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Effects of Chromophore Environment on the Photophysics of Poly(2-isopropenylnaphthalene)

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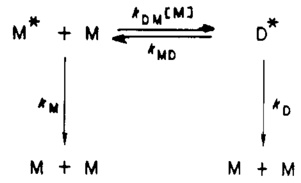
ABSTRACT: The fluorescence and phosphorescence decays of poly(2-isopropenylnaphthalene) (PIPN) samples of narrow polydispersity were measured in several solvents and in the neat film. In fluid solution at room temperature the excimer fluorescence decays are nonexponential, having rise times of less than 1 ns and two decaying components with characteristic lifetimes of 30 and 83 ns. Similar behavior is observed for the solid polymer except that the deviation of the excimer decay from exponentiality is even more pronounced. At 77 K, samples of PIPN dissolved in 2-methyltetrahydrofuran show no excimer emission at low excitation intensity, but the fluorescence decay of the free chromophore is biexponential, with typical decay times of 40 and 95 ns. The decay of naphthalene phosphorescence is exponential with a lifetime on the order of 2 s, whereas the 400- and 340-nm components of the delayed fluorescence give nonexponential decay, the latter having a considerably faster decay rate. These results are interpreted by using the concept of chromophores in inequivalent environments which do not interconvert during the time scales of the decay measurements. The proposed origin of the heterogeneity is the distribution of isotactic, heterotactic, and syndiotactic repeating units in the polymer samples.

Introduction

Reactions of functional groups attached to polymers exhibit complex kinetics because of the broad distribution of reactant separations and mobilities. These effects are particularly evident in studies of polymer photophysics, where the time scale of the experiment is on the order of the time scale of rotational and translational diffusion of polymers in fluid solution.[1,2]

Scheme I



The phenomenon of excimer fluorescence has some features which suggest that excimer formation between aromatic chromophores attached to a polymer chain might serve as a simple model for reactions on polymers. The excited-state complex has a well-defined structure: a sandwich dimer with a typical separation between aromatic rings of 0.3 nm. Excimer formation reflects segmental diffusion and a characteristic emission spectrum at a new wavelength is indicative of "product formation". Furthermore, since the excimer decays ultimately to two ground-state chromophores, the complications arising from depletion of reactants are absent. Nevertheless, recent studies of excimer decay kinetics in polymers have merely shown through the discovery of a number of new effects just how complex the problem of reactions on polymers can be.[3-10]

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The starting point for the interpretation of the fluorescence decay kinetics of excimer systems is the Birks scheme (Scheme I), which describes the formation of an excimer D* between a monomeric excited chromophore M* and a ground-state chromophore M.[11-13] When the formation of D* is described by a single rate constant k_{DM} and the excimer population is homogeneous, the decay of the excimer fluorescence intensity following pulsed excitation is described by

$$I_D(t) = \frac{k_{FD}k_{DM}[M]}{\lambda_2 - \lambda_1}[\exp(-\lambda_1 t) - \exp(\lambda_2 t)] \quad (1)$$

where

$$\lambda_1 = \tfrac{1}{2}(X + Y + \{(Y - X)^2 + 4k_{MD}k_{DM}[M]\}^{1/2}) \quad (2)$$

$$\lambda_2 = \tfrac{1}{2}(X + Y - \{(Y - X)^2 + 4k_{MD}k_{DM}[M]\}^{1/2}) \quad (3)$$

$$X = k_M + k_{DM}[M] \quad (4)$$

$$Y = k_D + k_{MD} \quad (5)$$

and k_{FD} is the rate constant for fluorescence.

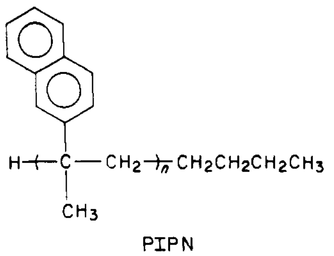
The monomer decay is given by

$$I_M(t) = \frac{k_{FM}}{\lambda_2 - \lambda_1}[(\lambda_2 - X)\exp(-\lambda_1 t) + (X - \lambda_1)\exp(-\lambda_2 t)] \quad (6)$$

Monomer and excimer fluorescence decays should correspond to a sum and a difference, respectively, of two exponentially decaying terms, and analysis of the two decays should give the same values of λ_1 and λ_2.

While in some early work on excimer kinetics of polymers attempts were made to derive rate constants within the Birks scheme,[14] other investigators subsequently showed that the monomer fluorescence decays were more complex than the Birks scheme predicts.[3-10,15] Recent work has established that (1) λ_1 and λ_2 values of monomer and excimer decay curves do not coincide,[15] (2) quenching of the free chromophores is not described by a single rate constant k_{MD},[4,6-9,15] and (3) the excimer population is not necessarily homogeneous.[10] The kinetics are complicated by the fact that the excitation can be transferred from one chromophore to another,[16-20] a process which enhances the efficiency with which the excimers are formed.

