Coil Size and Long Range Excimers. 1. Solvent–Solvent Mixtures

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Received May 11, 1993; Revised Manuscript Received November 29, 1993®

ABSTRACT: Fluorescence spectra of polyacenaphthylene (PAN) were determined in dilute solution at a constant temperature, 25.0 °C. Solvents were prepared by mixing two good solvents in different proportions. Solvent viscosity (η) and polymer intrinsic viscosity ($[\eta]$) were also measured at 25.0 °C for each solvent composition. Solvent mixtures were chosen to show a monotonous change of only solvent fluidity (η^{-1}) (benzene-dioxane) and both η^{-1} and $[\eta]^{-1}$ simultaneously (tetrahydrofuran–dioxane, chloroform–tetrahydrofuran, and cyclohexane–diethyl ether). A single solvent, toluene, was also used. The dependence of the excimer to monomer fluorescence ratio on solvent viscosity and segmental density (directly proportional to $[\eta]^{-1}$) has been discussed in terms of a kinetic scheme which takes into account energy migration, ground state preformed dimers, and unquenched monomeric units. It predicts that the excimer to monomer fluorescence ratio depends on the product $\eta^{-1}[\eta]^{-1}$.

Introduction

The intrinsic fluorescence of the homopolymers and copolymers with monomeric units bearing chromophores is a very complex phenomenon. In this work we will be concerned only with excimer emission, a powerful tool to study conformational transitions with relaxation times in the nanosecond time scale.[1]

Intramolecular excimer emission depends on many different variables: chain configuration and molecular weight, solvent, temperature, pressure, etc. The original Birks scheme and some modifications have been employed to explain the temperature dependence of the steady state fluorescence spectra and the time correlated emission of polymers with intrinsic fluorescence.[1] But many different aspects remain unexplained.

A particular set of kinetic constants may be necessary for each polymer configuration. For example, the rate constant for excimer formation through rotation of the backbone bonds is quite different for racemic and meso dyads.[2,3] As a consequence, atactic polymers must be considered a mixture of subsystems with different photophysical behaviors,[4] of which the relative contribution depends on the polymer microstructure.

The existence of ground state preformed dimers may also determine the characteristics of excimer emission and, in particular, its dependence on temperature and solvent viscosity.[4–6] The role of energy migration has also been broadly discussed.[7]

Solvent may influence the fluorescence of the polymer through different pathways: solvent viscosity determines chain mobility, and polymer–solvent interactions control the equilibrium average conformation or may cause quenching.

There are a number of works on the influence of solvent viscosity on excimer emission, but most of them are concerned with dichromophoric or small size compounds.[8–13] To form excimers in polymers, a photon must move to an excimer forming site (EFS) or the chain must move through a frictional medium to form an EFS. According to the last mechanism, the rate constant for excimer formation (k_a) depends inversely on solvent viscosity (η) and different theories[14–17] have been applied to express the functionality of such a dependence. The excimer to monomer fluorescence ratio (I_E/I_M) depends on a set of rate constants which correspond to chain movements and other processes which take place without friction with the solvent medium. In some cases, the nonradiative decay processes depend on solvent viscosity[18] but it is not usually the case for polymer anchored chromophores. In the low temperature limit (LTL), the fluorescence ratio depends on solvent viscosity only through k_a and, as expected, I_E/I_M increases upon decreasing solvent viscosity.[19–22] Something different occurs in the high temperature limit (HTL) because the fluorescence ratio depends not only on k_a but also on the rate constant for excimer dissociation k_d, which itself depends inversely on viscosity. Thus, in the HTL, the fluorescence ratio I_E/I_M increases upon increasing solvent viscosity, as observed for phenylsiloxanes.[23] It was also found[10,21] that the crossover temperature between the HTL and the LTL is influenced by solvent viscosity, and therefore it can be concluded that solvent viscosity and temperature are two interdependent variables.

