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Influence of Isolated Chromophores on the Temperature Dependence of the Excimer Emission in Steady-State and Time-Resolved Fluorescence of Polysiloxanes

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ABSTRACT: Steady-state fluorescence spectra and time-correlated emissions of a copolymer of dimethylsiloxane and methylphenylsiloxane were measured, as a function of temperature, in the range −70 to 30 °C. The stationary results indicate that the system is always, apparently, in the low-temperature limit, with a very low activation energy for excimer formation. Monomer decays are triexponential, and one of the components shows, at any temperature, a lifetime very similar to the monomeric analog. ^{29}Si NMR spectra demonstrate that the chromophore sequence distribution is very close to random and that about 79% of the phenyl units are isolated. The fluorescence results can be explained in light of a kinetic scheme which takes into account the existence of isolated chromophores (64%, as calculated from the monomeric decays) and chromophores which form excimers with the same photophysical characteristics as in a homopolymer diad. Such a kinetic scheme has been used to develop the equations for steady-state and time-resolved experiments, and with use of them, apparent and corrected values of some kinetic parameters, such as the rate constant for excimer formation and the corresponding activation energy, have been determined.

Introduction

In siloxane copolymers containing both methylphenyl and dimetyl units, the fluorescence emission depends critically on the comonomer composition.[1,2] For the methylphenyl homopolymer (PMPS) the fluorescence consists of a broad band, mainly due to excimer emission at 325 nm, with a small shoulder corresponding to monomer emission at 285 nm. In the copolymers, as the methylphenyl contents diminishes, the excimer emission also diminishes and the monomer emission becomes more important. For a copolymer composition of only 9% in methylphenyl units, the fluorescence band is almost exclusively monomer emission with the excimer practically hidden as a long tail of such emission.[1]

The temperature variation of the fluorescence emission in the homopolymer and in the copolymers of not so low methylphenyl content shows that they are in the high-temperature limit (HTL), for temperatures in the vicinity of ambient.[2] Thus, the excimer to monomer fluorescence ratio, I_E/I, diminishes on increasing T, due to excimer dissociation.[3] The low-temperature limit (LTL) is reached, in the case of the homopolymer, only at temperatures much lower than ambient. A crossover between the HTL and LTL takes place at about −6 °C.[4] This peculiar behavior is not particular of the polymer, since the dimeric analog (disiloxane) also shows the same pattern, with the crossover between the HTL and LTL occurring at about −24 °C.[3,4] The rate constant for excimer formation, as determined from transient experiments, is also similar in polymer and dimeric molecules, at room temperature.[4,5]

However, the copolymer having very low methylphenyl content does not fit into this pattern, its behavior being somehow opposite.[2] In the present work, we analyze the fluorescence emission of such low phenyl containing copolymer, by studying the temperature dependence of its stationary spectra and of its decay. The chromophore sequence length has also been determined by ^{29}Si NMR spectroscopy.

Experimental Part

Two copolymers of dimethylsiloxane and methylphenylsiloxane were employed in this work: Co8240 and Co8241. They were provided by Polysciences and used in a previous work.[1] Their molecular weights, determined by vapor-pressure osmometry, are $M_n = 6.4 \times 10^3$ and 4.2×10^3, respectively. The mole fraction of methylphenyl units in the copolymers, determined spectrophotometrically, is 0.095 and 0.543, respectively.

Solvent used for fluorescence measurements, methylcyclohexane (MCH) (from BDH, laboratory reagent), was purified as previously described.[6] The monomeric analog,[7] methylphenyldimethoxysilane (MS), was purchased from Petrarch Systems and it was purified by HPLC preparative.

Steady-state fluorescence spectra were recorded with a Spex Fluorolog F212I. The spectra were corrected, as previously described in ref 6. 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. The temperature ramps were repeated at least three times, and the reproducibility was found to be quite acceptable.

The methodology followed in the analysis of the fluorescence decay times measured using time-correlated single-photon counting is the same as described before.[5] Samples were the degassed ones employed for the steady-state experiments. The excitation wavelength was 250 nm and the monomer emission was analyzed at 280 nm.

^{29}Si NMR spectra were obtained on a Bruker FT spectrometer, at 79.5 MHz. Chemical shifts are given relative to tetramethylsilane internal reference. Bulk samples and 30% solutions in chloroform-*d*, with 0.02 M Cr(acac)$_3$ as relaxation agent,[8–10] yield about the same spectra. Their integrals reproduce (see Table 1) the copolymer composition determined by different method (spectrophotometrically). The number average molecular weights, calculated from the ratio of the total integral to the integral of the end groups ($M_n = 7 \times 10^3$ and 5×10^3, for Co8240 and Co8241, respectively) reproduce well the order of magnitude of the M_n values determined by vapor-pressure osmometry (see above).

