

Fluorescence Behavior of a Pyrene-End-Capped Poly(ethylene oxide) in Organic Solvents and in Dioxane–Water Mixtures

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A poly(ethylene oxide) polymer end-labeled with two pyrene units ($M_w = 9500$ g/mol and abbreviated as Py₂PEO) was investigated in dioxane–water mixtures and several organic solvents by steady-state and time-resolved fluorescence techniques. In dioxane–water mixtures, the fluorescence emission spectra indicate that with the gradual addition of dioxane to the solvent mixture, the maximum of the pyrene monomer band remains practically constant, whereas the excimer band displays a blue shift of ≈ 8 – 10 nm. From time-resolved fluorescence data, two- and three-exponential decays at the pyrene monomer and excimer emission wavelengths, respectively, were obtained. Two of the decay times (τ_1 and τ_2) are identical at all emission wavelengths. The additional shorter decay time (τ_3), which is only observed at the excimer emission wavelength, was attributed to the component responsible for the blue-shifted excimer maximum, that is, to a second excimer, uncoupled to the other two species. Thus, the time-resolved fluorescence data suggests that one pyrene monomer is able to form either one or two excimers (E_1 and E_2 , coupled and uncoupled, respectively). The sum of the pre-exponential factors, associated with the coupled species, at the excimer emission wavelength in dioxane–water mixtures always differs from zero. This, together with differences in the excitation spectra when collected at the monomer and excimer wavelengths, revealed that a static route is partially responsible for E_1^* formation. In the case of pure organic solvents, the proposed kinetic scheme can be simplified. In this case, the sum of the pre-exponential factors at the excimer emission wavelength is practically zero, which is a direct consequence of the dynamic mechanism being the only route for E_1^* formation. The kinetic scheme has been solved, and the rate constants for excimer formation (k_a), dissociation (k_d), and excimer decay (k_E) are presented.

Introduction

Intramolecular excimer formation in polymeric and oligomeric molecules where the chromophore units are linked in the extremities has been extensively studied using pyrenyl,^{1–11} naphthyl,¹² and phenyl¹³ groups. The main chain can be a hydrocarbon,^{1–3} fluorocarbon,¹⁴ or oligosilane;^{4,15} polymers such as polystyrene^{5–10,16} and poly(ethylene oxide)^{11,17} are also often used, and the results of studies on these systems provide valuable information on both the conformational states and dynamic behavior in these systems. With polymers, the capacity of end-to-end cyclization or, in this case, intramolecular excimer formation has been shown to be influenced by several factors, chain length,^{1–4,10,13,17} temperature,^{6,9,15} hydrostatic pressure,^{5,18} and solvent quality.^{6–9,17} Zachariasse et al. performed an exhaustive study on the effect of the chain length in a series of 1,*n*-di(1-pyrenyl)alkanes¹ and 1,*n*-bis(1-pyrenylcarboxy)alkanes³ ($n = 1$ – 16 , 22 , and 32). In the former, excimer formation was detected in all studied cases with a maximum at $n = 3$, in agreement with Hirayama's rule.¹³ A particularly strong inhibition of intramolecular excimer formation occurs when n ranges between 5 and 8 , while for longer chains, an increase of the excimer formation was observed. In the latter case, a different behavior was found due to the presence of carboxylic groups. The maximum is attained at $n = 5$ and is followed by a gradual decrease with increasing of the chain length. These two sets of experiments tell us that the end-to-end cyclization of the

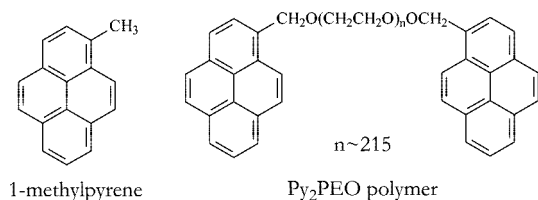
hydrocarbon chain also depends on the probe, that is, if it is the pyrene probe itself or a derivative of it.

The chain length also has a strong impact on the relative orientation of the chromophores. When the chromophores are separated by short chains, the restrictions imposed by the chain are greater than those in the case of long chains. This is particularly visible in the case of 1,*n*-di(1-pyrenyl)alkane when we compare the fluorescence decays at the excimer emission wavelength for $n = 3$ and 13 .² With $n = 3$, triexponential decays are obtained, corresponding to the emission of a monomer and two conformationally different excimers, that is, due to the restrictions of the hydrocarbon chain, a less stable excimer is also formed. When $n = 13$, only the decay times attributed to the monomer and to the more stable excimer emission are obtained. Due to the higher conformational flexibility, all relative orientations are, in principle, possible, and the two pyrene groups arrange themselves to adopt the most stable conformation. In addition, and very relevant for the present study, with bis((1-methoxypyrene)carbonyl) alkanes, with $n = 1$ – 22 , it was found that for $n < 6$, the excimer emission was blue shifted relative to the intermolecular excimer emission. This shift was attributed to the high-energy strain of the cyclized chains which, by increasing the chain length, becomes negligible, and no shift could be observed.^{19,20}

The effects of temperature, hydrostatic pressure, and solvent on the end-to-end cyclization (excimer association) rate constant, which is directly proportional to the excimer-to-monomer (I_E/I_M) ratio,^{5,9} have been studied using polystyrene with both ends labeled with pyrene. The following general conclusions have

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SCHEME 1



been given: the cyclization rate constant increases with temperature,⁹ decreases with pressure,⁵ and is higher in poor solvents (where segment–segment contacts are more favorable than the segment–solvent contacts) than in good solvents (where segment–solvent interactions become favorable).⁹

In the case of water-soluble polymers hydrophobically modified in the extremities, the solvent has a strong effect on the end-to-end cyclization of the polymer chain. Hydrophobically modified poly(ethylene oxide)s (PEO) are of particular relevance and, in addition to their pure scientific interest, are of industrial importance as thickeners. Hydrophobic modifications have included introduction of aliphatic chains,^{21,22} adamantane,²³ fullerenes,²⁴ and pyrene.¹⁷ Because of the fluorescence properties of the group, pyrene-end-capped PEO polymer has been widely studied and has provided considerable information on the structure and dynamics of these polymers in solution and their interaction with surfactants,²⁵ cyclodextrins,²⁶ and other macromolecules.²⁷ The choice of the solvent is of major importance to determine the behavior of these polymers in solution. An anomalous behavior was found for these polymers in water, methanol, and methanol–water mixtures, where unusual excimer-to-monomer ratios were obtained. In these solvents, the end-to-end cyclization is not a pure diffusion-controlled process, probably due to the hydrophobic attraction between the pyrene groups, which is strongly decreased in pure methanol compared with that in aqueous mixtures.^{11,17}

The aim of the present work is to study the effect of solvent on a pyrene-end-capped poly(ethylene oxide) conformation and its influence on the kinetics of excimer formation.