There are several examples in the literature of polymers whose fluorescence ratios are independent of coil size ($[\eta]$) or segmental density ($[\eta]^{-1}$).[19,23–25] They are polymer systems in both the HTL and LTL but are characterized by the formation of excimers between nearest neighbor chromophores (we call them short range excimers, SRE). On the other hand, the fluorescence ratio of polymers forming long range excimers (LRE), that is to say, excimers between nonnearest neighbor chromophores, depends very much on segmental density.[21,26,27] For end to end excimers, which are a particular kind of LRE, it was found that excluded volume effects modify not only the rate constant for excimer formation (which implicitly depends on the intramolecular concentration of chromophores and therefore on $[\eta]^{-1}$) but also the first order rate constant for excimer dissociation.[26]

® Abstract published in *Advance ACS Abstracts*, March 1, 1994.

0024-9297/94/2227-2297$04.50/0

In this work we intend to analyze the solvent influence on LRE. With that purpose, we have employed mixed solvents chosen to change monotonously only solvent fluidity (η^{-1}) (benzene–dioxane, Bz–Dx) and both η^{-1} and $[\eta]^{-1}$ simultaneously (tetrahydrofuran–chloroform, THF–Clf, tetrahydrofuran–dioxane, THF–Dx, and diethyl ether–cyclohexane, DEE–Ch). Polyacenaphthylene (PAN) was chosen for this work because both LRE[27,28] and SRE[29] have been reported for this polymer and, thus, changes of the coil conformation and solvent viscosity must be reflected in its fluorescence spectra. Here we have considered solvent mixtures which cause only relatively small changes of the fluorescence ratio because of the small changes in solvent viscosity. We could get larger effects using solvents like ethylene glycol, but the dependence of the rate constants on η is different in that viscosity range[18] and we are interested in the behavior of polymers dissolved in common organic solvents. In a following paper solvent–precipitant mixtures will be studied.[30]

Experimental Section

Most measurements were performed on sample PANL (which was sythesized by cationic polymerization[31]) and only a few were made with a lower molecular weight sample PANA purchased from Aldrich. It was twice reprecipitated in chloroform–methanol as the solvent–precipitant system and dried under vacuum. The characteristics of samples were previously described.[27] Solvents used were of high-quality grade for fluorescence; they were purchased from Carlo Erba.

Liquid mixtures were prepared by assuming volume additivity. Polymer solutions were made by mixing two solutions in the single solvents of identical optical density.

Emission spectra have been recorded in a Hitachi F4000 spectrofluorometer at a constant temperature (25 °C), using excitation and emission band-passes from 1.5 to 5 nm; the excitation wavelength was 295 nm. The fluorescence ratio of the PAN samples was determined as the ratio of the intensities measured at the wavelengths corresponding to the maximum excimer and monomer emissions (400 and 340 nm, respectively). Measurements were done carefully to minimize the exposure time to the incident light, since PAN is easily decomposed.

The absorbance at the excitation wavelength was always below 0.4, which corresponds to polymer concentrations much below the critical value for coil overlap, and that makes improbable intermolecular chain contants in the homogeneous solutions. On other hand, the low absorbance of the samples prevents auto-absorption or similar artifacts.

It will be shown below that nitrogen bubbling increases appreciably the fluorescence ratio of PAN solutions but maintains the same trend with respect to $\eta^{-1}[\eta]^{-1}$ than an aerated solution. Air equilibrated solutions in solvent mixtures were employed in order to get more reproducible compositions.

Viscosities of solvent mixtures and polymer solutions were measured with an Ubbelhode modified viscometer insert in a Lauda Viscoboy automatic viscometer. The temperature was maintained at 25.00 ± 0.05 °C. Viscosities were calculated by applying corrections for kinetic energy (always less than 2%) and density (always less than 1%). Polymer intrinsic viscosity was taken as the reduced viscosity measured with a very low polymer concentration, 0.10 g/dL. The experimental viscosities of single solvents differ by less than 1% with values taken from literature.[32]

Theoretical Expressions

Scheme 1

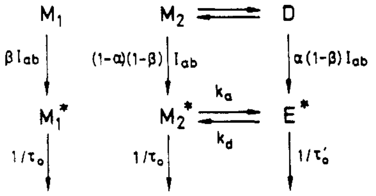
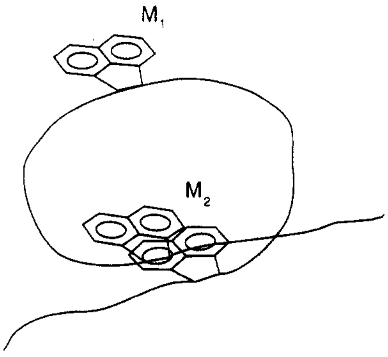


