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Fluorescence Properties of Poly(ethylene terephthalate-*co*-2,6-naphthalene dicarboxylate) with Naphthalene Contents Ranging from 0.01 to 100 mol %

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ABSTRACT: Several samples of poly(ethylene terephthalate-*co*-2,6-naphthalene dicarboxylate) were synthesized with different contents of dimethyl-2,6-naphthalene dicarboxylate (DMN). The polymer samples were ground into powders, and steady-state and time-resolved fluorescence measurements were carried out on these copolymers. The lifetimes of the excited DMN monomer and dimer were found to be 12 and 26.5 ns, respectively. By monitoring the overlap between the fluorescence excitation and emission spectra of the different species, it was concluded that energy migration occurs among the DMN monomers and among the DMN dimers, that energy can be transferred from an excited DMN monomer to a ground-state DMN dimer, but that energy transfer from an excited DMN dimer to a ground-state DMN monomer is unlikely. Increasing the DMN content induces the formation of energy traps for the DMN monomer fluorescence, which results in increasing DMN monomer quenching. When the DMN content reaches 25 mol %, the polymer matrix is saturated with DMN dimers, and no further quenching is observed.

Introduction

2,6-Naphthalene dicarboxylate, the building block of poly(ethylene 2,6-naphthalene dicarboxylate) (PEN), contains the well-known chromophore naphthalene. Although the photophysical properties are relatively well understood for naphthalene-based polymers in solution (an excited naphthalene can (1) fluoresce, (2) form an excimer via encounter with a ground-state naphthalene, and (3) undergo energy migration by transferring its excess energy to a nearby ground-state naphthalene),[1−12] this comprehensible picture is not directly transposable to PEN in the bulk.[1,13] This is due mostly to the inherent differences of physical properties encountered when switching from a liquid to a solid sample. These differences include the very high local chromophore concentration and the frozen nature at the molecular level of a solid-state PEN sample which results in a very limited long-chain motion of the DMN units when compared to a PEN chain in solution where the chromophores associate and dissociate on a rapid time scale.

In PEN, chromophore aggregates are formed in which the DMN moieties will stack on one another to form ground-state dimers. It is commonly agreed that in the PEN matrix (1) these ground-state dimers act as traps for the excited DMN monomer and (2) the energy can migrate.[1] However, a detailed assessment of the various photophysical processes occurring in the PEN matrix has not yet been published.

The relevant photophysical processes occurring in the PEN matrix can be listed as follows. The excited DMN monomer and dimer can fluoresce with a lifetime τ_M and τ_D, respectively. Energy can migrate between DMN monomers or DMN dimers with energy migration rates k_M^{Mig} and k_D^{Mig}, respectively. Energy can also be transferred from the excited DMN monomer to the ground-state DMN dimer with a rate constant k_{DM}^{ET}. The reverse process, where energy is transferred from the excited DMN dimer to the ground-state DMN monomer, is characterized by a rate constant k_{MD}^{ET}. In the case of formation of excited dimers, the conventional Birks' scheme[13] for excimer formation has been deliberately disregarded because it assumes that excimer formation occurs via a diffusional process which is highly unprobable in a solid-state matrix.

The key element in regulating these photophysical processes is the DMN concentration. All theories that aim at describing the photophysical processes occurring in the PEN matrix assume that energy migration is governed by energy transfer (ET).[15−18] ET depends strongly on the distance between the excited chromophore and the ground-state trap.[19] As a result, adjusting the DMN concentration allows one to vary the distances between DMN monomers and dimers and thus alter the relative importance of one process over the other, making it easier to differentiate each one individually.

