

# Dynamics of macromolecular chains. Excimer formation of poly( $\alpha$ -methylstyrenes) in solution

Liliane Bokobza and Lucien Monnerie

Laboratoire de Physico-Chimie Structurale et Macromoléculaire E.S.P.C.I. — 10, rue Vauquelin, 75231 Paris Cédex 05, France

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Intramolecular excimer formation has been investigated in two samples of poly( $\alpha$ -methylstyrenes) over the temperature range  $-80^{\circ}$  to  $+80^{\circ}\text{C}$ . The ratio of the emission intensities of dimer and monomer ( $I_D/I_M$ ) is very sensitive to the tacticity of the polymer. The results reveal a rather large difference in excimer stability between polystyrene and poly( $\alpha$ -methylstyrene). On the other side, poly( $\alpha$ -methylstyrene) exhibit a higher efficiency of excimer formation than polystyrene. Activation energy for excimer formation in the case of a syndiotactic diad is lower in poly( $\alpha$ -methylstyrene) than in polystyrene. This is consistent with conformational energy calculations.

## INTRODUCTION

Intramolecular excimer formation occurs in many vinyl aromatic polymers. The formation of the excimer state results from the association of two aromatic groups separated by a three carbon chain, one of which has been electronically excited. The configurational requirements for intramolecular excimer formation was first outlined by Hirayama<sup>1</sup> in his study of diphenyl and triphenyl alkanes which are model compounds for vinyl polymers.

Excimer fluorescence of dilute solutions of polystyrene has been a subject of considerable interest<sup>2-8</sup>. Intramolecular excimer formation in poly-*o*-, *m*- and especially *p*-methylstyrenes has been largely investigated by Ishii *et al.*<sup>5,6,8,9</sup> but little attention has been paid to excimer formation in poly( $\alpha$ -methylstyrenes)<sup>10,11</sup>. The purpose of the present work is to discuss the influence of temperature on monomer chromophore and excimer emissions in fluid solutions of two samples of poly( $\alpha$ -methylstyrene) of different tacticity. It will be shown that the effect of temperature on the emission spectrum is different to that observed in polystyrenes and its model molecules.

## EXPERIMENTAL

The cationically polymerized poly( $\alpha$ -methylstyrene) (c-P $\alpha$ MS), was prepared at  $-78^{\circ}\text{C}$  with  $\text{BF}_3\text{OEt}_2$  as catalyst and had a number average molecular weight of 336 000. The anionically polymerized poly( $\alpha$ -methylstyrene) used, (a-P $\alpha$ MS), was a commercial sample supplied by the Polymer Laboratories Ltd. Its molecular weight was 90 000. Polystyrenes and their model compounds were also used for purpose of comparison with poly( $\alpha$ -methylstyrenes): atactic polystyrene (at-PS) ( $M_w = 110\,000$ ) was obtained from the Pressure Chemical Company; isotactic polystyrene (it-PS) was polymerized with  $\text{Al}(\text{C}_2\text{H}_5)_3 - \text{TiCl}_4$  in benzene at  $60^{\circ}\text{C}$ ; the 2,4-

diphenylpentane was prepared by the method of Overberger and Bonsignore<sup>12</sup>.

The study was carried out in 1,2-dichloroethane between  $-30^{\circ}$  and  $80^{\circ}\text{C}$  and in methylene chloride between  $-80^{\circ}$  to  $25^{\circ}\text{C}$ , the two solvents were supplied by Merck and used without further purification.

Emission spectra were recorded on a Fica Model 55 MK II spectrofluorometer equipped with a 450 W Xenon lamp and a R 212 photomultiplier tube. Emission spectra were automatically corrected for instrumental response. The excitation wavelength was 260 nm in all cases. The concentrations of solutions were adjusted to the same optical density at 260 nm (0.2). Measurements were made on solutions that were carefully degassed by a repetitive freeze-pump-thaw cycle. Sample heating was accomplished by circulating a temperature controlled aqueous solution of ethylene glycol in the cell holder. Sample cooling was accomplished by a flow of gaseous nitrogen precooled to the desired temperature and obtained from liquid nitrogen. The  $^{13}\text{C}$  n.m.r. spectra of poly( $\alpha$ -methylstyrenes) were observed in *ortho*-dichlorobenzene at  $80^{\circ}\text{C}$ , and that of atactic polystyrene in chloroform at  $55^{\circ}\text{C}$ . These spectra were measured using a Jeol PS 100 spectrometer. The microtacticity of the polymers was determined from the relative areas of the  $\text{C}_1$  aromatic peaks interpreted according to Inoue *et al.*<sup>13</sup>.

c-P $\alpha$ MS, a-P $\alpha$ MS and at-PS were found to contain about 90, 70 and 74% syndiotactic diads respectively. These results are in qualitative agreement with those obtained by Inoue *et al.*<sup>13</sup>.

