Excimer Formation in Chain Self-Contact Points

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ABSTRACT: Fluorescence spectra of poly(indene) (PIN) and poly(acenaphthylene) (PAN) samples of molecular weight ranging from 1.8×10^3 to 2.9×10^5 were measured in dilute solution at different temperatures (2, 10, 25, and 40 °C). The fluorescence ratio (I_E/I_M) of PIN decreases upon increasing the chain molecular weight and becomes zero for chains of about 500 monomeric units. By contrast, the fluorescence ratio of PAN increases with molecular weight. The temperature dependence is also different for both polymers: in the range of temperatures studied here, PIN is in the high-temperature limit and PAN is in the low-temperature limit. These results are interpreted in terms of the number of chain self-contact points in the equilibrium conformation and also taking into account segmental diffusion. Monte Carlo simulation results of the number of self-contact points in Gaussian chains of different length are also presented.

Introduction

Excimers[1] are electronic excited-state complexes formed by two chromophores that have the following characteristics: (i) they are placed in a sandwiched parallel disposition, (ii) the distance between their centers is about 3 Å, and (iii) originally one is in the ground state and the other one is in the electronic excited state (generally in the first singlet excited state).

Excimers have a red-shifted emission with respect to the emission of single chromophores or monomer emission. The analysis of the excimer to monomer intensity ratio (I_E/I_M) is potentially very useful for polymers bearing chromophores in the monomeric unit because it is related to both dynamic and equilibrium properties of the macromolecule. Nevertheless, the relationship between the fluorescence ratio (I_E/I_M) and the dynamic or equilibrium molecular parameters is not always evident or easy to find because excimer formation is a very complex phenomenon even if it takes place only with chromophores of the same chain (intramolecular excimers).

Intramolecular excimer-forming sites (EFS) can be formed by two rings joined by a 1,3-propane-like structure (short-range excimers, SRE)[2] or can be placed in a chain self-contact point where two rings that belong to nonneighbor monomeric units overlap (long-range excimers, LRE).[3] On the other hand, excimers can be formed in an EFS (SRE or LRE) by direct absorption of light or by energy migration from a different point of the chain; in such a case, excimer formation is controlled by the population of EFS in the average equilibrium conformation of the chain. But even if the excitation is not placed in an EFS, an excimer can be formed if during the excited-state lifetime an EFS is reached by segmental motions that take place in the same time scale (nanoseconds): rotations through backbone bonds,[4] segmental diffusion,[5] etc. In this case, excimer formation is controlled by the rate of such motions.

Each excimer formation process and each type of excimer has a different set of rate constants for excimer formation, excimer dissociation, and nonradiative decay of the excited-state species. Very often, polymers show both SRE and LRE, and both types of EFS, in some conditions, may form excimers in the equilibrium conformation or after some motions. The observed excimer emission is thus the balance of many different overlapping independent phenomena, and the situation can be still more complicated if the stereochemical composition of the polymer is taken into account. That explains why excimer emission of vinyl aromatic polymers or other homologous polymers is a complex phenomenon enclosing a lot of interesting information.

Fortunately, some polymers may form only one type of excimer, and in some conditions, segmental motions can be frozen or enhanced and that makes it easier to understand the excimer formation process. It is generally accepted[1] that the monomeric structures of poly(indene) (PIN) and poly(acenaphthylene) (PAN) may not form SRE, and since both show excimer emission, it must be due to LRE.

The photophysics of PAN has been broadly studied.[6-15] It has been proposed that PAN excimers are formed by a chromophore and its next to nearest neighbor,[6,8] which is a particular case of LRE. The basis for this conclusion was, on one side, the dependence of the fluorescence ratio of acenaphthylene copolymers on their composition and, on the other, geometrical considerations based on the RIS model. Recently, it was shown[14] that, by considering optimized structures, the contribution of EFS formed by nearest neighbors or SRE in threo-disyndiotactic PAN can be nonnegligible. It is also known[3] that about 20% of the excimer emission of high molecular weight PAN comes from excimers formed by segmental diffusion of the chain, whereas the rest is formed in self-contact points of the chain that exist in the ground-state equilibrium conformation.