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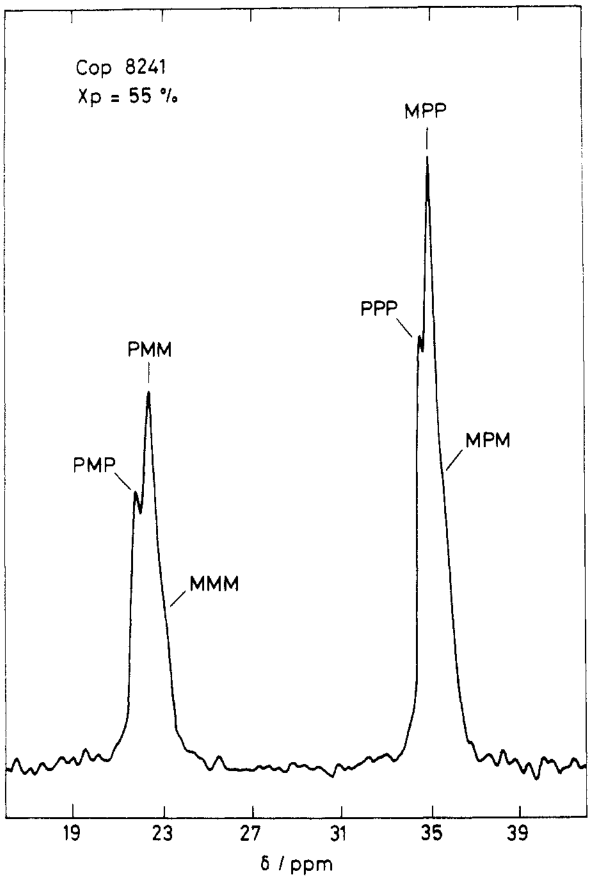


Figure 1. ^{29}Si NMR spectra of copolymer 8241.

Results

NMR Spectra. ^{29}Si NMR spectra (Figures 1 and 2) of Co8240 and Co8241 show three bands centered at chemical shifts of about -7, 22, and 35 ppm. The first band corresponds to the end groups (trimethylsilane, represented by E in Table 1), and it is decomposed into two peaks corresponding to methylphenyl or dimethyl preending groups. The band placed at 22 ppm corresponds to comonomer sequences centered in a dimethyl unit (represented by M in Table 1). It is resolved in three peaks corresponding to the three types of triads formed by a central dimethyl unit and two lateral units, which can be dimethyl or methylphenyl.[8-10] The band centered at about 35 ppm corresponds to triads centered in a methylphenyl unit (represented by P in Table 1), and the three peaks correspond to the three types of triads shown in Table 1. It is also remarkable that M or P units in cycles give signals centered at 16 and 30 ppm, respectively, whereas they cannot be distinguished of linear structures by ^{1}H NMR spectroscopy, and thus, it can be concluded from Figures 1 and 2 that these copolymer samples are free of residual cyclic compounds.

Table 1 summarizes the proportion (x in percent) of the different sequences and end groups and compares them with the calculated values[11] assuming a random distribution (x_R in percent). For both copolymers, the experimental sequence length distribution is very close to the random one, which is typical of copolymers synthesized under equilibrium conditions. It is very interesting to notice that about 79% of the P units of Co8240 are isolated in the chain (MPM triads in Table 1), and the remaining 21% P units are directly joined to at least one other P unit (triads MPP and PPP, in Table 1).

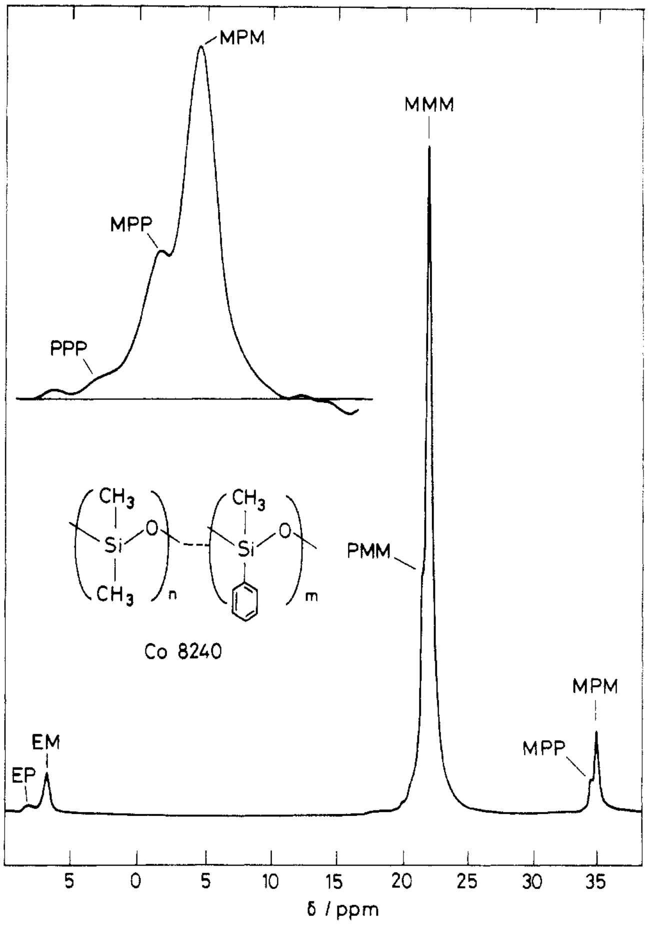


Figure 2. ^{29}Si NMR spectra of copolymer 8240. Overimposed is the enlarged band corresponding to sequences centered in a methylphenylsiloxane unit.

