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Decay of Poly(phenylsiloxane) Fluorescence Emission. Kinetic Parameters and Rotational Motion

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ABSTRACT: Time-correlated single-photon-counting measurements were performed on the monomer and excimer emissions of very dilute solutions of methylphenylsiloxane polymers. The homopolymer (PMPS) and three copolymers of methylphenylsiloxane with dimethylsiloxane of different compositions have been studied. Results in two solvents of widely different viscosity (cyclohexane and heavy oil) and at two temperatures (21 and 40 °C) were obtained. The decays are in all cases multiexponential. No rise time of excimer emission was observed in the low-viscosity solvent. In heavy oil, a rise time of a few hundred picoseconds is detected but, still, there remains an important contribution of excimer species with no rise time. The analysis of the decays is made in the light of a kinetic scheme that is consistent with a previous ground-state conformational analysis of PMPS. In such a kinetic scheme, a significant part of the excimers come from preformed dimers in the diads of the polymer. The possible distinction of two excimeric states, one due to meso diads and the other due to racemic diads, is discussed. The rate constant for the formation of excimer by rotational motion ($k_a = 10^9$–10^{10} s^{-1}) is larger than in hydrocarbons polymers.

Introduction

Phenylsiloxanes are materials with very important technical applications. They are also very interesting systems from the photophysical point of view because of the peculiarities that they show when compared with hydrocarbon polymers. A conformational analysis of poly(methylphenylsiloxane) (PMPS) reveals[1] that more than half of its monomeric units are in ground-state preformed excimer-forming sites (EFS), regardless of temperature and chain molecular weight. The fluorescence ratio (I_E/I_M, excimer to monomer intensity ratio) is nevertheless smaller than what could be expected according to that large population of EFS. It is for example very similar to the fluorescence ratio of polystyrene whose population of ground-state EFS is much smaller: 2.6%.[2] The observation of an isosbestic point in the steady-state fluorescence spectra recorded in the high-temperature limit[3–5] (HTL) made us conclude that excimer dissociation was a nonnegligible process in these systems.

The fluorescence ratio is directly correlated with the molar fraction of MPS in copolymers.[3] Energy migration is not likely in phenylsiloxanes because of their large number of energy traps,[1] and therefore, the sequence length of chromophores should not influence[6] their photophysical behavior.

The fluorescence spectra of copolymers with a very low percentage of MPS show a temperature dependence typical of the low-temperature limit (LTL),[5] whereas copolymers with more MPS are in the HTL in the same range of temperatures. To explain this result, it was suggested[5] that a real excited-state equilibrium was not reached in the copolymer of low chromophoric intramolecular concentration because the rate constant for excimer formation was smaller than or similar to the rate constant for monomer and excimer radiative and nonradiative decay.

All these previous studies on phenylsiloxane polymers and copolymers were based on stationary spectra and so discussion about rate constants and relative importance of different processes contributing to excimer and monomer emissions was only conjectural. Direct time-resolved measurements are needed to gain further insight into the mechanism involved and, if possible, to determine the appropriate rate constants of the process. This is the objective that has guided the work reported in the present paper.

Experimental Section

Samples were kindly donated by Drs. I. Hernández-Fuentes and C. Salom (Madrid). The characteristics of these samples, which were previously described,[3] are summarized in Table I. PMPS was atactic[7] as expected for any phenylsiloxane.[8]

The solvents used, cyclohexane (Ch) (Merck Uvasol) and heavy oil (HO) (U.S. Pharmacopeia), were of the highest quality (no residual fluorescence upon excitation at 250 nm).

The concentration of polymer solutions was adjusted to give an optical density less than 0.6. They were purged with nitrogen or argon for 15–20 min.

The fluorescence decays were measured in a single-photon-counting system described in ref 9. The excitation source was a D_2-filled coaxial flash lamp (Edinburgh Instruments) run at 50 kHz and 7 kV. The photomultiplier (Philips XP 2020 Q) wavelength shift is 1 ps nm^{-1} at 2.35 kV.[9] The experimental conditions were chosen to ensure that there were no light scattering artifacts, while the number of counts per second was enough to collect 10–20 kilocounts at the maximum in ca. 20 h, the period of time in which the lamp pulse remains stable. As an exception, in the experiment in HO only 4 kilocounts was

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Table I
Characteristics of the Samples: Average Molecular Weight (M), Molar Fraction of Methylphenylsiloxane (x_{MP}) in the Copolymers, and Number Average of Monomeric Units (N) and of Chromophores (N_{MP}) in a Macromolecule

sample	$M \times 10^{-3}$	x_{MP}	N	N_{MP}
PMPS	106[a]	1	443	443
Co 710	2.5[b]	0.663[c]	22	14
Co 8241	4.2[b]	0.543[c]	39	21
Co 8240	6.4[b]	0.095[c]	80	8

[a] M_w determined by GPC (M_w/M_n = 1.76). [b] M_n determined by vapor pressure osmometry. [c] Determined spectrophotometrically.