Very little is known about PIN from the photophysical point of view.[3,15,16] Its fluorescence spectra in dilute solution show only one band formed by the spectral overlap of very close monomer and excimer bands (292 and 322 nm, respectively).[15] The fluorescence ratio of PIN is practically independent of solvent viscosity,[3] and therefore, it can be concluded that their excimers are formed (i) 100%

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

sample	$10^{-3}M_w$	$10^{-3}M_n$	r	N
PIN173	2.3			20
PIN290	4.5		2.9	39
PIN284	7.2			62
PIN286	10.0		2.1	86
PIN285	18.6			160
PIN170	55.9		1.9	481
PIN126	276		2.3	2379
PIN195	291		1.9	2508
PAN181	1.85			12
PAN293	2.35	1.62	1.45	15
PAN294	4.33	3.34	1.30	28
PAN(A)	5.77	4.25	1.36	38
PAN(L)	140		1.44	921

[a] Molecular weight (M_w determined by GPC and M_n by VPO), polydispersity ($r = M_w/M_n$ with M_n determined by VPO if the data are available and otherwise determined by GPC), and weight-average number of monomeric units (N).

in ground-state preformed self-contact points without excimer dissociation or (ii) 100% in a dynamic process so fast that the equilibrium excimer formation–dissociation is established before the emission takes place. Since no isosbestic point was observed[16] in the temperature dependence of the PIN fluorescence spectra, the first explanation was accepted.[3]

There are also in the literature some other studies on long-range excimers.[17-23] They are concerned with alternating copolymers,[17,18] random copolymers with a very small fraction of chromophores isolated in the chain,[19-21] or pyrene end labeled chains.[22,23]

Long-range excimers provide a tool for studying the number of segment–segment contacts and the dynamics of segmental diffusion. In the present paper, we report the results of the molecular weight dependence of LRE.

Experimental Section

Three PIN samples (PIN195, PIN126, PIN170) were synthesized by cationic polymerization.[24] Five more PIN samples were obtained by electropolymerization[25] in the same conditions as those used for PAN samples (PAN181, PAN293, and PAN294). PAN(A) was purchased from Aldrich, and PAN(L) was synthesized by cationic polymerization.[26] Solvents used (THF and dioxane) were purchased from Carlo Erba SA; they were high-quality solvents specially prepared for fluorescence or HPLC.

The weight-average molecular weight (M_w) of the fractions was determined by size exclusion chromatography (SEC), using a Perkin-Elmer chromatograph equipped with a 6000 psi pump, a Perkin-Elmer differential refractometer LC-25, and an injector of 175 μL. Five columns (three Waters Assoc. Ultrastyragel of 10^3, 10^4, and 10^5 Å and two Shodex, A-803 and A-805) in series were used. Samples were eluted with THF, and the flow rate was 1.0 mL/min. The columns were first calibrated with standard poly(styrene) (PS) samples of narrow molecular weight distribution. This classical calibration based on PS standards yields different results than universal calibration, and since the last one is valid for high enough molecular weights, we have employed it for PAN(L) and PIN170, PIN126, and PIN195. The calibration with PS standards was employed for oligomers.

Polymer intrinsic viscosity [η] in THF was determined from efflux time measured with an Ubbelhode modified viscometer fit in a Laude Viscoboy automatic viscometer. The temperature was kept at 25.00 ± 0.05 °C. [η] was determined by means of the Huggins and Kramer extrapolations. The intrinsic viscosity of PS in THF at 25.0 °C was calculated with the viscometric equation of ref 27.

