Excimer-Forming Sites of Poly(methylphenylsiloxane)

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ABSTRACT: The percentage of possible conformers and their relative averaged configurational energies have been calculated for atactic (50% meso) poly(methylphenylsiloxane) (PMPS), as a function of temperature (5–60 °C) and molecular weight (2–30 monomeric units). The simulation method employed uses the rotational isomeric chain model, modified to include fluctuations in the rotational angles and excluded volume interactions. Of all the equilibrium conformers, 60.3% are excimer-forming sites (EFS) at 25 °C, for long chains. Contrary to similar polymers, the $\bar{g}$ conformers contribute significantly to the total EFS population in PMPS. The proportion of EFS is different for the dimer (78.1%) and a long chain (60.3%), but the distribution of conformers reaches a constant value at very low degrees of polymerization (about 14). End-group effects are less than 6%. With a rise in temperature, the proportion of EFS decreases slightly, with an effective balance of energy of 0.2 kcal/mol. Rotational sampling of EFS is exothermic for meso diads even in the electronic ground state. For racemic diads, rotation from the predominant conformer (r(tt), 10.8% for long chains) to the corresponding EFS (r(t$\bar{g}$) or r($\bar{g}$t)) is practically athermic. Excimer formation is therefore expected to be very efficient both through preformed EFS and through rotation. On the other hand, torsional barriers and excimer-binding enthalpy are much lower in PMPS than for similar hydrocarbon polymers. This makes excimer dissociation also very efficient in such a way that a real excited-state equilibrium can be reached before emission (in accordance with experimental results), in particular for racemic diads.

Introduction

Poly(methylphenylsiloxane) (PMPS) has an asymmetrically substituted chain. Its configurational properties, such as unperturbed dimensions and dipole moment, have been studied.[1–4] One of the substituents (phenyl) is a typical fluorescing chromophore. The fluorescence spectrum of PMPS shows a double band with a large proportion of excimer emission,[5] much the same as the one observed for the phenyl chromophore in vinyl polymers. The typical phenyl-containing vinyl polymer whose photophysics has been more extensively studied is polystyrene (PS). Although the emitting chromophore is the same in PS and in PMPS, however, the molecular structure of both polymers is very different (PMPS has a Si–O backbone, PS a C–C). The different bond lengths and bond angles involved in the two structures, as well as their different conformational flexibilities, should be reflected in the formation of their corresponding excimers.

The purpose of this paper is to relate the conformational characteristics of PMPS to its photophysical behavior (recently reported)[5–7] and to show what the differences with regard to PS are.

Excimer emission[8] of polystyrene (PS) and PS-like polymers in very dilute solutions is determined (i) by the average equilibrium conformation, (ii) by segmental rotation through bonds of the skeleton, and (iii) by segmental intramolecular diffusion. The two first factors determine the formation of excimers by two chromophores belonging to consecutive monomeric units, whereas segmental diffusion determines the formation of long-range excimers,[9] that is to say, excimers formed by two nonneighbor rings.

Excimer emission from dilute solutions reflects, therefore, conformational and dynamical characteristics of the coil, but in some cases,[10] it has been shown that the equilibrium rotational isomeric states model calculations (RIS) can give a good account of the results because of the time scale involved. The same holds for miscible blends when segmental movements are frozen (below T_g), and only conformational characteristics and energy migration determine excimer emission.[11]

In vinyl asymmetric polymers (PS-like) in dilute solution, the contribution of long-range excimers to the total excimer emission can be neglected for long chains[9,12–14] having chromophores of short lifetimes.[15] They will not be considered in this work.

The possible excimer-forming sites (EFS) for short-range excimers are, a priori, conformers tt and $\bar{g}\bar{g}$ of meso diads and t$\bar{g}$ and $\bar{g}$t of racemic diads.[16] Conformer $\bar{g}$ is in general sterically prohibited,[17] and therefore only meso diads in the tt conformation (m(tt)) are usually considered EFS in PS-like polymers. But this is not necessarily the case in polymers having other chemical structures, like PMPS, as we will try to show below.

The concentration of EFS in the electronic ground state (preformed EFS) for a given polymer depends on the chain configuration, tacticity, head-to-head unions, etc. For example, preformed EFS are 13.4% for isotactic PS and only 2.6% for atactic PS[11] (for long chains and at 300 K). It seems that the proximity of racemic diads decreases the probability of conformation tt in meso diads, and this makes the proportion of preformed EFS in atactic PS less than half that in isotactic PS.

