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Viscosity Dependence of the Excimer to Monomer Fluorescence Ratio. Cyclic and Linear Polysiloxanes

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ABSTRACT: Fluorescence spectra of cyclic and linear samples of poly(methylphenylsiloxane) (PMPS) have been measured at 25 °C, in two solvent mixtures (tetrahydrofuran/dioxane and tetrahydrofuran/methanol), as a function of the solvent composition. The viscosity of the medium (η) and the segmental density of the macromolecule are varied by changing the solvent composition. The ratio of excimer to monomer intensities (fluorescence ratio, I_E/I_M) is independent of segmental density. I_E/I_M of linear PMPS is also almost independent on solvent viscosity, but for cyclic PMPS, a direct dependence of I_E/I_M on η is observed. The analysis of results allows several conclusions: (i) long range excimers are disregarded in the high molecular weight sample; (ii) only less than 10% excimers of any phenylsiloxane, cyclic or linear, are formed in ground-state preformed excimer-forming sites, due to the high dynamic flexibility of siloxanes in the nanosecond time scale; and (iii) excimer dissociation plays a significant role and takes place through a viscosity-dependent mechanism. A model is proposed to explain the viscosity dependence of the fluorescence ratio, which applies both to the high-temperature limit (like the present results of PMPS), and also to some other previously reported results on polymers in the low-temperature limit.

Introduction

The fluorescence spectra of poly(methylphenylsiloxane) (PMPS) solutions show two bands:[1–5] monomer, or single ring emission, centered at about 285 nm, and excimer emission, at about 325 nm at 25 °C. The conformational analysis of PMPS shows[6,7] that at equilibrium a large proportion of conformers (between 40% and 80%) are ground-state preformed excimer-forming sites (EFS), in atactic samples. Besides, Si–O–Si backbones have a larger mobility than hydrocarbon chains,[8] and therefore excimer formation through bond rotation of conformers close to an EFS is expected to be very efficient.[7] PMPS is in the high-temperature limit[4,5] at temperatures close to room temperature, and dissociation of excimers is also an important process in the photophysical behavior of these molecules.

The excimers mentioned above are short-range excimers (SRE), that is to say, they are formed by chromophores joined by a 1,3-propane-like structure. But, in principle, long-range excimers (LRE), formed by rings which belong to nonconsecutive monomeric units separated by a closed loop, cannot be disregarded.

Some of us have recently reported[9,10] a very simple model to discern between the short-range and long-range excimer formation in the low-temperature limit, that is to say, without taking into account the excimer dissociation. According to such a model, the total fluorescence ratio in the low-temperature limit, can be written[10]

$$I_E/I_M = k_1 + k_2[\eta]^{-1} + k_3\eta^{-1} \qquad (1)$$

The two first terms take into account the contribution from ground-state preformed EFS, either in long-range chain self-contacts between units separated by a loop, which is dependent on segment density (hence on $[\eta]^{-1}$), or from ground-state preformed short-range EFS. Ground-state preformed EFS may form excimers by direct absorption or by energy migration. The term $k_3\eta^{-1}$ corresponds to the formation of excimers by bond rotation (SRE), or by segmental diffusion (LRE), which are processes whose rates are inversely proportional to the viscosity of the medium. The relative contribution of each mechanism to excimer formation, in the low-temperature limit, can be obtained with the help of eq 1, as follows. The fluorescence ratio of each sample is determined, at constant temperature, in solvent mixtures of different composition. The solvent viscosity and polymer intrinsic viscosity must also be determined, at the same temperature, as a function of the solvent mixture composition. The fluorescence ratio is then correlated with η^{-1} and $[\eta]^{-1}$ according to eq 1, and the value of each term in eq 1 divided by the corresponding fluorescence ratio to obtain a measurement of the relative contribution of each mechanism to excimer formation. This method has been applied to hydrocarbon polymers in the low-temperature limit. For high molecular weight samples with phenyl-type chromophores, the relative contribution of LRE to the observed fluorescence ratio has been found negligible.[9,10]

In the case of phenylsiloxanes which are[4,5] in the high-temperature limit, the model has to be modified in order to consider the contribution from excimer dissociation. The purpose of this paper is to study the fluorescence ratio of PMPS as a function of solvent viscosity and polymer-reduced viscosity, in order to quantify the relative contribution from each type of excimer, taking into account excimer dissociation of this polymer. Different types of phenylsiloxanes are studied here: linear and cyclic. As we shall see, the behavior of the cyclic molecules adds important light into this problem.