The number-average molecular weight of the same samples was determined in chloroform with a Knauer vapor pressure osmometer (VPO) at 60 °C. The calibration was made with benzil.

Table I summarizes the characteristics of the samples employed in this work, M_w, M_n, the polydispersity index $r = M_w/M_n$, and the weight-average number of monomeric units (N). End groups have not been considered in calculating N.

UV absorption spectra were obtained on a Shimadzu UV-240 spectrophotometer. Optical density was always kept below 0.5 at the excitation wavelength.

Emission spectra have been recorded in a Hitachi F4000 spectrofluorometer with 280-nm excitation wavelength for PAN and 270 nm for PIN. The excitation and emission band-passes were from 1.5 to 5 nm in both cases. The spectra were corrected for the spectral sensibility of the system. The spectral overlap has been considered negligible for PAN, but it has been calculated with monomer and excimer pure bands for PIN. The PIN monomer band is obtained with a solution of high molecular weight sample for which only monomer emission is observed.[16] Excimer emission is obtained with a PIN sample in bulk by reflection. In this way, it has been found[16] that

$$I_E = I_{322} - 0.373I_{292} \quad (1)$$

$$I_M = I_{292} - 0.117I_{322} \quad (2)$$

where I_{322} and I_{292} represent the intensity of the emission at 322 and 292 nm, respectively. Very dilute solutions in dioxane (Dx) for PIN and in THF for PAN were employed to ensure that only intramolecular excimers are formed. They were purged with nitrogen to avoid quenching by oxygen.

PAN fluorescence spectra were not reproducible at 40 °C due to some photoreactions. At lower temperatures, measurements were performed with special care to minimize the time exposition to the incident light and changing the sample for repeating any run. The same precautions were taken with PIN, and in that way, the spectra were reproducible.

Theoretical Considerations

Although the cyclization of a chain has been the object of considerable theoretical work both from equilibrium and dynamical points of view,[28] its obvious extension to predict properties depending on multiple contributions from different internal cycles (as the long range excimer formation) deserves some comments. The simplest approach consists of assuming a small probability for the formation of each of the cycles so that the global probability of excimer formation in a chain composed of N elements is given by

$$P_E = \sum_{x=x_m}^{N-1} (N-x)P_x \quad (3)$$

where P_x is the probability for an internal cycle of x units and x_m is the minimum of units required to form a cycle (depending on the chain rigidity). $x_m = N-1$ corresponds to end-to-end EFS. For a unperturbed and completely flexible chain, a Gaussian function can describe the equilibrium distribution of distances between units separated by a given number of bonds, and therefore $P_x = x^{-3/2}$ if an equilibrium process is considered. If the cyclization is a diffusion-controlled kinetic process,[5,23] the cyclization rate (and P_x) can also be approximately considered proportional to $x^{-3/2}$, though now, it depends strongly on the solvent's viscosity (and temperature). The introduction of excluded volume should decrease the exponent in the scaling law for P_x down to 2 due to both the increase of the chain volume and to a correlation hole effect[29] in the distribution function at R (end-to-end distance) = 0. Then we can express in general $P_x = x^{-a}$ with a larger or equal to $^3/_2$, and neglecting finite size effects, we can write

$$P_E = \int_{x_m}^{N} (N-x)x^{-a}\,dx \quad (4)$$

Moreover, we can assume that most of the units are not cycled so that the monomer emission probability P_M can