A Dupont Curve Resolver (Model 310) was used to analyze the  $^{13}\text{C}$  n.m.r. spectra as well as the fluorescence spectra.

## RESULTS

Figure 1 shows the fluorescence spectra of the samples in methylene chloride at  $25^{\circ}\text{C}$ . They consist of two emission

bands appearing for P $\alpha$ MS at 288 and 335 nm, for polystyrenes and their respective model compounds at about 285 and 330 nm. The higher energy band is assigned to the fluorescence of the monomer phenyl group, the lower energy band is attributed to the fluorescence of the intramolecular excimer.

Figure 2 shows temperature-dependent fluorescence spectrum of a-P $\alpha$ MS in methylene chloride and that of at-PS ( $M_w = 110\,000$ ) for purpose of comparison.

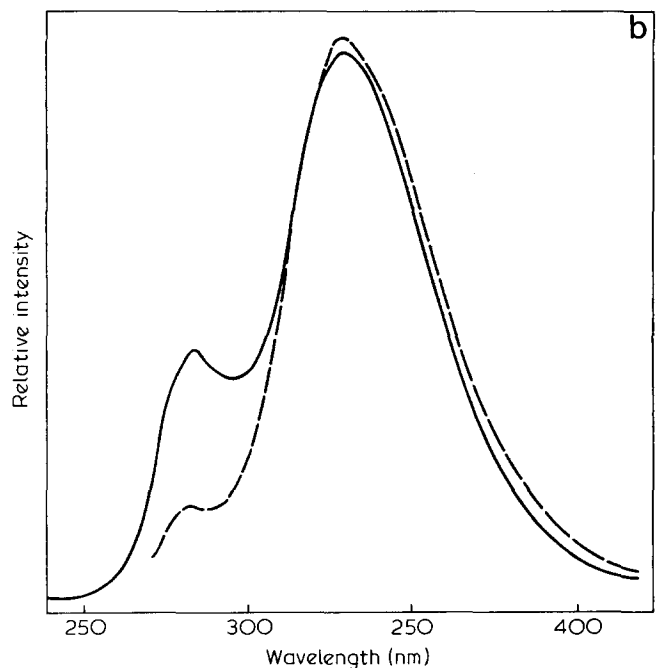
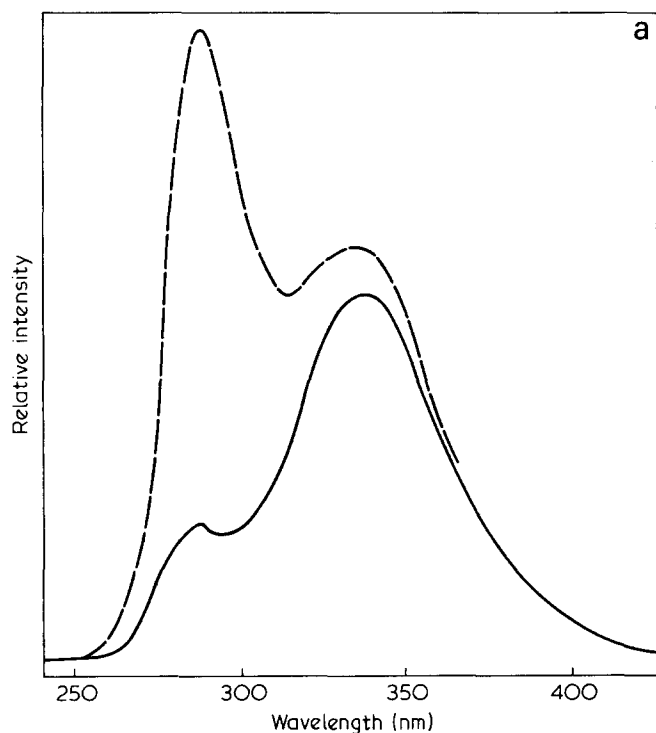


Figure 1 Corrected fluorescence spectra of degassed methylene chloride solutions at 25°C of: (a) poly( $\alpha$ -methylstyrenes), ---, cationically polymerized sample; —, anionically polymerized samples; (b) polystyrenes, —, atactic polystyrene; ---, isotactic polystyrene; (c) 2,4-diphenylpentanes, ---, *dl* isomer; —, *meso* isomer

The intensities of normal ( $I_M$ ) and excimer ( $I_D$ ) fluorescence in arbitrary units as a function of temperature are given in Figure 3.