In an effort aimed at monitoring the photophysical properties of the DMN monomer in a polymer matrix as a function of DMN concentration, we have synthesized a series of poly(ethylene terephthalate-*co*-2,6-naphthalene dicarboxylate) (T*X*N(2), where *X* represents the DMN mole percent in the polymer matrix) where *X* was varied from 0.01 up to 100 mol % (PEN). The comonomer terephthalic acid was chosen to ensure that the DMN comonomer be embedded in an aromatic-like matrix. Steady-state and time-resolved fluorescence measurements were performed on these samples, and the results are reported hereafter.

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Experimental Section

Melt Polymerizations. Ethylene glycol (Eastman), dimethyl terephthalate (DMT) (Eastman), and dimethyl-2,6-naphthalene dicarboxylate (DMN) (Amoco Chemicals) were used without further purification. The appropriate amounts of starting materials were charged into a 500 mL one-neck round-bottom flask, along with catalyst metals, and polymerized under conditions similar to those previously reported.[20] The polymers were allowed to slowly cool at 23 °C before isolation, yielding polymers with various levels of crystallinity for the PET, PEN, and copolymers with DMN concentration in PET ranging from 0.01 to 100 mol %. The polymers typically had inherent viscosities (in 60/40 phenol/tetrachloroethane) at 23 °C of 0.3−0.4 dL/g.

Sample Preparation. Samples of each polymer were micropulverized in a lab grinder into a fine powder and sieved through a 120 mesh screen (hole size 0.0049 in.). The powders were then introduced into a 1 cm square quartz fluorescence cell, and fluorescence measurements were performed on the solid-state samples without degassing.

Steady-State and Time-Resolved Fluorescence Measurements. All fluorescence measurements were acquired on a Photon Technology International, Inc., spectrofluorometer. Fluorescence excitation and emission spectra used a xenon-arc lamp for excitation. For the time-resolved fluorescence measurements, excitation was provided by a hydrogen-filled flash lamp. All powdered samples were studied in the front-face configuration. Before acquisition of any fluorescence decay, an instrument response was collected at the excitation wavelength. The usual conditions to study the fluorescence of the polymer samples were $\lambda_{ex} = 350$ nm and $\lambda_{em} = 365$ nm for the monomer (380 nm when the signal at 365 nm was too low as for high DMN contents) and $\lambda_{ex} = 350$ nm and $\lambda_{em} = 480$ nm for the excimer. Times per channel of 0.191 and 0.382 ns/channel over 512 channels were used for the monomer and the excimer, respectively. All decays held a minimum of 10 000 counts at the decay maximum. The fluorescence decays were fitted with a sum of exponentials according to eq 1 with k equal to 2 or 3, and the fitting software corrected for the presence of light scattering in the monomer decays.[21]

$$f(t) = \sum_{i=1}^{k} A_i \exp(-t/\tau_i) \tag{1}$$

No scattering contribution was detected in the excimer decays, and the light scattering correction was not applied to these decays. The parameters of the fit were optimized by using the Marquardt−Levenberg algorithm.[22] The quality of the fits was estimated from the χ^2, the residuals, and the autocorrelation function of the residuals. Error bars for the parameters obtained from analysis of the fluorescence decays were obtained by simulating 20 fluorescence decays with different Poisson noise patterns, fitting the simulated decays, and calculating the standard deviations of the retrieved parameters.

Results and Discussion

Figure 1 shows the normalized fluorescence emission spectra of the polymer samples obtained with an excitation at 350 nm. As the DMN content is increased from 1 up to 100 mol %, the spectrum maximum shifts from 380 up to 428 nm. This is also illustrated in Figure 2 which shows the position of the fluorescence maximum as the DMN content is increased. The emission maximum appears to stabilize at about 425 nm for polymer matrices having a DMN content larger than 50 mol %. We attribute this transition to the increased formation of DMN dimers, which is favored at high DMN concentrations. This transition is also probed by the excitation spectra recorded with an emission wavelength of 430 nm as shown in Figure 3. A broadening of the excitation spectra is clearly seen in Figure 3 as the DMN content is increased. Figure 2 shows the full width at half-maximum ($\Delta\lambda$) of the excitation spectra as a function of DMN content. A transition in the excitation broadening occurs between 1 and 25 mol % DMN content. We assigned this broadening to the appearance of DMN dimers, which can be produced via direct excitation. Qualitative agreement is obtained for the DMN con-