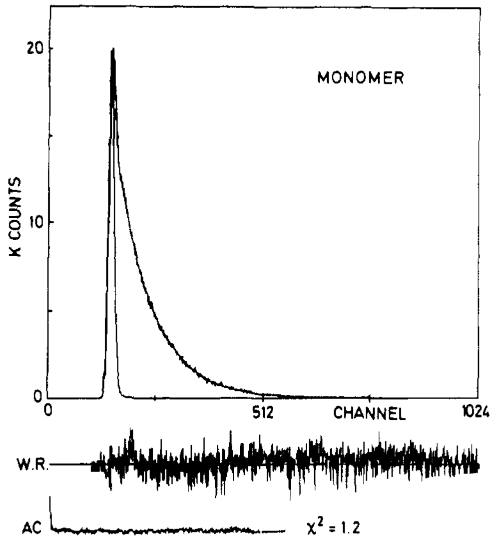


Figure 1. Fluorescence decays of PMPS in cyclohexane at 21 °C. Monomer emission (280 nm) with double-exponential fit. Weighted residuals (WR), autocorrelation function (AC), and χ^2 values are indicated.

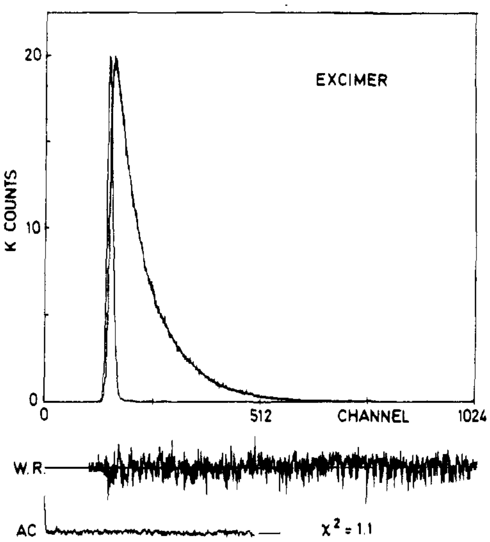


Figure 2. Same as in Figure 1, but for the excimer emission (345 nm).

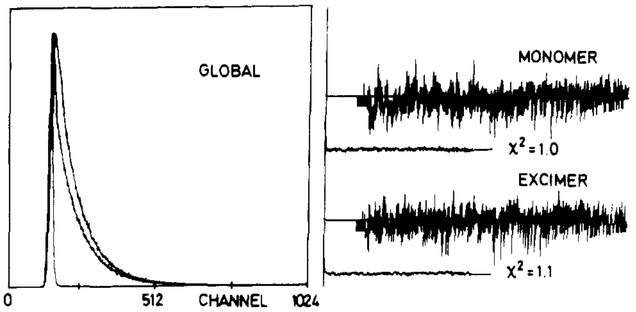


Figure 3. Same as in Figures 1 and 2, but with global fit to a sum of three exponentials.

collected at the maximum. Alternate measurements (1 × 10^3 counts at the maximum per cycle) of the pulse profile at 250 nm, the monomer emission at 280 nm, and the excimer emission at 345 nm were performed until the desired number of counts was reached.

The time resolution of the apparatus was checked by measuring the lifetimes of 8-methoxypsoralen in acetonitrile (τ = 0.10 ns) and in ethanol (τ = 0.39 ns),[10] which were both reported and measured with a picosecond laser system.[11] The concordance is excellent, and thus it can be concluded that decay times down to 100 ps can be measured with that equipment.

The fluorescence decays were deconvoluted either by independent analysis of the monomer and excimer decays or by global analysis, where both decays are jointly fitted with the same set of decay times. In some cases an additional component of fixed τ is introduced in the analysis to account for some impurities whose emission overlaps with the sample emission.