Figure 4 gives a logarithmic plot of the ratio of excimer to monomer intensity ( $\ln I_D/I_M$ ) as a function of temperature.

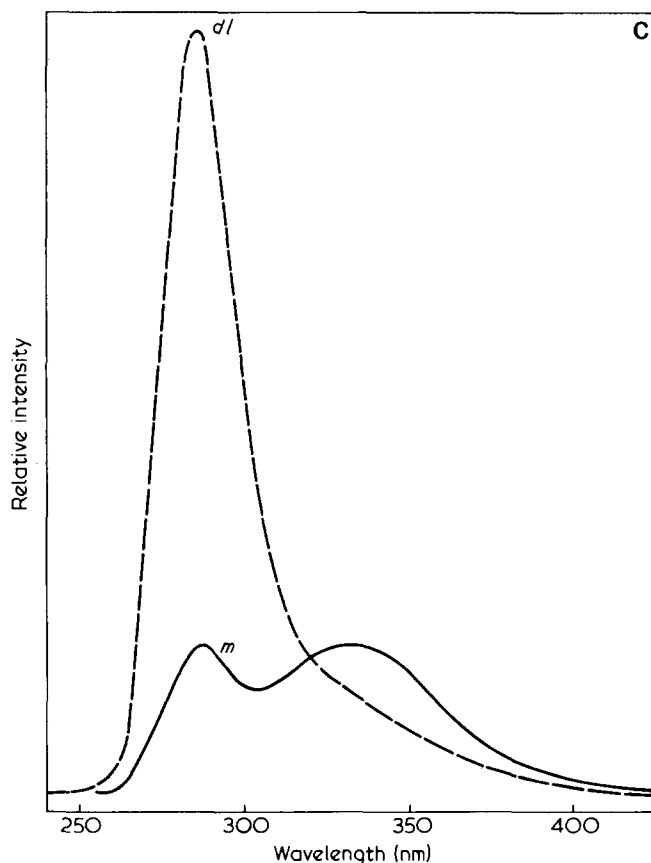
For poly( $\alpha$ -methylstyrenes), as the temperature of the solution is increased from low temperatures, the intensity of the monomer is observed to decrease while the intensity of the excimer band increases. But at temperatures exceeding  $-60^\circ\text{C}$  for a-P $\alpha$ MS and  $-30^\circ\text{C}$  for c-P $\alpha$ MS, the excimer band decreases greatly with increasing temperature (Figure 3). This behaviour is quite different from that of polystyrene for which Heisel and Laustriat<sup>4</sup> found that both excimer intensity (Figure 5) and lifetime are approximately independent of temperature between  $-40^\circ$  to  $+80^\circ\text{C}$ . A similar result has been obtained for 2,4-diphenylpentanes, the polystyrene model molecules<sup>14</sup>.

## DISCUSSION

To analyze the observed temperature dependence, we can recall the solution of the standard kinetic treatment<sup>15</sup>:

$$\frac{I_D}{I_M} = \frac{K_{FD}}{K_{FM}} \left[ \frac{K_a}{K_d + K_{ID} + K_{FD}} \right],$$

where  $I_D$  and  $I_M$  represent the intensities of normal and excimer fluorescence,  $K_{FD}$  and  $K_{FM}$  are the fluorescence rate constants of excimer and monomer,  $K_a$  is the association rate constant for excimer formation between a ground state and excited monomer,  $K_d$  is the rate constant for excimer dissociation and  $K_{ID}$  represents internal quenching of the excimer. This expression is used if several assumptions are valid.



