Photophysics of Siloxanes. Influence of Preformed Dimers and Transition from Low-Temperature to High-Temperature Behavior of Dimeric and Polymeric Methylphenylsiloxane

Antonio L. Maçanita

Departamento de Química, Centro de Tecnología Química e Biológica, 2780 Oeiras, Portugal

Arturo Horta and Inés F. Piérola*

Departamento de Química Física, Facultad de Ciencias, Universidad a Distancia (UNED), 28040 Madrid, Spain

Received July 28, 1993; Revised Manuscript Received November 22, 1993[⊗]

ABSTRACT: Fluorescence spectra and fluorescence decays of dimethylphenyldisiloxane (DS) and of poly(methylphenylsiloxane) (PMPS), in methylcyclohexane dilute solution, were measured in a range of temperatures (−132 to +50 °C). This range is shown to cover both the low- and high-temperature limits and the crossover region. The steady-state results for DS show a typical Arrhenius behavior, compatible with a simple Birks kinetics. DS monomer fluorescence decays are biexponential, showing evidence for excimer dissociation, compatible with an isoemissive point observed in the range 5–27 °C. An excimer rise time could be observed for DS at the lowest temperatures, but the sum of the preexponential factors is larger than zero, proving that a certain fraction of the excimers come from ground-state dimers. In order to account for the presence of such preformed dimers, the kinetic scheme has been modified and the proper equations for this modified scheme have been derived. The steady-state results for PMPS indicate that about 50% of the chromophores form part of the ground-state preformed dimer conformations. Fluorescence decays of PMPS are too complex to yield kinetic parameters with physical meaning, but the steady-state results allow the extraction of the rate constant for excimer formation and its activation energy. A complete set of the Birks scheme rate constants was obtained as a function of temperature for DS, both from steady-state and transient experiments, with a good coincidence of the results obtained by the two methods. Apparent and corrected values of the rate constant for excimer formation, taking into account the contribution of ground-state preformed dimers, were also obtained.

Introduction

Methylphenylsiloxane chain molecules have very interesting photophysical behavior. Their fluorescence spectra are dominated by the emission from excimer, which in the homopolymer overshadows that of the monomer.[1-6] The temperature dependence of such excimer–monomer emission presents an isoemissive point indicative of an excited-state equilibrium.[2,3] At room temperature the behavior is typical of systems which are in the high-temperature limit (HTL),[2-4] contrary to what is usual in other phenyl-containing polymers, in which at ambient temperature the behavior is typical of the low-temperature limit (LTL).[2,7] In order to explain this accessibility of the siloxanes to the HTL, the great conformational flexibility of these molecules has been invoked.[2,5,8,9]

The analysis of flexibility in the polymer requires knowledge of what happens in the more simple structure of a diad, which can be represented by the dimer molecule. The stationary spectrum of such a dimer shows that, similar to what happens with the polymer, the ambient-temperature behavior of disiloxane is also typical of the HTL, with the same isoemissive point.[2]

The question is, by lowering the temperature sufficiently, will it be possible to block the attainment of excited-state equilibrium and reach the LTL in these compounds? The effect of lowering the temperature may be different in the long-chain polymer and in the dimer, hence the interest of studying both in parallel.

In the present work we study the photophysics of methylphenylsiloxane polymer in comparison with that of the disiloxane molecule. The emphasis is on the temperature dependence of their emission spectra in a broad range extending down to very low temperatures, from −132 to +50 °C. Our study covers both the stationary spectra and the transient-state emissions of these molecules. As we shall see, the decay of the polymer is more complex than that of the dimer and both types of molecules differ in their conformational behavior at low temperatures.

Conformational analysis of these molecules has shown that a large fraction of their ground-state conformers are preformed dimers.[8] It is then to be expected that an important part of the excimer emission (which is dominant in these systems) will come from such preformed dimers. The results to be presented below provide experimental evidence confirming the influence of such preformed dimers on the fluorescence of these molecules. Hence, excimer emission takes place by (at least) two mechanisms: kinetic (chain rotation) and equilibrium (preformed dimers). Defining a rate constant for excimer formation gives then only an apparent value. In the present paper we take into account both mechanisms of excimer formation in the kinetic scheme and use proper equations which allow us to distinguish the true rate constant from the apparent one.

Experimental Part

The homopolymer PMPS ($M_w = 1.15 \times 10^5$, $M_w/M_n = 1.71$) was part of a sample used in a previous work.[2] The dimeric analog, dimethylphenyldisiloxane (DS), and two monomeric analogs, phenylmethyldimethoxysilane (MS) and phenyldimethylethoxysilane (MSET), were purchased from Petrarch Systems and purified by preparative HPLC.[10] MS was the monomeric analog of PMPS, and MSET was the analog of DS as explained in ref 10.

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1994.