Although naphthalene-containing polymers have been investigated intensively, only one publication has dealt with the photophysics of poly(2-isopropenylnaphthalene) (PIPN).[21] Since this polymer can be prepared in high purity with narrow polydispersity by low-temperature anionic polymerization,[22,23] it is ideal for luminescence studies, which are particularly sensitive to the presence of impurities. The present publication describes systematic investigations of the singlet and triplet decay kinetics of PIPN in fluid solution, neat films, and low-temperature glasses. The high purity and low polydispersity of PIPN obtained by anionic polymerization afforded an opportunity to see whether the complex decay kinetics observed for many naphthalene-containing polymers was real or a consequence of insufficient sample purity.



PIPN

Table I
Properties of the Polymer Samples

polymer	sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
P2VN	1	130 000	2.1
PIPN	2	3 300	1.3
	3	7 580	1.05
	4	11 700	1.19
	5	28 400	1.08
	6	39 900	1.07
	7	46 400	1.07
	8	119 000	1.05
	9	135 000	1.06
	10	157 000	1.09
	11	183 000	1.12
	12	278 000	1.11
	13	29 100	2.00
	14	22 000	1.28

Experimental Section

Materials. The synthesis of poly(2-vinylnaphthalene) (P2VN) has been described previously.[20] Poly(2-isopropenylnaphthalene) samples were kindly made available by Professor R. C. Schulz of the University of Mainz, Mainz, West Germany. Samples of different molecular weights were prepared by *n*-butyllithium-initiated anionic polymerization of solutions of the monomer in THF at −78 °C. Full details of the preparation and characterization of the polymer samples are found in previous publications.[21,23] Table I lists the properties of the polymer samples used in the present study.

The 2-isopropenylnaphthalene used in the preparation of the above polymers was an industrial sample obtained by the pyrolysis of 2-isopropylnaphthalene. In order to ensure that certain aspects of the luminescence behavior of PIPN did not arise from impurities present in the monomer, additional polymer samples were prepared from monomer synthesized by an entirely different route, similar to that developed by Hopff and Lüssi.[22] 2-Acetonaphthone (J. T. Baker) was recrystallized from ethanol–H_2O and dried thoroughly. It was then converted to 2-(2-naphthyl)-2-propanol by a Grignard reaction with MeMgI in refluxing ether. The isolated alcohol was recrystallized from petroleum ether (bp 60–70 °C) to give 45 g of product, mp 64–65 °C, which was dehydrated by heating to 180 °C with 0.2 g of powdered $NaHSO_4$. The monomer was distilled under high vacuum and sublimed three times to give 20 g of white flat crystals: mp 52.5–53 °C; NMR ($CDCl_3$) δ 2.25 (s, 3 H), 5.2 (m, 1 H), 5.5 (m, 1 H), 7.2–7.9 (m, 7 H). The purified compound was stored over a sodium mirror in an atmosphere of dry nitrogen and was distilled under high vacuum directly into the polymerization vessel. Polymerization was carried out by the method of Engel and Schulz.[23] Two samples were prepared: one was initiated with *n*-BuLi at −78 °C and had a polydispersity of 2.0; the other was obtained by addition of *n*-BuLi in hexane to the stirred solution of monomer in THF at 20 °C. As soon as the green color of the PIPN terminal anion appeared, the solution was immersed in dry ice–acetone and allowed to polymerize slowly at −78 °C. This procedure gave a sample with a polydispersity of 1.28. Polymerization was terminated by the addition of dry methanol, and the polymers were recovered and purified by several reprecipitations from $CHCl_3$ into methanol.

For luminescence work toluene and benzene (J. T. Baker Photrex grade) were distilled from P_4O_{10}. THF and 2-MeTHF were distilled from $LiAlH_4$ under N_2 and were stored under nitrogen at 0 °C.

Sample Preparation for Luminescence Measurements. For studies of fluid solutions, samples were prepared having optical densities of 0.2 in a 1-cm square Suprasil fluorescence cuvette with a 10-cm stem (Hellma) and were deoxygenated through a pair of syringe needles with high-purity nitrogen. All samples were used for a single experiment only. For studies on low-temperature glasses, solutions were prepared having optical densities of 0.1 in a 1-mm cell and were transferred to quartz tubes of 3 mm outside diameter. After thorough degassing the sample tubes were sealed and cooled slowly in the vapor over the liquid nitrogen before being fully immersed. The liquid nitrogen was filtered through a pad of glass wool to minimize scattering from ice crystals. For decay measurements on polymer films samples were prepared by spin-coating of PIPN solutions in benzene at 5000 rpm on 13-mm-diameter Suprasil disks (Hellma) using a Headway Research Model EC 101 D photoresist spinner. The films were dried under high vacuum for 48 h before being mounted at an angle of 20° relative to the normal to the excitation beam.