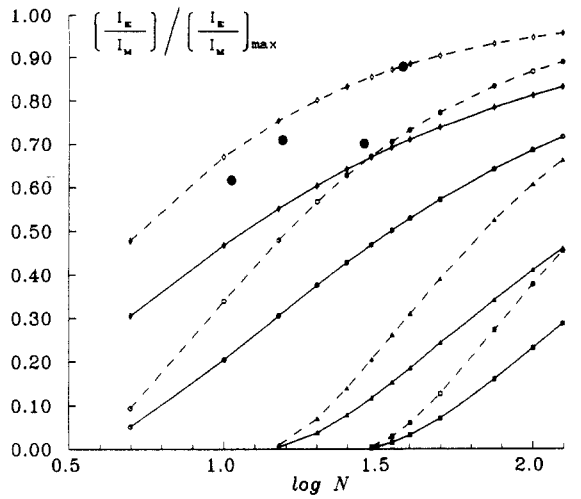

Figure 1. Fluorescence ratio (I_E/I_M) normalized to its maximum value ($(I_E/I_M)_{max}$) and calculated by means of eqs 6 (solid line) and 7 (dashed line), as a function of the number of monomeric units (N) for different x_m values: (△) 1, (○) 13, and (□) 27. The experimental results of PAN at 25 °C are superimposed (●).

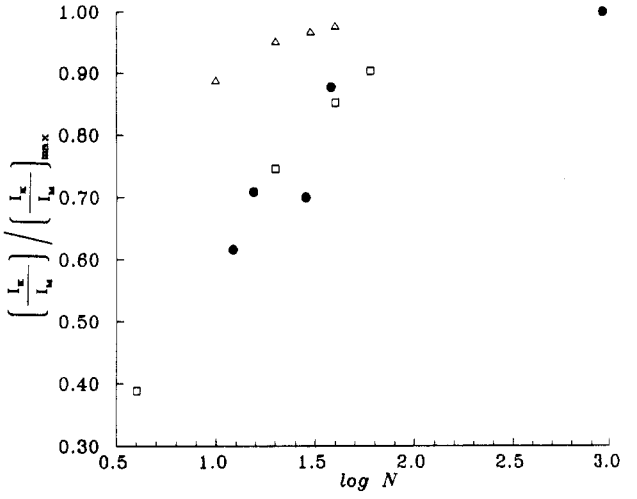

Figure 2. Fluorescence ratio (I_E/I_M) normalized to its maximum value ($(I_E/I_M)_{max}$) and determined by Monte Carlo simulation methods: (□) SIMU I ($x_m = 1$), (△) SIMU III ($x_m = 1$). The experimental results of PAN have also been plotted (●).

be taken as approximately proportional to N. We will show below that this approach introduces a 30% error, but the proportionality can be accepted for $N > 20$.

If chain motions are slower than emission and, consequently, excimers are formed in ground-state preformed EFS, the fluorescence ratio is proportional to P_E/P_M[30,31]

$$\frac{I_E}{I_M} = \frac{Q_E}{Q_M}\frac{P_E}{N} \tag{5}$$

where Q_E/Q_M represents the ratio of excimer to monomer intrinsic fluorescence quantum yields. If, by contrary, excimer formation is a diffusion-controlled process, a kinetic scheme should be considered to find the relationship between the fluorescence ratio and P_E, which, as mentioned before, depends on N as in the previous case (ground-state preformed EFS). Assuming a simple Birks scheme[1] in the particular case where excimer dissociation is a negligible process,[32] the fluorescence ratio can be described again by eq 5.

In order to compare experimental and calculated values, it is convenient to calculate reduced values of the fluorescence ratio:

$$\frac{I_E/I_M}{(I_E/I_M)_{max}} = [2x_m^{-1/2} - 4N^{-1/2} + 2x_m^{1/2}N^{-1}]/2x_m^{-1/2} \tag{6}$$

($a = {}^3/_2$, no excluded volume)

$$\frac{I_E/I_M}{(I_E/I_M)_{max}} = [x_m^{-1} - N^{-1}\ln N + N^{-1}(\ln x_m - 1)]/x_m^{-1} \tag{7}$$

($a = 2$, excluded volume)

In both cases, we obtain similar qualitative trends: an increase of I_E/I_M for increasing values of N until an asymptotic value ($(I_E/I_M)_{max}$) depending only on x_m (or the polymer rigidity) is reached. The aspect of such a dependence can be inspected in Figure 1. The excluded volume effects decrease the fluorescence ratio with respect to Gaussian chains, but in reduced values, they cause the opposite effect. Chain flexibility (lower x_m) increases the formation of LRE, as expected.