0024-9297/94/2227-0958$04.50/0

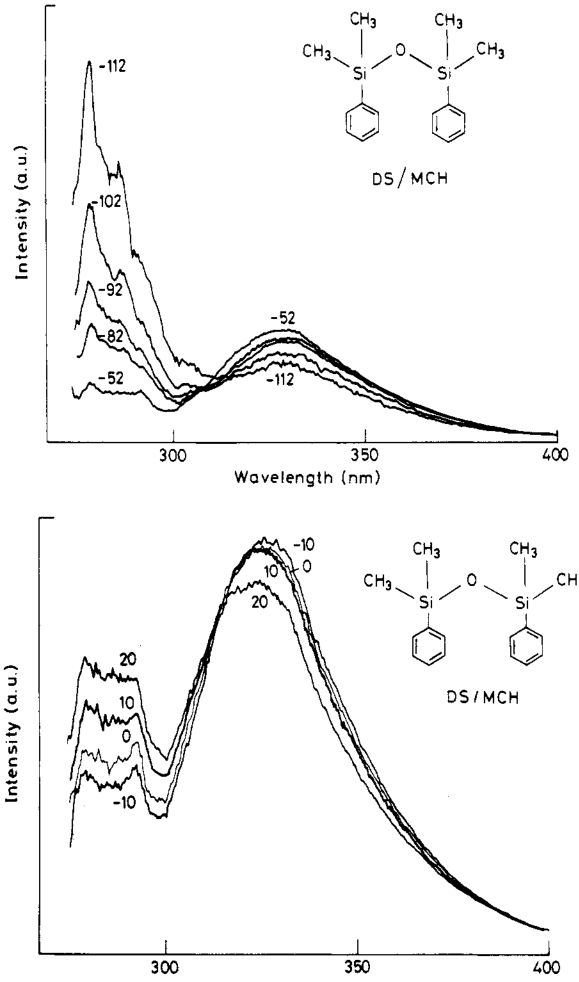


Figure 1. Fluorescence spectra of DS, in a MCH dilute solution, at different temperatures.

Solvent used for fluorescence measurements, methylcyclohexane (MCH; BDH, laboratory reagent), was purified as previously described.[11]

Steady-state fluorescence spectra were recorded with a Spex Fluorolog F212I. The spectra were corrected as previously described in ref 11. Solutions of optical density less than 0.6 at the excitation wavelength (260–270 nm, depending on the experimental conditions) were degassed by the freeze–pump–thaw technique (six cycles at 10^{-4} Torr) and then sealed. Solutions of the monomeric analog and of DS or PMPS to be compared with the first one were prepared with exactly the same optical density at the excitation wavelength. The temperature ramps were repeated at least three times, and the reproducibility was found quite acceptable.

The methodology followed in the analysis of the fluorescence decay times measured using the method of time-correlated single photon counting is the same as described before.[5] Samples used were the degassed samples employed for the steady-state experiments. The excitation wavelength was 250 or 260 nm (depending on the experimental conditions), and the monomer and excimer emissions were analyzed at 280 and 330 nm, respectively.

Results

Steady-State Results for DS. The stationary fluorescence of DS at several temperatures is shown on Figure 1. The highlights of these spectra are as follows: (i) In the range of temperatures 5–27 °C, the monomer band increases and the excimer band decreases, as the temperature rises; the monomer increase is at the expense of the excimer, so that an isoemissive point exists. (ii) For temperatures above 27 °C, the trend is similar, but the isoemissive point is no longer present; a new mechanism of deactivation enters into play at about 27 °C,[2,3] that breaks the isoemissive point. (iii) On decreasing T below 5 °C, the trend of the excimer band is opposite; the excimer decreases with T, until it almost disappears at −115 °C. This vanishing of the excimer band at very low T is a surprising result, if we consider that a large fraction of ground-state preformed dimers is predicted for disiloxane from conformational analysis.[8,9] According to the present results, such preformed dimers are almost nonexistent at the lowest T in the dimer.

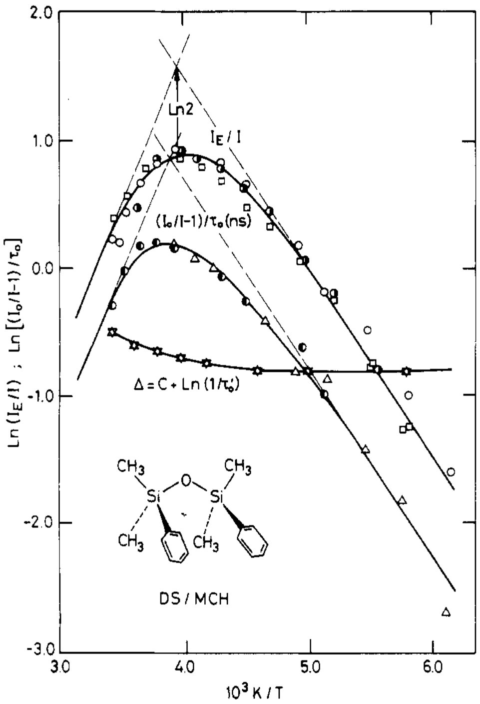
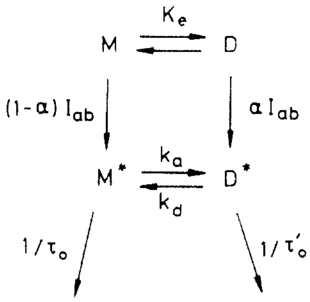


Figure 2. Arrhenius type plots of the fluorescence ratios I_E/I and $(I_0/I - 1)\tau_0^{-1}$, for DS in a MCH dilute solution. The different symbols correspond to different ramps of temperature. Δ is the difference of the two logarithmic functions.