Table 1. Probability of Comonomer Sequences, Determined by Means of ^{29}Si NMR Spectroscopy

	Co8240		Co8241	
sequence[a]	x_R/%[b]	x/%[b]	x_R/%	x/%
P		9		55
M		91		45
PMP	1	2	30	32
PMM	16	14	50	46
MMM	83	84	20	22
PPP	1	1	30	31
PPM	16	20	50	45
MPM	83	79	20	24
PE	9	17	55	58
ME	91	83	45	42

[a] M, dimethylsiloxane unit; P, methylphenylsiloxane unit; E, trimethylsilane terminal unit. [b] x was estimated from the detailed peak structure of the bands. x_R was estimated from the overall comonomer composition assuming a random distribution.

It is also quite noticeable that in a copolymer of 55% P units in the chain (Co8241), a non-negligible proportion of chromophores (24%; see Table 1) are isolated in the chain. They should be taken into account in any analysis of the fluroescence decay. But this may not be easy because isolated chromophores are only one of the reasons for the complex emission decays of copolymers; meso and racemic diads with different kinetic parameters may give rise to tetraexponential decays[4,5] and the analysis considering one more component looses its physical meaning. Co8241 was used only in the NMR measurements to check the validity of the method.

Steady-State Fluorescence Spectra. In Figure 3 we show the temperature variation of the results obtained from the stationary spectra. For the lifetime and the emission intensity of the isolated chromophore, τ_0 and I_0, we take the values determined for a MCH solution of the monomeric model compound, methylphenyldimethoxy-

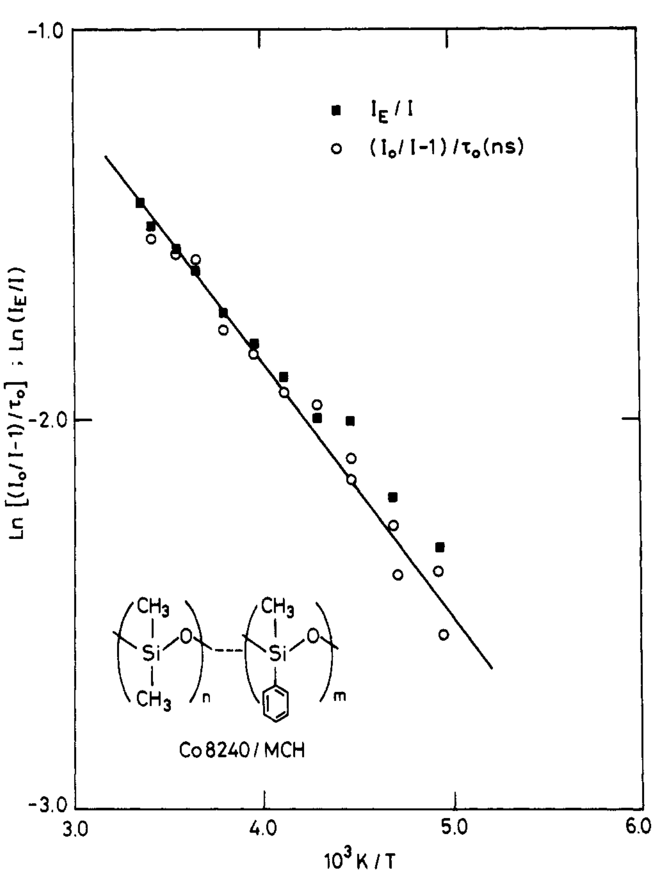


Figure 3. Arrhenius type plot of the fluorescence ratios I_E/I and $(I_o/I - 1)\tau_o^{-1}$ for the copolymer 8240 in dilute MCH solution.

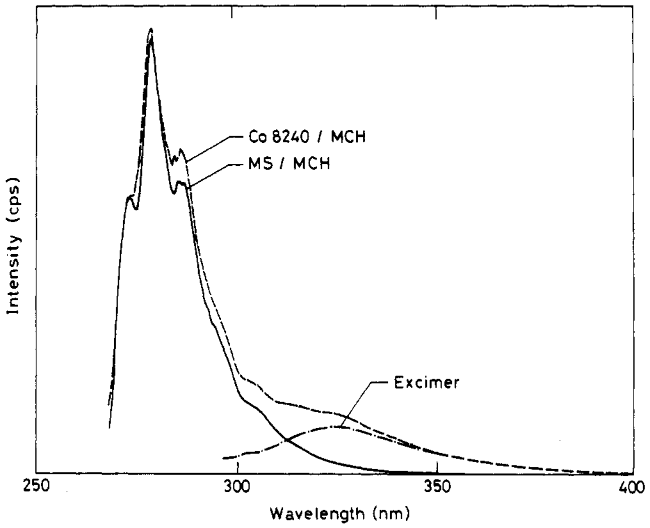


Figure 4. Fluorescence spectra of copolymer 8240 and of monochromophoric model compound MS in dilute MCH solution and the excimer band obtained by subtracting the MS spectrum normalized to 270 nm. λ_{ex} = 265 nm and T = -70 °C.