Excimers can be formed not only by preformed EFS but also by rotation during the monomer excited-state lifetime from a conformation close to an EFS (rotational excimers). Rotational excimers have, as preformed EFS, a larger contribution to the total excimer emission for isotactic PS than for atactic PS. It has been estimated that 70% of the isotactic PS excimers are formed by rotation, although only 30% of the atactic PS excimers are formed by that mechanism in the same conditions.[9] This has been understood by taking into account the conformational energies of meso and racemic diads, since the most populated conformer is closer in energy to the corresponding EFS for meso diads than for racemic diads.[16,17]

In this work, we report a conformational analysis of PMPS, with the purpose of establishing the proportion of

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Table I
Different Averaged Components of the End-to-End Vector, ⟨R⟩ or ⟨$\mathbf{RR}^T$⟩, and ⟨R^2⟩ (in Å or Å^2) for Atactic PMPS Chains with $N = 20$ and $\delta\varphi = 0$. Values at 30 °C Obtained with Monte Carlo (MC) and Quasianalytical (QA) Methods

	MC	QA
$\langle x \rangle$	−0.32 ± 0.06	−0.4 ± 0.5
$\langle y \rangle$	0.40 ± 0.09	0.5 ± 0.1
$\langle z \rangle$	4.66 ± 0.004	4.3 [illegible] 0.6
$\langle x^2 \rangle$	85.8 ± 0.8	89 ± 2
$\langle y^2 \rangle$	87.4 ± 0.6	87 ± 1
$\langle z^2 \rangle$	97.7 ± 0.8	95 [illegible] 6
$\langle xy \rangle$	−0.7 ± 0.5	0.6 ± 0.4
$\langle xz \rangle$	−18.3 ± 0.4	−18 ± 3
$\langle yz \rangle$	3.6 ± 0.6	3.8 ± 0.9
$\langle R^2 \rangle$	271 ± 1	271 ± 1

EFS in this polymer and of interpreting its observed photophysical behavior.[5-7] With that aim, we have represented atactic PMPS chains through a Monte Carlo simulation method, using the rotational isomeric state model parameters.[18]

Methods and Theoretical Calculations

General Simulation Method. We have used a slightly modified version of the Monte Carlo scheme established previously for symmetric[19] (polymethylene) and asymmetric[20] chains (pure isotactic or pure syndiotactic PMPS). This scheme was previously employed in calculations of the distribution function of the end-to-end vector, ⟨**R**⟩. Modifications are required in order to perform calculations for intermediate tacticities (i.e., atactic PMPS). In this case, the chains have different stereochemical sequences, though a given replication probability, p_r, can be fixed (p_r is the probability that a repeat unit being added to the chain will have the same configuration, *d* or *l*, as its predecessor). We obtain a random distribution of racemic and meso diads by means of a subroutine that yields pseudorandom numbers.

Once we have generated a given stereochemical sequence, the probability for each rotational angle in the fourth element of the chain, i.e., the second rotational angle, is computed as

$$p_2(\varphi_k) = \frac{\omega_k[(\prod_{h=3}^{N-1} \mathbf{U}_h)q]_{\varphi_k}}{\mathbf{U}_2(\prod_{h=3}^{N-1} \mathbf{U}_h)q} \qquad (1)$$

where ω_k is the statistical weight that corresponds to the isomeric state with φ_k as the second rotational angle, $\mathbf{U}_2$ is a row vector containing all the statistical weights for the different values of this angle, $\mathbf{U}_h$ is a statistical weight matrix (see below), $q = (1,1,1)$ (column), and N is the number of chain bonds. The conditional probability that each rotational angle is in state φ_k, given that its predecessor is in state φ_j, is calculated as[20]

$$f_i^c(\varphi_j/\varphi_k) = \frac{\omega_{jk}^{\ i}[(\prod_{h=i+1}^{N-1} \mathbf{U}_h)q]_{\varphi_k}}{[(\prod_{h=i}^{N-1} \mathbf{U}_h)q]_{\varphi_j}} \qquad (2)$$

Here, $\omega_{jk}^{\ i}$ is the statistical weight including first-order and second-order interactions.

In the simulation of an atactic polymer (with a fixed value of p_r), each chain of a statistical sample has a different distribution of meso and racemic diads and, therefore, it also has a different sequence of matrices in eq 2. The computational effort is thus much larger than for the purely isotactic or purely syndiotactic chains.