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Table I
Characteristics of the Samples Used in This Work[a]

sample				
kind	identification	x_n	I_E/I_M	α
cyclic	PMPSC3	3	2.82	
cyclic	PMPSC4	4.4	1.68	0.43
cyclic	PMPSC9	9.0	1.84	0.66
linear	PMPSF5	443	4.08	0.60
copolymer	Co710	14	1.80	0.62
dimer	DS	2	1.42	0.78

[a] Number average degree of polymerization (x_n, determined by GPC), fluorescence ratio (I_E/I_M, measured in THF at 25 °C), and fraction of monomers in EFS in the ground-state equilibrium conformation (α, theoretically determined).

Experimental Section

Several phenylsiloxane samples, whose characteristics appear in Table I, were used in this work. One of them is linear (PMPSF5), atactic and of high molecular weight.[3] The other three samples, are cyclic and have low molecular weights. 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisiloxane (PMPSC3) was purchased from Petrarch Systems Inc. The cyclics with larger degrees of polymerization (PMPSC4 and PMPSC9) were prepared as described in ref 11. The dichromophoric model compound 1,3-diphenyltetramethyldisiloxane (DS) was synthesized as described in ref 4. Finally, a linear copolymer of dimethylsiloxane and methylphenylsiloxane (Co710), with 66.3% in moles of the phenyl comonomer, was employed.[3,5] Table I summarizes the number average degrees of polymerization of the six samples. Those of samples PMPSF5, PMPSC4, PMPSC9, and Co710 were determined by GPC. For the copolymer, x_n represents only the number of phenylsiloxane units in the chain. The data for α, the fraction of monomeric units in EFS in the equilibrium conformation, were taken from refs 6 and 7. The value of α is not available for the cyclic trimer because the rotational isomeric state model is not valid for that planar ring.[6]

Solvents used (tetrahydrofuran (THF), dioxane (Dx), and methanol (MeOH)) were purchased from Carlo Erba. They were of different quality, RS for fluorimetry and RPE for viscometry.

An Ubbelohde modified viscometer, fitted in a Lauda automatic viscometer, was employed to measure solvent and polymer solution viscosities. The temperature was kept at 25.00 ± 0.05 °C, and polymer concentration was very low, 0.18%. In this way, $\eta_{sp}/c \simeq [\eta]$.

Emission spectra have been recorded on a Hitachi F4000 spectrofluorimeter, at 25 °C. The excitation wavelength was 250 nm, and the optical density of samples was always below 0.5. In this way, self-absorption was absent, and the fluorescence ratio was independent of the polymer concentration, that is to say, only intramolecular excimers were observed. The fluorescence ratio was determined on aerated samples, by the ratio of fluorescence intensities at 330 and 285 nm.

Results and Discussion

In order to study separately the influence of solvent viscosity and sample segmental density, two solvent mixtures have been chosen for this work: THF/Dx and THF/MeOH.

The first one is a mixture of two good solvents of about the same quality. In fact, η_{sp}/c of PMPSF5 at 25 °C is practically the same in both solvents: 0.40 dL/g in THF and 0.35 dL/g in Dx (Figure 1). Solvent viscosity η changes monotonically in a broad range (from 0.486 to 1.187 cP[12] at 25 °C, see Figure 1) upon increasing ϕ_2, the Dx volume fraction in the solvent mixture. The mixture THF/MeOH shows the opposite behavior: η is about the same for both solvents (0.486 cP for THF and 0.547 cP for MeOH both at 25 °C),[12] but η_{sp}/c decreases by adding MeOH (precipitant) to the PMPS solution in THF (good solvent) keeping the polymer concentration constant (Figure 2). Phase separation takes place at 25 °C in solutions with 56% v/v MeOH or larger precipitant fractions and polymer concentrations of about 5 × 10^{-4}M.