silane (MS), of exactly the same optical density as the copolymer solution. MS was considered the best monomeric analog of the copolymer, among a set of monophenylsilanes, because of its spectral characteristics.[7] The excimer emission, I_E, was determined at 330 nm, with the fluorescence spectrum of the copolymer dilute solution, by subtracting the MS spectrum normalized at 270 nm (see Figure 4). The monomer emission intensity, I, was measured, as for I_o, at 290 nm.

The plot of $\ln(I_o/I - 1)/\tau_o$ and of $\ln(I_E/I)$ vs $1/T$ both yield the same habit. As we can see, the behavior is typical of the LTL, in the whole range of temperatures studied: -70 to 24 °C here and 5 to 60 °C in ref 2. No crossover to the HTL is present, although the temperature reaches the range where the homopolymer and a dimeric analog show HTL behavior.[3]

In accordance with a simple Birks scheme, the following equations are derived:[4,6,12]

$$\left[\frac{I_o}{I} - 1\right]\tau_o^{-1} = \frac{k_a}{1 + k_d\tau_o'} \tag{1}$$

$$\frac{I_E}{I} = \frac{k_F'}{k_F}\tau_o'\frac{k_a}{1 + k_d\tau_o'} \tag{2}$$

where k_F and k_F' represent the rate constants for monomer and excimer radiative decays, respectively, the ratio of which is approximately temperature independent. k_a is the rate constant for excimer formation, k_d the rate constant for excimer dissociation, and τ_o' the excimer lifetime. Assuming that in the LTL the rate constant for excimer dissociation, k_d, is much smaller than the rate constant for excimer decay, $k_E = 1/\tau_o'$, then $k_d\tau_o' \ll 1$, and the linear fit of the results shown on Figure 3 yields the preexponential factor, $k_a°$, and the activation energy, E_a, for the monomer to excimer formation process:

$$E_a = 1.2 \text{ kcal/mol} \tag{3}$$

$$k_a° = 1.7 \times 10^9 \text{ s}^{-1}$$

This activation energy is larger than 0.8 kcal/mol, the value previously reported for the same copolymer[2] in a range of higher temperatures, 5-60 °C, and both values are much lower than the activation energy determined for the homopolymer (3.2 kcal/mol)[4] and than the activation energy of viscous flow, $E(T/\eta)$ = 3 kcal/mol in this solvent, MCH.

Extrapolating to 20 °C gives

$$k_a = k_a° e^{-E_a/RT} = 2.2 \times 10^8 \text{ s}^{-1} \tag{4}$$

and thus, the rate constant is more than one order of magnitude smaller than that of the homopolymer at 21 °C: 6.7 × 10^9 s^{-1}, from steady state results,[4] and (7.7-8.3) × 10^9 s^{-1}, from time resolved measurements[5] with two different analysis. But we shall show below that the results of Co8240 represent only apparent values.

Fluorescence Decays. The transient experiments throw some light on the possible origin of such differences between Co8240 and the homopolymer. Figure 5 contains a typical example of the transient results obtained with Co8240, at a given temperature. These results can be reasonably described by a triexponential decay (see Figure 5), although a fourth component seems to improve the fit. Table 2 contains the values obtained for the three components of the decay at different temperatures.

One of the components has a time parameter (τ_3) which is very close to the lifetime (τ_o) of the monomeric model compound (also included in Table 2 for comparison). Since in such a monomeric model only isolated chromophores are present, our results suggest that in Co8240 there are also some phenyl rings which are isolated along the chain, with no other phenyl as next-neighbor.

In the case of the dimeric siloxane, the simple Birks scheme holds[4] with only two emitting species: monomer and excimer, which are interconvertible. Here, a third emitting species is required to explain the decays. The picture would then be as follows (Scheme 1). The two first components (τ_1 and τ_2) come from phenyl rings having another ring as next-neighbor along the chain capable of