Chart 1



In this system it is necesary to take into account a kinetic scheme[6] which includes all the processes shown in Scheme 1, where τ_0 and τ_0' represent the monomer and excimer intrinsic lifetime, respectively. It is essentially a Birks scheme since it considers only one excimer whose kinetic constants should be an average of those formed in the different polymer configurations. But it is more general because it includes the possibility of having (i) a fraction β of light absorbed by chromophores (M_1) in positions which are not able to form excimers (as we show in Chart 1) and (ii) a fraction $\alpha(1-\beta)$ of the light absorbed by chromophores in ground state preformed dimers (D). The rest of the light, a fraction equal to $(1-\alpha)(1-\beta)$ is absorbed by chromophores like M_2 in Chart 1, they may form excimers through diffusion but they are not in a ground state dimer conformation.

Applying the steady state conditions to Scheme 1 yields

$$\frac{I_E}{I_M} = \frac{k_{FE}}{k_{FM}} \frac{\tau_0(k_a + \alpha\tau_0^{-1})(1-\beta)}{1-\alpha(1-\beta) + \beta k_a\tau_0 + k_d\tau_0'} \qquad (1)$$

where k_{FE} and k_{FM} represent the excimer and monomer fluorescence rates the ratio of which is expected to be solvent independent.[21] k_a and k_d are the rate constants for excimer formation and dissociation through segmental diffusion. Excimers can also be formed by direct absorption of light by D or by energy migration through M_1 type monomer sequences until the photon is trapped in a self-contact point of the chain or ground state dimer conformation, D. Energy migration increases the probability of excimer formation but it does not affect the lifetime of isolated chromophores M_1, which is expected to be equal to τ_0, the lifetime of the monochromophoric model compound. The contribution of direct absorption of light by D is represented in eq 1 by the term $\alpha\tau_0^{-1}$; evidently, its contribution would be significative only if τ_0 and/or k_a is small enough.

Lets assume now that k_a results from the additive contribution of solvent independent energy migration (k_a°) and segmental diffusion in a bimolecular process ($k_a'[M_2]$). This second contribution would depend on the intramolecular concentration $[M_2]$ of monomer able to form excimers, which can be considered proportional to $[\eta]^{-1}$. It would depend too on solvent viscosity through the second order rate constant k_a' and since it is a diffusional movement, it can be assumed that the dependence is on T/η.

Under the assumption that energy migration (k_a°) and excimer formation by segmental diffusion ($C\eta^{-1}[\eta]^{-1}$, where C is a proportionality constant) are additive contributions to k_a, it gives $k_a = k_a^{\circ} + C\eta^{-1}[\eta]^{-1}$. k_d is a first order rate constant and it may depend on η^{-1} but not on $[\eta]^{-1}$.

Table 1. Solvent Viscosity and Inverse of Intrinsic Viscosity (Directly Proportional to Polymer Segmental Density) at 25.0 °C, in the Pure Components of the Solvent Mixtures Here Employed

solvent 1	solvent 2	η_1 (mPas)	η_2 (mPas)	$[\eta]_1^{-1}$ (g/dL)	$[\eta]_2^{-1}$, (g/dL)
THF	Dx	0.47	1.19	3.35	10.07
Bz	Dx	0.60	1.19	11.26	10.07
THF	Clf	0.46	0.54	3.35	3.8[a]
DEE	Ch	0.22	0.89		
Tl		0.59		6.54	

[a] From turbidity measurements; see ref 33.