Experimental Section

Materials. The poly(ethylene oxide) polymer end-labeled with two pyrene units used in these studies (Scheme 1) was provided by Prof. M. Almgren, has a $M_w = 9500$ g/mol, and shows very low polydispersity ($M_w/M_n = 1.1$). Dynamic light scattering studies (to be published) show that in dilute aqueous solutions, the polymer is present as isolated chains and shows little tendency to aggregate. 1-Methylpyrene (Scheme 1) was purchased from Aldrich and was used as received. This latter compound was recrystallized, and its purity was confirmed by the single exponential decay behavior observed. The solvents used were of spectroscopic or equivalent grade. The chromophore concentration (c_{Py}) used in the Py₂PEO solutions ranged, for all fluorescence experiments, from 1×10^{-5} to 1×10^{-6} M. Prior to experiments, the solutions were deoxygenated by bubbling with nitrogen or argon and sealed.

Instrumentation. Absorption and fluorescence spectra were recorded on Shimadzu UV-2100 and Jobin-Ivon SPEX Fluorog 3-22 spectrometers, respectively. All of the fluorescence spectra were corrected for the wavelength response of the system.

Fluorescence decays were measured using a home-built TCSPC apparatus with a N₂-filled IBH 5000 coaxial flashlamp as the excitation source, a Jobin-Ivon monochromator, a Philips XP2020Q photomultiplier, and Canberra instruments TAC and MCA. Alternatively, as an excitation source, a Horiba-JI-IBH

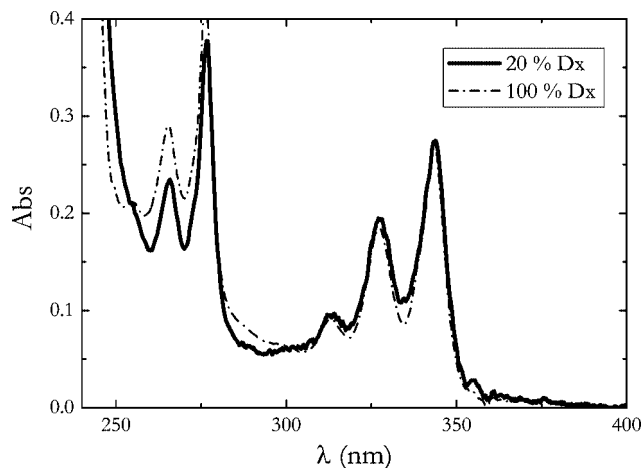


Figure 1. Absorption spectra of the Py₂PEO polymer in 2:8 and 10:0 (v:v) dioxane–water solutions.

NanoLED, $\lambda_{exc} = 339$ nm, was also used. The fluorescence decays were analyzed using the modulating functions method of Striker.²⁸

Temperature control was achieved using a home-built system based on cooled nitrogen and electric heating, which is automatically controlled by the difference between the input value and the actual sample temperature, determined with a PT100 thermometer.

Results and Discussion

The study of a poly(ethylene oxide) polymer (hydrophilic) end-capped with pyrene (hydrophobic) permits the evaluation of the conformational behavior of this polymer in a varied range of solvents with different polarities. This can be probed both by the pyrene (monomer) emission and also by using the excimer-to-monomer ratio (I_E/I_M) and the kinetics of excimer formation. Attempts were made to dissolve the polymer in various solvents. It was found to dissolve in water, various alcohols, tetrahydrofuran, dioxane, and benzene. For initial studies on solution behavior, dioxane–water mixtures were used as these allow the examination of polarity effects over the range from aqueous to low-polarity media.

Absorption and Steady-State Fluorescence. Dioxane–Water Mixtures. The pyrene-end-capped Py₂PEO polymer shows the characteristic absorption spectra of the pyrene probe itself; see Figure 1. The molar fraction of dioxane was found to influence the peak-to-valley ratio (P_A)²⁹ of the $S_0 \rightarrow S_2$ absorption transition band. The changes in the absorption spectra with the gradual increase of dioxane content (increase of the P_A ratio) and of the solvent mixture suggests the presence of two absorbing species, pyrene monomers and ground-state dimers (GSD).

Figure 2A shows the emission spectra of the Py₂PEO polymer (in water, dioxane, and dioxane–water mixtures). It can be seen that under these conditions, the emission spectra of the pyrene-end-capped polymer displays the characteristic bands of both the monomer ($\lambda_{max} = 375$ nm) and the excimer ($\lambda_{max} \approx 480$ – 490 nm) species. Three main conclusions could be drawn from the observation of the emission spectra of the Py₂PEO polymer. First, the increase of the dioxane content in the mixture leads to a decrease in the intramolecular interaction. These interactions are here measured in terms of the excimer-to-monomer ratio (I_E/I_M ratio). The gradual addition of dioxane to the mixture solution, even in small amounts, has a pronounced effect on the I_E/I_M ratio (Figure 2B). However, even in a good solvent