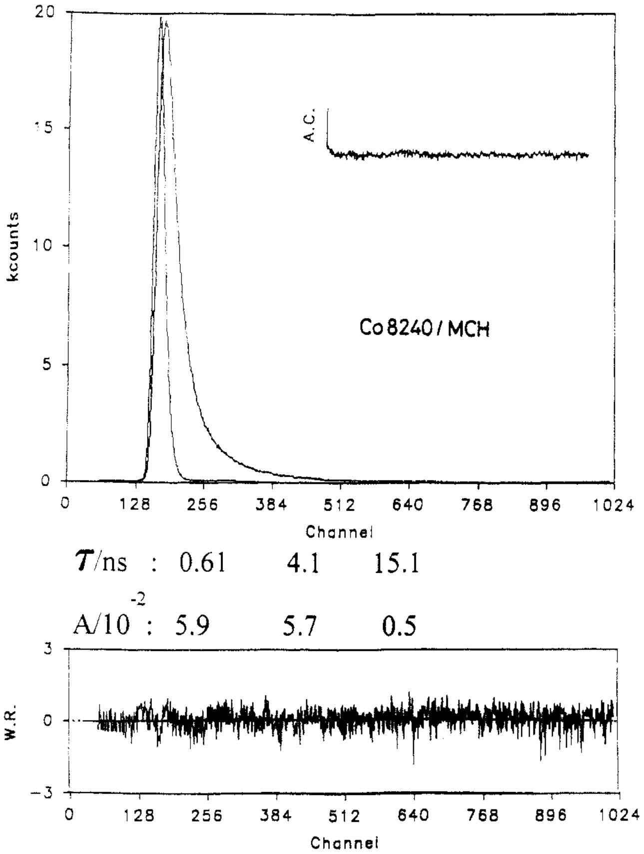
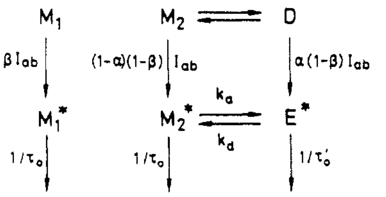


Figure 5. Fluorescence decay of copolymer 8240 monomer emission in dilute MCH solution at 20.5 °C. λ_{em} = 290 nm.

Table 2. Best-Fit Parameters ($\tau_i = 1/\lambda_i$) of Monomer Emission for Copolymer 8240, and Lifetime, τ_o, of the Monomeric Analog, MS, in Methylcyclohexane Dilute Solution, as a Function of Temperature

T/°C	τ_1/ns	τ_2/ns	τ_3/ns	a_{11}	a_{12}	a_{13}	χ^2	τ_o/ns
−35	2.0	28.4	14.0	0.49	0.09	0.42	1.48	14.9
−30	1.8	27.5	13.6	0.48	0.06	0.46	1.39	13.8
−20	1.2	24.8	11.7	0.53	0.05	0.42	1.50	11.8
−10.3	1.0	22.1	9.7	0.48	0.05	0.46	1.28	9.5
0	0.85	20.0	7.4	0.46	0.05	0.48	1.16	7.3
12.0	0.91	16.0	5.0	0.42	0.07	0.51	1.12	5.0
12.5	0.95	15.9	5.0	0.44	0.07	0.49	1.24	5.0
20.5	0.61	15.1	4.1	0.49	0.04	0.47	1.49	3.7

Scheme 1



forming excimers, and the third component, τ_3, which is very similar to τ_o, comes from isolated phenyl rings having dimethylsiloxane units at both sides of the chain.

Let us call β the fraction of light absorbed by isolated chromophores M_1 having dimethyl units at both sides along the chain. Then, $1 - \beta$ is the fraction of light absorbed by chromophores having one or two methylphenyl neighbor units (M_2 and D). We can determine this β from our fluorescence data.

Results of the homopolymer have shown that a sizeable fraction of the excimer emission arises from preformed dimers (D) in these compounds.[4,13,14] The complete kinetic scheme should take into account that the fraction of light nonadsorbed by M_1 has two components, $\alpha(1 - \beta)$, the fraction of light directly absorbed by ground-state dimers, and $(1 - \alpha)(1 - \beta)$, the fraction of light absorbed by M_2 type chromophores, as shown in Scheme 1.

Theoretical Model

Kinetic Scheme and Steady-State Equations. When applying the steady-state conditions to Scheme 1, the following equations are obtained, instead of eqs 1 and 2:

$$\left[\frac{I_o}{I} - 1\right]\tau_o^{-1} = \frac{(k_a + \alpha k_M)(1-\beta)}{1 - \alpha(1-\beta) + \beta k_a\tau_o + k_d\tau_o'} \qquad (5)$$

$$\frac{I_E}{I} = \frac{k_F'}{k_F}\,\frac{\tau_o'(k_a + \alpha k_M)(1-\beta)}{1 - \alpha(1-\beta) + \beta k_a\tau_o + k_d\tau_o'} \qquad (6)$$

where $k_M = 1/\tau_o$ represents the rate constant for monomer radiative and nonradiative decay. When a system with isolated chromophores and preformed dimers is analyzed by means of the simpler Birks scheme using eqs 1 and 2, then apparent values of k_a^{ap} and E_a^{ap} are obtained. The relationship between the real k_a from Scheme 1 (eqs 5 and 6) and the apparent k_a^{ap} from the Birks scheme (eqs 1 and 2) is:

$$k_a = \frac{[1 - \alpha(1-\beta) + k_d\tau_o']k_a^{ap} - \alpha(1-\beta)k_M(1 + k_d\tau_o')}{1 + k_d\tau_o' - \beta(1 + k_d\tau_o' + k_a^{ap}\tau_o)} \qquad (7)$$