Fluorescence Decay Measurements. Two single-photon-counting instruments were used to record fluorescence decays. One of these has been described previously;[24] the other was a PRA System 2000 instrument with dual excitation and emission monochromators and aberration-corrected optics. Equivalent results were obtained with the two instruments. Samples were excited at 280 nm (or 300 nm in the case of benzene or toluene solutions) and the fluorescence decay of the PIPN excimer was observed at 420 nm. In a study to determine whether the excimer decay was wavelength-dependent, decays were recorded at wavelengths from 380 to 480 nm. For fluorescence measurements on low-temperature glasses sample tubes were held in a quartz Dewar and the emission was detected at 337 nm through the combination of a monochromator and a Corning 7-37 filter (330–370-nm band-pass). Fluorescence decays were analyzed over a 100-fold range of intensity by the technique of iterative reconvolution. Equivalent results were obtained with routines incorporating Marquardt's algorithm for gradient search[25] or a Simplex algorithm (the latter avoiding the need to evaluate the derivatives of the trial function). No analysis of the monomer decay of PIPN at room temperature was possible, as it was obvious that the very weak emission was contaminated by overlap with the excimer emission band.[10]

Phosphorescence and Delayed Fluorescence Decays. A Hitachi Perkin-Elmer MPF-2A spectrofluorimeter with phosphorescence accessories provided by the manufacturer was used for all steady-state spectra. The decay curves of phosphorescence and delayed fluorescence were recorded by connecting the photomultiplier output of the detector to a sampling oscilloscope and photographing the decay trace obtained when the excitation beam was cut off by means of an electromechanical shutter. Intensities of delayed fluorescence, delayed excimer fluorescence, and phosphorescence were monitored at 340, 400, and 490 nm, respectively. In order to yield sufficiently intense triplet emission spectra, the excitation and emission spectral bandwidths were increased to 18 and 14 nm, respectively. Decay curves were subsequently replotted on a semilogarithmic scale and the best-fit decay times were evaluated by a least-squares linear regression method.

Results

Fluorescence Decays at Room Temperature. Figure 1 compares the excimer fluorescence decays of poly(2-vinylnaphthalene) and poly(2-isopropenylnaphthalene). The excimer decay curves of all samples are similar and deviate markedly from the predictions of the Birks scheme. The rise time of the excimer fluorescence is less than 1 ns and the decay beyond the point of maximum intensity is described within experimental error by a sum of two exponentially decaying terms:

$$I_D(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2); \qquad A_1, A_2 > 0 \tag{7}$$

In eq 7 and throughout this article the fitting parameters are represented as decay times τ_j in order to avoid identification with the Birks scheme quantities λ_1 and λ_2.

Tables II and III list values of the best-fit parameters A_1, A_2, τ_1, and τ_2 for the excimer decays of P2VN and PIPN in several solvents. The excimer decays are essentially the same in various solvents and are almost unaffected by the molecular weight of the PIPN samples. Only the ratio A_2/A_1 appears to change with molecular weight, with the contribution of the more slowly decaying component becoming more prominent as the molecular weight increases. Figure 2 shows that the quantity $A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$, a measure of the fraction of the total fluorescence arising from the long-lived component, is a very slowly varying function of molecular weight. It may reflect the fact that the triad composition of PIPN is also a slowly varying function of molecular weight, as the NMR data of Engel and Schulz, replotted in Figure 2, illustrate. (Note that the data for sample 9, $\bar{M}_n = 1.35 \times 10^5$, deviate from the general trend but that the tacticity of this sample is also anomalous.)

Table II
Fitting Parameters of Excimer Fluorescence Decay Curves at 25 °C[a]

polymer	solvent	A_2/A_2	τ_1, ns	τ_2, ns	χ_R^2 [b]
P2VN	toluene	1.37	32.5	83.8	1.03
	2-MeTHF	0.80	26.4	84.1	1.23
PIPN (sample 14)	toluene	1.61	38.4	82.1	1.10
	2-MeTHF	1.21	28.6	82.7	1.36
	benzene	1.68	34.6	82.3	1.14
	THF	1.66	33.6	83.2	1.14

[a] Fitting from two channels past decay maximum according to eq 7. [b] Reduced χ^2.

Table III
Fitting Parameters for Excimer Fluorescence Decays of PIPN Samples of Different Molecular Weights[a]

sample	$\bar{M}_n$	A_2/A_1 [b]	τ_1, ns	τ_2, ns	χ_R^2
2	3 300	1.22	30.3	84.0	1.04
3	7 580	1.20	29.4	83.2	1.30
5	28 400	1.48	29.6	83.2	1.23
7	46 400	1.55	27.8	82.5	1.06
9	135 000	1.54	29.1	83.3	1.06
12	278 000	1.76	26.2	81.8	1.24

[a] In 2-MeTHF at 25 °C. [b] Fitting from two channels past decay maximum according to eq 7.