The PMPS chain has been modeled by using the molecular description given by Mark and Ko.[18] Thus, we use the following RIS model parameters: length of the Si–O bond $l = 1.64$ Å; supplementary bond angles $\theta_{\text{Si–O–Si}} = 37°$ and $\theta_{\text{O–Si–O}} = 70.5°$; and statistical weights included in the matrices

$$\mathbf{U}_2 = (1,\sigma,\sigma)$$

$$\mathbf{U}_d = \mathbf{U}_l = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & 0 \\ 1 & 0 & \sigma \end{pmatrix}$$

$$\mathbf{U}_{ll} = \begin{pmatrix} \omega'\omega''' & \sigma\omega'' & \sigma\omega''\delta \\ \omega''\delta & \sigma\delta & \sigma\omega\omega' \\ \omega'' & \sigma\omega\omega''' & \sigma\delta \end{pmatrix}$$

$$\mathbf{U}_{dl} = \begin{pmatrix} (\omega'')^2 & \sigma\omega'''\delta & \sigma\omega' \\ \omega'''\delta & \sigma & \sigma\omega\omega'' \\ \omega' & \sigma\omega\omega'' & \sigma\delta^2 \end{pmatrix}$$

with the associated conformational energies $E_\sigma = 0.35$, $E_\omega = 1.60$, $E_{\omega'} = -2.50$, $E_{\omega''} = -0.90$, $E_{\omega'''} = -0.50$, and $E_\delta = -1.00$, in kcal/mol. Rows and columns in the matrices contain the statistical weights corresponding to rotational isomers for the different bond pairs. Specifically, $\mathbf{U}_d$ and $\mathbf{U}_l$ are associated to bond pairs O–Si–O bracketing a Si atom of either *d* or *l* stereochemical configuration (*d* is assigned when the attached phenyl group is in front of the chain backbone and *l* when it is behind that plane). $\mathbf{U}_{ll}$ and $\mathbf{U}_{dl}$ are associated to bond pairs Si–O–Si with stereochemical sequences *ll* and *dl*. The matrices for the sequences *dd* and *ld* around the Si–O–Si bonds are obtained by interchange of rows 2 and 3, followed by interchange of columns 2 and 3 in matrices $\mathbf{U}_{ll}$ and $\mathbf{U}_{dl}$, respectively.

When a new O atom is added to the chain and a meso diad is formed, matrix $\mathbf{U}_{ll}$ or $\mathbf{U}_{dd}$ (depending on the configurations of the Si atoms) is chosen. If the formed diad is racemic, matrix $\mathbf{U}_{ld}$ or $\mathbf{U}_{dl}$ is chosen. When a Si atom is added to the chain, we do always consider $\mathbf{U}_l = \mathbf{U}_d$.

The PMPS chains are generated with 50% meso diads ($p_r = 0.5$), which is the tacticity of the samples[1] whose photophysical behavior[5-7] will be compared with the results of the simulation.

In any case, the chains generated are initiated by the sequence O–Si(CH$_3$)(C$_6$H$_5$)–, with the Si atom being in the *d* configuration. No end effects have been considered except for the dimer.

Model Modifications. We have introduced in the general scheme of simulation two modifications. First, we take into account independent Gaussian fluctuations of the rotational angles around their rigid values, with a given root-mean-square deviation $\delta\varphi = 15°$. The procedure to introduce these fluctuations is explained in ref 19. Second, we consider long-range interactions between units separated by more than four bonds along the chain to represent the excluded volume effect. We have employed a hard-sphere potential,[19] so that, if the distance between any pair of units of the skeleton separated by five or more bonds is smaller than $R_0 = 3$ Å, the whole conformation is neglected and the generation of a new chain is initiated.

Calculation of EFS Population and Conformational Energies. In order to check the validity and precision of this simulation, we have performed calculations of other quantities such as end-to-end distance and different averaged components of ⟨**R**⟩ and ⟨$\mathbf{RR}^T$⟩ for which we have results obtained with a quasianalytical (nonsimulation) method[4,21] for the same atactic PMPS chain. The results for those properties obtained previously with the quasia-

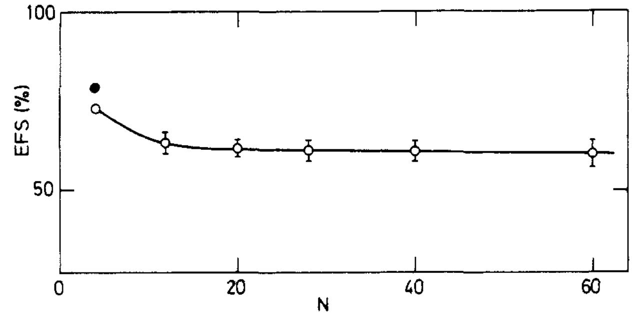


Figure 1. Excimer-forming sites (EFS) population for atactic PMPS chains, as a function of the number of chain bonds, N, at 25 °C: (○) without end groups; (●) with end groups.

nalytical method (which can be considered as exact for the model but cannot be applied to the present problem) and the results obtained with our simulation procedure are practically coincident in all cases (Table I). This coincidence stresses our confidence in the simulation procedure.