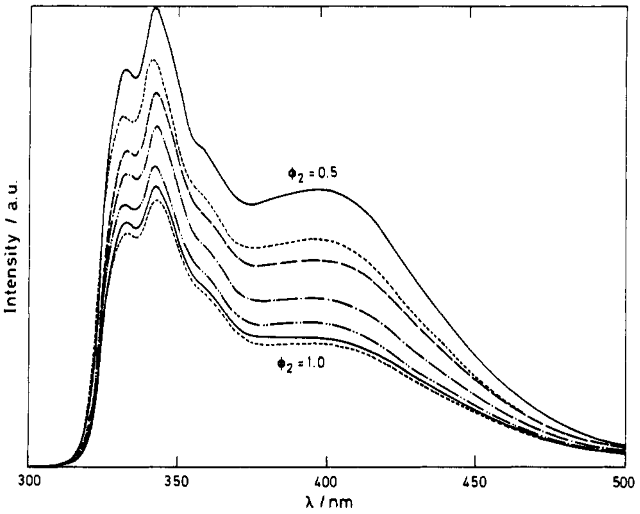


Figure 1. Fluorescence spectra of PAN in dilute solution in several THF-Clf mixtures, at 25.0 °C. The scales of intensity are not correlative.

Nevertheless in the low temperature limit $k_d\tau_o'$ is negligible and eq 1 becomes

$$\frac{I_E}{I_M} = \frac{a_1 + a_2\eta^{-1}[\eta]^{-1}}{a_3 + a_4\,\eta^{-1}[\eta]^{-1}} \tag{2}$$

where

$$a_1 = (\alpha + k_a^o\tau_o)(1 - \beta)Q_E/Q_M$$

$$a_2 = \tau_o(1 - \beta)CQ_E/Q_M$$

$$a_3 = 1 - \alpha(1 - \beta) + k_d\tau_o' + \beta k_a^o\tau_o$$

$$a_4 = \tau_o\beta C$$

and all of them can be considered solvent independent if $k_d\tau_o'$ is about 0 (in the low temperature limit).

Results

Fluorescence spectra and the intrinsic viscosity of PAN at 25.0 °C were determined in four solvent mixtures summarized in Table 1, as a function of solvent composition. Solvent viscosity was also determined for each mixture and composition at 25.0 °C. Solvent mixtures better than single solvents are used to ensure a monotonous change of any property of the medium providing a large number of solvents with different viscosities and polymer-solvent interactions.

Figure 1 shows some representative fluorescence spectra and Figures 2 and 3 show the polymer intrinsic viscosity and solvent viscosity as a function of the composition of the solvent mixtures. It must be noticed that $[\eta]$ is about constant in the Bz-Dx mixture and solvent viscosity suffers the smallest change in the mixture THF-Clf. For the other mixtures both η and $[\eta]$ change simultaneously when going from a pure solvent to the other.

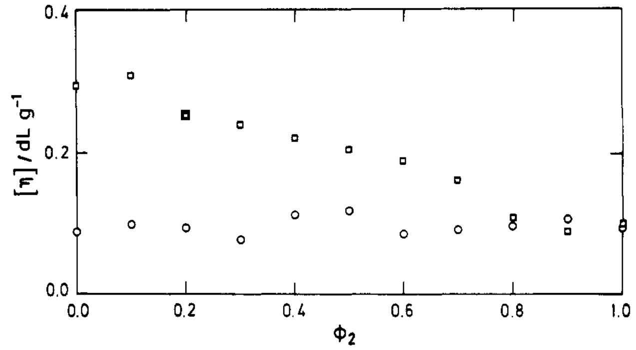


Figure 2. Intrinsic viscosity of PAN at 25.0 °C in two solvent mixtures, (□) THF-Dx and (○) Bz-Dx, as a function of the Dx volume fraction.