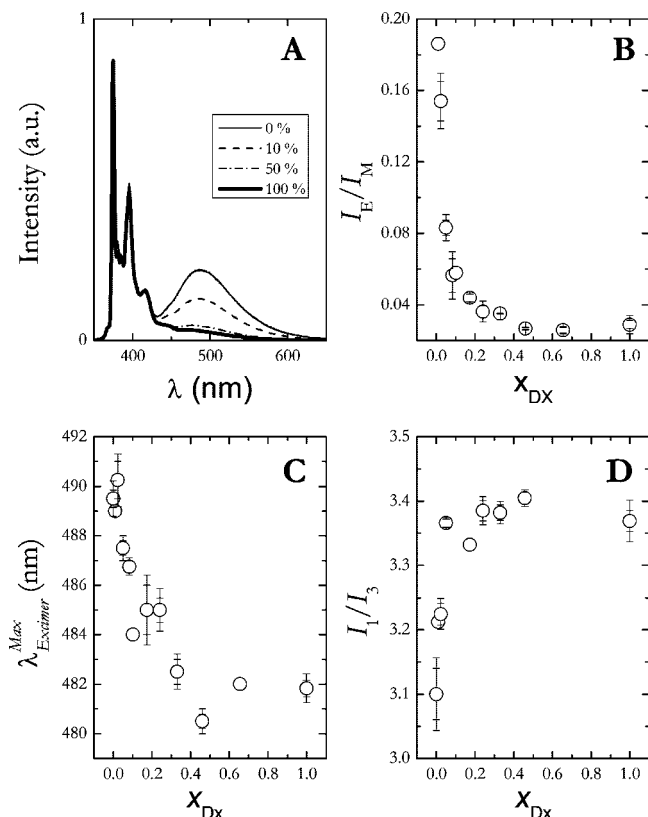


Figure 2. Emission spectra of the Py₂PEO polymer in water and dioxane–water solutions, $c_{\text{Py}} = 5 \times 10^{-6}$ M (A). Dependence of the I_E/I_M ratio (B), maximum emission wavelength of the excimer (C), and I_1/I_3 ratio (D) with the molar fraction of dioxane in dioxane–water mixtures for the Py₂PEO polymer at room temperature.

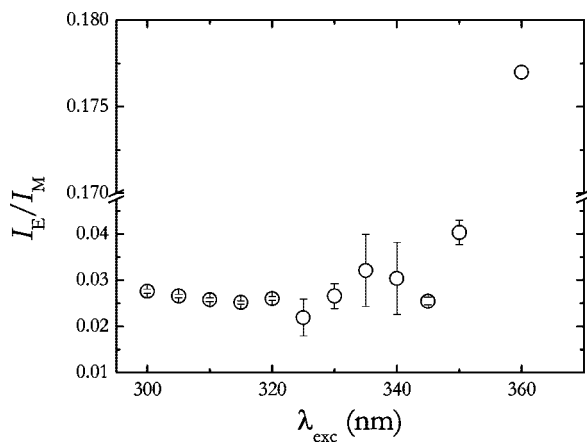


Figure 3. Variation of the excimer-to-monomer ratio (I_E/I_M) as a function of the excitation wavelength for the Py₂PEO polymer in dioxane.

for the end groups, such as dioxane, ground-state dimers are still present, as can be observed by the increase in the I_E/I_M ratio when excitation is made at the red edge of the absorption spectra ($\lambda_{\text{exc}} = 350\text{--}360$ nm); see Figure 3. This is also supported by the excitation spectra collected at the monomer and excimer (long-wavelength emission band) regions, which show that these two excitation spectra do not fully overlap for all dioxane–water mixtures (data not shown). Second, the wavelength maximum for the monomer emission band remains practically constant, whereas the excimer maximum emission wavelength ($\lambda_{\text{Excimer}}^{\text{max}}$) displays a gradual blue shift (maximum of $\approx 8\text{--}10$ nm) with increasing dioxane percentage in the mixture (Figure 2C). This is a somewhat surprising observation

TABLE 1: Photophysical Parameters Taken from the Absorption and Fluorescence Excitation Spectra for the Py₂PEO Polymer in Several Solvents^a

solvent	n_D	η^0 (Pa·s)	ϵ^{25}	P_A	$P_E - P_M$	$\Delta\lambda$ (nm)
methanol	1.3284	0.55×10^{-3}	32.66	2.86	0.06	0
THF	1.4072	0.575×10^{-3}	7.58	3.22	0.26	0
benzene	1.5011	0.649×10^{-3}	2.28 ^d	2.99	0	0
water	1.3323	1.002×10^{-3}	80.16 ^d	2.44	0.35	1.1
ethanol	1.3614	1.200×10^{-3}	24.55	3.00	0.09	0
dioxane	1.4224	1.439×10^{-3b}	2.21	3.29	0.07	0
propan-1-ol	1.3855	1.943×10^{-3c}	20.45	3.04	0	0
butan-1-ol	1.3993	2.948×10^{-3}	17.51	3.40	0.5	0

^a P_A are obtained from the absorption spectra and consist, respectively, in the peak-to-valley ratio and in the difference between the maxima absorption wavelength of the polymer and of the model compound of the $S_0 \rightarrow S_2$ pyrene absorption band. The parameters ($P_E - P_M$) and $\Delta\lambda$ are the differences between the peak-to-valley ratio and between the maxima wavelength, respectively, of the excitation spectra collected at the excimer and monomer emission wavelengths. The viscosity at 20 °C (η^{20}), refractive indexes at 20 °C (n_D), and dielectric constants at 25 °C (ϵ^{25}) are also presented.⁴⁵ ^b Obtained at 15 °C; ^c Obtained at 25 °C; ^d Obtained at 20 °C.

since it is well-known that excimers do not show sensitivity to the polarity of the media.³⁰ Therefore, this shift can only result from the presence of an additional species emitting in a similar region to the excimer.

Pure Solvents. The effect of solvent on the photophysical behavior of the Py₂PEO polymer was also studied using a range of solvents. The photophysical parameters, refractive indexes, viscosities, and dielectric constants are presented in Table 1. The effect of the solvent on the behavior of the Py₂PEO polymer in solution is related both to the physical properties of the solvent itself and to its quality toward both PEO chain and end-capped pyrene (Py) groups, that is, the excimer formation results from the balance between the solvent–PEO, solvent–Py, and Py–Py interactions. This balance has a strong effect on the pyrene–pyrene interactions and consequently on the presence of ground-state association. Table 1 shows the photophysical parameters taken from the absorption and excitation spectra, which provide qualitative information of the presence of GSD in solution. It can be seen that the most marked differences in the absorption spectra of the Py₂PEO polymer (seen in the P_A parameter), together with differences between the excitation spectra collected at the monomer and excimer emission wavelengths ($P_E - P_M$ and $\Delta\lambda$), are found in water and methanol. Although these are considered to be good solvents for the PEO chain, they are not so good for the pyrene end-caps. Thus, in these solvents, the end-to-end cyclization of the PEO chain is promoted, leading to GSD formation. In THF, benzene, dioxane, 1-butanol, and 1-propanol, these differences are very much smaller, and the P_A values become equal to or greater than 3, values generally considered to be indicative of the absence of GSD.^{29,31} The pyrene–solvent interactions become favorable in these solvents, and dynamic excimer formation becomes more important than the formation of ground-state dimers.