What is most interesting from the temperature variation of these spectra is that, on lowering the temperature, we are able to change the regime, from the HTL, observed at room temperature, to the kinetically controlled LTL, with a crossover region in between them. The two limits, and the crossover, can be seen in Figure 2, where we show plots of $\ln(I_0/I - 1)/\tau_0$ vs $1/T$ and $\ln I_E/I$ vs $1/T$. I_0 represents the integral of the emission spectrum from the monomeric analog (MSET for DS; see the Experimental Part), and I_E and I are the integrals of the excimer band and of the monomer band of the DS spectrum, respectively. τ_0 is the lifetime of the monomeric analog, taken from ref 10. The results clearly describe two straight lines of opposite slopes, which correspond to the LTL and to the HTL, respectively. The transition point between them can be situated at −24 °C.

From the slopes of these straight lines drawn, we determine the activation energy, E_a (LTL), and the enthalpy, ΔH (HTL), corresponding to the monomer to excimer formation process, with the following results (kcal/mol): $E_a = 3.2$; $\Delta H = -4.0$ (previous results in cyclohexane had given $\Delta H = -3.4$).[2,3] Some more kinetic parameters can be determined from the plots shown in Figure 2, if a proper kinetic scheme is used. Ground-state preformed dimers[8,9] must be, in principle, taken into account for phenylsiloxanes. Thus, the kinetic scheme shown as Scheme 1 has been proposed[5,12] for these systems. α is the fraction of ground-state conformers which are

Scheme 1



preformed dimers, and K_e is their equilibrium constant: $K_e = \alpha/(1-\alpha)$. The kinetic equations deduced from such a scheme for the stationary state are as follows:

$$\left(\frac{I_0}{I}-1\right)\tau_0^{-1} = \frac{k_a + \alpha\tau_0^{-1}}{1-\alpha+k_d\tau'_0} \qquad (1)$$

$$\frac{I_E}{I} = \frac{k'_F}{k_F}\,\frac{\tau'_0(k_a+\alpha\tau_0^{-1})}{1-\alpha+k_d\tau'_0} \qquad (2)$$

k_a is the rate constant for the monomer to excimer formation, k_d is the rate constant for excimer to monomer dissociation, τ'_0 is the lifetime of the excimer, and k_F and k'_F are the rate constants for monomer and excimer decays, respectively.

The usual procedure for determining the rate constant for excimer formation, k_a, is to neglect preformed dimers ($\alpha = 0$) and to assume $k_d\tau'_0 \ll 1$ (LTL). Thus, the left-hand side of eq 1 yields k_a. From the intercept of the line corresponding to the LTL in the Arrhenius type plot of $(I_0/I - 1)\tau_0^{-1} \sim k_a = k_a{}^\circ \exp(-E_a/RT)$, we get, for DS $k_a{}^\circ = 2 \times 10^{12}$ s^{-1} and E_a = 3.2 kcal/mol. The k_a extrapolated to 20 °C with the Arrhenius expression gives the value 8 × 10^9 s^{-1}, which will be compared below with the result of transient experiments.

The difference between $(I_0/I - 1)/\tau_0$ or I_E/I values measured at the crossover transition temperature and the corresponding ones extrapolated from the LTL and HTL straight lines is equal to $\ln(2-\alpha)$, and since, for this system, it is approximately equal to ln 2, this means that only a very small fraction of ground-state conformers (below 10%) are dimers at the crossover temperature (−24 °C). This result is in accordance with the transient-state results (see below), but it is unexpected as mentioned before.

It can be seen in Figure 2 that there is a difference ($\Delta = C + \ln(1/\tau'_0)$) between $\ln(I_0/I - 1)/\tau_0$ and $\ln I_E/I$ which is about constant for the lowest temperatures but increases sharply in the high-temperature range. This is due to the fact that τ'_0 is temperature dependent, and this is especially important for the higher temperatures ($T > -20$ °C). It is also worth noting that we attain a good result with the $(I_0/I - 1)/\tau_0$ representation because we are using a proper model compound (MSET) for the monomer, as discussed in ref 10.