Thin films of PIPN show only excimer emission, as Figure 3 shows. The excimer fluorescence decay of a PIPN film, shown in Figure 4, is typical of behavior observed by us for a number of polymers containing pendant naphthalene chromophores.[26] The decay curve has a rise time too short to measure and a complex decay which is concave upward and which can be represented only very poorly by a sum of two exponential terms (eq 7) beyond the peak maximum. Within experimental error the decay curves are the same all across the excimer band, a result which indicates that this band corresponds to a single-emission spectrum, but that the species which give rise to this spectrum decay in a kinetically inhomogeneous manner.

Fluorescence Decays at 77 K. When dissolved in 2-methyltetrahydrofuran glasses at 77 K, PIPN and P2VN both show only monomer fluorescence,[20,21] but the fluorescence spectrum of PIPN shows changes with increasing molecular weight.[21] Figure 5 illustrates the fluorescence decay of a PIPN sample in a 77 K glass. The monomer emission at 337 nm is described by a sum of exponentials with approximately equal contributions from terms with decay times of 36 and 94 ns. Thus, even in a rigid matrix at low temperature, the fluorescence of PIPN decays inhomogeneously. Table IV summarizes the low-temperature decay data for PIPN samples of different molecular weights. Difficulties in rejecting scattered light completely cause the errors in the fitting parameters to be considerably greater than those observed for the decays recorded at 25 °C and made it necessary to skip the first several channels of the decay curves in the analysis. Nevertheless, the contribution from the slowly decaying component increases very gradually with increasing molecular weight, just as in the excimer decays recorded at room temperature.

Phosphorescence and Delayed Fluorescence Decays. As described in a previous publication,[21] the delayed