Figure 4 shows the dependence of the I_E/I_M ratio on the inverse of the solvent viscosity. There is a maximum in the I_E/I_M ratio when water is used as a solvent. The Py₂PEO polymer excimer formation is not a pure diffusion-controlled process and will depend on both the viscosity of the solvent and the conformation and dynamics of the PEO polymer chain. From the excitation spectra at three wavelengths, the presence of ground-state association with the Py₂PEO polymer is confirmed in all of the solvents studied. However, it is higher when water is used as a solvent as can be concluded from the photophysical

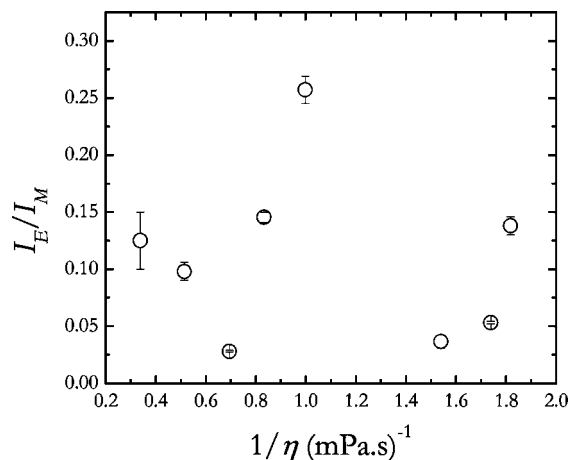


Figure 4. Dependence of the I_E/I_M on the solvent viscosity at room temperature for the Py₂PEO polymer $c_{Py} = 1 \times 10^{-6}$ M.

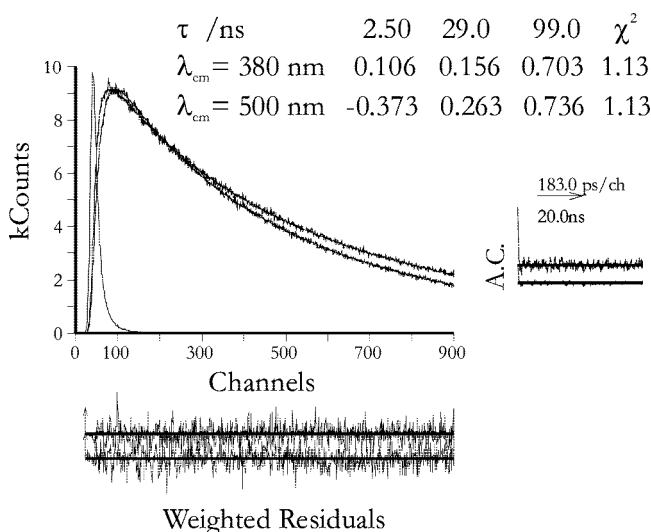
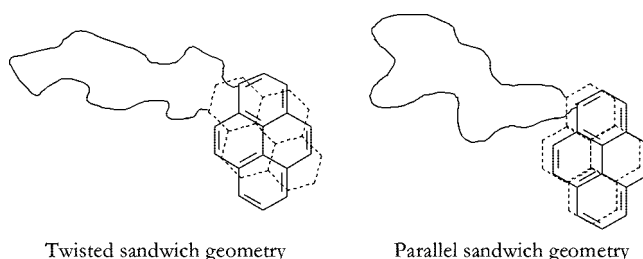


Figure 5. Fluorescence decays obtained for the Py₂PEO polymer at $\lambda_{em} = 370$ and 500 nm and with $\lambda_{exc} = 335$ nm in water (pH = 5.5), obtained with global analysis. Decay time values (τ_i) and pre-exponential values (a_{ij}) are shown as insets of the decays. For a better judgment of the quality of the fits, shown as insets are the weighted residuals, autocorrelation (A.C.) functions, and chi-squared (χ^2) values.

parameters taken from the absorption and excitation spectra (Table 1) and from the sum of the pre-exponentials at the excimer emission wavelength (see below Figure 5). These observations explain the unusually high I_E/I_M values found in this solvent when compared with those of the other pure solvents.

Time-Resolved Fluorescence. The fluorescence decays of the Py₂PEO polymer in water (Figure 5) were found to be multiexponential in both the monomer (375 nm) and excimer (520 nm) emission regions. The global and individual analyses of the decays were best fitted with three exponentials at the two emission wavelengths, with decay time values in water at room temperature of 2.5, 29.0, and 90.0 ns. The shortest decay time appears with a negative pre-exponential at the excimer emission wavelength and is associated with pyrene monomers that form an excimer in the excited state. It can be seen that the sum of the pre-exponential factors at the excimer emission wavelengths is not zero, which again provides convincing evidence for the presence of ground-state association. The two longer decay times, which are identical at the two emission wavelengths, are attributed to the emission from two confor-

SCHEME 2



mationally different excimers. The existence of two conformationally different excimers was first reported for intramolecular excimer formation with 1,3-(1,1'-dipyrenyl) propane³² and subsequently with hydrophobically modified polymers.³³ In the case of the poly(acrylic acid) randomly labeled with pyrene in water, it has been observed that the decay times associated with the shortest-lived (more stable) and longer-lived (less stable) excimers display values in the ranges of 40–65 ns and 90–130 ns, respectively.³³ From these, we suggest that we can attribute the decay times displayed by the Py₂PEO polymer to the emission of an excimer with a twisted sandwich geometry (~29 ns) and that with a parallel sandwich (~99 ns) conformation (see Scheme 2).

However, in pure dioxane and in dioxane–water mixtures, a dramatic change in the fluorescence decays was observed, which can be visualized by comparing the decay profiles in Figures 5 and 6. The individual analyses of these were found to follow bi- and triexponential decays at the monomer and long-wavelength emissions, respectively, in organic solvents and in all dioxane–water mixtures; see Figure 6. The two longest decay times are identical at all emission wavelengths and correspond to the emission of monomers that are able to form an excimer (τ_2 , which is associated with a negative pre-exponential factor at the excimer emission wavelength) and to an excimer, E_1 (τ_1). The additional decay time, the shorter decay time, which is now essentially observed only at the excimer emission wavelength (τ_3), appears to be attributable to the component responsible for the shorter wavelength excimer maximum, that is, to an additional species, uncoupled from the other two. This is also seen from the global analysis of the fluorescence decays (presented in Table 2), where the pre-exponential factor associated with τ_3 at the monomer emission wavelength corresponds to less than 1% of the total emission at this wavelength in all studied solvents. This negligible contribution, which is not present when the independent analysis is made, is an obvious consequence of the need for an equal number of exponentials at the two emission wavelengths when the global analysis is used.