As we shall see in the next section, τ'_0 obtained from transient experiments is $\tau'_0 = 12.5 \times 10^{-9}$ s, at the crossover T = −24 °C. Hence, the rate constant for the excimer to monomer dissociation, k_d, at this temperature, is $k_d = 1/\tau'_0 = 8.0 \times 10^7$ s^{-1}. The activation energy for such excimer dissociation, E_d, can be estimated from the values of E_a and ΔH quoted above: $E_d = E_a - \Delta H$ = 7.2 kcal/mol. From k_a, k_d, E_a, and E_d, we obtain, for T = 20 °C, the values shown in Table 1.

Transient-State Results for DS. The results obtained with the single-photon-counting technique for the decays of DS are shown on Figure 3 for a representative temperature. For other temperatures the results are similar (see Table 2). The decays are in all cases biexponential, which is again compatible with a Birks

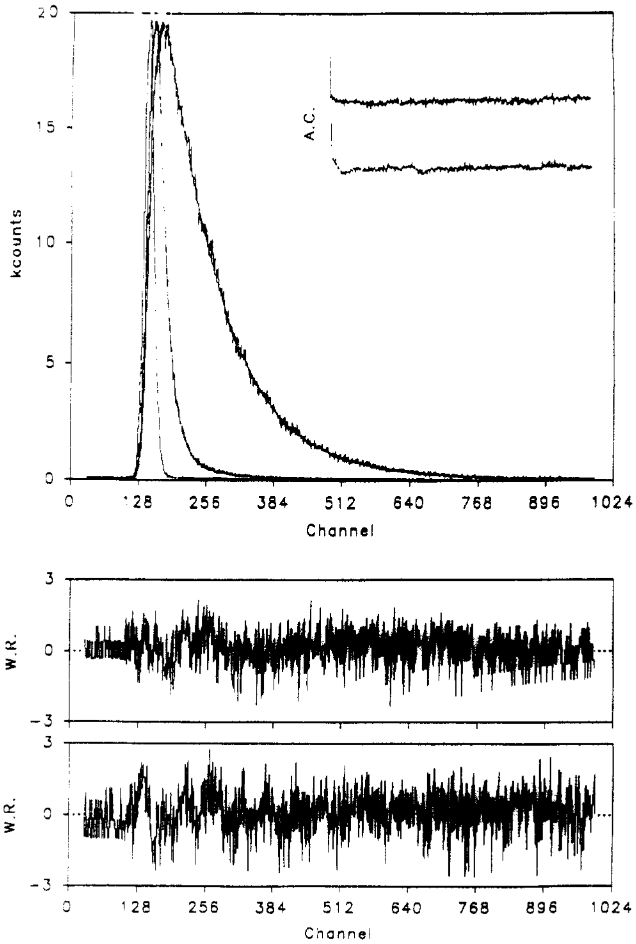


Figure 3. Monomer (290-nm) and excimer (330-nm) decay of DS, in a MCH solution, at −100 °C (parameters in Table 2).

Table 1. Comparison of the Kinetic Parameters Obtained from Stationary Spectra and from Transient Experiments (Decays), for the Dimer (DS), in Methylcyclohexane Solutions

	stationary	transient
crossover LTL–HTL	−24 °C	−21 °C
E_a (kcal/mol)	3.2	2.8
E_d (kcal/mol)	7.2	6.5
ΔH (kcal/mol)	−4.0	−3.3
$k_a{}^\circ$ (s^{-1})	2 × 10^{12}	1.2 × 10^{12}
$k_d{}^\circ$ (s^{-1})	1.6 × 10^{14}	3.4 × 10^{13}
k_a (20 °C) (s^{-1})	8.0 × 10^9	9.8 × 10^9
k_d (20 °C) (s^{-1})	6.7 × 10^8	4.8 × 10^8

Table 2. Best Fit Parameters of Monomer and Excimer Emission Decays for DS in a MCH Dilute Solution, as a Function of Temperature, from Global Analysis

T/°C	τ_2/ns	τ_1/ns	a_2	a_1	χ^2
−100	2.83	15.3	9.6^a	0.18^a	1.1
			−1.3	5.1	
−70	0.93	13.3	20	0.19	1.3
			0.23	5.9	
−40	0.36	13.7	49	0.57	1.4
			−1.6	6.1	
−30	0.20	13.0	83	0.71	1.2
			1.2	5.9	
−20	0.23	10.7	67	1.1	1.3
			−1.8	4.9	
21.5^b	0.11	9.7	36	2.2	1.2

[a] First row, monomer; second row, excimer. [b] At 21.5 °C, only monomer emission decays were analyzed.

Table 3. Kinetic Parameters for the Dimer (DS), from Transient Experiments (Decays), in Methylcyclohexane Solutions ($\alpha = 0$)

T/°C	$k_a/10^9\ s^{-1}$	$k_d/10^7\ s^{-1}$	$\tau'_0/10^{-9}$ s	$\tau_0/10^{-9}$ s
-100	0.32	0.46	15.2	30.2
-70	1.03	0.91	13.2	28.0
-40	2.7	3.1	13.7	18.7
-30	4.2	4.5	12.9	16.6
-20	4.2	7.1	10.7	13.0
21.5	8.3	53.0	11.1	3.1

scheme (see Scheme 1). Both the monomer and the excimer decay have a third component of very small amplitude, which represents less than 6% of the total intensity at -100 °C with a very long time constant (78 ns at -100 °C). It could be due to impurities, although repeated HPLC purification did not eliminate it. It seems reasonable to neglect this long component and interpret the results with a global biexponential analysis.