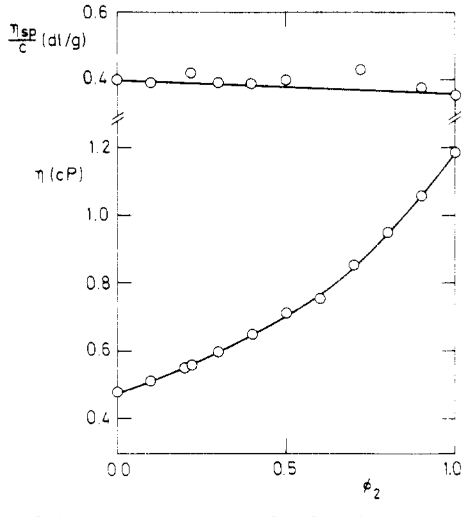


Figure 1. Solvent viscosity (η) and reduced viscosity (η_{sp}/c) of PMPSF5 at 25 °C as a function of Dx volume fraction in the solvent mixture THF/Dx.

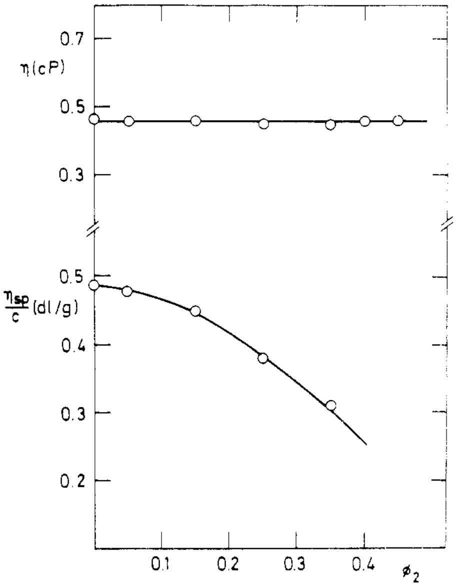


Figure 2. Solvent viscosity (η) and reduced viscosity (η_{sp}/c) of PMPSF5 at 25 °C as a function of MeOH volume fraction in the solvent mixture THF/MeOH.

Figure 3 shows the fluorescence spectra of PMPSC4 in THF/Dx mixtures. The other phenylsiloxane samples show similar spectra with monomer and excimer bands centered at about 285 and 330 nm, respectively. The fluorescence ratio of linear and cyclic PMPS in the two solvent mixtures have been depicted in Figure 4, as a function of the volume fraction of the second component (MeOH or Dx). Lets consider first the influence of segmental density on the fluorescence ratio of poly(phenylsiloxanes) (THF/MeOH mixture).

Long-range excimers may be formed in principle only in some of the samples here studied, Co710 and PMPSF5. Only the sample PMPSF5 has been studied in the mixture THF/MeOH, because segmental density changes significantly by addition of a precipitant only in the high molecular weight linear chains. Its fluorescence ratio is practically constant (Figure 4) with solvent composition, in spite of the fact that reduced viscosity (and in consequence segmental density ($[\eta]^{-1}$)) changes by a factor of 2 (Figure 2) keeping constant solvent viscosity (Figure