Short-lived components have also been found in other systems such as 1,12-bis(1-pyrenyl)dodecane in hybrid sol–gel systems,³⁴ Zn–Al-layered double hydroxides intercalated by anionic pyrene derivatives,³⁵ and randomly labeled poly(acrylic acid) polymer ($M_w = 150$ kg/mol⁻¹) in dioxane.²⁹ In all of these situations, the existence of a short decay component at the excimer emission wavelength was attributed to the direct excitation of ground-state dimers. This can be associated with two different effects. The first is the possibility of formation of micelle-like structures, which have been observed at high concentrations (>8 g/L) in a short PEO chain labeled at one end with pyrene.³⁶ Intermolecular interactions were also detected in a similar Py₂EO₈₇ polymer.³⁷ However, this possibility was discarded for the dilute solutions studied here since the I_E/I_M ratio is constant within the Py₂PEO polymer concentration

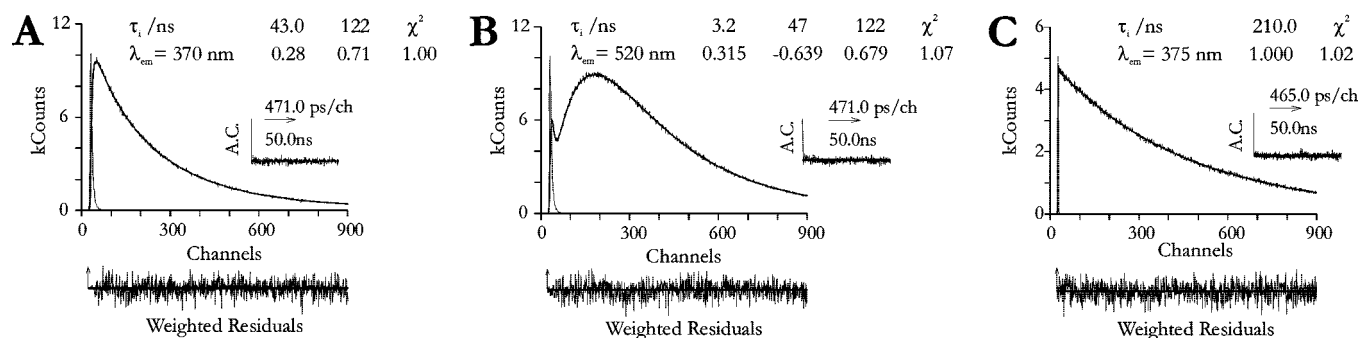


Figure 6. Fluorescence decays obtained for the Py₂PEO polymer in methanol obtained with independent analysis at the monomer (A) and excimer (B) emission wavelengths and for the 1-methylpyrene in methanol (C), $c_{\text{Py}} = 1 \times 10^{-6}$ M. The instrument profile curve is also shown.

TABLE 2: Fluorescence Decay Times (τ_i) and Pre-exponential Factors (a_{ij}) Obtained from the Global Analysis of the Fluorescence Decays of the Py₂PEO Polymer in Different Solvents, $c_{\text{Py}} = 5 \times 10^{-6}$ M along with the Decay Times (τ_M) of the Model Compound 1-Methylpyrene

solvent	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	a_{i1}	a_{i2}	a_{i3}	χ^2	τ_M (ns)
THF	375	2.4	41	134	0.032	0.085	0.879	1.05	140
	520				0.698	-0.278	0.302	1.12	
benzene	375	1.9	42	144	0.038	0.046	0.910	0.98	163
	520				0.645	-0.325	0.355	1.06	
methanol	370	3.2	43	120	0.000	0.309	0.683	1.00	210
	520				0.361	-0.599	0.635	1.02	
ethanol	375	2.5	42	133	0.039	0.096	0.856	0.98	204
	520				0.300	-0.637	0.700	1.07	
dioxane	370	2.3	50	163	0.061	0.003	0.935	1.09	166
	520				0.698	-0.244	0.302	1.01	
propanol	375	2.2	40	148	0.049	0.075	0.866	0.97	206
	520				0.232	-0.677	0.768	1.11	
butanol	375	3.2	34	147	0.091	0.053	0.845	1.08	205
	520				0.233	-0.439	0.767	1.07	

investigated (Figure 7). If intermolecular interactions between Py₂PEO polymer chains were present in the system, an increase of the I_E/I_M ratio with concentration would be observed.^{11,36,38} With the Py₂EO₈₇ polymer, where intermolecular interactions were observed, the poly(ethylene oxide) (where the two pyrene groups are linked) is smaller than the PEO chain of the polymer under investigation; this means that the former polymer possesses a greater hydrophobic character than the latter, suggesting a reasonable explanation for the absence of intermolecular interaction with the Py₂EO₂₁₅ polymer. The second possibility is attributed to the fact that the short-lived component may be

associated with restrictions imposed by the PEO polymer chain. This component is indeed observed in all of the used solvents, with the exception of water (see Table 2), which seems to be a strong indication that it is related to the interactions between the PEO chain and the solvent. Although water is considered to be a poor solvent for the pyrene groups, it is a good solvent for the PEO chain. This leads to the idea that in aqueous solution, the PEO chain will adopt a random coil conformation, as suggested by dynamic light scattering (to be published), whereas in the other studied solvents, the PEO chain is less soluble, and it becomes more compact to avoid the contact with the solvent. The pyrene groups are entrapped in the polymer, favoring the static excimer formation and the formation of a new species, excimer E₂.