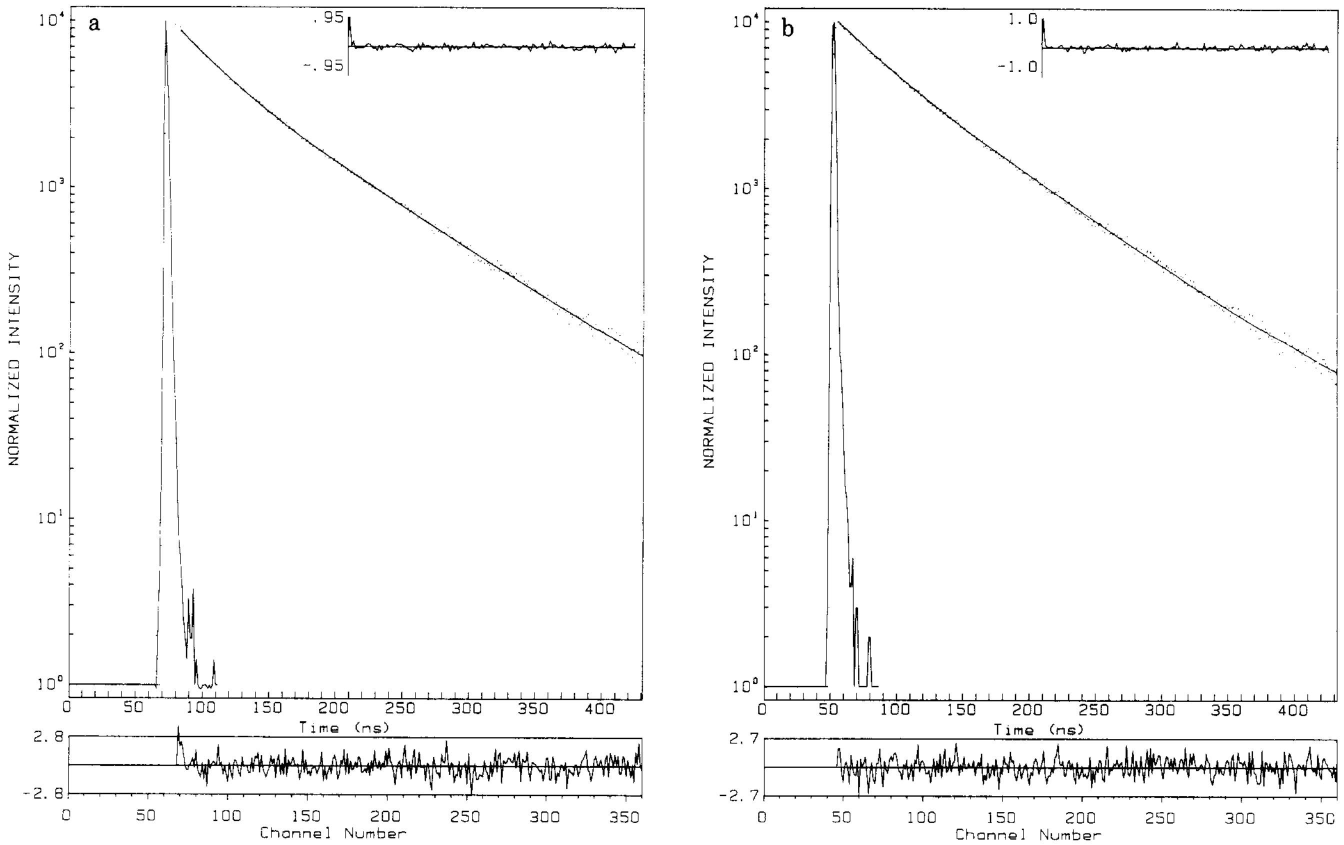


Figure 1. Excimer fluorescence decays of polymers in deoxygenated toluene at 25 °C on excitation at 305 nm: (a) P2VN; (b) PIPN (sample 14). The solid line is the convolution of the best-fit double-exponential decay parameters with the lamp profile. Under each decay curve is the channel-by-channel plot of the normalized differences between experimental and calculated decay curves. The inset at the top right of each curve shows the autocorrelation function of the residuals.

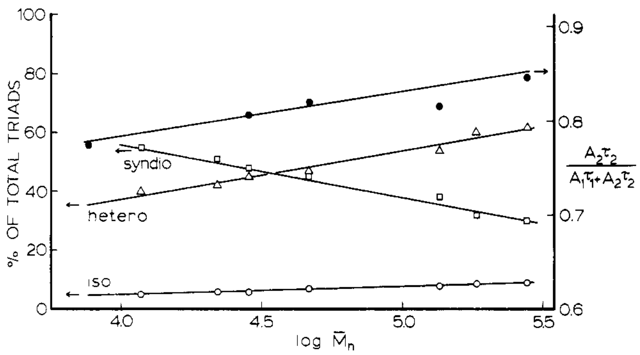


Figure 2. Molecular weight dependence of triad distribution and ratio $A_2\tau_2/(A_1\tau_1 + A_2\tau_2)$ of the excimer decays in 2-methyltetrahydrofuran at 25 °C, for PIPN samples of narrow polydispersity. The triad distributions are taken from NMR data of Engel and Schulz[23] with permission.

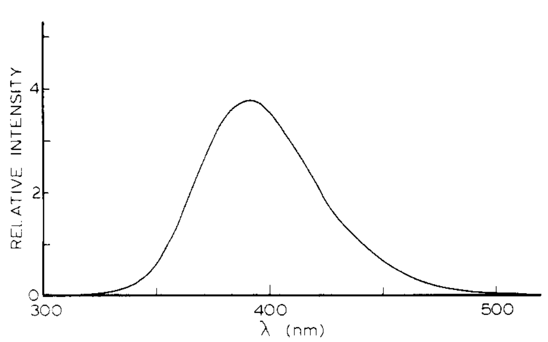


Figure 3. Fluorescence spectrum of a PIPN film (sample 14) on 285-nm excitation. The emission bandwidth is 2 nm.

Table IV
Fitting Parameters for the Monomer Fluorescence Decays of PIPN Samples in 2-Methyltetrahydrofuran Glasses at 77 K[a]

sample	A_2/A_1	τ_1, ns	τ_2, ns	χ_R^2
2	0.649	50.2	97.4	0.99
3	0.845	42.6	90.5	1.18
4	0.908	38.8	92.0	1.16
5	1.20	40.1	97.5	1.21
7	1.09	35.9	94.1	1.31
9	1.46	36.2	99.4	0.97
11	1.53	29.4	94.5	1.38

[a] Fitting from four channels past decay maximum according to eq 7.

Table V
Mean (1/*e*) Decay Times τ of Delayed Fluorescence and Phosphorescence for PIPN Samples in 2-Methyltetrahydrofuran Glasses at 77 K

	τ, s		
sample	340 nm[a]	400 nm[a]	490 nm
2	*b*	2.4	2.3
4	0.3	2.6	1.6
7	0.4	2.7	1.7
8	0.4	2.1	1.6
9	0.4	1.9	1.6
11	0.4	2.0	1.6
12	0.4	2.1	1.7
13	0.3	1.8	1.6
14	0.3	2.0	1.7

[a] Decay is nonexponential. [b] 340-nm band is too weak to allow decay measurements.

luminescence of PIPN samples dissolved in low-temperature glasses contains contributions from emitting species with maxima at 340, 400, and 490 nm. Figure 6 shows typical decays of the emission at these three wavelengths. In contrast to the decay of the 490-nm emission, the decays