Table II
Monte Carlo Simulation Results of P_E/P_M as a Function of N ($x_m = 1$)

N	SIMU I	SIMU II	SIMU III	ref 33
4	0.136			
10		0.755	0.497	
16				0.181
20	0.261	0.809	0.527	
30		0.822	0.540	
32				0.213
40	0.298	0.830	0.547	
60	0.316			
64				0.260

Since the occurrence of multiple cyclizations may somewhat complicate the scheme, we have also performed some simulation calculations to check this description for ground-state preformed EFS. We have generated Monte Carlo samples of chains whose bond lengths follow a Gaussian distribution. First, we have not considered any intramolecular potential between units, so we are dealing with the Gaussian chain model. For this model, the Monte Carlo samples are obtained by generating totally independent conformations. We have verified the validity of the assumption $P_x = x^{-3/2}$ (in fact, we have also verified the expected quantitative coefficient in the proportionality corresponding to a Gaussian distribution). The average total number of cycles found in our samples closely follow eq 4 with $a = {}^3/_2$. Qualitatively, they show the same dependence on N as the values obtained with eqs 6 and 7. Figure 2 shows reduced values of I_E/I_M calculated with this simulation procedure that we call SIMU I, for $x_m = 1$. The number of self-contact points (n_c) per unit ($P_E/P_M = n_c/N$) is shown in Table II together with similar Monte Carlo simulation results taken from ref 33 for the case where there is no intramolecular attractive interaction ($x_m = 1$ in both cases). It is remarkable the large fraction of monomeric units that are closing intramolecular cycles; this introduces an error in P_M if it is assumed, as before, that n_c is negligible with respect to N, but since n_c is almost constant for large N values, it is correct to assume that P_M is proportional to N.

Moreover, we have randomly chosen a given unit and have found whether this unit is in close contact with other unit or not (i.e., whether it is at a distance $R < R_c$, where R_c is a cyclization[34] or long-range excimer formation distance parameter). In this way, we have evaluated P_E/P_M as the ratio between the number of cases where we

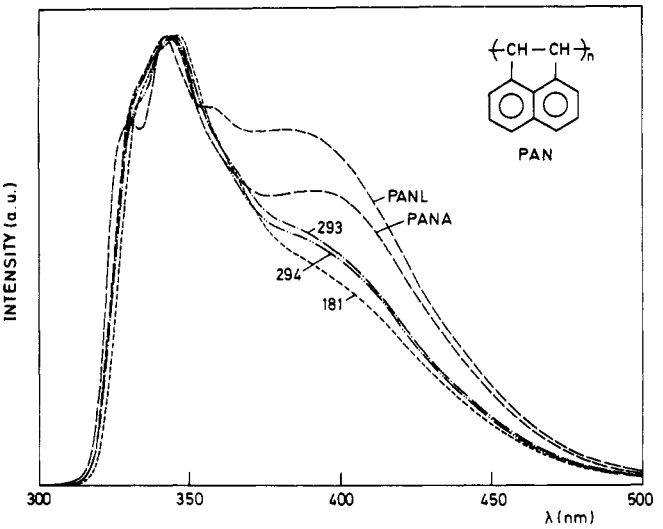

Figure 3. Fluorescence spectra of PAN dilute solutions in dioxane at 2 °C. Samples symbols are indicated.