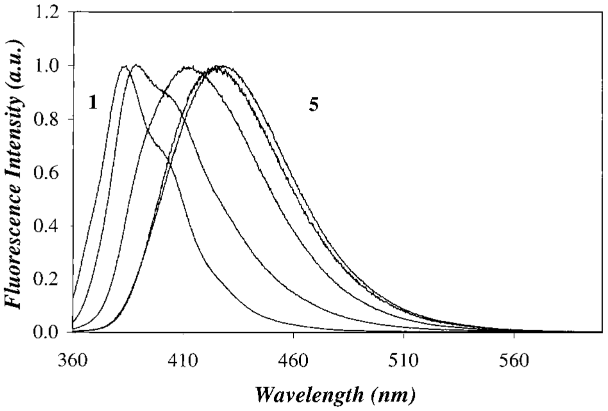

Figure 1. Emission spectra of six copolymers with $\lambda_{ex} = 350$ nm. The spectra were normalized at the fluorescence maximum. (1) T1N(2), (2) T8N(2), (3) T25N(2), (4) T50N(2), and (5) PEN.

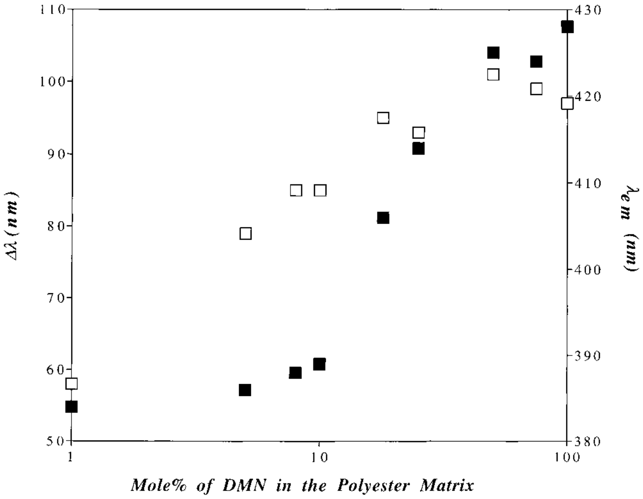

Figure 2. Position of the peak maximum of the fluorescence emission spectra (λ_{em}, ■) and full width at half-maximum of the excitation spectra ($\Delta\lambda$, □).

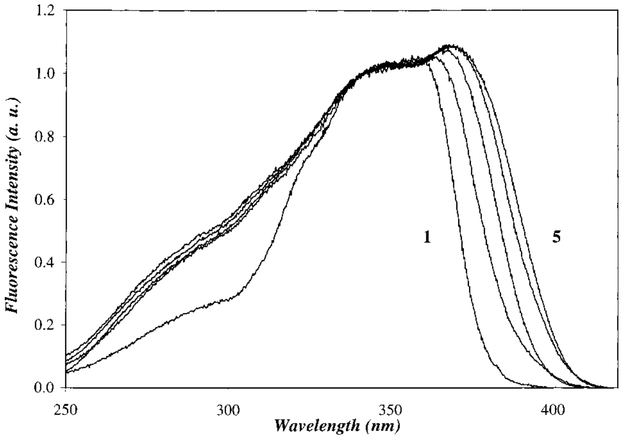

Figure 3. Excitation spectra of the same copolymers as in Figure 1 with $\lambda_{em} = 430$ nm.

centration regime where the transitions, observed with the excitation and emission spectra, occur (cf. Figure 2).