$K_{FM}$  and  $K_{FD}$  have generally been found to be independent of temperature. The existence of an isoemissive point in solution spectra of dinaphthylalkanes between  $-100^\circ$  and  $-30^\circ\text{C}$  leads Chandross and Dempster<sup>15</sup> to infer that quenching processes are not competing with fluorescence:  $K_{ID} \ll K_{FD}$ . They further found that as the

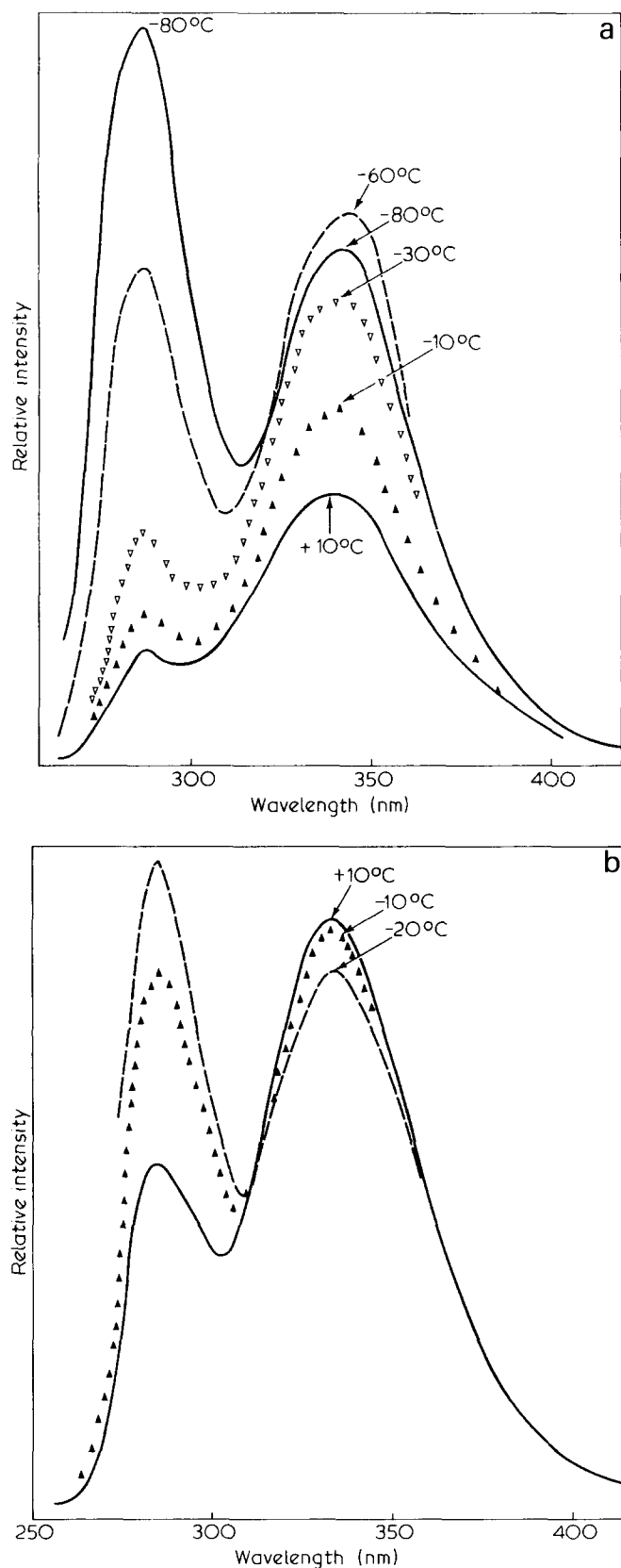


Figure 2 Temperature dependence of the emission spectrum in methylene chloride: (a) a-P $\alpha$ MS; (b) at-PS