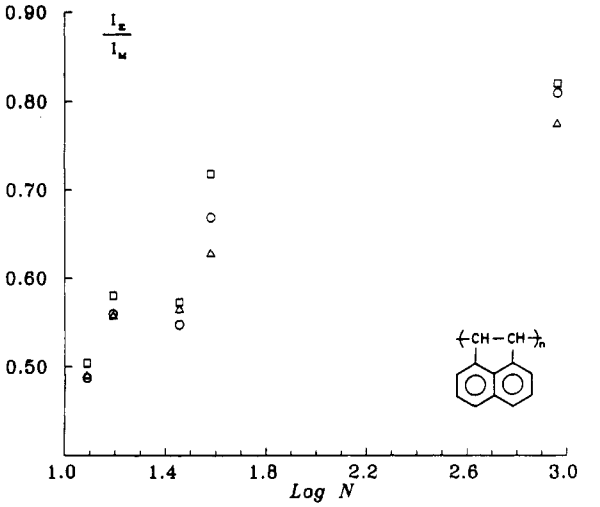

Figure 4. Fluorescence ratio of PAN diluted solutions in dioxane at 2 (△), 10 (○), and 25 °C (□), as a function of the number of monomeric units in the chain on a log scale.

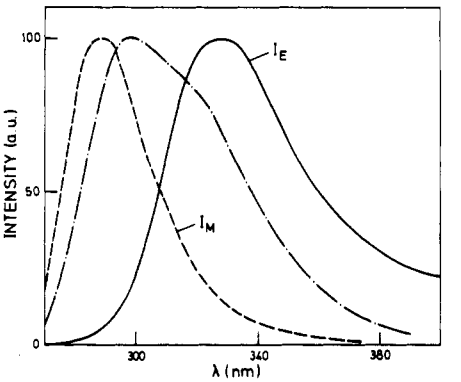

Figure 5. Monomer (I_M) and excimer (I_E) bands of PIN195 and fluorescence spectra of PIN173 in THF dilute solution.

have obtained $R < R_c$ to those where we have found $R > R_c$. The results of this simulation (SIMU II) $P_E/P_M = n_c/(N - n_c)$ with $x_m = 1$ are also shown in Table II.

Finally, we have performed the same type of evaluation for P_E/P_M using samples of chains with excluded volume, introduced by means of the hard-sphere potential between nonneighboring units, so that conformations where any distance between pairs of units is smaller than a given value R_o[34] are discarded. In order to obtain an adequate number of accepted conformations, we have used an stochastic procedure that only changes a portion of the chain in each simulation step. This procedure has been employed in previous work with the same type of chains and is described elsewhere.[35] In this case, we have worked with the somewhat artificial restriction $R_c > R_o$. This type of simulation (SIMU III) yields, as expected, lower $P_E/P_M = n_c/(N - n_c)$ values than SIMU II (see Table II for $x_m = 1$), but both of them are larger than SIMU I values because of the approximation introduced in $P_M = N - n_c = N$.

All those different simulations have provided results that follow closely the pattern for the behavior of I_E/I_M versus N shown in Figure 1. It should also be remarked that this trend is very similar to those expected for other processes or energy migration that may be competing in some experiments.[30,31] Excimer dissociation was implicitly neglected both in the model and in simulations.

Results

The normalized fluorescence spectra of PAN dilute solutions in dioxane at 2 °C are depicted in Figure 3. They show monomer and excimer bands centered at 345 and 400 nm, respectively. The absorption spectra of the different samples are superimposable, but the vibrational resolution of monomer emission is molecular weight dependent. Upon increasing chain length, there is an enhancement of the emission in the blue side of the band that may correspond to a Ham effect.[36] In dichromophoric compounds, that effect was attributed[37] to a conformational distribution with large percentages of conformers with closely spaced chromophores, which causes a mutual enhancement of the overall polarizability. Following this interpretation, longer PAN chains may become richer in chromophore–chromophore contacts or chain self-contact points, and this is in accordance with previous theoretical predictions (see Figures 1 and 2).