The kinetic equations deduced from Scheme 1 for the transient-state decays are as follows:

$$I_M(t) = a_{11}e^{-\lambda_1 t} + a_{12}e^{-\lambda_2 t} \qquad (3)$$

$$I_E(t) = a_{21}e^{-\lambda_1 t} + a_{22}e^{-\lambda_2 t} \qquad (4)$$

where λ_1 and λ_2 have the same meaning as in a simple Birks scheme:[7]

$$\lambda_{2,1} = \frac{1}{2}\{X + Y \pm [(X - Y)^2 + 4k_ak_d]^{1/2}\} \qquad (5)$$

with $X = k_a + 1/\tau_0$ and $Y = k_d + 1/\tau'_0$. But now the preexponential amplitudes are

$$\begin{aligned} a_{11} &= k_F[(\lambda_2 - X)(1 - \alpha) + \alpha k_d]/(\lambda_2 - \lambda_1) \\ a_{12} &= k_F[(X - \lambda_1)(1 - \alpha) - \alpha k_d]/(\lambda_2 - \lambda_1) \\ a_{21} &= k'_F[k_a(1 - \alpha) + \alpha(X - \lambda_1)]/(\lambda_2 - \lambda_1) \\ a_{22} &= k'_F[-k_a(1 - \alpha) + \alpha(\lambda_2 - X)]/(\lambda_2 - \lambda_1) \end{aligned} \qquad (6)$$

Table 2 shows the best fit parameters of a global analysis of monomer and excimer decays at different temperatures, and Table 3 summarizes the values determined for the rate parameters of Scheme 1, assuming $\alpha = 0$. They are also shown in Figure 4 as a function of temperature. We can see thatn τ'_0 is much less sensitive to temperature than τ_0 is. From the temperature variation of the rate constants, we get the corresponding activation energies. In Table 1 we show the result in comparison with the corresponding values determined from the stationary spectra. In general, there is good agreement and a single picture emerges.

A rise time can be observed (Table 2) for the excimer, but the sum of the preexponential factors is larger than zero. A rise time could be detected at room temperature in a copolymer, only when using a very viscous solvent (heavy oil).[5] The preexponential factors did not add up to zero in that case either.[5] Here, with DS, we find a similar situation by lowering T.

From the results of Table 3 shown in Figure 4, we can see that, although k_d is always smaller than k_a at the temperatures studied, the increase with T is larger for k_d so that, extrapolating the experimental results, it is possible to predict that k_d will reach the same value as k_a at about 70 °C. On the other hand, k_a follows a typical Arrhenius behavior, whereas the other rate constants of Scheme 1 do not.

Steady-state Results for PMPS. The results for polymer PMPS obtained from the stationary spectra are shown in Figure 5. The most important features are the following: (i) The same isoemissive point of the dimer is observed in the polymer, this time in the range 5–32 °C. (ii) At higher temperatures also some other deactivation mechanism breaks this isoemissive point.[2,3] (iii) The same as with the dimer, the polymer shows the two temperature limits, LTL and HTL, and a crossover between them; the transition temperature for this crossover is -6 °C, somehow higher than that of the dimer. (iv) Both $\ln(I_0/I - 1)/\tau_0$ and $\ln I_E/I$ vs $1/T$ yield noticeable curvature in the LTL, which can be attributed to a predominance of preformed dimers in the formation of excimer since if we make $k_a = 0$ in eq 1 simplified to the LTL, $(I_0/I - 1)/\tau_0 = \alpha\,\tau_0^{-1}/(1 - \alpha)$. At such a low temperature as -110 °C, I_E/I is larger than 1 (Figure 6) and even at -132.9 °C (solid solvent); so preformed dimers persist at very low temperatures.

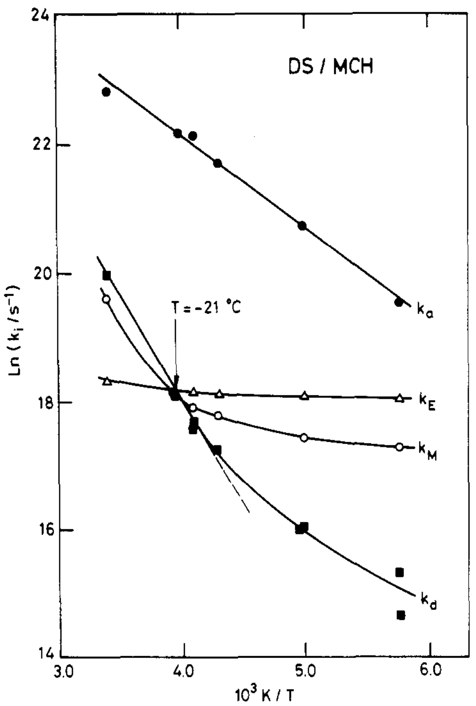


Figure 4. Rate constants for the excited-state process of DS, in a MCH dilute solution, as a function of temperature. $k_M = 1/\tau_0$; $k_E = 1/\tau'_0$.