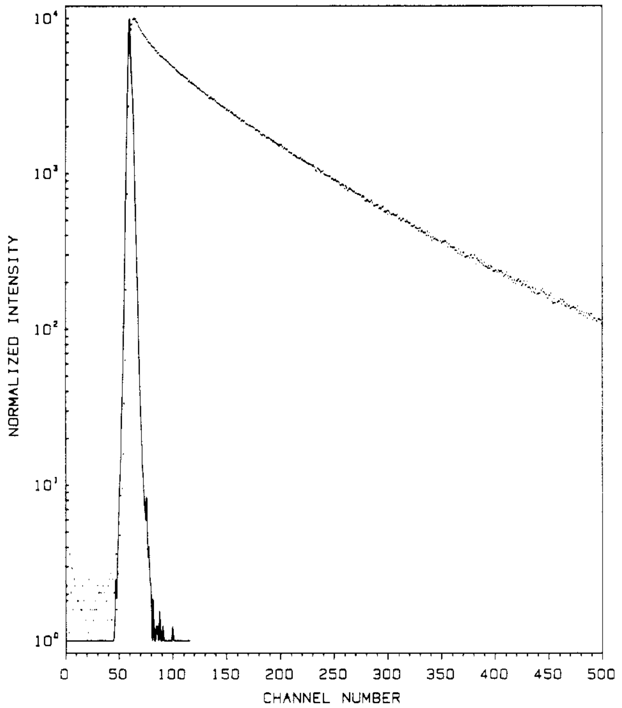


Figure 4. Excimer fluorescence decay at 420 nm on 280-nm excitation of a PIPN film (sample 14). The instrumental time settings correspond to 0.656 ns per channel.

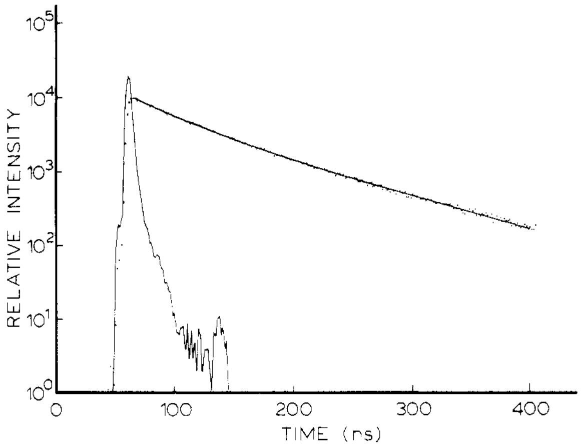


Figure 5. Fluorescence decay of PIPN (sample 7) in 2-methyltetrahydrofuran at 77 K. The excitation and emission wavelengths are 280 and 337 nm. The solid line is the convolution of the best-fit double-exponential decay function with the lamp profile.

at 340 and 400 nm are nonexponential. The 1/*e* decay time of the 340-nm emission is considerably shorter than those of the other two bands. Table V summarizes decay data for the PIPN samples. Variations in the decay times of the three emitting species with molecular weight were smaller than the experimental error. Only the relative intensities of the three components change significantly with molecular weight, as shown by the compilation of results in Table VI. Included for comparison in Tables V and VI are results for the two PIPN samples prepared from monomer synthesized by the alternate route. These samples and those prepared by the Mainz group display almost identical delayed luminescence behavior.

Discussion

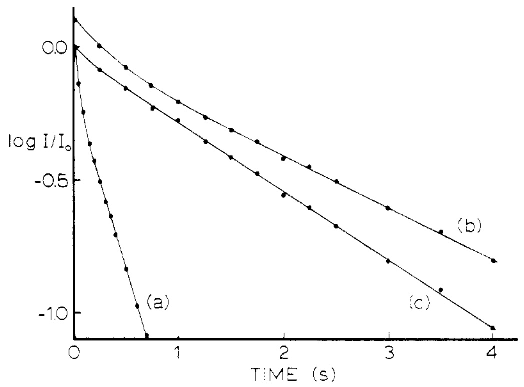


Figure 6. Delayed luminescence decays of PIPN (sample 14) in 2-methyltetrahydrofuran at 77 K on 293-nm excitation: (a) delayed fluorescence at 340 nm; (b) delayed fluorescence at 400 nm; (c) phosphorescence at 490 nm. Curve b is shifted vertically by 0.1 unit for clarity.

Table VI
Relative Contributions of Delayed Fluorescence and Phosphorescence for PIPN Samples at Constant Excitation Intensity[a]

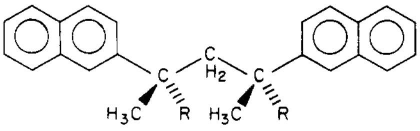
sample	delayed fluorescence 340 nm	400 nm	phosphorescence 490 nm
2	0.01	0.71	0.28
3	0.10	0.51	0.39
4	0.42	0.16	0.42
11	0.55	0.15	0.30
13	0.36	0.19	0.44
14	0.43	0.13	0.43

[a] Solutions in 2-MeTHF at 77 K; λ_{ex} = 293 nm.