Results

Cyclohexane. Figures 1–3 show the decays of PMPS monomer and excimer emissions in Ch at 21 °C. Similar curves were obtained for the copolymers, except for Co 8240, whose excimer decay was not measured because of the spectral overlap with monomer emission (see Figure 4). The wavelengths for analysis of monomer and excimer emission (280 and 345 nm, respectively) were chosen to minimize the spectra overlap.

Biexponential Fit. In all cases, a biexponential fit appears to give acceptable statistical parameters (χ^2 between 1 and 1.6). Table II summarizes the fitting parameters of the biexponential independent analysis of the monomer and excimer emission decays at two temperatures for the different samples in Ch dilute solution. A third exponential of fixed τ equal to ca. 30 ns was incorporated in the analysis of the PMPS monomer emission to account for minor amounts of impurities not involved in the kinetics.

No rise time of the excimer emission is detected in these fits at either temperature. Moreover, the shortest component (τ_2) is different for the excimer and monomer decays (e.g., 3.5 and 0.13 ns, respectively, for PMPS at 21 °C). This shows the complexity of the mechanism.

Global Analysis. In order to analyze the monomer and excimer decays simultaneously with the same time parameters (global analysis), at least three exponentials are needed. The fitting parameters obtained with three exponentials in such global analysis of monomer and excimer emission are listed in Table III. (A fourth component of fixed lifetime, τ = 30 ns, was again incorporated in the analysis of PMPS monomer emission.) This fitting procedure improves slightly the statistical parameters over the previous ones. The autocorrelation function and the weighted deviations of PMPS monomer emission can be compared in Figures 1–3, and the χ^2 for all the samples can be compared in Tables II and III. Here, as in the previous biexponential fit, no rise time of the excimer emission is observed at either temperature.

The influence of temperature on the decay parameters is as expected; namely, all τ's decrease upon increasing temperature (Tables II and III).

The influence of polymer composition is as follows: the longest component (τ_1 in either type of fit) and the intermediate component of Table III are practically independent of the polymer composition (Tables II and III) and about the same for monomer and excimer emission. The shortest component (τ_2 in Table II, τ_3 in Table III) of monomer decay decreases appreciably upon increasing

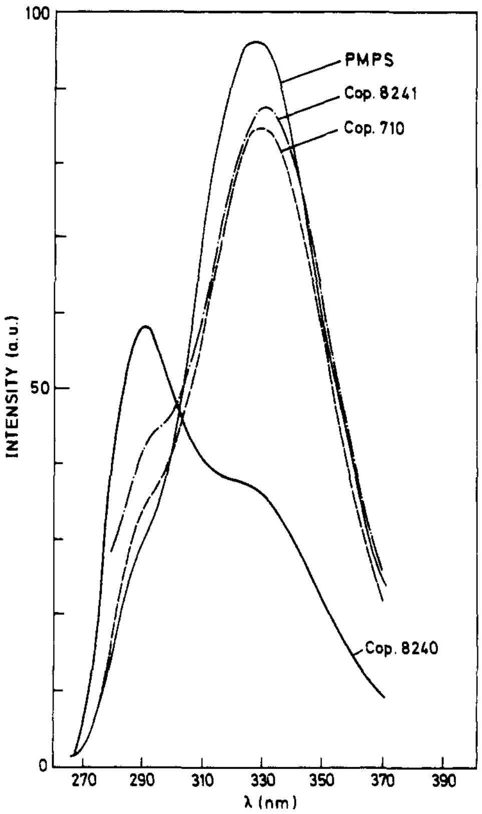


Figure 4. Uncorrected emission spectra of the homopolymer and copolymers.

the methylphenylsiloxane content of the chain and is always smaller than the corresponding τ of the excimer decay.

Heavy Oil. Trying to discern the complex mechanism of excimer formation in these systems, we studied one of the samples (Co 710) in a very viscous solvent: USP heavy oil (HO), whose viscosity is (at 20 °C) η = 193 cP. The influence of such high solvent viscosity on the decay parameters has been studied at 21 °C.

Table IV summarizes the decay parameters of this sample obtained with biexponential and triexponential fits and with global or independent analysis. The biexponential fit with independent analysis is again good enough from the statistical point of view. A rise time of the excimer emission is observed in this case. With independent fit to a biexponential, the rise time is 430 ps, shorter than the decay for the monomer (1.3 ns), but using three exponentials with independent analysis the excimer emission rise time is split into two components (i.e., 150 and 970 ps). Such low τ values almost reach the limits of what can be done with a nanosecond flash lamp but it is still inside the time resolution of the apparatus (see Experimental Section).