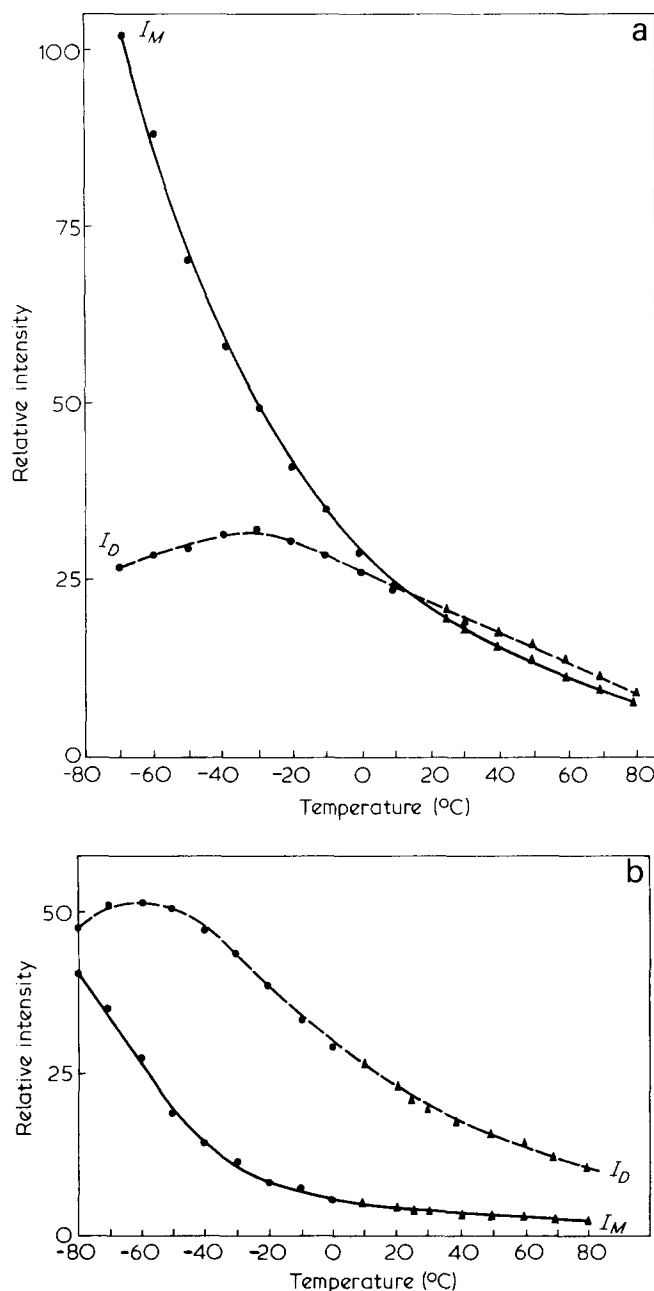


Figure 3 Temperature dependence of fluorescence intensity of excimer ( $I_D$ ) and monomer ( $I_M$ ) bands for poly( $\alpha$ -methylstyrenes):  $\bullet$ , in methylene chloride;  $\blacktriangle$ , in 1,2-dichloroethane. (a) c-P $\alpha$ MS; (b) a-P $\alpha$ MS

temperature was increased in the range  $-100^\circ$  to  $-30^\circ\text{C}$ , the excimer fluorescence also increased, implying that the region in which dissociation competes with dimer fluorescence has not been approached:  $K_d \ll K_{FD}$ . Under these conditions,  $I_D/I_M$  should be proportional to  $K_a$  and the slope of the curve at low temperatures in plots of  $\ln I_D/I_M$  against the reciprocal of temperature yields the activation energy for excimer formation.

Above  $-60^\circ\text{C}$  for a-P $\alpha$ MS and  $-30^\circ\text{C}$  for c-P $\alpha$ MS, excimer dissociation is responsible of the decrease of the excimer emission band. So activation energies were calculated from the slope of the lowest part of the temperature plot (Figure 4). Values of 1.9 and 2.5 Kcal  $\text{mol}^{-1}$  are obtained for a-P $\alpha$ MS and c-P $\alpha$ MS respectively in methylene chloride solution. It is interesting to note that a linearity of  $\ln(I_D/I_M)$  against  $1/T$  is obtained well beyond the temperature where dissociation becomes

efficient. It is probably due to a temperature variation of the non radiative decay  $K_{IM}$ .

As is seen in Figure 3, the monomer emission bands decrease from  $-80^{\circ}$  to  $+80^{\circ}\text{C}$ . This indicates that excimer dissociation does not lead to excited monomer. Harrah<sup>16</sup> drew a similar conclusion from solution studies of poly(2-vinylnaphthalene) and postulated that if it is assumed that the reduction in excimer fluorescence at high temperature results from dissociation of the excimer, this must be accompanied by either internal conversion to the ground state or intersystem crossing to the triplet. Similarly Vala *et al.*<sup>2</sup> postulated that normal fluorescence in PS solution is due to radiative decay of a chromophore excited by direct absorption of incident radiation and not by excimer destabilization.