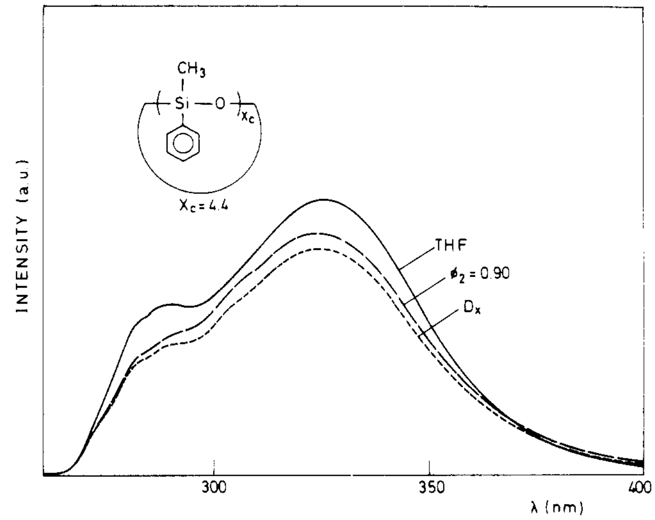


Figure 3. Fluorescence spectra of PMPSC4 in THF, in Dx, and in a THF/Dx mixture (90% Dx).

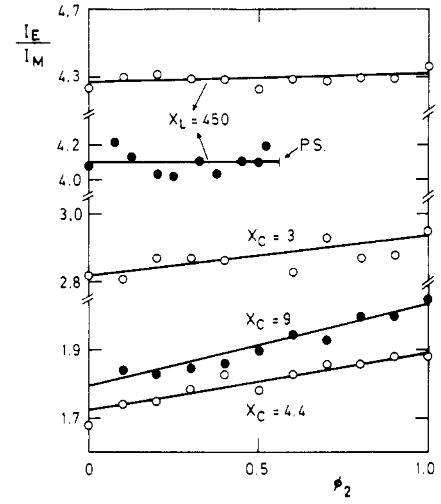


Figure 4. Fluorescence ratio of several samples at 25 °C, as a function of the volume fraction of the second component in the solvent mixture: PMPSC3 (x_c = 3, ○), PMPSC4 (x_c = 4.4, ○), PMPSC9 (x_c = 9, ●) and PMPSF5 (x_L = 450, ○) in THF/Dx, and PMPSF5 (x_L = 450, ●) in THF/MeOH. In the last system, the composition at which phase separation takes place is indicated (P.S.).

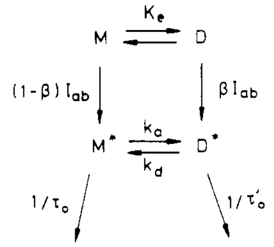
2). In consequence, long range excimers can be disregarded in that high molecular weight sample.

The same result was previously obtained in similar solvent mixtures with atactic and isotactic polystyrene[9] high molecular weight samples. It is also in accordance with some other results on polymers bearing phenyl groups, e.g., high molecular weight polyindene[13] and random copolymers with diluted styrene units in the chain[14] can form excimers only of the long range type, but they do not show excimer emission. Only low molecular weight samples of polyindene[13] and random copolymers with long-lived chromophores, like pyrene, show excimer emission, and the fluorescence ratio is then[15] proportional to segmental density $[\eta]^{-1}$.

In the solvent mixture THF/Dx, the fluorescence ratio of cyclic PMPS increases with the volume fraction of Dx in the solvent mixture, and therefore, it increases with solvent viscosity. Linear samples show a much slower increment.

This is a rather surprising result if it is compared, for example, with polystyrene,[9] polyacenaphthylene,[10] or dichromophoric compounds[16-18] (low-temperature limit), whose fluorescence ratios depend directly on η^{-1}. As far as we know, only polyindene[10] and poly[(aryloxy)phosphazenes][19] show a fluorescence ratio with the same dependence on solvent viscosity as the present poly(phenylsiloxanes). These other polymers having behavior similar to PMPS are also in the high-temperature limit at room temperature. It seems, therefore, that polymers in the low- or the high-temperature limit show opposite dependencies on solvent viscosity. This point will be considered in the theoretical model described below.

Scheme I



Theoretical Model

To explain the above mentioned results, it is necessary to find a general relationship of the fluorescence ratio with the viscosity of the medium. That will be the objective of the following paragraphs.