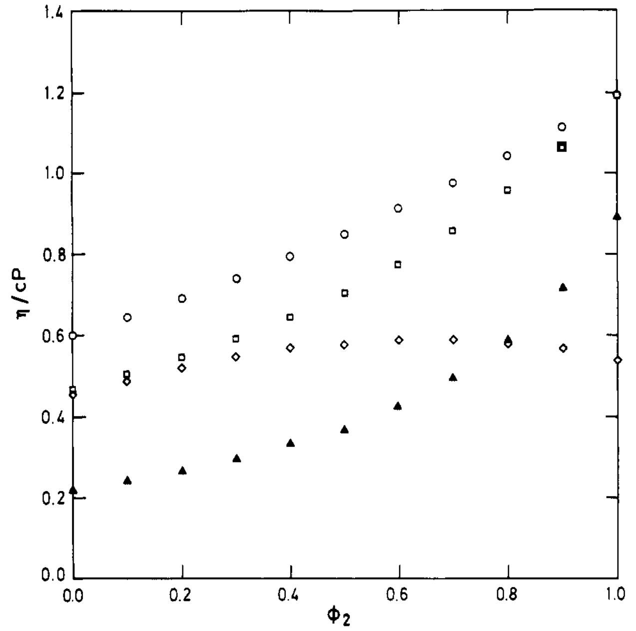


Figure 3. Viscosity of several solvent mixtures as a function of the volume fraction of the second component: (□) THF-Dx; (○) Bz-Dx; (△) DEE-Ch; (◇) THF-Clf.

The polymer sample employed for measurements in the DEE-Ch mixture is of a lower molecular weight (PANA; see the Experimental Section) because this is a cosolvent mixture whose components are nonsolvents of the high molecular weight sample (PANL) employed in the other solvent mixtures. Even though the solubility is sufficient for performing fluorescence measurements, it is too low for intrinsic viscosity measurements.

The excimer to monomer fluorescence ratio I_E/I_M is shown in Figure 4 for all the systems here studied. Measurements were reproducible except for pure THF, for which data obtained in two sets of measurements give different values, with an incertitude about 0.05; but it is well-known that THF is a very hygroscopic and unstable solvent. Measurements in the mixture THF-Dx were previously reported.[20] The reproducibility in the other single solvents is about 0.003 for Dx and 0.001 for Bz, and the dispersion in solvent mixtures with respect to the best fit line is also very small.

Lets consider first the mixture Bz-Dx for which $[\eta]$ of PAN is about independent of solvent composition (Figure 2) and solvent viscosity (Figure 3) changes in a range which covers most of the typical organic solvents. The fluorescence ratio of PAN in this mixture increases upon

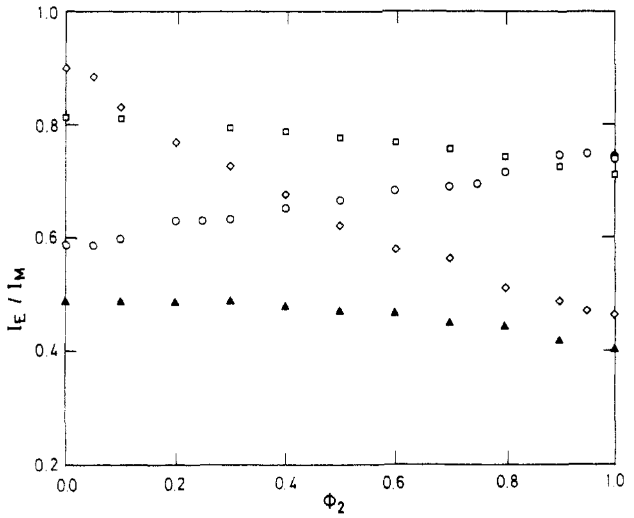


Figure 4. Fluorescence ratio of PAN as a function of the volume fraction of the second component: (□) THF–Dx; (○) Bz–Dx; (△) DEE–Ch; (◇) THF–Clf.

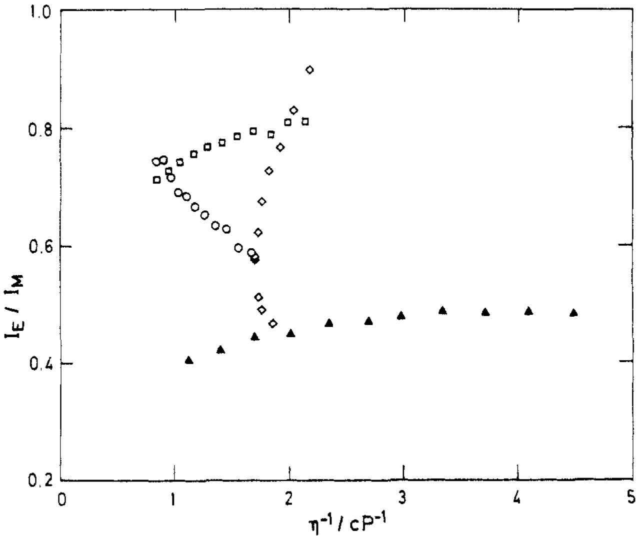


Figure 5. Fluorescence ratio of PAN as a function of solvent fluidity for the different solvent mixtures and a single solvent, Tl (☆). Symbols are the same as in previous figures.