#### Discussion on some important features of the data

The ratio of excimer to monomer fluorescence intensity  $I_D/I_M$  which is an approximate measure of the excimer sampling mechanism is greater for a-P $\alpha$ MS than for c-P $\alpha$ MS by a factor of about five at  $25^{\circ}\text{C}$ . The rather large difference in efficiency of excimer formation is probably due to the difference in tacticity of the two samples. In a previous paper<sup>17</sup> dealing with intramolecular excimer formation in polystyrene model molecules, we pointed out that the intramolecular excimer state is easier to obtain in isotactic conformations than in syndiotactic ones. As an example, Figure 1c shows the emission spectra of *meso* and *dl* 2,4-diphenylpentanes, the simplest polystyrene model molecules which can be considered as the first step of the isotactic and syndiotactic chains. It is clear that the

spectral patterns of the two compounds differ significantly, the *meso* isomer exhibiting a greater ratio of excimer to normal fluorescence intensity than the *dl* isomer. A similar conclusion can be drawn by comparing fluorescence spectra of isotactic and atactic polystyrenes (Figure 1b). So the higher efficiency of excimer sampling rate is the result of a higher content of isotactic diads in a-P $\alpha$ MS. These results suggest that excimer formation is extremely sensitive to conformational changes due to a change of tacticity.

Another interesting aspect of the results is the fact that the activation energies for excimer formation (Table I) are approximately equal in the two samples of P $\alpha$ MS. We have previously shown that the apparent activation energies related to the rotational barrier between the ground and excimer states are different for the two diphenylpentanes. Similarly, the activation energy for excimer formation in isotactic polystyrene is smaller than for the corresponding atactic polymer. The results show (Table I) that the activation energy for excimer formation is about  $4\text{--}5\text{ kcal mol}^{-1}$  for a syndiotactic diad in the case of the polystyrene while it decreases largely in the case of poly( $\alpha$ -methylstyrene). Conformational analysis of Gorin and Monnerie<sup>18</sup> for 2,4-diphenylpentanes shows that, in the case of a syndiotactic diad, the rotational process between the ground state conformation ( $tt$  or  $g^-g^-$ ) and the higher energy excimer conformation  $g^+t$  (or  $tg^+$ ) can hardly be reached. From conformational energy calculations undertaken in our laboratory by Froelich<sup>19</sup>, it appears that P $\alpha$ MS presents more stable conformations than PS on account of the similar bulkiness of the phenyl,

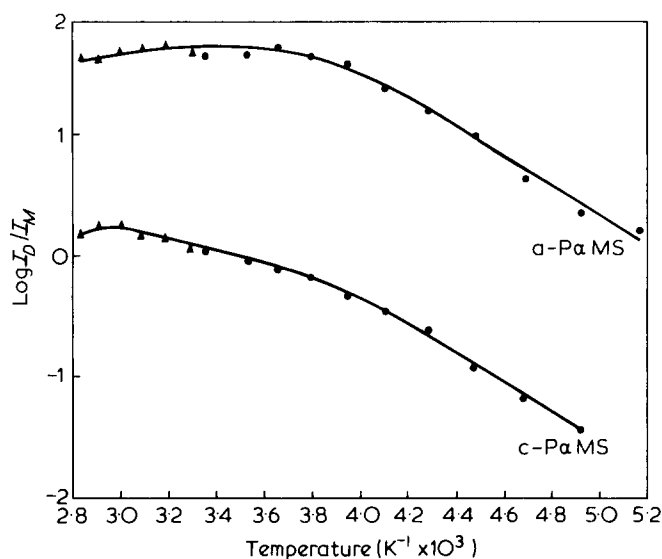


Figure 4 Temperature dependence of the ratio of excimer to monomer fluorescence intensities of poly( $\alpha$ -methylstyrenes):  $\bullet$ , in methylene chloride;  $\blacktriangle$ , in 1,2-dichloroethane

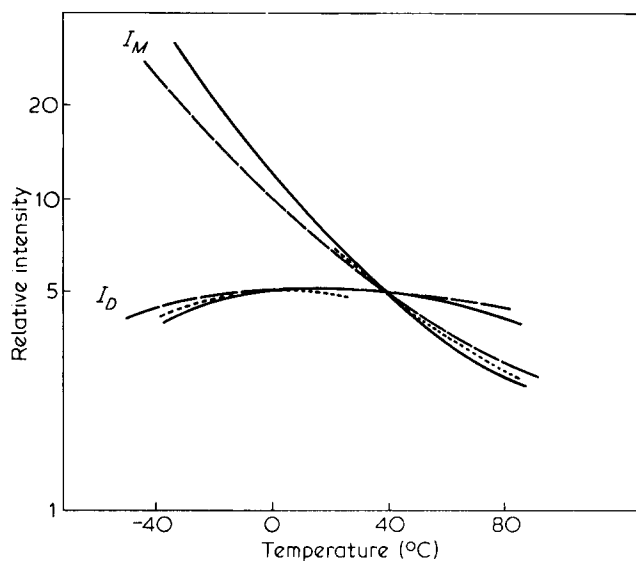


Figure 5 Temperature dependence of fluorescence intensity of excimer ( $I_D$ ) and monomer ( $I_M$ ) bands for polystyrene: — — —, in *p*-dioxane; — — —, in methylene chloride; — — —, in 1,2-dichloroethane. (After Heisel and Laustriat<sup>4</sup>)