The fluorescence decay of phenylsiloxanes is a complex multiexponential phenomenon[8] that has been qualitatively explained on the basis of kinetic Scheme I taken from ref 8. It recognizes the possibly existence of two monomer–EFS equilibria, one in the ground state and another in the excited state. For the purposes of the present discussion, it will be sufficient to consider only two excited state species: monomer, M*, and excimer, D* (which amounts to simplififying Scheme I by assuming, as a first approximation, that the rate constants for the meso and racemic diads are about the same). Applying the steady-state conditions to kinetic Scheme I (with such simplification), it results:

$$\frac{I_E}{I_M} = \frac{k_{FE}\tau_o'}{k_{FM}\tau_o}\,\frac{\beta + k_a\tau_o}{1 - \beta + k_d\tau_o'} = \frac{Q_E}{Q_M}\,\frac{\beta + k_a\tau_o}{1 - \beta + k_d\tau_o'} \tag{2}$$

where k_{FM} and k_{FE} are rate constants for monomer and excimer radiative decay, τ_o and τ_o' are the monomer and excimer intrinsic fluorescence lifetimes, and k_a and k_d are the rate constants for excimer formation and dissociation through segmental rotation. Formation of excimers by energy migration is also included in k_a (see below). β represents the fraction of light which is absorbed by preformed dimers in the ground-state average equilibrium conformation, and Q_E/Q_M is the intrinsic fluorescence quantum yields ratio. β is related to the fraction of monomeric units which are forming part of EFS in the equilibrium conformation, α, and with the extinction coefficient of the dimers, ϵ_D, and of single chromophores, ϵ_M:

$$\beta = \frac{\epsilon_D\alpha}{\epsilon_D\alpha + \epsilon_M(1 - \alpha)} \tag{3}$$

Equation 2 corresponds to a general case:

(i) It implicitly considers excimer formation through direct absorption of light by ground-state dimers (β) and through energy migration and segmental motion (k_a).

(ii) It can be applied to LRE as much as to SRE, or to samples in which both types of excimers coexist.

(iii) It can be applied both to the low-temperature limit and to the high-temperature limit, and to the transition regime in between, because it includes no assumption on the relative values of the rate constants for excimer dissociation (k_d) and excimer decay ($1/\tau_o'$).

Its largest limitation is that it considers only one type of monomer and excimer species without taking into account the different configurational states of a macromolecule. Each type of configurational state would require a particularized kinetic scheme like Scheme I.

The nonradiative decay processes depend in some cases on the solvent viscosity. The deactivation of the excited state of some molecular rotors, through torsional relaxation, gives place to a reorientation of the surrounding media which depends[20] on η^{-1}, in the range of low viscosity media with $\eta < 2$ cP. We can expect no dependence of τ_o on solvent viscosity for hydrocarbon polymers where packing of chromophores is very compact and therefore side groups are almost immobilized.[6] For inorganic polymers, bond distances are longer, and side groups may almost freely rotate,[6] but conformational changes by rotation through bonds of the skeleton and segmental diffusion, can be considered much more strongly dependent on solvent viscosity. Therefore, we will assume that $1/\tau_o'$ and $1/\tau_o$ do not depend on solvent viscosity and that the rates of segmental motion depend inversely on solvent viscosity. The rate constants for rotation depend in general on η^{-x} (ref 20 and references therein), with $x = 1$ in the limit of low viscosity solvents, and $x < 1$ for solvents of medium and high viscosity. With the η^{-1} law for segmental motions, the rate constants for the formation and dissociation of excimers can be written as

$$k_a = k_a'\eta^{-1} + k_a^{o} \tag{4}$$

$$k_d = k_d'\eta^{-1}$$

where k_a' and k_d' are viscosity independent constants, and k_a^o is the contribution to excimers from energy migration. With these hypotheses, eq 2 becomes

$$\frac{I_E}{I_M} = \frac{k_{FE}\tau_o'}{k_{FM}\tau_o}\,\frac{\beta + \tau_o(k_a'\eta^{-1} + k_a^{o})}{1 - \beta + \tau_o'k_d'\eta^{-1}} = \frac{k_1 + k_2\eta^{-1}}{k_3 + k_4\eta^{-1}} \tag{5}$$

High-Temperature Limit. The model described above allows one to understand the unexpected dependence of the fluorescence ratio on solvent viscosity, for polymers in the high-temperature limit, like poly(phenylsiloxanes) at temperatures close to room temperature.