The fluorescence ratio (I_E/I_M) of PAN increases with molecular weight (Figure 4) at low N values, and it seems to reach a constant value for the highest molecular weight. There is a certain dispersion of the results that, since the fluorescence ratio is totally reproducible, must be attributed to the different configuration and molecular weight distributions of the samples obtained by different procedures. In spite of that dispersion, it can be observed that the curves at the three temperatures studied here are shifted toward each other, and thus, changes with temperature are equivalent for the different molecular weights.

The fluorescence spectra of PIN dilute solutions show only one band when they are obtained with normal excitation and emission band-passes (1.5 nm in Figure 5). It is due[16] to the spectral overlap of monomer and excimer emissions, which are centered at very close wavelengths (292 and 322 nm, respectively), and as a consequence cannot be resolved. The shape of the monomer pure band (Figure 5) can be obtained from the emission of indane or PIN195 dilute solutions because excimer emission is negligible in that polymer sample.[16] The shape of the excimer pure band (Figure 5) can be obtained by subtracting the monomer band from any other spectrum or from the emission of PIN in bulk with front face excitation. The fluorescence ratio (I_E/I_M) is then calculated from the shape of the monomer and excimer pure bands by means of eqs 1 and 2.

Figure 6 shows the normalized fluorescence spectra of eight PIN samples in THF dilute solutions over a molecular weight range of 2300–291 000. There is an apparent blue shift of the emission upon increasing chain length,

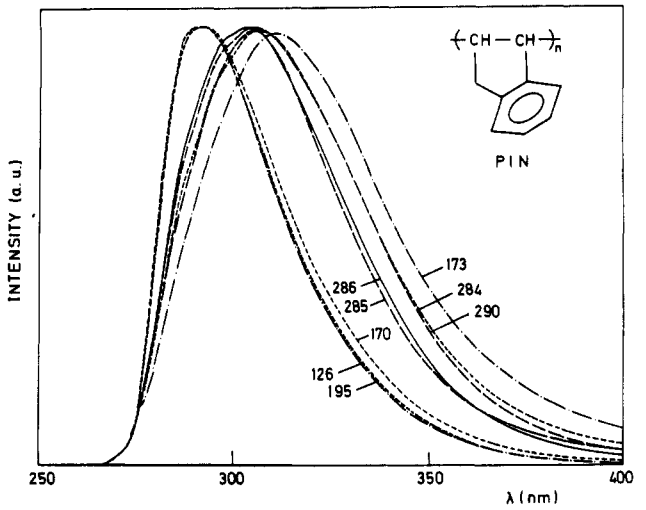

Figure 6. Fluorescence spectra of PIN diluted solutions in THF at 40 °C. Sample symbols are indicated.

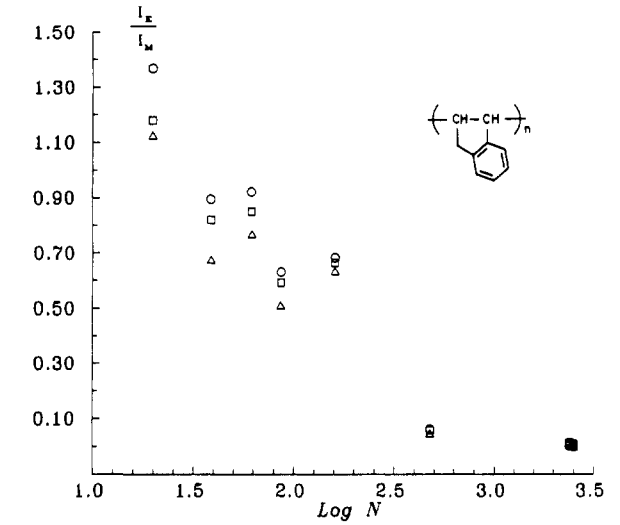

Figure 7. Fluorescence ratio of PIN diluted solutions in THF at 10 (○), 25 (□), and 40 °C (△), as a function of the number of monomeric units (N) on a log scale.

which is equivalent to a descent of the fluorescence ratio (I_E/I_M).