PET absorbs 350 nm UV light and emits fluorescence in the same wavelength range as naphthalene does. To assess whether the fluorescence observed in our experiments came from the PET matrix or the naphthalene chromophores, polymer matrices were also prepared, which contained very low amounts of naphthalene (0 mol % $\leq$ DMN mol % $\leq$ 1 mol %). Their fluorescence excitation and emission spectra are shown in parts a and b of Figure 4, respectively. The emission spectrum of the PET matrix exhibits two maxima at 390 and 410 nm and a shoulder at 370 nm. When DMN is added to the PET matrix, the emission spectrum is altered. The spectra of T0.01N(2) and T0.1N(2) exhibit a maximum at 380 nm, flanked by two shoulders which could be due to the PET matrix. As increasing amounts of DMN are introduced into the polymer matrix, the left shoulder disappears, and the maximum originally at 380 nm shifts slightly to the right. The excitation spectrum of pure PET exhibits two resolved maxima at 342 and 358 nm. These features are preserved up to a 1 mol % DMN content for which the top of the fluorescence excitation spectrum flattens. The excitation spectra of the polymer matrices broaden with increasing DMN content. Since the spectroscopic features displayed by polymer matrices having a DMN content larger than 1 mol % are rather different from those exhibited by the PET matrix, one can conclude that the PET matrix contributes little to the overall fluorescence of the polymer matrices with DMN content of 1 mol % and higher.

This was further supported by fluorescence time-resolved measurements, which are reported later on. These decay measurements show that PET contributes 11% to the fluorescence decay of T1N(2) and that PET fluorescence cannot be detected for DMN contents larger than 1 mol %. Since PET and DMN excitation and emission spectra overlap to some extent, an energy transfer mechanism from the PET matrix to the DMN monomer is certainly present. This energy transfer mechanism occurs at a rate that must be faster than the PET own rate of emission estimated at 8.3×10^8 s^{-1}, as measured with our time-resolved fluorescence spectrofluorometer. This fast rate being very close to the detection limit of our fluorometer, the energy transfer process between the PET matrix and the DMN monomer was not investigated in the present study, which focuses on the fluorescence properties of polymer matrices having DMN contents larger than 1 mol %.

Upon excitation, the chromophore naphthalene is known to transfer its energy to a nearby naphthalene, a phenomenon described as energy migration. Energy transfer mechanisms are usually evoked to model the phenomenon of energy migration.[15-18] For instance, Spies and Gehrke[1] have analyzed the fluorescence decays of PEN, using a kinetic scheme developed by Mollay and Kauffmann.[15] They assumed that energy hopping between sites occurs following an energy transfer mechanism between a donor site and an acceptor site. To fit their decays, they assumed that the back-reaction from the excited trap to the ground-state donor is occurring at a nonnegligible rate; i.e., energy transfer from the DMN excited dimer to the DMN ground state monomer is taking place. The energy transfer process is characterized by the Forster radius which depends essentially on the spectral overlap between the absorption spectrum of the acceptor and the emission spectrum of the donor.[19]

Our excitation and emission spectra can be used to qualitatively assess the relative importance of the various physical processes, which are occurring in the energy hopping mechanism taking place in the PEN matrix. Assuming that the DMN electronic environment is similar in the PET matrix to that of the PEN matrix, the excitation spectra of the polymer samples can be considered as an approximate representation of the absorption spectra. We further assume that polymer matrices with DMN contents of 1 mol % (very low DMN content and small probability of having two neighboring DMN monomers capable of forming an excimer) and 100 mol % (highest possible DMN content and highest probability of having two neighboring DMN monomers capable of forming a dimer) are characteristic of the DMN monomer and dimer, respectively. Figure 5 shows the overlap between the excitation and emission spectra of different species. The best overlap is observed between the fluorescence spectrum of the DMN monomer and the excitation spectrum of the DMN dimer. Intermediate overlaps are observed between the excitation and fluorescence spectra of the DMN monomer, as well as between those of the DMN dimer. However, there is little overlap between the excitation spectrum of the DMN monomer and the emission spectrum of the excited DMN dimer.