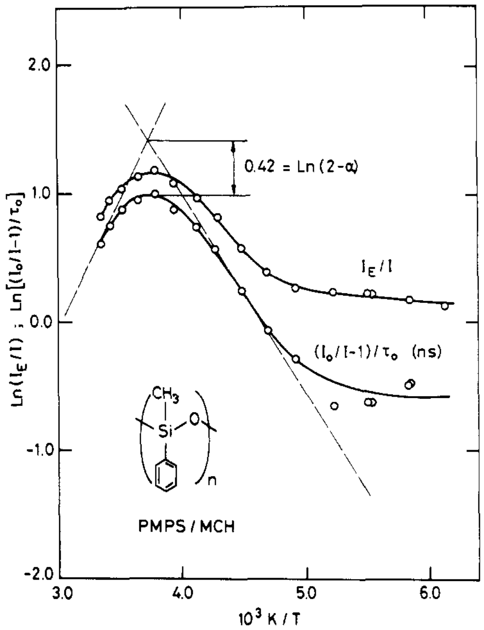


Figure 5. Arrhenius type plots of the fluorescence ratios I_E/I and $(I_0/I - 1)\tau_0^{-1}$, for PMPS in a MCH dilute solution.

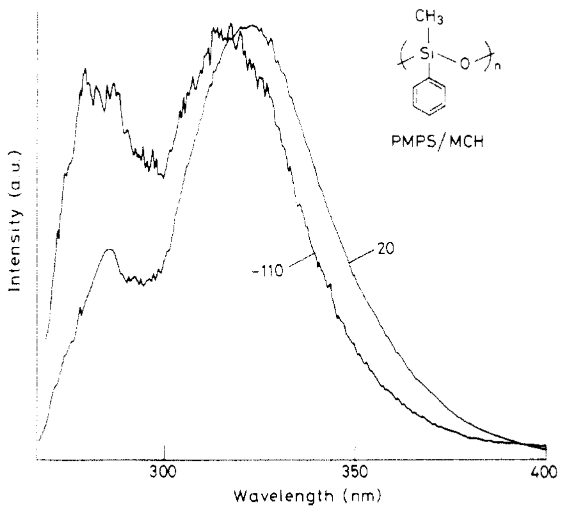


Figure 6. Fluorescence spectra of PMPS, in a MCH dilute solution, at different temperatures.

Table 4. Kinetic Parameters for the Polymer (PMPS), Obtained from Stationary Spectra, in Methylcyclohexane Solutions

crossover LTL–HTL	−6 °C
E_a (kcal/mol)	3.2
ΔH (kcal/mol)	−3.9
k_a° (s^{-1})	1.7×10^{12}
k_a (20 °C) (s^{-1})	6.7×10^9
α (−6 °C)	0.48

This is in contrast with what is observed in the disiloxane, where no significant curvature of the plots appears (and I_E/I tends to vanishingly small values).

The difference between $(I_0/I - 1)/\tau_0$ or I_E/I values measured at the crossover transition temperature and the corresponding ones extrapolated from the LTL and HTL straight lines is equal in this case to about 0.42, that corresponds to $\alpha = 0.48$, much larger than for DS and not far from the theoretical prediction: 0.6.[8,9] Above this temperature, the behavior is dominated by equilibrium in the excited state. Below it, the control is mainly kinetic, but with a large proportion of preformed dimers.

The similarity of the two representations, $(I_0/I - 1)/\tau_0$ and I_E/I (Figure 5), is attained only when the proper model compound is used. For the polymer PMPS this model is MS, as discussed in ref 10.

The analysis of the data in Figure 5 in the linear part of the LTL yields (assuming $\alpha = 0$ and $k_d\tau'_0 \ll 1$) for the monomer to excimer formation the values $E_a = 3.2$ kcal/mol and $k_a^\circ = 1.7 \times 10^{12}$ s^{-1}, which extrapolate to $k_a = 6.7 \times 10^9$ s^{-1} at 20 °C. It is interesting to compare these values of the polymer with those obtained for the dimer. As we can see in Tables 1 and 4, they are very similar. Extrapolation to 20 °C yields for k_a a value very close to that of the dimer. Hence, the kinetic formation of excimer seems to be as fast in the polymer as it is in the dimer. Notice that the order of magnitude of k_a at 20 °C is almost 10^{10} s^{-1}, hence a very fast process compared to other phenyl-containing polymers.[7]