Equation 7 allows us to analyze the separate influence of isolated chromophores and of preformed dimers on the rate constant k_a. First, we will examine the influence of isolated chromophores. For $\alpha = 0$, eq 7 simplifes to

$$k_a = k_a^{ap}\left[1 - \beta\left(1 + \frac{k_a^{ap}\tau_o}{1 + k_d\tau_o'}\right)\right]^{-1} \qquad (8)$$

The real rate constant for excimer formation, k_a, is larger than the apparent value obtained ignoring isolated chromophores, k_a^{ap}, and the difference between apparent and real values increases with β. In other words, as the fraction of chromophores which are isolated grows, the apparent rate constant obtained by ignoring them decreases.

Let us consider now the influence of preformed dimers. For $\beta = 0$, eq 7 reads

$$k_a = k_a^{ap} - \alpha\left(k_M + \frac{k_a^{ap}}{1 + k_d\tau_o'}\right) \qquad (9)$$

The real k_a is smaller than the apparent value k_a^{ap} and the difference between both increases with α. Namely, the apparent rate constant grows as the proportion of preformed dimers increases.

Something similar happens with the activation energy. The apparent value

$$E_a^{ap} = -\mathrm{R}\ \mathrm{d}(\ln k_a^{ap})/\mathrm{d}(1/T) \qquad (10)$$

is related to the real one, E_a, and to E_e, the dimer binding enthalpy in the ground state:

$$E_e = -\mathrm{R}\ \mathrm{d}(\ln K_e)/\mathrm{d}(1/T) \qquad (11)$$

with $K_e = \alpha/(1 - \alpha)$. In the LTL ($k_d\tau_o' \ll 1$)

$$E_a^{ap} = \frac{k_a\tau_o(1-\alpha)}{(k_a\tau_o + \alpha)[1 - \alpha(1-\beta) + \beta k_a\tau_o]}E_a + \frac{\alpha(1-\alpha)(1 + k_a\tau_o)}{(k_a\tau_o + \alpha)[1 - \alpha(1-\beta) + \beta k_a\tau_o]}E_e \qquad (12)$$

We can consider separately the influence of isolated chromophores and of preformed dimers on the apparent activation energy. For $\alpha = 0$, eq 12 reduces to

$$E_a = (1 + \beta k_a \tau_o) E_a^{ap} \tag{13}$$

Thus, the real activation energy is larger than the apparent one, when isolated chromophores are present, and the difference between real and apparent values is an increasing function of β. For $\beta = 0$ and assuming $k_a\tau_o \gg 1$, eq 12 simplifies to

$$E_a = E_a^{ap} - \alpha E_e \tag{14}$$

the real activation energy is smaller than the apparent one, due to preformed dimers, and the difference between both increases with α.

In the case of phenylsiloxanes, E_e is very small, about 0.2 kcal/mol,[13] and the real activation energy is, as expected, larger than the apparent value which is deduced for the copolymer ignoring the influence of isolated chromophores.

Scheme 1 and eq 7 and 12 explain thus why k_a and E_a of Co8240 are smaller than the corresponding values of the homopolymer: the isolated chromophores give place to apparent values which are smaller than the real ones. Scheme 1 also explains why Co8240 is apparently always in the LTL, even at 60 °C, the temperature at which the homopolymer and other related systems are in the HTL.[2-4]

In the LTL, $k_d\tau_o' \ll 1 - \alpha(1-\beta) + \beta k_a \tau_o$, whereas in the HTL the term $k_d\tau_o'$ dominates in eqs 5 and 6. Therefore, at the crossover temperature, T_c, between the two temperature limits

$$k_d\tau_o' = 1 - \alpha + \beta\tau_o(k_a + \alpha k_M) \tag{15}$$

In copolymers with larger β, the $k_d\tau_o'$ value which must be reached to cross between the two temperature limits becomes larger and, since $k_d\tau_o'$ increases with temperature, it means that T_c shifts to higher values in copolymers with increasing fractions of isolated chromophores. Thus a copolymer with high enough β and/or k_a values may be apparently in the LTL, in the whole range of temperatures experimentally accessible, even though it has $k_d\tau_o' > 1 - \alpha$, which is the characteristic of the HTL when $\beta = 0$. And such is the case of Co8240.