The percentage of possible conformations in meso and racemic diads of a chain with N bonds in the skeleton ($N/2$ monomeric units), at 25 °C and with $p_r = 0.5$, has been determined by the following steps: (i) the stereochemical sequence of each chain is generated; (ii) the rotational angles determining the conformations are obtained; (iii) the coordinates of the $N + 1$ atoms in the skeleton, referring to a determined frame[19] centered in the first unit, are calculated; (iv) the overlap of nonneighboring units is checked, and the chain is neglected if the result is positive; (v) finally, if the chain is accepted, the population of each conformation of meso and racemic diads is counted.

This sampling process is repeated a number of times. The accuracy of the Monte Carlo results depends on the size of the samples. We have used four samples, each one containing 5×10^3 independent stereochemical sequences and characterized by a specific seed number, which initiates the generation of pseudorandom values.

The energy of any conformational state (E_i) of meso and racemic diads, in a given generated chain, has been computed from the corresponding population (f_i) by using the Boltzmann equation:

$$f_i = \exp(-E_i/RT) \qquad (3)$$

Relative values of E_i referring to the energy of the racemic diad in the tt conformation have always been considered.

The averages of every quantity $X_{q(\alpha\beta)}$ (with X denoting E_i or f_i; q = meso or racemic diad; $\alpha, \beta = \mathrm{t}, \mathrm{g}, \text{or } \bar{\mathrm{g}}$) are evaluated separately for the different samples as the sum of all the values normalized to the number of chains chosen in that sample. Then the mean value of the four samples is made. The error interval associated with the mean value is estimated as usual from the root-mean-square deviations.

Results and Discussion

Molecular Weight Dependence of EFS. For an isolated meso or racemic diad of PMPS, the populations of its nine conformers can be calculated directly from the interaction energies of ref 18. The results of such calculations are as follows (25 °C). For a meso diad, the conformations that are EFS (m(tt) plus m($\bar{\mathrm{g}}\bar{\mathrm{g}}$)) represent 81.8% of all nine conformers. For a racemic diad, the population of EFS (r($\mathrm{t}\bar{\mathrm{g}}$) plus r($\bar{\mathrm{g}}\mathrm{t}$)) is lower: 63.1%. And for a diad representative of an atactic polymer (50% meso, 50% racemic), the population of EFS is 72.5%.

Table II
Population (f_i) and Conformational Energy (E_i), Relative to the r(tt) State, of the Most Frequent Conformers of an Isolated Diad Representative of Atactic PMPS (50% m, 50% r), at 25 °C[a]

conformer	f_i	E_i, kcal/mol
m(tt)	0.406	−0.88
r($t\bar{g}$)	0.158	−0.34
r($\bar{g}t$)	0.158	−0.34
r(tt)	0.087	0.00
r($\bar{\mathrm{g}}\bar{\mathrm{g}}$)	0.037	0.48
m($\mathrm{t}\bar{\mathrm{g}}$)	0.035	0.52
m($\bar{\mathrm{g}}\mathrm{t}$)	0.035	0.52
m($\bar{g}\bar{g}$)	0.004	1.83

[a] Conformers corresponding to EFS are italic.

Table III
Population (f_i) of the Most Frequent Conformers of Atactic PMPS Chains of N Backbone Bonds and Conformational Energy (E_i) for N = 60, All at 25 °C[a]