The assumption $\alpha = 0$ in eqs 1 and 2 is reasonable for DS, but it cannot be made for PMPS. Thus, the above k_a and E_a values are apparent values (k_a^{ap} and E_a^{ap}) which should be corrected to take into account the contribution of preformed dimers. The relationships between the true values, k_a and E_a, and the apparent ones deduced above, k_a^{ap} and E_a^{ap}, are[6]

$$k_a = k_a^{ap} - \alpha\left(k_M + \frac{k_a^{ap}}{1 + k_d\tau'_0}\right) \qquad (7)$$

Table 5. Apparent and Corrected Values of the Rate Constant for Excimer Formation of PMPS in a MCH Dilute Solution, Determined from the Steady-State Results, at Several Temperatures

T/°C	$k_a^{ap}/10^9$ s^{-1}	$k_a/10^9$ s^{-1}
−100	0.6	0.3
−70	1.7	0.9
−30	2.3	1.4
−20	2.9	1.9
0	4.7	3.8
20.5	7.0	6.2

$$E_a = E_a^{ap} - \alpha E_e \qquad (8)$$

with $E_e = -R\, d[\ln K_e/(1/T)]$, which for phenylsiloxanes takes a very low value, 0.2 kcal/mol.[8,9] Apparent k_a values, calculated with $E_a = 3.2$ kcal/mol and $k_a^\circ = 1.7 \times 10^{12}$ s^{-1} at several temperatures, and the corresponding corrected values, calculated from eqs 7 and 8 for $\alpha = 0.6$, can be compared in Table 5. We can see that the difference between the corrected k_a values and those assuming $\alpha = 0$ is only about 10% at temperatures close to room temperature and that it grows to 100% at the lower temperatures. Nevertheless, α has been considered constant in these calculations and its temperature dependence could make even more important the correction. For E_a, the correction with $\alpha = 0.6$ is very small, within the range of the experimental error.

Evidence for ground-state preformed dimers has also been observed in other systems.[13,14] In some of them, there is a driving force for dimer formation due to hydrophobic interactions or to mesogenic groups.[13] In others, the chromophore is of a very short lifetime precluding the dynamic formation of excimers and only preformed dimers contribute.[14]

Transient-State Results of PMPS. The decays of the homopolymer are complex and cannot be fitted to any simple kinetic scheme. From the shortest decay time of PMPS in cyclohexane, approximate values $k_a = 8 \times 10^9$ s^{-1}, at 21 °C, and $k_a = 10 \times 10^9$ s^{-1}, at 40 °C, were obtained.[5] We can see that these results are in very good accord with the ones obtained from stationary spectra in methylcyclohexane, shown on Table 4. They also fit very well in the trend obtained for DS (Table 3), confirming the similar kinetic formation of excimer in the dimeric and polymeric molecules.

Independent analysis of monomer and excimer decays of PMPS at several temperatures requires three or four exponentials in all cases to get reasonable χ^2 values. Both monomer and excimer decays have a first component with a very short lifetime, lower than 0.2 ns, which represents less than 1% of the total emission. Most of the emission corresponds, at any temperature, to the component having the longest τ_i.

No rise time is detected for the excimer at any temperature. This is in accord with the relative importance which preformed dimers have in the polymer, and it is in contrast with what happens for DS, where a rise time can be detected.

Discussion

In spite of the similar values for the kinetic constants in polymer and dimer, there still remains the big dissimilarity that in the polymer a large fraction of excimers come from preformed dimers, in particular at the lowest temperatures attainable (see Figure 5), while in the dimer these preformed dimers have no observable contribution (see Figure 2). So, the persistence of preformed dimers is a genuine polymer effect.

On the other hand, the difference between DS and PMPS with regard to their low-temperature behavior which was interpreted in terms of differences in ground-state preformed dimers could also be interpreted assuming that energy migration can take place along the chain in PMPS and, of course, it cannot in DS. In this way k_a for the homopolymer would have two terms, a temperature-independent term due to energy migration and the Arrhenius type term due to the segmental mobility. At high temperatures, the second term would dominate due to the high flexibility of siloxanes, but for low temperatures k_a would level off to the energy migration contribution. This argument would explain the habit of Figure 5.

In order to discern whether energy migration is to be expected in PMPS or not, we can look at conformations. If we look in the traditional way, by considering just the states of diads, then we find that the most probable diad conformations are EFS.[8] The conclusion then is that energy migration should not be expected, because of the abundance of such diad light traps. But if we extend the analysis of conformations to consider the states of triads, then the picture changes. According to recent calculations,[15] the most stable state of a triad (units 1, 2, and 3) contains none of its two constituting diads (1,2 and 2,3) in a EFS state. To find a triad containing one of its diads in an EFS state, one has to go to higher energies (lower probabilities), the energy needed depending very much on tacticity. In any case, the conformational analysis of triads[15] suggests that the diad traps are not so abundant and hence that energy migration is a possibility in PMPS. With this hypothesis, the rate constant for energy migration $k_a{}^\circ$ would be the level off value of k_a in the range of the lowest temperatures, when the rate constant for excimer formation through rotation is negligible with respect to the temperature-independent $k_a{}^\circ$. That would make $k_a{}^\circ$ equal to about 5.7×10^8 s^{-1}.