Time-Resolved Equations. Scheme 1 can also be used to derive the equations of the transient experiments. It results in a biexponential equation for the excimer decay and a triexponential monomer decay, in accordance with the experimental results of Co8240.

$$I_M(t) = \alpha_{11}e^{-\lambda_1 t} + a_{12}e^{-\lambda_2 t} + a_{13}e^{-\lambda_3 t} \tag{16}$$

$$I_E(t) = a_{21}e^{-\lambda_1 t} + a_{22}e^{-\lambda_2 t} \tag{17}$$

where λ_1 and λ_2 have the same meaning as in a simple Birks scheme[12]

$$\lambda_{1,2} = \frac{X + Y \pm [(X-Y)^2 + 4k_a k_d]^{1/2}}{2} \tag{18}$$

(with $X = k_a + 1/\tau_o$ and $Y = k_d + 1/\tau_o'$), and $\lambda_3 = 1/\tau_o$, whereas the preexponential factors are, for monomer emission

$$\alpha_{11} = \frac{(\lambda_2 - X)(1-\alpha) + \alpha k_d}{\lambda_2 - \lambda_1}(1-\beta)$$

$$\alpha_{12} = \frac{(X - \lambda_1)(1-\alpha) - \alpha k_d}{\lambda_2 - \lambda_1}(1-\beta) \tag{19}$$

$$\alpha_{13} = \beta$$

and for excimer emission

$$\alpha_{21} = \frac{k_a(1-\alpha) + \alpha(X - \lambda_1)}{\lambda_2 - \lambda_1}(1-\beta) \tag{20}$$

$$\alpha_{22} = \frac{-k_a(1-\alpha) + \alpha(\lambda_2 - X)}{\lambda_2 - \lambda_1}(1-\beta)$$

Thus, β could be obtained from the preexponential factors of the monomer emission decay as

$$\beta = \frac{1}{1 + \frac{A+B}{1-\alpha}} \tag{21}$$

with $A = a_{11}/a_{13}$ and $B = a_{12}/a_{13}$. Table 3 shows β values calculated at different temperatures by means of eq 21. An average value of 0.47 can be given for β in Co8240 from the time-resolved fluorescence results. β can now be related to β_g, the fraction of ground-state isolated chromophores. Since the extinction coefficient of the diad is twice that of the isolated chromophore,

$$\beta_g = \frac{[M_1]}{[M_1] + [M_2] + [D]} = \frac{2\beta}{1+\beta} \tag{22}$$

Table 3 shows β_g values calculated at several temperatures. It is rather encouraging that β_g is about constant with temperature, as expected, but the average value of 0.64 ± 0.03 (for $\alpha = 0$) is somewhat lower than 0.79, the value obtained from ^{29}Si NMR measurements.

Table 3 summarizes also the k_a values calculated for $\alpha = 0$, as usual for a Birks scheme,[12] taking into account only the two first components of the decay. For $\alpha \neq 0$, the following equations were derived from eqs 19 and 20:

$$X(\alpha) = X(\alpha{=}0) + k_d\frac{\alpha}{1-\alpha} \tag{23}$$

$$k_a(\alpha) = X(\alpha) - k_M \tag{24}$$

where, in a first approach, k_d can be substituted by the value corresponding to $\alpha = 0$ and then this value can be improved with a new $k_d(\alpha)$ calculated with the expression

$$k_d(\alpha) = \frac{X(\alpha)Y(\alpha) - \lambda_1\lambda_2}{k_a(\alpha)} \tag{25}$$

where

$$Y(\alpha) = \lambda_1 + \lambda_2 - X(\alpha) \tag{26}$$

An iterative method could be applied, but the experimental error of k_d is so large that the second cycle yields reproducible values with respect to such errors.

Discussion of Kinetic Parameters

Long-range excimers can be overruled in Co8240 for the following reasons. According to the number average molecular weight of Co8240 (6.4×10^3), each chain has about 100 monomeric units and about 10 of them are methylphenylsiloxane. About 8 of the MPS units are

Table 3. Calculated Values of the Fraction of Isolated Chromophores, β, and Rate Constant for Excimer Formation, k_a, with and without Ground-State Preformed Dimers

	$k_a/10^8$ s^{-1}		β		β_g	
T/°C	(α = 0)	(α = 0.6)	(α = 0)	(α = 0.6)	(α = 0)	(α = 0.6)
−35	3.5	4.6	0.42	0.23	0.59	0.37
−30	4.2	5.2	0.48	0.27	0.65	0.42
−20	7.1	8.3	0.42	0.22	0.59	0.36
−10.3	8.0	9.6	0.46	0.26	0.63	0.41
0	9.2	11.1	0.48	0.27	0.65	0.42
12.0	7.5	10.1	0.50	0.29	0.67	0.45
12.5	7.2	9.5	0.49	0.28	0.66	0.44
20.5	12.4	14.7	0.47	0.26	0.64	0.41

isolated and the other two are consecutive and would therefore form short-range excimers. We have thus eight chromophores able to form long-range excimers, in a chain of 100 units, and on average, those chromophores will be separated by 12 dimethylsiloxane units. If we take as reference the results of Winnik[16] on the rate for end to end segmental diffusion of polydimethylsiloxane in a good solvent (toluene) at 22 °C, the rate constant to form cycles of 13 monomeric units is about 1.2×10^8 s^{-1}. That means that 8 ns will be required to form cycles of 13 units whereas the lifetime of isolated chromophores in those conditions is less than 4 ns (see Table 2), and besides, the probability of such a cycle to put in contact two chromophores is less than 0.01. Under these conditions it is practically impossible that long-range excimers would be formed in this polymer and only excimers between neighboring groups should be considered.