The fit of the results described above to eq 5 yields always k_3 values much smaller than k_4 (by a factor of 10^{-4}) and good correlations are obtained only with linear functions of I_E/I_M versus η:

$$I_E/I_M = k_{PE}\eta + k_{RE} \tag{6}$$

The physical meaning of the parameters in eq 6 are the following ones:

$$k_{PE} = \frac{Q_E}{Q_M}\,\frac{\beta + \tau_o k_a^{o}}{k_d'\tau_o'} \tag{7}$$

$$k_{RE} = \frac{Q_E}{Q_M}\,\frac{k_a\tau_o}{k_d\tau_o'} = \frac{k_{FE}k_a}{k_{FM}k_d} \tag{8}$$

Energy migration is not expected in phenylsiloxanes, because of the large population of ground-state preformed dimers,[7] and so, the term $k_a^o\tau_o$ can be neglected in eq 7.

Table II shows the parameters of the best fit to eq 6 of the fluorescence ratio, at 25 °C, in THF/Dx solvent mixtures, for several samples. For those systems at 25 °C, the steady-state results allow one to conclude that $k_d \gg \tau_o'^{-1}$, the excimer dissociation process is faster than the excimer decay through radiative and nonradiative pathways. This is in accordance with the results obtained by single photon counting measurements[21] on DS in cyclohexane at 25 °C: $k_d\tau_o'$ is larger than 30 and $k_a\tau_o$ is about 20. Those large values of $k_a\tau_o$ make the intercept of eq 6 (see Table II) larger than the slope, which depends on β ($\beta < 1$).

Table II
Standard Deviation (σ) and Best-Fit Parameters (k_{PE}, k_{RE}) to Eq 6 of the Fluorescence Results for Several Samples in the THF/Dx Mixture at 25 °C

sample	k_{PE}	k_{RE}	$\sigma \times 10^2$
PMPSC3	0.161	2.74	2.8
PMPSC4	0.298	1.57	2.8
PMPSC9	0.405	1.59	1.5
PMPSF5	0.187	4.25	5.0
Co710	0.142	1.73	
DS	0.113	1.36	

Table III
Relative Contribution of Preformed Excimers to the Fluorescence Ratio Observed in THF (%PE), Equilibrium Constant of the Excited State, K_e* (Relative to PMPSF5), and Ground-State Equilibrium Constant, K_e, Calculated from α Values of Table I (also Relative to PMPSF5)

sample	%PE	$k_a\tau_0$	$(k_d\tau_0)/(k_d\tau_0)_r$	K_e^*/K_e^*	K_e/K_{er}
PMPSC3	2.7			0.64	
PMPSC4	8.3	4.6	0.45	0.37	0.50
PMPSC9	10.9	5.3	0.50	0.37	1.29
PMPSF5	2.1	27.9	1.00	1.00	1.00
Co710	3.8	15.5	1.36	0.32	1.09
DS	3.8	19.2	2.15	0.41	1.15

The fitting of the results to eq 6 means too that in all cases, excimer dissociation follows a mechanism that depends inversely on solvent viscosity, and that there is not a complete equilibrium in the excited state.

In fact, there is an equilibrium in the excited state, only when k_a and k_d are much larger than τ_o^{-1} and $\tau_o'^{-1}$, respectively, and there results no dependence on solvent viscosity in that case, because $I_E/I_M = (k_{FE}/k_{FM})K_e^*$. There is another limit in which the fluorescence ratio does not depend on solvent viscosity: when k_a and k_d are much smaller than τ_o^{-1} and $\tau_o'^{-1}$ respectively. Then the fluorescence ratio

$$\frac{I_E}{I_M} = \frac{Q_E}{Q_M}\,\frac{\beta}{1 - \beta} = \frac{Q_E}{Q_M}\,\frac{\epsilon_D}{\epsilon_M}K_e$$

is a function of the ground-state equilibrium population of EFS. In general, systems are in between those two previous limits, and therefore, the fluorescence ratio depends on solvent viscosity. Cyclics have a larger dependence on solvent viscosity than open chains and therefore they are further away from equilibrium, with $k_a\tau_o$ still larger than β but closer to it (the fluorescence ratio is thus smaller for cyclics than for the linear homopolymer, see Table I).