	f_i		
conformer	N = 12	N = 60	E_i, kcal/mol
m(tt)	0.42 ± 0.02	0.42 ± 0.02	−0.81
r(tt)	0.106 ± 0.005	0.108 ± 0.009	0.00
r($\bar{g}t$)	0.106 ± 0.004	0.09 ± 0.01	0.09
r($t\bar{g}$)	0.102 ± 0.005	0.09 ± 0.01	0.09
r(tg)	0.083 ± 0.005	0.089 ± 0.005	0.11
r(gt)	0.074 ± 0.006	0.088 ± 0.007	0.12
m($\bar{\mathrm{g}}\mathrm{t}$)	0.022 ± 0.003	0.018 ± 0.006	1.07
m($\mathrm{t}\bar{\mathrm{g}}$)	0.020 ± 0.003	0.017 ± 0.007	1.08
r($\bar{\mathrm{g}}\bar{\mathrm{g}}$)	0.018 ± 0.003	0.014 ± 0.008	1.2
m(tg)	0.016 ± 0.002	0.017 ± 0.006	1.10
m(gt)	0.015 ± 0.002	0.016 ± 0.005	1.12
r(gg)	0.011 ± 0.001	0.013 ± 0.003	1.25
m($\bar{g}\bar{g}$)	0.002 ± 0.001	0.001 ± 0.001	2.7

[a] Conformers corresponding to EFS are italic.

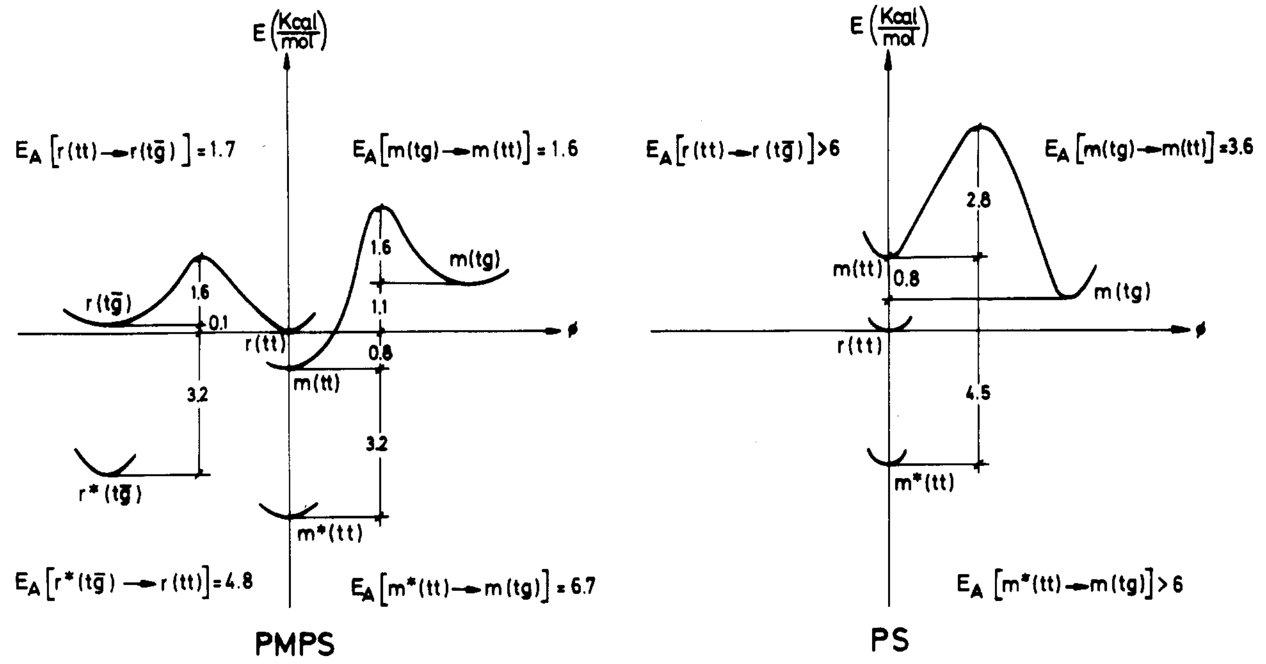
Since an isolated diad is a rather fictitious species, we have done the same calculation for the real dimer: 1,3-diphenyltetramethyldisiloxane (DS), which was also studied experimentally. The result for DS is that 78.1% of its conformational states are EFS. The end groups thus alter, but not much (less than 6%; see Figure 1), the population of EFS with respect to that of a diad representative of an atactic polymer, and in any case, they bring that population closer to the value for the meso diad.

Table II shows the population (f) of the most frequent conformers for an isolated diad of PMPS together with their conformational energy (E) relative to the r(tt) state. It is interesting to notice that, in an isolated diad, three of the four EFS types (m(tt), r($\mathrm{t}\bar{\mathrm{g}}$), and r($\bar{\mathrm{g}}\mathrm{t}$)) are lower in energy than r(tt), and therefore, they represent the conformational ground state of m and r diads. Even the m($\bar{\mathrm{g}}\bar{\mathrm{g}}$) state, which in the case of the dimeric analogue of PS (*meso*-2,4-diphenylpentane) represents less than 0.05% of the total conformers,[22] has here an appreciable, though small, contribution to the concentration of EFS (0.7%). Bond distances are larger for siloxanes than for hydrocarbon compounds,[18] and this makes such $\bar{\mathrm{g}}$ conformations sterically possible.