With global analysis the excimer rise time is larger than 1 ns, both with bi- and triexponential fits. It should be noted that in all cases the amplitudes of the components of the excimer decay do not add to zero, which corresponds to the existence of ground-state preformed excimers.

The very weak dependence of the decay parameters on solvent viscosity is remarkable. The longest component (τ_1 from monomer and excimer emission in any type of fit) is insensitive to η, its value being practically the same in Ch and HO at 21 °C (see Co 710 in Tables II–IV). The shortest component of monomer emission (τ_2 in Table II or τ_3 in Tables III and IV) increases by a factor of ca. 3 (τ_2) or 5 (τ_3) from Ch to HO, which is a small variation considering that the increase of η is 200-fold. The same insensitivity toward variations in η is observed in the excimer to monomer fluorescence ratio of Co 710, which is only slightly different in HO relative to Ch at the same temperature.

Kinetic Parameters. According to the classical treatment of copolymers, which is based on the Birks scheme[12]

$$\sum_i \lambda_i = k_a + k_d + \tau_0^{-1} + \tau_0'^{-1} \qquad (1)$$

where $\lambda_i = \tau_i^{-1}$; k_a and k_d are the rate constants for excimer formation and dissociation, respectively; and τ_0^{-1} and $\tau_0'^{-1}$ account for the rate constants of monomer (τ_0) and excimer (τ_0') decays through radiative and nonradiative pathways. In general, when n kinetically coupled species are considered, the decays are sums of n exponentials whose reciprocal decay times are related to the rate constants through $\sum_{i=1}^{n}\lambda_i = \sum_{j=1}^{m}k_j$.

On the right-hand side of eq 1 only k_a is expected to depend on copolymer composition. The question is: What is the nature of this dependence? Several proposals can be found in the literature,[6] which differ in the way they consider energy migration and chain microstructure. In the systems that we consider here, energy migration is not expected. On the other hand, the copolymers used are commercial and their finer microstructure is unknown, so that only the variable x_{MP} of Table I can be considered.

We consider first only λ_i from the monomer emission in the biexponential fit (Table II), since λ_i from excimer emission or in multiexponential fits require a more complex mechanism (see below). Figure 5 shows the dependence of $\lambda_1 + \lambda_2$ versus x_{MP}, which is nonlinear but seems to indicate that the extrapolation to $x_{\mathrm{MP}} = 0$ yields a very low intercept, and, therefore, $k_d + \tau_0^{-1} + \tau_0'^{-1}$ can be considered negligible compared with k_a for the high and medium values of x_{MP}.[13] At low x_{MP} values (e.g., Co 8240), however, k_a can become comparable to τ_0^{-1} (Figure 5),[13] in accordance with a previous suggestion.[5]

Since λ_1 is only ca. 5% of λ_2, we can simplify eq 1 to $k_a = \lambda_2$, with an error less than 10%. The results thus obtained for k_a are shown in Table V for the two temperatures studied. The activation energy is calculated with only those two temperatures.

In Figure 6 the sum of the reciprocal decay times ($\lambda_1 + \lambda_2 + \lambda_3$) obtained from global analysis is plotted against x_{MP}. In this case, the variation is quasi-linear and, again, a very small intercept is obtained. The k_a values can be approximated by $k_a = \lambda_3$ in this analysis. The results thus obtained for k_a and the corresponding activation energies are shown in Table V.

Discussion

There are three main mechanisms for intramolecular excimer formation in polymer systems:[14] (a) ground-state preformed EFS; (b) rotational excimers (whose relative contribution depends on solvent viscosity); (c) long-range excimers (formed by chain recoiling). The first two mechanisms should be very important in siloxanes according to conformational analysis,[1] which predicts a large number of ground-state preformed EFS and very low torsional barriers, making it very easy for the bonds to rotate, forming and dissociating the excimers.