The first term in eq 6 is proportional to β, and thus it depends on α, the fraction of monomers which are in EFS in the ground state. The second term is proportional to $k_a\tau_o$, the fraction of monomers in the excited state which form an EFS by rotation through a backbone bond. The contribution to the observed fluorescence ratio from preformed dimers (%PE) in the ground state is therefore:

$$\%\text{PE} = 100k_{PE}\eta/(I_E/I_M) \tag{9}$$

and of course the rest is the contribution from rotational excimers. The contribution of preformed excimers (%PE

$= \beta/(k_a\tau_o + \beta)$) to the observed fluorescence ratio is very low (Table III) if it is compared with α values. Two reasons can be considered; one of them is that $\epsilon_D < \epsilon_M$, which makes β smaller than α. On the other hand, k_a is very large,[8] due to the high dynamic flexibility of siloxanes, and that makes rotational motions more efficient for excimer formation than the capture of a photon in a preformed EFS.

Some more information may be obtained from previous equations and if it is assumed that β is about the same as α (Table I), $k_a\tau_o$ can be estimated. Table III shows $k_a\tau_o$

$$k_a\tau_o = \frac{k_{RE}}{k_{PE}}\beta\eta^{-1}$$

estimated values in THF. Besides, by choosing one system as reference (PMPSF5), and assuming again that $\beta = \alpha$, the product $k_d\tau_o$ and the apparent equilibrium constant of the excited state, K_e^*, can then be calculated with respect to the reference system (subscript r), to compare it with

$$\frac{k_d\tau_o}{(k_d\tau_o)_r} = \frac{(\beta/k_{PE}\eta)}{(\beta/k_{PE}\eta)_r}$$

$$\frac{K_e^*}{K_e^*} = \frac{k_{RE}}{k_{REr}} = \frac{(k_a/k_d)}{(k_a/k_d)_r}$$

the ground state equilibrium constant, $K_e = \alpha/(1-\alpha)$ (see Table III).

Table III shows that there is a clear difference between cyclic and linear samples. The very small cycles have lower dynamic flexibility (lower $k_d\tau_o$ and $k_a\tau_o$ values) than linear samples. The geometrical constrains of cycles avoid the formation of EFS and thus K_e of the very small cycles is smaller than for linear chains[6] (Table III) but K_e^* is even much smaller and that means that the excimer binding enthalpy (absolute value), or excimer stability, is also lower in cycles. It is in accordance with the blue shift[1] of the excimer emission observed in the small cycles with respect to long chains. The contribution of preformed excimers (%PE in Table III) to the fluorescence ratio is relatively larger in cycles than in linear chains, because both β and $k_a\tau_o$ decrease in cycles, for different reasons, but $k_a\tau_o$ decreases more.

K_e is about the same for low and high molecular weight linear samples, but K_e^* increases with chain length (Table III). The reason is that $k_d\tau_o$ decreases by a factor of 2 when going from the dimeric analogue to the high molecular weight sample (Table III), whereas $k_a\tau_o$ increases much more slightly. There is no reason to think that chain flexibility may increase with chain length, and in fact $k_a\tau_o$ does not change much. If $k_a\tau_o$ of Co710 is divided by the molar fraction of the methylphenylsiloxane in the copolymer, it becomes even closer to the PMPSF5 value (23.5 and 27.9, respectively). Therefore, to explain why $k_d\tau_o$ decreases upon increasing chain length it must be admitted that more efficient mechanisms for excimer dissociation are operative in the dimeric analogue.