Moreover, from the fluorescence decays collected at the excimer emission wavelength and with three different excitation wavelengths (316, 335, and 350 nm) for the Py₂PEO in methanol (Figure 8), two main observations could be made: at $\lambda_{\text{em}} = 520$ nm, the sum of preexponential factors (associated with the τ_2 and τ_3 decay times) is zero, independent of the excitation wavelength; and the contribution of the short-lived (uncoupled) component increases considerably when excitation is made at 350 nm. The first observation shows that in methanol (and, as will be shown below, in the pure solvents except water), the excimer E₁ is only formed in the excited state (dynamic excimer formation). The second observation fully supports the fact that E₂ is preassociated in the ground state since the excitation in the red edge of the absorption spectra leads to the preferential excitation (and emission) of ground-state dimers (the uncoupled species associated to τ_3). The dependence of the decay times

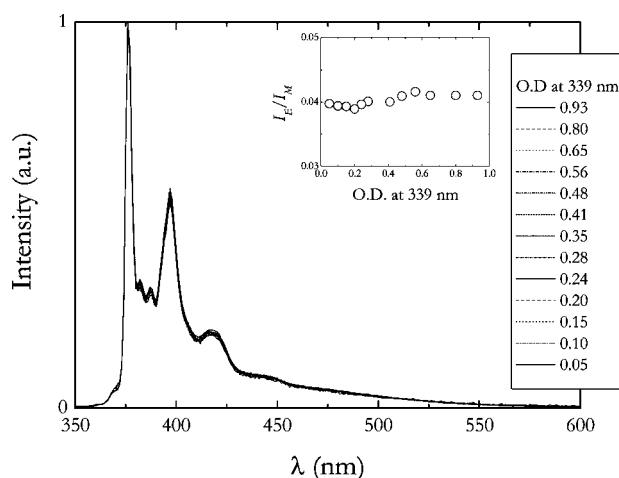


Figure 7. Fluorescence spectra, normalized at the monomer emission maxima, for the Py₂PEO polymer in dioxane at various concentrations. Shown as insets are the different I_E/I_M ratio values versus the (pyrene) O.D. at 339 nm.

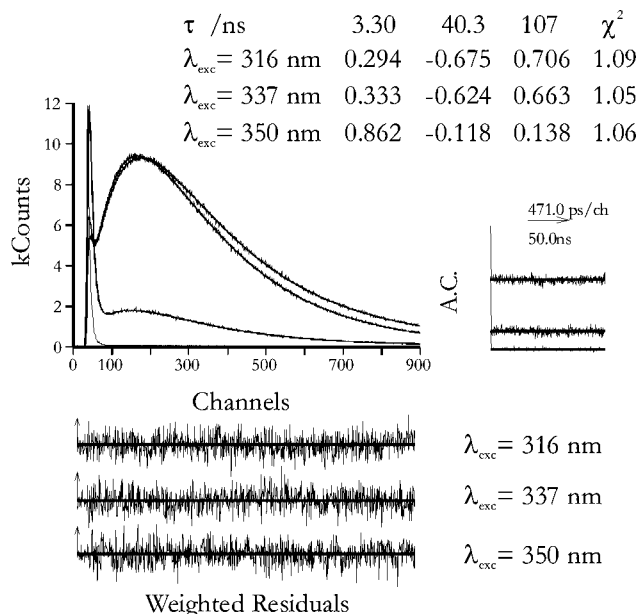


Figure 8. Fluorescence decays collected at 520 nm for the Py₂PEO polymer in methanol at three different excitation wavelengths, 316, 337, and 350 nm.

(τ_i) and of the associated pre-exponential factors at the monomer (a_{1j}) and excimer (a_{2j}) emission wavelengths are depicted in Figure 9.

From the variation of the pre-exponential factors at the monomer emission wavelength, it can be noted that the a_{11} factor increases and that a_{12} (fraction of monomers that form an excimer in the excited state) decreases. The a_{11} pre-exponential factor is related to the back reaction excimer \rightarrow monomer (reversibility), which means that this deactivation process becomes more important with the increase of the dioxane content in the mixture. In contrast, at the excimer emission wavelength, it can be seen that the sum of the pre-exponential factors ($a_{21} + a_{22}$) of the coupled species, that is, the monomer and E_1 excimer, gradually approaches the zero value with the increase on the mole fraction of dioxane, without, however, ever actually reaching zero, revealing that a static route for excimer formation must be partially responsible for the formation of E_1^* . This is also supported by the steady-state fluorescence results (emission and excitation spectra). The pre-exponential factor associated with the excimer E_2 gains weight with increasing dioxane content. This gradual increase on the a_{23} pre-exponential factor provides a strong hint that the excimer E_2 appears to be responsible for the deviation to shorter wavelength of the “excimer” band maximum. In fact, Langmuir–Blodgett films of pyrene derivatives showed the coexistence of two different excimers,^{39,40} one with a maximum emission wavelength at 480 nm (E_1) and a blue-shifted excimer (E_2) with a maximum at 430 nm. The former has been assigned to be an excimer with a sandwich-like conformation; the latter, with a very short decay time, has been assigned to a partially overlapped excimer, which loses weight with time. In our system, with increasing dioxane content, more restrictions are imposed on the pyrene groups, and more excimer E_2 is formed. We believe that the excimer E_2 will not be converted into excimer E_1 ; each excimer will instead be deactivated by itself through excimer emission or, in the case of E_1 , by dissociation.

Duhamel and co-workers^{16,31,41,42} have developed an alternative model, known as the fluorescence blob model, to interpret excimer formation kinetics in different kinds of pyrene randomly

labeled polymers based on the fact that different distances between the interacting chromophores will give rise to a distribution of excimer formation rate constants since cyclization rate constants depend on the chain length between the chromophores. Recently, Duhamel et al.¹⁶ have studied a series of double-labeled end-capped polystyrene and randomly labeled polymers using two different methods of analysis, the classical Birks’s model and the fluorescence blob model. From this study, they could observe that both steady-state (I_E/I_M ratio) and time-resolved fluorescence (k_{cy}) data led to similar tendencies in the variation of the different systems under investigation (randomly labeled and end-capped), which implicitly suggests that excimer formation depends on the polymer backbone and not the nature of the labeling. In contrast, the tendencies in the variation of the k_{cy} and k_{blob} values, obtained from the Birks analysis and from the blob model, respectively, were found to be similar. However, with the pyrene-end-capped polystyrene system, the (essential) biexponential nature of the decays allowed the use of the Birks’s kinetic scheme, a situation that is not possible in the present investigation, where the end-to-end cyclization rate constant was determined using a modified model, from Birks’s model, whose formalism, validity, and equations will be presented below.

Kinetic Scheme. From the above discussion, the kinetic processes that occur in the Py₂PEO polymer in solution can be explained by Scheme 3. In this, M^* and E_1^* are the monomer and excimer kinetically coupled through the associative (k_a) and dissociative (k_d) rate constants and E_2 is an additional excimer, uncoupled to the other two species. The $(1 - \alpha)(1 - \beta)$, $\alpha(1 - \beta)$, and β values are the fractions of light leading to the formation of the species M^* , E_1^* , and E_2^* .