Since no rise time is observed in the low-viscosity solvent (Ch) with any type of fit, it can be concluded that either the excimer species already exist in the ground state (preformed EFS) or rotational motions required to form them take place in times shorter than the experimental resolution (100 ps), or both. Rotational motions are slowed

Table II
Monomer and Excimer Emissions (Measured at 280 and 345 nm, Respectively) for the Different Samples in Cyclohexane at 21 and 40 °C[a]

sample	T, °C	τ_2, ns	τ_1, ns	$A_2 \times 10^2$	$A_1 \times 10^2$	χ^2
			Monomer			
PMPS	21	0.13	12.4	63	4.8	1.2
Co 710	21	0.54	11.4	22	3.5	1.6
Co 8241	21	0.52	11.8	19	4.1	1.5
Co 8240	21	3.0	9.8	9.1	1.1	1.4
PMPS	40	0.11	8.9	46	6.0	1.3
Co 710	40	0.39	8.1	24	4.9	1.6
Co 8241	40	0.36	7.1	20	5.7	1.1
Co 8240	40	1.9	7.4	12	0.7	1.3
			Excimer			
PMPS	21	3.5	12.4	1.7	6.3	1.1
Co 710	21	3.3	12.2	1.5	5.9	1.2
Co 8241	21	2.5	11.5	2.1	5.2	1.2
PMPS	40	1.3	8.8	3.7	8.3	1.2
Co 710	40	2.3	8.7	1.7	5.9	1.1
Co 8241	40	2.1	7.0	2.4	6.5	1.1

[a] Decay parameters (τ) and amplitudes (A) obtained by fitting separately the monomer and excimer emissions to the sum of two exponentials.

Table III
Monomer Emission (280 nm) and Excimer Emission (345 nm) for the Different Samples in Cyclohexane at 21 and 40 °C[a]

sample	T, °C	τ_3, ns	τ_2, ns	τ_1, ns	$A_3 \times 10^2$	$A_2 \times 10^2$	$A_1 \times 10^2$	χ^2
PMPS	21	0.12	6.4	13.0	64	0.7	4.3	1.0
					1.5	2.3	5.2	1.1
Co 710	21	0.22	3.8	12.0	38	1.7	2.9	1.0
					1.8	1.4	5.0	1.1
Co 8241	21	0.28	5.1	12.1	27	1.8	3.2	1.3
					2.5	2.1	4.8	1.2
PMPS	40	0.095	4.1	9.6	44	1.0	5.3	1.0
						2.0	3.9	1.0
Co 710	40	0.16	3.6	8.9	37	2.3	3.9	1.0
					1.5	1.6	5.5	1.1
Co 8241	40	0.19	4.4	7.7	27	2.7	3.3	1.0
					1.6	3.0	4.2	1.3

[a] Decay parameters (τ) and amplitudes (A) obtained by fitting both emissions to the sum of three exponentials by the method of global analysis (i.e., same τ's for both emissions). In each case, the first row shows A for the monomer and the second row shows A for the excimer.

Table IV
Monomer Emission (280 nm) and Excimer Emission (345 nm) for Co 710 in Heavy Oil at 21 °C[a]

type of fitting	λ, nm	τ_3, ns	τ_2, ns	τ_1, ns	$A_3 \times 10^2$	$A_2 \times 10^2$	$A_1 \times 10^2$	χ^2
II	280	1.32		10.7	18		2.0	1.2
	345	0.43		12.6	−6.0		8.0	1.2
IIG	280	1.49		12.3	17.8		1.6	1.0
	345	1.49		12.3	−3.0		8.4	1.2
III	280	0.02	1.48	10.9	20	16	1.9	1.0
	345	0.15	0.97	12.6	−8.9	−1.7	8.1	1.2
IIIG	280	1.0	3.9	12.8	17.8	2.9	1.3	0.7
	345	1.0	3.9	12.8	−4.5	1.0	7.8	1.0

[a] Decay parameters (τ) and amplitudes (A) obtained by different types of fitting: II and III, independent analysis of the sum of two (II) or three (III) exponentials; IIG and IIIG, global analysis to the sum of two (IIG) or three (IIIG) exponentials.

down in high-viscosity solvents such as HO, and, therefore, the decay parameters related with such processes are the ones expected to change with respect to those in Ch. The only component changing with solvent is the shortest one, which we have ascribed here to the rotational formation of excimer ($k_a = \lambda_2$ or λ_3). However, even in HO, the amplitudes of the excimer decay components do not add to zero, and, therefore, we can conclude that these results are in accordance with the conformational analysis:[1] there seems to be a large percentage of preformed EFS whose rate constant for excimer formation is independent of solvent viscosity, and the rest of the excimers are formed in very fast rotational motions, which in Ch correspond to a rise time below 100 ps and in HO give rise to very small rise times of ca. 400 ps.