Low-Temperature Limit. In the low-temperature limit, $k_d\tau_o'$ can be neglected with respect to $1 - \beta$, and eq 5 becomes

$$\frac{I_E}{I_M} = \frac{k_{FE}\tau_o'}{k_{FM}\tau_o}\frac{\beta + \tau_o(k_a'\eta^{-1} + k_a^{\circ})}{1-\beta} = k_{PE} + k_{RE}\eta^{-1} \quad (10)$$

where k_{PE} represents the contribution from ground-state preformed EFS through direct absorption or energy migration, and $k_{RE}\eta^{-1}$ represents the contribution from motions, rotation, or segmental diffusion:

$$k_{PE} = \frac{Q_E}{Q_M}\frac{\beta + \tau_o k_a^{\circ}}{1-\beta}$$

$$k_{RE} = \frac{Q_E}{Q_M}\frac{\tau_o k_a'}{1-\beta}$$

Equation 10 has already been applied to analyze the results of polystyrene[9] and polyacenaphthylene.[10] Those two polymers are in the low-temperature limit at 25 °C and yield good fits to the linear function on η^{-1}. The slope and intercept of such fits have now a physical meaning.

For those two polymers, β is about zero ($\alpha = 0.026$ for atactic PS, for example[14]), and thus energy migration can easily play a very important role in increasing the contribution of ground-state preformed EFS (%PE) to the fluorescence ratio:

$$\%\text{PE} = 100k_{PE}/(I_E/I_M) = \frac{\beta + \tau_o k_a^{\circ}}{\beta + \tau_o k_a} \simeq \frac{k_a^{\circ}}{k_a}$$

That, together with the lower k_a' values of hydrocarbon chains with respect to siloxanes,[8] makes the contribution %PE much larger in the first case (%PE = 30–70%[9,10]).

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References and Notes

(1) Horta, A.; Semlyen, J. A.; Piérola, I. F. To be submitted for publication.

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

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

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

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

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

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

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

(9) Masegosa, R. M.; Hernández-Fuentes, I.; Piérola, I. F.; Horta, A. *Polymer* **1987**, *28*, 231.

(10) Renamayor, C. S.; Gómez-Antón, M. R.; Piérola, I. F. *J. Appl. Polym. Sci., Symp. Ser.* **1990**, *28*, 231.

(11) (a) Clarson, S. J.; Semlyen, J. A. *Polymer* **1986**, *27*, 1633. (b) Clarson, S. J.; Dodgson, K.; Semlyen, J. A. *Polymer* **1987**, *28*, 189.

(12) Riddik, J. A.; Bunger, W. B. *Techniques of Chemistry. Vol. II, Organic Solvents*; Wiley: New York, 1970.

(13) Renamayor, C. S.; Gómez-Antón, M. R.; Calafate, B.; Mano, E. B.; Radic, D.; Gargallo, L.; Freire, J. J.; Piérola, I. F. *Macromolecules* **1991**, *24*, 3328.

(14) Semerak, S. N.; Frank, C. W. *Adv. Polym. Sci.* **1983**, *54*, 31.

(15) Cuniberti, C.; Perico, A. In Luminescence from Biological and Synthetic Macromolecules. *Ann. N.Y. Acad. Sci.* **1981**, *366*, (Morawetz, H., Steinberg, I. Z., Eds.).

(16) Goldenberg, M.; Emert, J.; Morawetz, H. *J. Am. Chem. Soc.* **1978**, *100*, 7171.

(17) Zachariasse, K. A.; Duveneck, G.; Busse, R. *J. Am. Chem. Soc.* **1984**, *106*, 1045.

(18) Maçanita, A. L.; Kühnle, W.; Zachariasse, K. A. Submitted for publication.

(19) Yeung, A. S.; Frank, C. W.; Singler, R. E. *Polymer* **1990**, *31*, 1092.

(20) Loutfy, R. O.; Arnold, B. A. *J. Phys. Chem.* **1982**, *86*, 4205.

(21) Maçanita, A.; Horta, A.; Piérola, I. F. To be submitted for publication.

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