In small-molecule systems it is generally observed that differences in the instantaneous environments around chromophores in solution are averaged out on the time scale of fluorescence. As a result, the luminescence decays of these systems are described by a single lifetime τ. This is not necessarily the case for chromophores attached to polymers, where the differences in environment may be more pronounced and the relaxation times longer.

Studies on diastereomeric model compound dimers[27-33] have recently proven very useful in clarifying the effects of chromophore inequivalence on excimer kinetics of polymers. The excimers formed in meso and racemic diastereomers of 2,4-diarylpentanes can form at different rates, emit in different wavelength regions, and have different decay times. A particularly marked example is provided by *dl*- and *meso*-2,4-di-*N*-carbazolylpentane, model compounds for poly(*N*-vinylcarbazole).[30] These exhibit excimer fluorescence with emission maxima at 370 and 420 nm and excimer decay times of 15 and 40 ns, respectively. The corresponding vinyl polymers have mixed tacticity, with the result that their excimer fluorescence is a superposition of the behavior of isotactic and atactic sequences.

While such dimers are useful as model compounds for a number of vinyl polymers, PIPN presents the problem that its simplest model dimer, 2,4-dimethyl-2,4-di-2-naphthylpentane (1) (R = CH_3) shows no diastereomerism



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and thus would convey no information on the effects of tacticity in the polymer. Although diastereomers of the compound having R = CH_2CH_3 would exist, the dominant steric effect of the polymer chain would be lost in these compounds. This has necessitated the present experimental approach, involving studies of the photophysics of PIPN samples whose tacticities vary in a known way with molecular weight.

PIPN displays excimer fluorescence of two components with decay times of 30 and 83 ns. The contribution of the long-lived component increases with increasing isotactic and heterotactic content in the polymer. On the basis of this we propose that the short-lived excimer population involves chromophores in racemic (*r*) diads, whereas the long-lived component arises from excimers formed between chromophores in diads with meso (*m*) configurations.

Several authors have proposed the existence in naphthalene-containing polymers of two or more excimers having different emission maxima and spectral widths.[10,34-36] This does not seem to be the case for PIPN and P2VN. The excimer population has a single-emission spectrum within experimental error and differs only in the individual decay rates.

In contrast to the $n = 3$ polymers such as P2VN and PIPN, naphthalene-containing polymers in which the chromophores are separated by more than three atoms do not show inhomogeneous excimer decay beyond the decay maximum. Such "non-Hirayama" systems include polymers of 1- and 2-naphthyl acrylates and methacrylates,[26] 1-naphthylmethyl methacrylate, and 2-(1-naphthyl)ethyl methacrylate.[15] It appears that in polymers not obeying the $n = 3$ rule the effects of tacticity are less marked. Possibly the greater number of conformations available to the side chains allows formation of the energetically most stable excimer regardless of stereochemical environment.

When a polymer is dissolved in a glass at 77 K, the chromophores are immobile on the time scale of fluorescence. The fraction of chromophores in excimer sites is very small, being given approximately by a Boltzmann distribution at the temperature at which vitrification occurred. As a result the emission from such glasses contains little or no excimer fluorescence. In contrast to the behavior observed for PIPN in fluid solution at room temperature, however, the fluorescence of PIPN dissolved in 2-methyltetrahydrofuran glasses is inhomogeneous, not only in decay rate but also in wavelength. The contribution from a highly structured emission spectrum resembling that of 2-*tert*-butylnaphthalene is greatest for low molecular weight samples of high syndiotactic content.[21] With increasing molecular weight (and decreasing syndiotactic content) the contribution from less structured emission red-shifted about 5 nm becomes more prominent. The decays of the overlapping spectra are described by two decay times of 40 ± 10 and 95 ± 5 ns for all samples. We suggest that the long-lived red-shifted emission arises from weak excited-state interactions between chromophores which are close together, but whose overlap is considerably less than that in the sandwich excimer geometry. The apparent variations of spectra and decay with molecular weight may arise because such interactions are more probable in *mr* and *mm* triads, whereas the chromophores in syndiotactic (*rr*) triads give fluorescence more like that of an isolated naphthalene chromophore.

Identification of delayed monomer and excimer fluorescence with chromophores in specific environments is not quite so straightforward. The appearance of the 400-nm band and its long decay time of 2.1 s rule out a number of impurities. These include ketones, aldehydes, terminal alkenylnaphthalene residues, or 2-isopropenylnaphthalene monomer, all of which would either have very different phosphorescence or delayed fluorescence spectra or very much shorter decay times. We can speculate that a terminal chromophore pair or a minute fraction of preformed excimer sites could give rise to excimer-like delayed fluorescence whose intensity decreases with increasing molecular weight. In view of the considerable range of triplet energy migration the mole fraction of traps giving rise to delayed excimer fluorescence could be very small, too small to be detectable by NMR spectroscopy, for example.