The rate constant for excimer formation that we obtain is very large, with values of k_a (Table V) in the range 10^9–10^{10} s^{-1}, which indicates that the formation of rotational excimers in these macromolecules is a faster process than it is in most hydrocarbon polymers, for which values about an order of magnitude smaller are usually found.[15]

The activation energy for the homopolymer PMPS is practically the same as the one predicted by the conformational analysis. The activation energy of the copolymers is, nevertheless, higher than expected for siloxane rotations. In the previous discussion, only rotational excimers were considered. However, in low molecular weight chains, as is the case of the copolymers included in this study, diffusional or long-range excimers could be contributing. In these conditions, the experimental activation energy will

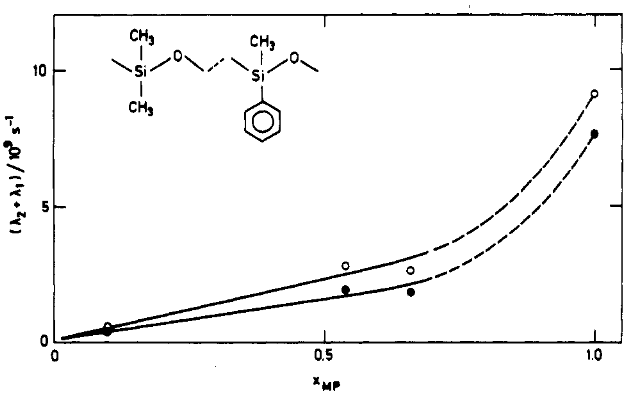


Figure 5. Plot of the sum of the reciprocal decay times in cyclohexane at 21 °C (open circles) and 40 °C (filled circles) as a function of the molar fraction of methylphenylsiloxane (x_{MP}). $\lambda_1 + \lambda_2$ from monomer double-exponential fits.

Table V
Apparent First-Order Rate Constant for Excimer Formation, k_a (Cyclohexane, at 21 and 40 °C), and Activation Energy, E_a, for the Same Process

sample	$k_a \times 10^{-9}$, s^{-1} 21 °C	$k_a \times 10^{-9}$, s^{-1} 40 °C	E_a, kcal/mol
	From λ_2		
PMPS	7.7	9.1	1.5
Co 710	1.9	2.6	2.9
Co 8241	1.9	2.8	3.3
	From λ_3		
PMPS	8.3	10.5	2.2
Co 710	4.6	6.3	3.0
Co 8241	3.6	5.3	3.6

be a function both of rotational motion and of diffusional motion.

Long-range excimers of low stability (small excimer binding enthalpy as here) are in the low-temperature limit at temperatures close to room temperature.[16] The only sample showing this type of behavior is Co 8240. The average number of chromophores in this copolymer is lowest (Table I), so that the formation of excimers between nonneighboring chromophores could be of importance in it. This would explain in part the difference of Co 8240 with respect to the other systems.

Excited-State Species. It is evident from previous results that a simple Birks scheme is not sufficient to explain the photophysical behavior of these systems. Even more than three excited-state species can be expected, although it is not known whether the global triexponential analysis is still amenable to improvement because of the relatively small number of counts that are attainable with these systems.

Besides, close inspection of the ground-state conformational analysis[1] allows the identification of several species, as we try to demonstrate now. Phenylsiloxanes have two types of diads, which cannot interconvert to one another: meso (m) and racemic (r) diads. They are in about the same proportion (50%) in the homopolymer[7] and other known siloxanes.[8] In high molecular weight PMPS, 42% m diads and 20% r diads are preformed EFS, and 8% m diads and 10% r diads may reach an EFS by means of one rotation through a chain bond requiring a very low activation energy: 1.6–1.7 kcal/mol. The rest, 20% r diads, require two rotations of the same activation energy to reach an EFS. This suggests that, in principle, two types of monomers could be considered from the point of view of rotational isomers: those monomers requiring one bond rotation and those requiring two bond rotations to form an excimer. Both should have different rates.