Table III summarizes the molecular weight dependences of the populations of the most interesting conformers of an atactic PMPS chain at 25 °C. Conformers whose contribution is less than 0.4% have been omitted. Several sets of chains with a different number of monomeric units in the range 6–30 have been studied (Figure 1). There is a slight molecular weight dependence of EFS population for oligomers with less than 14 monomeric units, but it can be considered constant for larger chains. The same result was found for atactic PS.[11,23]

It is clear from comparing Tables II and III that steric interactions of each diad with the neighboring diad change

Chart I



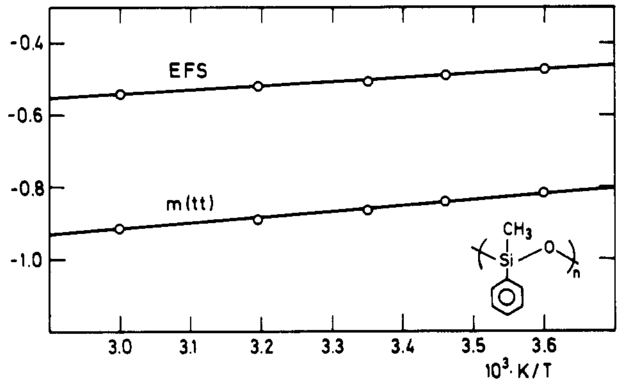


Figure 2. Temperature dependence of m(tt) conformers and total EFS population for an atactic PMPS chain of $N = 60$.

the diad population with respect to an isolated diad. Racemic diads are more influenced than meso diads, and the general trend is to decrease the proportion of $\bar{g}$ states in longer chains.

Even so, the proportion of EFS in a PMPS long chain at 25 °C is still very large: 60.3%. In the same conditions, the proportion of EFS for atactic PS is considerably lower; 2.6%.[11] The explanation for this large difference must be found in the interactions between neighboring phenyl rings.[5,18] The distance between phenyl rings that belong to neighboring monomeric units is such that their interaction is attractive for PMPS and repulsive for PS.

Temperature Dependence of EFS. Figure 2 shows the temperature dependence of EFS population in an Arrhenius-type plot. The proportion of m(tt) conformers decreases slightly with a rise in temperature, and since the proportion of the other EFS remains practically constant, the total concentration of EFS decreases with temperature with an effective balance of energy of 0.21 kcal/mol. Conformational energies of PMPS change less than 0.1 kcal/mol when going from 5 to 60 °C.

On the contrary, the population of PS EFS strongly depends on temperature, to the opposite sign; with a rise in temperature, m(tt) increases with an effective activation energy of 1.7 kcal/mol.[11] The reason for such a different temperature dependence is that EFS are minor conformers for PS but predominant conformers for PMPS. Temperature changes in the range 5–60 °C produce small changes in the conformational distribution of both polymers. But in the case of PS, such small changes represent a very large relative change of the EFS proportion, while the relative change is very small for PMPS.

Conformational Energies. Chart I compares the conformational energies of atactic PMPS (Table III, highest molecular weight) and atactic PS (taken from ref 17) at 25 °C. Rotational sampling of EFS is exothermic (m(tg) → m(tt)) or practically athermic (r(tt) → (t$\bar{g}$,$\bar{g}$t)) for PMPS, whereas it is endothermic for PS. Moreover, intrinsic torsional barriers are about one-half for PMPS[24] than for PS,[17] and therefore, activation energies for excimer formation through rotation are much smaller in the first case (1.6–1.7 kcal/mol for PMPS and 3.6 kcal/mol for PS m diads; Chart I). Rotational excimers are therefore highly probable for PMPS as compared to atactic PS.

Comparison with Experimental Results. Calculated EFS on equilibrium conformations do not explain the photophysical behavior of PMPS. Thus, considering only the formation of excimers in preformed EFS, the fluorescence ratio I_E/I_M should be much larger for PMPS than for PS, but the experimental results are $I_E/I_M = 2.7$ for PMPS and 2.0 for PS, at 40 °C, and 3.8 and 1.7, respectively, at 20 °C (see Figure 3). The difference depends on temperature, but it is not as large as expected. Also, the calculation of preformed EFS gives a higher proportion of EFS in the dimer than in the polymer (Figure 1), while the experimental I_E/I_M values are just the opposite[6] (I_E/I_M = 1.55 for DS and 5.1 for high molecular weight PMPS, under the same conditions).