Equations derived in Theoretical Model could be used to calculate the real k_a and E_a values of Co8240 from the apparent values and compare them with the corresponding values of the homopolymer. When comparing Co8240 with the homopolymer, we are entitled to envisage the following situation. The homopolymer contains preformed dimers (α = 0.6, from refs 14 and 15) but no isolated chromophores (β_g = 0). The copolymer contains a fraction of chromophores which are isolated (β_g = 0.79, from ^{29}Si NMR; β_g = 0.64, from monomeric decays), and the remaining fraction of chromophores ($1 - \beta$) can be preformed dimers with the same characteristics as in the homopolymer (thus, the same α).

Let us consider first the kinetic parameters obtained from time-correlated measurements. k_a values (Table 3) calculated with α = 0 or with α = 0.6 are very similar and both sets change with temperature according to an activation energy (3.0 kcal/mol) about equal to the activation energy for excimer formation in the homopolymer and the dichromophoric model compound (3.1–3.2 kcal/mol)[4] and also very close to the copolymer E_a calculated through steady-state measurements (0.8[2]–1.2 kcal/mol) and corrected with equation 13 (3.3 kcal/mol).

Equations 7 and 8 can be used to calculate the real k_a values from the steady-state apparent results, provided that $k_d\tau_o'$ values are taken from the corresponding data of the dimeric analog, the only system for which it is possible to know them with enough confidence from time-resolved measurements.[4] For the lowest temperature limit, the results obtained with β = 0.7 and α = 0.6 or close values and eq 7 have no physical meaning, but at higher temperatures, for example at 20 °C ($k_d\tau_o'$ = 5.5), a real k_a = 7.6×10^8 s^{-1} is obtained versus an apparent value of 2.2×10^8 s^{-1}. The $k_d\tau_o'$ values calculated from the time-correlated measurements of the copolymer show a large dispersion, but at 20 °C ($k_d\tau_o'$ = 0.69) with α = 0, the corrected k_a is 7.2×10^8 s^{-1}. These values are still 1 order of magnitude smaller than the real or corrected value of k_a of the homopolymer[4] at the same temperature, 6.2×10^9 s^{-1} (from steady-state measurements).

The Arrhenius expression of k_a for Co8240 in MCH, compatible with the real or corrected values of E_a and k_a at 20 °C, is the following one:

$$k_a = 2.1 \times 10^{11} \exp(-3.3/RT) \tag{27}$$

These k_a values are larger than the apparent k_a^{ap} values obtained by steady-state measurements of Co8240, but they are very close to the k_a values obtained with time-correlated measurements shown in Table 3. Nevertheless, those time-resolved k_a values are still smaller than the typical values of the homopolymer, and thus, it may be concluded that rotations through the backbone bonds are faster for some reason in the homopolymer. It could be argued that energy migration is present only in the homopolymer and in copolymers with large enough sequences of chromophores and that that would increment k_a of the homopolymer with respect to Co8240, but the rate of energy migration in the homopolymer[4] is only 5.7×10^8 s^{-1} and that small value does not account for the difference of k_a in both systems.

On the other hand, since the quality of the three exponentials is not the highest, we may be losing information on fast events occurring in the picosecond time scale. This would lead to smaller k_a values. The amplitude of the first component is extremely low, and that introduces an important uncertainty in the k_a values and makes it impossible to calculate the other kinetic parameters of the Birks type scheme (Scheme 1).

Conclusions

The kinetic scheme and equations proposed in the present paper afford a general way to interpret the steady-state and transient fluorescence results of copolymers.

It has been shown that isolated chromophores cause a decrease of the apparent k_a and E_a values and shift the crossover between HTL and LTL to higher temperatures. The distortions caused by isolated chromophores ($\beta > 0$) on any magnitude are always much more important than those caused by preformed dimers ($\alpha > 0$). Therefore, caution must be taken in the analysis of the steady-state and time-correlated fluorescence results of copolymers and also of homopolymers in which isolated chromophores may exist for different reasons.

Some particular results for the siloxane copolymer Co8240 here studied suggest that the system has complexities which preclude a simple comparison with the homopolymer. Thus, chain mobility appears to be different in the copolymer and the homopolymer, and the copolymer shows no clear evidence for the existence of preformed dimers as they are found in the homopolymer. Besides, the temperature variation of monomer and excimer lifetimes and of the rate constants for excimer formation and dissociation suggest that the disiloxane DS may not be an adequate dimeric model for the bichromophoric diad in the case of the copolymer.

The kinetics of excimer formation appears to be faster in the homopolymer than in the copolymer. A possible reason may be that the homopolymer can form more kinds of excimers. According to recent conformational analysis,[15] the triads in PMPS can form excimers by coupling the chromophores of units 1 and 3. These second-neighbor excimers can occur in addition to the first-neighbor excimers between the two contiguous units in a diad.

However, in the copolymer of low phenyl content, probably only the diad excimers have any chance to occur.

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