The fluorescence decays follow sums of exponential laws described by eqs 1 and 2²⁹

$$I_M(t) = I_{375\text{nm}}(t) = A_{11}e^{-t/\tau_1} + A_{12}e^{-t/\tau_2} \quad (1)$$

$$I_E(t) = I_{520\text{nm}}(t) = A_{21}e^{-t/\tau_1} + A_{22}e^{-t/\tau_2} + A_{23}e^{-t/\tau_3} \quad (2)$$

where the decay times τ_1 and τ_2 and are given by

$$\tau_{2,1} = [k_X + k_Y \pm \sqrt{(k_X - k_Y)^2 + 4k_a k_d}] / 2 \quad (3)$$

and where $k_X = k_a + 1/\tau_M$, $k_Y = k_d + 1/\tau_E$, and τ_3 is the decay time of the uncoupled species, that is, the dimer.

From Scheme 3, the excited-state concentration time dependence of each species (E_2 , M , and E_1) is given by

$$[E_2^*](t) = a_{23}e^{-\lambda_3 t} \quad (4)$$

$$[M^*](t) = a_{11}e^{-\lambda_1 t} + a_{12}e^{-\lambda_2 t} \quad (5)$$

$$[E_1^*](t) = a_{21}e^{-\lambda_1 t} + a_{22}e^{-\lambda_2 t} \quad (6)$$

In pure organic solvents (Table 2), the proposed kinetic scheme can be simplified. In this situation, the sum of the pre-exponential factors of the two coupled species at the excimer emission wavelength ($a_{22} + a_{21}$), is approximately zero, mirroring the fact that excimer formation through a dynamic mechanism is the only route for E_1^* formation; see Figure 6

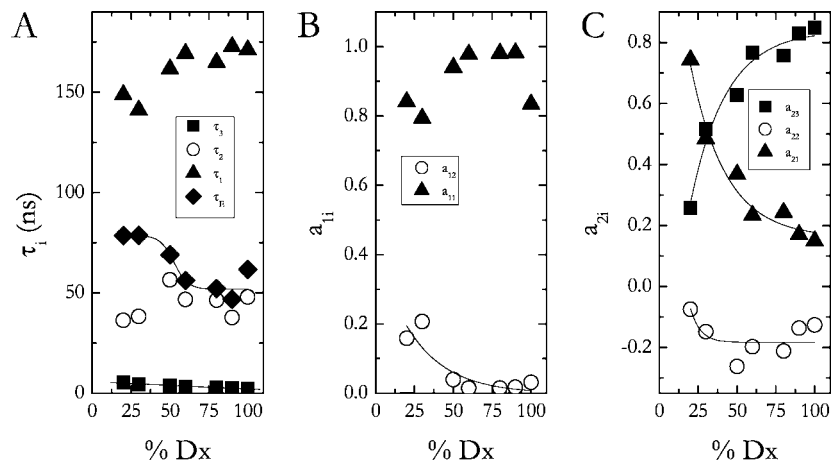
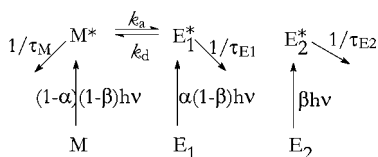


Figure 9. Dependence of the decay times (A) and pre-exponential factors at the monomer (B) and excimer (C) emission wavelengths as a function of the dioxane content for the Py₂PEO polymer in dioxane–water solutions. The lines are only meant to be guides for the eye.

SCHEME 3



and Table 2. As a consequence, α in Scheme 3 will be equal to zero, leading to a simplified kinetic scheme where the fractions of light that excite M and E₂ are $(1 - \beta)$ and β , respectively.

Rate Constants. In the case of organic solvents, where the presence of GSD is negligible ($\alpha = 0$ in Scheme 3) and where the E₂ species is uncoupled from the other excimer, the rate constants for the excimer E₁ in the simplified Scheme 3 were obtained through the following equations²⁹

$$k_a = \frac{\lambda_1 + \left(\frac{a_{12}}{a_{11}}\right)\lambda_2}{\left(\frac{a_{12}}{a_{11}}\right) + 1} - k_M \quad (7)$$

$$k_d = \frac{k_X k_Y - \lambda_1 \lambda_2}{k_a} \quad (8)$$

$$k_E = k_Y - k_d \quad (9)$$

1-Methylpyrene was used as parent compound to obtain the value of the unquenched lifetime, τ_M . The k_a values obtained for the Py₂PEO polymer in organic solvents are presented in Table 3 using the polymer and model compound. As can be seen from this, the rate constants k_a and k_d (Table 3) are within expected values found for pyrene excimer formation in polymers labeled with pyrene and may be attributed to end-to-end cyclization.^{3,9,43} The k_a values can also be compared with that obtained for a poly(acrylic acid) polymer ($M_w = 450 \text{ kg/mol}^{-1}$) in dioxane labeled with a low percentage of pyrene ($k_a = 0.009 \text{ ns}^{-1}$).³³ Larger k_a values were obtained for a highly labeled polymer ($k_a = 0.014 \text{ ns}^{-1}$).³³ This is explained by the shortest mean distance between the pyrene groups attached onto the PAA chain, when compared with those of the Py₂PEO polymer. It should be stressed that a direct comparison of these values with the intermolecular rate constant (diffusion-controlled) is not valid

because of the strong contribution of the poly(ethylene oxide) polymer chain to the activation energy and its effect on excimer-forming conformations. However, it is worth noting that k_a appears to be faster in methanol and ethanol than in the other solvents. Generally the end-to-end cyclization is faster in a poor solvent than it is in a good one.⁹ It consequently seems clear that methanol and ethanol are poor solvents for the Py₂PEO polymer.