Thanks to the kinetic model used, we have been able to obtain true rate constants for the excimer formation in PMPS, once the effect of the direct absorption of light by ground-state preformed dimers has been taken into account. Our results show that the influence of preformed dimers on E_a values is almost negligible. Regarding k_a, the absolute difference between the apparent and true values is in the range $(0.3\text{–}1.0) \times 10^9$ s^{-1}, which makes the correction important at the lowest temperatures but not so relevant at temperatures close to ambient temperature.

The results deduced from the stationary state and from the transient experiments are very much coincident, yielding support to the kinetic scheme that we have used to interpret them and also to the correct choice of model molecules for the monomeric unit.

The rate constant values deduced show that the chain mobility is very similar in the dimer and in the high polymer. In both cases, these rate constants are much higher than in other polymer systems, evidencing, from a photophysical point of view, the very high chain mobility of the siloxanes. This is also the reason why the role of preformed dimers is diminished in spite of their relatively large abundance in the siloxanes. As eqs 1 and 2 show, the fraction of preformed dimers, α, is modulated by τ_0^{-1} and the result $\alpha\tau_0^{-1}$ has to be large in comparison to k_a if the dimers are to represent a sizable contribution to fluorescence. Here, both k_a and α are much larger than in typical hydrocarbon chains, but, as the numerical results of Tables 3 and 5 show, k_a dominates over $\alpha\tau_0^{-1}$ at all temperatures. In other systems of lower α the contribution from preformed dimers can nevertheless be very large, if τ_0 is very small[14] or if k_a is small. This is in accordance with previous conclusions based on the dependence of excimer emission on the viscosity of the medium for the siloxanes.[12]

The rate constant values obtained also show that excimer dissociation is a very effective process, k_d attaining very high values as temperature increases and becoming the dominant effect.

Acknowledgment. This work was supported by Grant No. PB89/0198 from DGICYT (Spain), by CTQB (Portugal), and by Acción Integrada Spain–Portugal No. 20B.

References and Notes

(1) Salom, C.; Horta, A.; Hernández-Fuentes, I.; Piérola, I. F. *Macromolecules* **1987**, *20*, 696.

(2) Salom, C.; Hernández-Fuentes, I.; Piérola, I. F.; Horta, A. *Macromolecules* **1989**, *22*, 1874.

(3) Salom, C.; Gómez-Antón, M. R.; Horta, A.; Hernández-Fuentes, I.; Piérola, I. F. *Macromolecules* **1987**, *20*, 1627.

(4) Wu, S. K.; Jiang, Y. C.; Rabek, J. F. *Polym. Bull.* **1980**, *3*, 319.

(5) Maçanita, A. L.; Piérola, I. F.; Horta, A. *Macromolecules* **1991**, *24*, 1293.

(6) Maçanita, A. L.; Horta, A.; Piérola, I. F., submitted for publication in *Macromolecules*.

(7) (a) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 31. (b) Birks, J. B. *Photophysics of Aromatics Molecules*; Wiley: New York, 1971.

(8) Rubio, A.; Freire, J. J.; Piérola, I. F.; Horta, A. *Macromolecules* **1989**, *22*, 4014.

(9) Horta, A.; Rubio, A.; Freire, J. J.; Piérola, I. F. *Macromolecules* **1991**, *24*, 3121.

(10) Maçanita, A. L.; Danesh, P.; Peral, F.; Horta, A.; Piérola, I. F., submitted.

(11) Maçanita, A. L.; Costa, F. P.; Costa, S. M.; Melo, E. C.; Santos, H. *J. Phys. Chem.* **1989**, *93*, 336.

(12) Salom, C.; Semlyen, J. A.; Clarson, S.; Hernández-Fuentes, I.; Maçanita, A. L.; Horta, A.; Piérola, I. F. *Macromolecules* **1991**, *24*, 6827.

(13) (a) Duhamel, J.; Yekta, A.; Hu, Y. Z.; Winnik, M. A. *Macromolecules* **1992**, *25*, 7024. (b) Ganguly, T.; Farmer, L.; Li, W.; Bergeron, J. Y.; Gravel, D.; Durocher, G. *Macromolecules* **1993**, *26*, 2315. (c) Rauscher, V.; Bassler, H. *Macromolecules* **1990**, *23*, 398.

(14) (a) Mendicuti, F.; Patel, B.; Waldeck, D. H.; Mattice, W. L. *Polymer* **1989**, *30*, 1680. (b) Patel, B.; Mendicuti, F.; Mattice, W. L. *Polymer* **1992**, *33*, 239. (c) Mendicuti, F.; Mattice, W. L. *Polymer* **1992**, 4180.

(15) Horta, A.; Freire, J. J.; Piérola, I. F., submitted to *Macromolecules*.