Energy migration has been invoked[11] to explain the progressive increase of I_E/I_M for atactic PS when going from the dimer to the high molecular weight samples,[11,13,25-27] although such interpretation has been criticized.[28] In PMPS, energy migration should not be expected because almost two-thirds of the phenyl rings are forming part of preformed EFS, which are potential traps of the energy.

It must therefore be admitted that, to understand the PMPS fluorescence, it is necessary to take into account not only preformed EFS is equilibrium conformations but also the dynamic contribution to excimer formation and

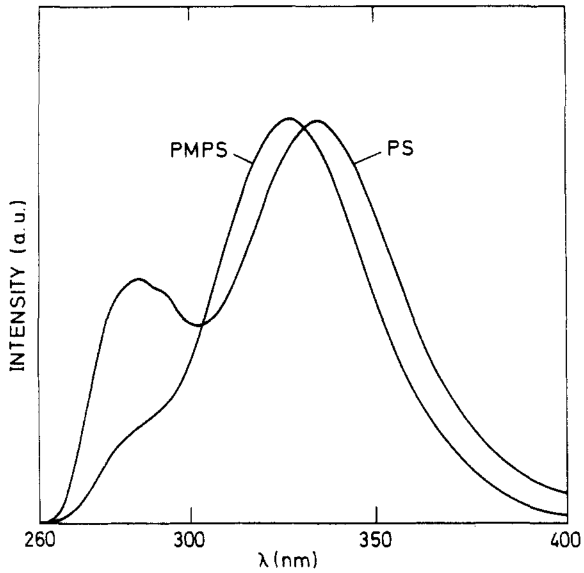


Figure 3. Fluorescence spectra of atactic samples of PS and PMPS. $T = 20$ °C. Solvent: dioxane (PS), cyclohexane (PMPS). $M_w = 1.0 \times 10^5$ (PS), 2.7×10^5 (PMPS). $M_w/M_n = 1.02$ (PS), 1.65 (PMPS). $\lambda_{ex} = 250$ nm. Optical density = 0.5.

excimer dissociation. Since PMPS is highly flexible, its conformational changes are very fast and compete with emission.

The activation energy for the excimer formation experimentally found must be attributed to the changes with temperature of preformed EFS and to the thermal activation of rotational excimer sampling. This explains why the experimental results are larger than those theoretically found for changes with temperature of the equilibrium conformation. (For example, in PMPS the experimental result is 0.7 kcal/mol,[7] and the one calculated for the EFS population is −0.2 kcal/mol. In PS the experimental results, 1.4, 3.1, and 3.8 kcal/mol,[29,30] are also larger (on average) than the one calculated for EFS: 1.7 kcal/mol[8b,11]).

Excimer Dissociation. An isosbestic point has been observed for PMPS[6] and other siloxanes[7,30] at temperatures close to room temperature in such a way that monomer emission intensity (I_M) increases when excimer emission intensity (I_E) decreases. That evidences the existence of an excited-state equilibrium between monomer and excimer in which excimer formation and excimer *dissociation* are faster than monomer or excimer fluorescence.[7]

There exists experimental evidence for no excimer dissociation of high molecular weight PS,[25,27,31-34] and no isosbestic point is observed in the fluorescence spectra of dilute PS solutions at temperatures close to room temperature.[6] This different contribution of excimer dissociation to the photophysical behavior of PS and PMPS can be explained with Chart I.

The influence of excimer dissociation on excimer emission cannot be rigorously discussed in terms of the conformational energies calculated based on the electronic ground state, like in Tables II and III. The strong interaction that gives rise to the excimer formation decreases the energy of the EFS with respect to the conformational energy found for the electronic ground state. Besides, the polarizability of the phenyl ring changes with the electronic excitation, and this would modify interactions with other groups and, consequently, the conformational distribution.

Since the electronic excitation is localized in a given chromophore only for a few nanoseconds, the excited-state equilibrium distribution of conformers is probably never reached. Therefore, it makes no sense to attempt the calculation of the equilibrium populations that correspond to interactions of electronic excited-state rings. Furthermore, these interactions are unknown. A good approach to reality could be to assume the following:

(i) Rotations to form excimers occur between conformational energy levels like those calculated for the electronic ground state. Torsional barriers are approximated by intrinsic torsional barriers in Chart I.