increasing solvent viscosity, which is equivalent to saying that I_E/I_M decreases for solvents of increasing fluidity, as shown in Figure 5. The dependence is the opposite for the mixtures DEE–Ch and THF–Dx, and for the THF–Clf mixtures the fluorescence ratio decreases or increases with η^{-1} depending on solvent composition. It is thus evident that solvent fluidity is not the driving force of the formation of excimers in this polymer.

The mixture THF–Clf is a good example of polymer–solvent specific interaction which in this case causes a quenching effect. The total fluorescence intensity decreases upon increasing the Clf content of the solvent mixture. Since the intrinsic lifetime of monomer and excimer excited states are different, the intensity of the emission coming from those two species changes in a different way and the dependence of the fluorescence ratio on solvent composition becomes quite complex. Solvents with specific interactions will not be considered in the analysis of the dependence of the fluorescence ratio on solvent physical constants.

Discussion

Qualitatively, the same result as given here was obtained[21] for LRE formation by pyrenyl side groups in a copolymer. In that case, in accordance with their own theoretical predictions,[16,21] the fluorescence ratio was proportional to $\eta^{-1}[\eta]^{-1}$ but the intercept was zero or slightly negative. In our case, the fluorescence ratio at infinite viscosity and/or zero segmental density ($\eta^{-1}[\eta]^{-1} = 0$) represents a large contribution to the observed fluorescence ratio (for example, 88% in THF at 25 °C) and the relationship is not direct but inverse; that is to say, the fluorescence ratio decreases upon increasing $\eta^{-1}[\eta]^{-1}$.

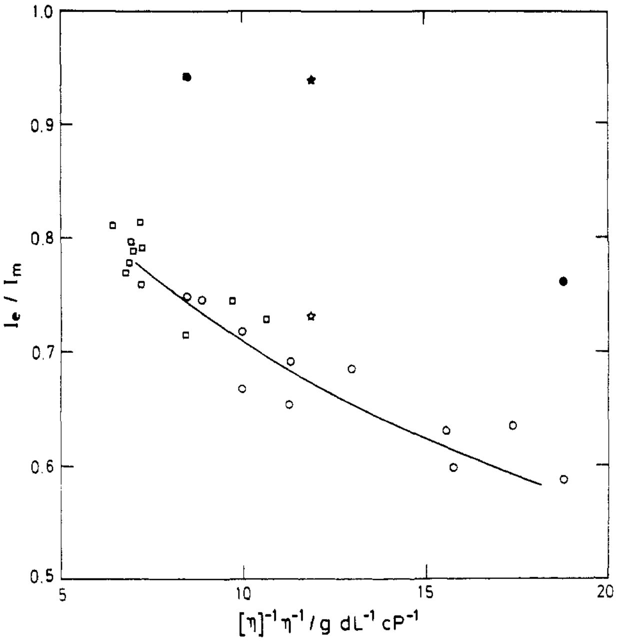


Figure 6. Experimental (points) and calculated (line) values (eq 3) of the PAN fluorescence ratio. Symbols are the same as in previous figures. Empty points correspond to aerated solutions and filled points to oxygen free solution in single solvents.

To interpret the differences between those two systems (ref 21 and this work) we have considered the following arguments.

(i) Energy migration is known to be very important in PAN,[7] and its contribution to excimer formation must be persistent even in solvents of low fluidity ($\eta^{-1} \rightarrow 0$). Energy migration is not expected in a copolymer of a very low labeling fraction, and it explains how the fluorescence ratio of the system in ref 21 tends to zero for mediums of very high viscosity whereas it is large for PAN.