The fluorescence ratio of PIN (Figure 7) decreases with increasing molecular weight at the three temperatures considered here. The values of the fluorescence ratio are reproducible, and the dispersion of the results must again by attributed to the different molecular weight distributions of the samples. In this polymer, changes with temperature of I_E/I_M are molecular weight dependent, the larger changes corresponding to the lower molecular weight samples (Figure 7). In the limit of high temperatures, no excimer emission is expected for any molecular weight. I_E/I_M is larger for PIN than for PAN in some cases, but the same cannot be concluded for the proportion of excimer forming sites in both polymers, which is related to ϕ_E/ϕ_M, the excimer to monomer ratio of fluorescence quantum yields, and it depends on the overall intensities rather than on intensities at fixed wavelengths.

PIN and PAN also show an opposite behavior in the temperature dependence of their fluorescence ratio. The fluorescence ratio of PIN decreases upon increasing temperature (Figure 7) without showing an isosbestic point. PIN is therefore in the high-temperature limit region, but it is not under "thermodynamic control"; that is to say, there is not a dynamic equilibrium excimer formation–dissociation faster than emission. Therefore, excimers are formed in ground-state EFS[3] by energy migration[16] or direct absorption of light, two processes independent of solvent viscosity, and since the PIN fluorescence ratio does not depend on solvent viscosity,[3] excimer dissociation must be considered a minor contribution. In such conditions, the descent of I_E/I_M with temperature is determined by the activation energy for excimer nonradiative decay[1] (assuming that the Birks scheme can be applied).

Contrary to PIN, the fluorescence ratio of PAN increases upon increasing temperature (Figure 4). It is therefore in the low-temperature limit or "kinetic control" region in which increasing temperature favors excimer formation through a descent of solvent viscosity and because thermal energy activates segmental diffusion. The dependence of the PAN fluorescence ratio on solvent viscosity[3] is in accordance with that result.

Discussion

The habit shown in Figure 4 of the dependence of the PAN fluorescence ratio on the number of chain monomeric units was also found for other polymers: poly(2-vinylnaphthalene),[30,38] poly(1-vinylnaphthalene),[39] poly(1-naphthyl methacrylate),[40] poly(styrenesulfonic acid),[41] and polystyrene[31,42-44] in solution and solid blends. Nevertheless, the dependence found for PIN has no precedent in the literature.

The experimental results of PAN are satisfactorily explained by the theoretical model described above, if it is assumed that $x_m = 1$ and there are excluded volume effects (Figure 1). This would correspond to the formation of EFS by neighbor statistical units which could be associated with SRE only for highly flexible chains. The simulation results (Figure 2, SIMU I) also support that conclusion.

Energy migration is very efficient in PAN,[10,11] and this favors preformed excimers with respect to dynamical excimers. But energy migration is strongly dependent on molecular weight[30,31] and gives way to a chain length dependence like that shown in Figure 4. Thus, energy migration reinforces the dependence of segmental diffusion and equilibrium EFS population on molecular weight found in this work, and the same can be said about the distribution of EFS among the macromolecules.[42,45]

The molecular weight dependence of the PIN fluorescence ratio is totally different from any other previously reported, and it is also different from the PAN molecular weight dependence. Its behavior can be explained only if it is assumed that (i) the number of self-contact points formed in the ground-state equilibrium average conformation increases with molecular weight but not as fast as the coil size and therefore they become progressively diluted or (ii) the rate constant for excimer nonradiative decay increases very much in longer chains. The first argument would require us to accept that there are some configurational and/or conformational properties peculiar to PIN and different from the PAN analogous properties. The second argument has a precedent in ref 44 but with changes much less dramatic than those found in this work; it may also be related to the molecular weight dependence of chain segmental mobility,[4] which is reflected in the different contribution of equilibrium and dynamic excimers in chains of different length.[3]

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