Deviations of polymer photophysics from behavior observed for small-molecular model systems must be interpreted with considerable caution because of the sensitivity of luminescence techniques to the presence of impurities. In the present work, identical excimer decay behavior was found for P2VN prepared by free-radical polymerization and 13 PIPN samples prepared by anionic polymerization of monomer obtained by two completely different synthetic procedures. The fact that samples of such different origin behave so similarly suggests that the unusual behavior is not produced by impurities.

The decay times of delayed fluorescence and phosphorescence are even more sensitive to quenching by impurities. These decay times, listed in Table V, are as long as, and generally considerably longer than those reported in the literature for other naphthalene-containing polymers[37-42] and are further evidence for the high purity of the P2VN and PIPN samples. The nonexponential decay of monomer delayed fluorescence agrees with the observations of other authors. Several explanations have been proposed, including the effects of a broad distribution of molecular weights on trapping rates.[37] Since nonexponential decay of delayed fluorescence is now observed in polymers of narrow polydispersity, molecular weight heterogeneity does not appear to be the sole explanation of this effect.

Conclusions

Careful luminescence decay measurements on highly purified naphthalene-containing polymers have allowed us to identify several effects arising from differences in chromophore environment. A likely cause of this microheterogeneity is differences in the excited-state interactions between chromophores in repeating units of different stereochemistry. These studies further emphasize that if analysis of the excimer decay kinetics of polymers is attempted within the confines of the Birks scheme, then important information on the polymer systems is lost.

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Registry No. Poly(2-isopropenylnaphthalene), 71114-00-6; 2-isopropenylnaphthalene, 3710-23-4; 2-isopropylanaphthalene, 2027-17-0; 2-acetonaphthone, 93-08-3; 2-(2-naphthyl)-2-propanol, 20351-54-6; MeMgI, 917-64-6.

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Electrostatic Interactions between Ions and DNA Estimated with an Electrolyte Tank

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ABSTRACT: By the use of an electrolyte tank, a device that is effectively an analog computer, we find expressions for the electrostatic interactions between models of small ions in solution around a model of a DNA molecule. In this way we can take account of the modifications of Coulomb's law produced by the polarization charges on the surface of discontinuity in dielectric constant (permittivity) between the low-permittivity DNA and the high-permittivity water. Both the simplest model for the DNA, a circular cylinder, and a more realistic model, a helix, were examined. The effects of the low permittivity of the DNA are (1) to create a short-ranged repulsion between the DNA and ions in the water as the result of an image-charge-like phenomenon; (2) to shield charges on opposite sides of the DNA from each other; (3) to enhance the interaction of charges on the same side of the DNA. The total effect is to raise the energy of charges in the grooves of the helix. The maximum energy increases are several times $k_\mathrm{B}T$, even for univalent ions, so the effects of the low permittivity on the ion distribution are expected to be substantial.

Introduction

In this paper we attempt to find improved expressions for the energy of electrostatic interactions between ions in solutions containing large polyelectrolyte molecules, in particular DNA molecules, expressions that can be used in Monte Carlo calculations of the ionic distributions in such solutions. These electrostatic interactions are fundamentally Coulomb interactions, but they are modified by the discontinuity in permittivity (dielectric constant) between the polyelectrolyte molecule and the solvent. Modifications of the bare Coulomb interaction are implicit in the well-known treatment of globular proteins by Tanford and Kirkwood,[1] but they have not hitherto been considered in any detail in the case of long polyelectrolytes such as DNA, as far as we know except for one study by Bailey.[2]

Electrostatic polarization fields are induced by the charged ions at a discontinuity in the permittivity. Each ion interacts with its own polarization field to produce a change in its self-energy. The interaction is dependent upon the geometry of the dielectric discontinuity and the distance of the ion from the discontinuity; for example, ions are repelled from the plane surface of a low-permittivity region by the well-known image-charge effect. Each ion also interacts with the polarization fields of other ions, an interaction that is dependent upon the geometry of the region and the distances of both ions from the discontinuity; this modifies the usual Coulomb interaction. Of course, the representation of the surface between a real molecule and the solvent as a surface between two regions of different permittivity can only be an approximation. However, in the present state of ignorance about the hydration layers around ions and macromolecules, the approximation of a simple surface seems to be reasonable. The magnitude of these interactions can be calculated analytically only for a few simple geometries. For others, the magnitudes can be obtained from an analog computer known as an electrolyte tank.[3-6]

The advantage of the electrolyte tank is simplicity and adaptability to a wide variety of shapes representing the

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