(ii) If an EFS is reached by rotation of an excited-state chromophore or if it gets an exciton by energy transfer or direct absorption, an excimer is formed[35] (m*(tt) or r*(t$\bar{g}$,$\bar{g}$t)), and the energy of the state decreases in ΔG, the Gibbs energy for excimer binding. Only the excimer-binding enthalpy, ΔH, is known for PMPS (−3.2 kcal/mol).[7] ΔG cannot be determined for PS because it does not reach the excited-state equilibrium, but we can assume that ΔH is the same as for its dimeric model compound: $\Delta H = -4.5$ kcal/mol for racemic 2,4-diphenylpentane.[36]

(iii) Excimer dissociation occurs by rotation from m*(tt) or r*(t$\bar{g}$,$\bar{g}$t) to another conformation that does not require a $\bar{g} \leftrightarrow g$ transformation. The energy of the final state can be considered to be like that calculated for the electronic ground state and torsional barriers to be like the intrinsic torsional barrier.

Chart I shows the activation energy for excimer dissociation. It is much smaller for PMPS than for PS (4.8 kcal/mol for PMPS racemic diads and above 6 kcal/mol for PS; Chart I), and this is in accordance with the appearance of an isosbestic point for PMPS but not for PS and with the similar fluorescence ratios for both polymers.

Molecular motion required for excimer dissociation is an easier process in a small dimer than in a long chain.[37] For example, racemic 1,3-diphenylpentane presents evidence[36,38] of a small dissociation, while high molecular weight PS does not.[25,27,31-34] Therefore, DS is expected to dissociate to a greater degree than PMPS, and this explains the smaller fluorescence ratio of the dimer.

Conclusions

Excimer dissociation contributes to decrease I_E/I_M in PMPS with respect to PS. That explains why the fluorescence ratio of both polymers is not as different as expected based on (a) their different EFS populations (large for PMPS, small for PS) and (b) the higher probability of rotational excimers in PMPS (because of lower rotational barriers in this polymer).

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Temperature Dependence of Polymer Film Properties on the Air–Water Interface: Poly(vinyl acetate) and Poly(*n*-butyl methacrylate)

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ABSTRACT: Surface dynamic light scattering is used to deduce the surface viscoelastic properties of poly(vinyl acetate) (PVAc) and poly(*n*-butyl methacrylate) (PnBMA) spread at the air–water interface. The two polymers were selected as group representatives of expanded (PVAc) and condensed (PnBMA) type films. Surface longitudinal viscosity, κ, and elasticity, ϵ, for the two types were calculated from the frequency shift and line broadening of the power spectrum of the scattered light with a dispersion relation over a range of temperatures and surface concentrations. In some cases, the wavevector dependence of the spectral characteristics necessitated the incorporation of a transverse viscosity term, μ, in the dispersion equation, subject to the assumption that ϵ and κ did not depend on the scattering wavevector. This transverse viscosity was shown to have an anomalous temperature dependence with characteristics different for the two polymers; an explanation of the temperature dependence in terms of a slow, collective transverse relaxation process is provided, which may be related to the orientational properties of the different polymers at the interface.

Introduction

Polymer conformation and dynamics at interfaces are important for scientific[1] and technological[2] reasons. It has been known for many years that a wide variety of polymers can be spread at the air–water interface and that measurements of the surface pressure of the resulting films as a function of surface polymer densities suggest grouping polymers according to qualitative differences in their tendency to spread and quantitative differences in their pressure–area curves.[3] For example, poly(vinyl acetate) (PVAc) spreads readily to form fluid (expanded) films stable up to high surface pressures (≤ 15 dyn cm^{-1}). It is now well established that the reduction in surface tension and the increased damping of surface waves motion, which result when a surface-active film is spread on a liquid surface, are ascribed to the viscoelastic properties of the film. The effects of a surface-active substance on surface waves motion have been examined extensively[4-8] by measuring the attenuation of mechanically excited waves. More recently, the study of the viscoelastic properties of monomolecular films has attracted renewed attention through the introduction of surface light scattering from thermally excited capillary waves since this technique is a noninvasive one. A variety of different materials have been studied by using surface wave scattering.[9-16] On the other hand, very few experiments[12,13] have been directed to probe the temperature dependence of the viscoelastic parameters, which is of major significance since the liquid substrate can be a good or poor "solvent" depending on temperature for a given polymer.[17,18] We present in this report a study of surface light scattering combined with static surface pressure with the use of two polymers,

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