Table I Apparent activation energies for excimer formation,  $E_a$ , in methylene chloride

	Poly( $\alpha$ -methylstyrenes)		Polystyrenes		2,4-Diphenylpentanes	
	c-P $\alpha$ MS	a-P $\alpha$ MS	at-PS	it-PS	<i>dl</i> isomer	<i>meso</i> isomer
$E_a$ (kcal mol $^{-1}$ )	2.5	1.9	3.8	2.0	4.6	2.4
Syndiotactic-diad content	0.90	0.70	0.74			

the methyl and the methylene group attached to the  $\alpha$  carbon. In particular for the syndiotactic diad, the excimer state  $g^+t$  is a stable conformation and has energy of similar order of magnitude as the other stable states. This result explains the low energy barrier found for c-P $\alpha$ MS.

Another striking feature of the data is the difference in excimer stability in PS and P $\alpha$ MS. While excimer dissociation is negligible between  $-40^\circ$  to  $+80^\circ$  C in PS<sup>4</sup>, it is sizable in P $\alpha$ MS. Another point of interest is to compare excimer formation in PS and P $\alpha$ MS. As excimer dissociation is important at  $25^\circ$  C, the  $I_D/I_M$  ratios must be compared at a temperature well below  $25^\circ$  C. For example at  $-40^\circ$  C, the  $I_D/I_M$  ratio is 3.26 for a-P $\alpha$ MS and 0.86 for at-PS, the two polymers exhibiting a similar content of isotactic diads. We can effectively point out that excimer formation is easier in P $\alpha$ MS than in PS. This result is surprising since it seems reasonable to expect that excimer state is more difficult to reach in P $\alpha$ MS than in PS on account of the additional interaction between the two  $\alpha$ -methyl groups in the former compound. Wand and Morawetz<sup>11</sup> found that a sample of P $\alpha$ MS exhibits a higher ratio of excimer to monomer fluorescence intensity than PS. The authors think that a parallel sandwich-like conformation of the two phenyl rings is more strained in P $\alpha$ MS than in PS, so the high efficiency of excimer sampling observed in the former compound leads them to believe that a perfect plane arrangement of the two aromatic chromophores is not a strict geometric requirement as was assumed.

The works of Sundararajan<sup>20</sup> and Froelich<sup>19</sup> show that the value of the methylene bond angle which minimizes the energy is close to  $126^\circ$ , a value significantly larger than the  $112^\circ$ – $114^\circ$  value, found for the polystyrene model molecules. Crystallographic results<sup>21</sup> on small molecular analogues also support this conclusion.

The variation of the methylene bond angle leads to a deviation from a parallel sandwich arrangement and to a distance between the two aromatic nuclei of about 3 Å. In the case of polystyrene, taking into account the likely value of  $112^\circ$  for the methylene bond angle, the interchromophore separation is about 2.6 Å. A maximum  $\pi$  orbital overlap is probably not allowed in P $\alpha$ MS which could explain the difference in excimer stability between PS and P $\alpha$ MS. If the variation of the methylene bond angle may explain the destabilization of the excimer conformation in P $\alpha$ MS, it could never explain the high efficiency of excimer formation in this polymer. The fact

that P $\alpha$ MS exhibits a rather large ratio of excimer to monomer fluorescence intensity with regard to polystyrene is probably due, as it has been seen above, to small energy barriers between the ground and excimer states, especially in the case of syndiotactic diads, and perhaps to the presence at room temperature of non negligible amounts of conformation corresponding to excimer sites.

A final point difficult to understand is that the excimer dissociation does not occur at the same temperature for the two samples of P $\alpha$ MS. The different behaviour may be due to different structures of the excimer forming sites in c-P $\alpha$ MS being predominantly syndiotactic and in a-P $\alpha$ MS which is a more isotactic-rich polymer.

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