer and excimer emission decreases and increases respectively and both reach limiting values at about 65% of isotactic dyads. The ratio of the relative quantum yields of excimer to monomer ( $F_D/F_M$ ) becomes also nearly constant above this limit (Fig.2B). The value of this ratio (4.5) found for our atactic PS sample of  $M_w=10^5$  is in very good agreement with that given by Ishii et Al.<sup>(2)</sup> for  $M_w > 10^4$ . For pure isotactic polystyrene, the quantum yield of monomer emission becomes very low and its determination is not as accurate as for atactic polystyrene. This explains the discrepancy between the literature data. For instance Ishii et Al. have found  $(F_D/F_M)=15.4$  while our value of  $(F_D/F_M)$  is 23. Nevertheless such results clearly show that the excimer formation does not depend on the tacticity if the isotactic dyad fraction is higher than 65%.



A



B

Fig. 2 : A : Tacticity dependence of the relative quantum yield of excimer (○) and monomer (●) emission bands  
 B : Tacticity dependence of the ratio of the relative quantum yields of excimer to monomer emission band

Frank and Harrah<sup>(5)</sup> have expressed the fraction of sites geometrically suitable to excimer formation according to:

$$f_E = \frac{W_E \cdot \exp(-\Delta E/kT)}{W_G + W_E \cdot \exp(-\Delta E/kT)}$$

where  $W_E$  and  $W_G$  are the degeneracies of the excimer and ground states respectively and  $\Delta E$  is the energy of the excimer site conformation with respect to the ground state. As recalled in introduction, it can be shown that  $\Delta E$  between the ground states ( $g^+t$  and  $tg^-$ ) and the simply degenerate excimer state ( $tt$ ) in the iso dyads is lower than  $\Delta E$  between ground states ( $tt$  and  $g^+g^+$ ) and excimer states ( $tg^-$  and  $g^-t$ ) in the syndio dyads. If it was possible to neglect the energy migration phenomenon, the ratio  $F_D/F_M$  could be expected to vary as  $1/m$  (where  $m$  is the fraction of iso dyads) since the fraction of excimer forming sites varies as  $m$ . In fig.3, it is clear that the variation of  $F_D/F_M$  with  $1/m$  is far to be linear and such a result is consistent with the suggestion of Semerak and Frank<sup>(1)</sup> according which the energy migration has sufficient range to "jump" over short sequences of monomers. By considering the statistical data of Table 1, it appears that the introduction of syndiotactic sequences of average and maximum length lower to 2.2 and 6 respectively does not modify the excimer formation with respect to the pure isotactic polystyrene.

From the Förster dipole-dipole estimate of the nearest neighbour energy migration rate, the range of the migration process should be 2-3 chromophores for polystyrene<sup>(1)</sup>. The same estimation for poly(2 vinyl naphthalene) gives a value of 10 chromophores while the experiments are only consistent with a range of migrating singlet state approximately 10 times higher. Although we have not tried to calculate the energy migration rate in epimerized polystyrenes, our work seems to show that the range of the migration is also higher than the theoretical value since the presence of syndio sequences as long as 6 chromophores does not induce a decreasing of the excimer yield. However, when the maximum length of these sequences becomes higher than 6, the behavior abruptly changes and we could conclude that the maximum range of energy migration is of the order of 6 chromophores.

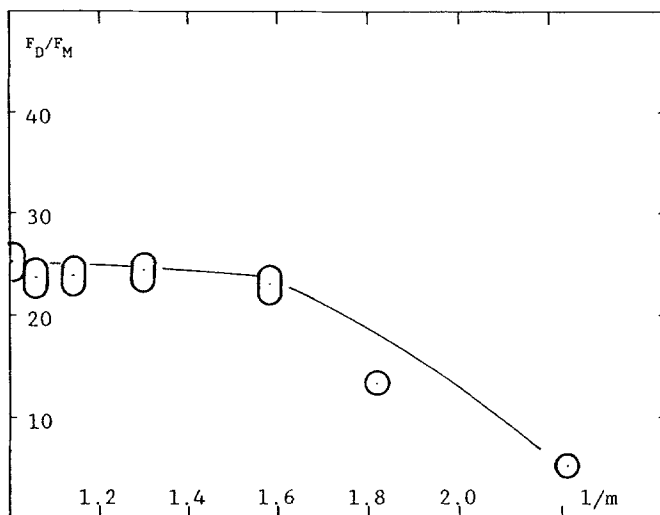


Fig.3 : Dependence of the ratio of the relative quantum yields of excimer band on the monomer band on the reciprocal isotactic dyad fraction

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