For a diffusion-controlled process, the I_E/I_M ratio should increase with $1/\eta$, while $\ln[k_a]$ should decrease with $\ln \eta$. This has been observed for pyrene-end-capped polystyrene chains and for pyrene randomly labeled polystyrene chains.¹⁶ However, neither of these types of behavior could be observed with Py₂PEO. In fact, this system is kinetically more complex than the above-mentioned cases,¹⁶ where no ground-state association was detected. In the present system, one monomer and two excimers were detected, which explains the deviation of the I_E/I_M ratio versus $1/\eta$ from linearity. However, in organic solvents where the excimer E₁ formation is described by a classical Birks's kinetic scheme, a typical behavior of a diffusion-controlled process would be expected for the k_a versus $1/\eta$ and $\ln[k_a]$ versus $\ln \eta$ (Table 3). Considering the solvent series methanol, ethanol, 1-propanol, and 1-butanol, a decrease of the k_a is observed with the increase of the solvent viscosity. The discrepant values are found when the polymer is dissolved in THF, benzene, and dioxane. In fact, in these solvents, the I_E/I_M ratios are lower than ~ 0.05 , which might result in monomer emission leaking into excimer decays. This behavior was found for long polystyrene chains labeled in the extremities with pyrene, where no reliable end-to-end cyclization rate constants were obtained.¹⁶

For the series of alcohols, where a linear dependence with the solvent viscosity was found, the following equation can be applied

$$\ln k_a = \ln a + \alpha \ln \eta \quad (10)$$

where a is a constant and α is the slope of the plot shown in Figure 10. The value obtained was $\alpha = 0.52$, which is much lower than that expected for a purely diffusion-controlled process. A similar value was obtained for a *p*-phenylenevinylene trimer containing 2-ethylexyloxy side chains ($\alpha = 0.63$).⁴⁴ Both cases reflect the difference between the frictional forces acting on the polymer chain and those predicted from the macroscopic solvent friction, that is, from the viscosity. In our case, this is

TABLE 3: Rate Constant for Excimer E₁ Association (k_a), Dissociation (k_d), and Excimer Decay [$k_E(1)$] for the Py₂PEO Polymer in Several Organic Solvents at $T = 20\text{ }^\circ\text{C}$ and $\lambda_{\text{exc}} = 337\text{ nm}^a$

solvent	η (Pa·s)	k_a (ns ⁻¹)	k_d (ns ⁻¹)	$k_E(1)$ (ns ⁻¹)	τ_E (ns)
methanol	0.55×10^{-3}	0.0081 ± 0.0007	0.0056 ± 0.0003	0.013 ± 0.001	77 ± 5
THF	0.575×10^{-3}	0.0018	0.012	0.010	96
benzene	0.649×10^{-3}	0.0021 ± 0.0003	0.0079 ± 0.0011	0.014 ± 0.0011	71 ± 4.8
ethanol	1.200×10^{-3}	0.0054 ± 0.0017	0.0055 ± 0.0002	0.0162 ± 0.0007	61.5 ± 6.6
dioxane	1.439×10^{-3}	0.0019 ± 0.0002	0.0048 ± 0.002	0.0161 ± 0.002	62.3 ± 6.6
1-propanol	1.943×10^{-3}	0.0046 ± 0.0018	0.0058 ± 0.0013	0.017 ± 0.0007	58.6 ± 1.4
1-butanol	2.948×10^{-3}	0.0033	0.0088	0.019	52

^a The values are the result of the average of 3–4 independent experiments and were determined using the 1-methylpyrene model compounds. The viscosities (η) of the solvents taken from ref 45 are also presented.

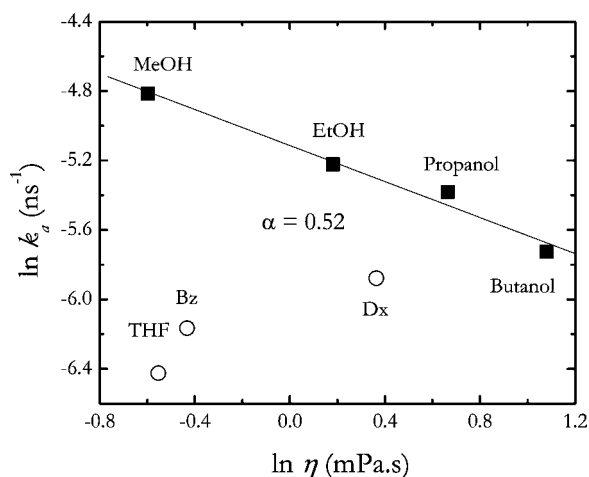


Figure 10. Dependence of the end-to-end cyclization rate constant [$\ln k_a$] on the solvent viscosity ($\ln \eta$) for the Py₂PEO polymer in tetrahydrofuran (THF), benzene (Bz), methanol (MeOH), ethanol (EtOH), dioxane (Dx), 1-propanol, and 1-butanol at room temperature. The k_a values were obtained with 1-methylpyrene as the model compound.

again the result of the influence of the polymer conformation (also conditioned by the solvent) on the rate constant of excimer formation. In solution, the PEO chain adopts a conformation of a random coil, and the k_a values are determined by the end-to-end distance.

The excimer decay rate constants [$k_E(1)$] (0.010 and 0.019 ns⁻¹) and excimer decay times ($\tau_{E1} = 52\text{--}96\text{ ns}$), presented in Table 3, follow into values usually observed with other pyrene-labeled polymer systems.^{29,33,43}

Summary and Conclusions

Fluorescence spectral and lifetime studies on a pyrene-end-capped poly(ethylene oxide) reveal different dynamic and static behavior in water and in organic solvents. In water, the fluorescence decays strongly suggesting that two conformationally different excimers are formed through both static and dynamic mechanisms. The addition of the nonpolar dioxane to the solution, even in small amounts, leads to a change in the kinetics of pyrene photophysics in this polymer, that is, two coupled species coexist with one uncoupled one. This new species has a decay time of 2–3.5 ns and seems to be due to ground-state association, attributed to restrictions imposed by the PEO chain with the increase of the dioxane content, which is a bad solvent (when compared with water) for the ethylene oxide chain. The contribution of this additional species becomes most important in water-free solutions. A (intramolecular) dimer is present and was found with all of the solvents investigated (the possibility of intermolecular interactions was discarded

because of the very low polymer concentrations, together with unpublished results from dynamic light scattering). Thus, the dimer formation is suggested to be due to intramolecular end-to-end cyclization. Rate constants for excimer E₁ formation [k_a], dissociation [k_d], and excimer decay [$k_E(1)$] were also determined for the Py₂PEO polymer in organic solvents. A linear increase of the k_a values with decreasing solvent viscosity was obtained in a series of alcohol solvents; minor changes were found in the k_d values with the solvent.

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