(ii) Ground state preformed dimers would explain excimer emission in solvents for which polymer segmental density would be low ($[\eta]^{-1} \rightarrow 0$). It has been shown above that the contribution of ground state preformed dimers becomes more important for chromophores of lower τ_0 and thus it must be larger for PAN than for a pyrene bearing polymer.

(iii) To explain the different sign of the dependence of I_E/I_M on $\eta^{-1}[\eta]^{-1}$, we first have to consider the influence of excimer dissociation which depends inversely on I_E/I_M. But we have finally discarded that possiblity because it was found for end-to-end excimers[26] that the rate constant for excimer dissociation depends directly on $[\eta]$ because of a correlation hole effect associated with end groups. Such a dependence of k_d on $[\eta]$ is incompatible with the experimental results of PAN and we must conclude that k_d plays a minor role because at room temperature the polymer is in the low temperature limit ($k_d\tau_0' \ll 1$).

A nonlinear regression fit of the experimental results shown in Figure 6 to eq 1 by means of a computational method yields positive coefficients with a minimum standard deviation (2×10^{-2}):

$$\frac{I_E}{I_M} = \frac{1.35 + 0.019\eta^{-1}[\eta]^{-1}}{1.27 + 0.090\,\eta^{-1}[\eta]^{-1}} \qquad (3)$$

Any other fitting attempt trying to include any solvent dependence of excimer dissociation (on η^{-1} or $\eta^{-1}[\eta]$) or additional contributions to k_a were unsuccessful and gave some negative coefficients without physical meaning. Figure 6 shows the good coincidence of the experimental results and those calculated with eq 3 in two solvent mixtures and a single solvent, toluene (Tl). It is also shown that oxygen free solutions in single solvents follow the same trend with larger values of the fluorescence ratio.

According to eq 3, a_4 is different from 0 and, as a consequence, β is too. These results suggest that for some configurational or conformational reason, there are isolated chromophores in a PAN chain which are not able to form excimers (M_1 in Chart 1). Its relative contribution to the observed monomer emission increases upon increasing solvent fluidity and polymer segmental density (larger $\eta^{-1}[\eta]^{-1}$) because, then, the monomer in equilibrium with the excimer (M_2) is very much quenched. According to eq 2, the fluorescence ratio of the systems with isolated chromophores decreases with respect to the $\beta = 0$ situation.

Holden and Guillet[1] have suggested that for polymer containing chromophores linked by more than three carbon atoms, a fraction of the chromophores can be locked into conformations which cannot achieve that corresponding to an excimer forming site, within the lifetime of the excited state τ_o. Although PAN cannot be considered in the set of polymers studied by Holden and Guillet, it is possible that the existence of isolated chromophores in polymers is even more general than they suggested.

Chromophores M_1 in Scheme 1 are, of any other chromophore, at a distance farther than that from which they can diffuse during τ_o, and therefore they cannot be considered in the excimer to monomer equilibrium process. They have next neighbor chromophores but they do not form short range excimers, and hence, we can consider them as isolated chromophores.

The relative contribution of energy migration and segmental diffusion to LRE formation can be calculated with the parameters of eq 3 since

$$\frac{a_1}{a_1 + a_2\eta^{-1}[\eta]^{-1}} = \frac{\alpha + k_a^o\tau_o}{\alpha + k_a\tau_o} = \frac{1.35}{1.35 + 0.019\eta^{-1}[\eta]^{-1}} \qquad (4)$$

For example, in THF at 25 °C, energy migration and the direct absorption of light by ground state preformed dimers, contribute 90% of the total excimer formation, and segmental diffusion contributes the rest, 10%.[20]

For diffusion controlled excimer formation processes the rate constant is usually reduced for the solvent viscosity effect by multiplying for η, but caution must be taken for the existence of an additive contribution that is solvent viscosity independent due to energy migration or direct absorption of light by ground state preformed excimers.

Acknowledgment. Financial support from DGICYT and from CAM (Spain) under Grant Nos. PB89/0198 and 247/92, respectively, and from Acción Integrada Spain-Portugal N. 20B is gratefully acknowledged.

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