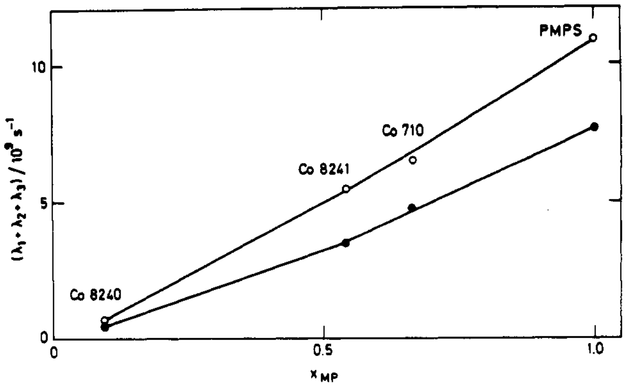
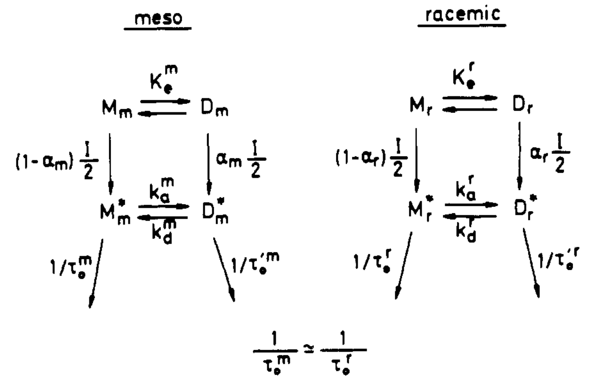


Figure 6. Same as in Figure 5, but $\lambda_1 + \lambda_2 + \lambda_3$ from global analysis.

Scheme I



Nevertheless, rotations seem to be so efficient that the excimer rise time is in any case below the time resolution in low-viscosity solvents, and, therefore, the experimental conditions do not allow one to distinguish between those two types of monomer or between preformed and rotational excimers.

Two types of excimers can also be distinguished with respect to their ability for dissociation. Excimers formed in meso diads (m*) require an activation energy for the rotational dissociation of 6.7 kcal/mol, whereas for excimers formed in racemic diads (r*), the activation energy is much smaller, 4.8 kcal/mol (assuming the same excimer binding enthalpy).[1] Consequently, it is reasonable to think that r* will dissociate much faster than m* and both types of excimer will have different decay parameters.

Without going into further details, at least three excited-state species can be expected: monomer (M*), m*, and r*. In light of this simplification, a kinetic mechanism can be proposed.

Mechanism. The kinetic mechanism proposed is shown in Scheme I. Of course, it is a simplification of the system, but it could be a first approach to the very complex problem.

An important feature of this mechanism is that it includes the monomer–dimer ground-state equilibrium, which is needed to account for the large proportion of EFS present in these siloxane polymers. α is the fraction of diads that are in an EFS conformation, and K_e is the corresponding monomer (M)–dimer (D) equilibrium constant: $K_e = \alpha/(1-\alpha)$. The formation of rotational excimers is included in a separate step described through the rate constant k_a. The influence of solvent viscosity enters into this step. Excimer dissociation is described through k_d. Meso and racemic diads are considered separately, since they have different proportions of EFS (described through α^m, K_e^m and α^r, K_e^r, respectively) and may also have different rates for bond rotation (k_a^m, k_d^m, and k_a^r, k_d^r, respectively).

According to this mechanism, the decays of monomer and excimer emissions would be expressed as sums of (2 + 2), or four, exponentials. However, the observed behavior can be somewhat simpler (requiring fewer exponentials) if certain conditions are met—for example, if the two excimers are similar (kinetically) or if any of the excimers is in the LTL. A special case is of interest here. When the rate constants for excimer formation are similar in both kinds of diads ($k_a^m = k_a^r$) and when only the r* excimer dissociates ($k_d^m \ll 1/\tau_0^{m'}$). Then the monomer simplifies to a biexponential decay and the excimer to a triexponential decay. This number of exponentials could be a good representation of our experimental decays, and the conditions imposed on k_a and k_d to obtain such simplification are reasonable according to the conformational analysis results.

A full verification of the mechanism described in Scheme I with the experimental data presently available is not possible. More experimental studies are in progress with the aim of determining the rate constants involved.

Conclusions

(1) The multiexponential nature of the decays indicates that the photophysical process is complex.

(2) There is coexistence of ground-state preformed excimers and rotational excimers in high molecular weight PMPS. Three excited-state species are proposed: M*, m*, and r*.

(3) In the low molecular weight copolymers, long-range excimers are also considered to coexist with the other two types of excimers.

(4) The rate constant for excimer formation by rotational motion is very large ($k_a = 10^9$–10^{10} s^{-1}), higher than that usually found in hydrocarbon polymers (10^8 s^{-1}).

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