These observations lead us to the following conclusions in terms of the efficiencies of energy transfer between the different species. Energy transfer will be most effective between an excited DMN monomer and a ground-state DMN dimer. The energy can hop among DMN monomers or among DMN dimers. However, the back-reaction from excited dimers to ground-state monomers is expected to be negligible. These conclusions can be summarized with the following sequence where the rate constants have been defined in the Introduction.

$$k_{\mathrm{DM}}^{\mathrm{ET}} > k_{\mathrm{M}}^{\mathrm{Mig}} \approx k_{\mathrm{D}}^{\mathrm{Mig}} \gg k_{\mathrm{MD}}^{\mathrm{ET}}$$

Negligible back-reaction was also observed by Cao et al. in the case of poly(oxytetramethylene glycol–naphthalene 2,6-dicarboxylate) (PTMN), a similar polymer.[8] They performed time-resolved emission spectra on this polymer, and their data unambiguously showed that the monomer emission at 380 nm disappears as the delay is increased. Only the dimer fluorescence at 430 nm remains at longer delays. This indicates that, in the PTMN system, the DMN monomer is not regenerated via dimer dissociation or back energy transfer to the DMN ground-state monomer. Mechanical dissociation of the DMN dimer into one excited and one ground-state DMN monomers is expected to be negligible in a solid-state sample. These conclusions disagree somehow with the assumption made by Spies and Gehrke whose decay analysis for the solid-state PEN was done assuming that dimer dissociation does take place.[1]

Time-resolved fluorescence decay measurements were also carried out on these polymer samples. The powders were excited at 350 nm, and the emission was observed at 365 or 380 nm for the DMN monomer (depending on signal intensity) and 480 nm for the DMN dimer. According to the steady-state fluorescence spectra (Figure 2), these wavelengths should ensure that DMN monomer and dimer fluorescence are observed with the

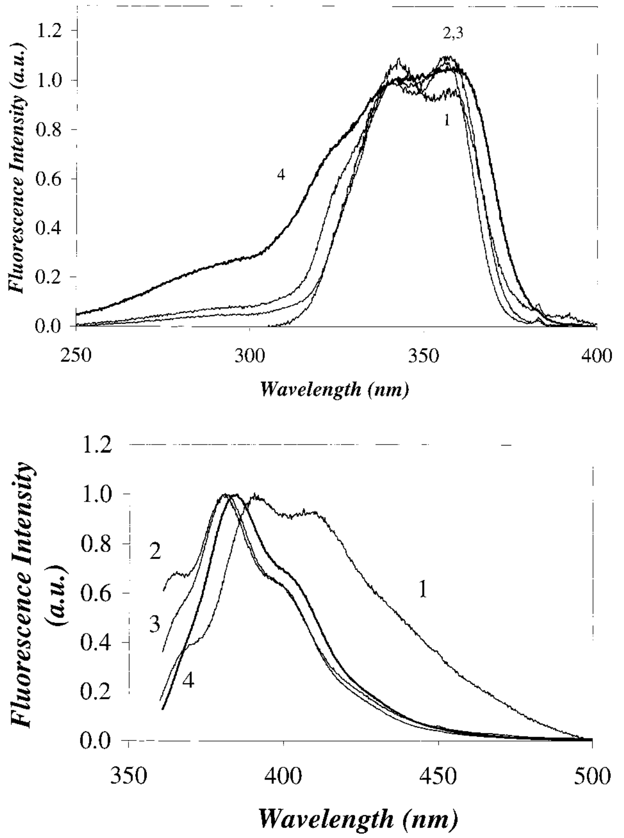

Figure 4. (a) Excitation spectra of PET and three copolymers with $\lambda_{em} = 430$ nm. The spectra were normalized at the fluorescence maximum. (1) PET, (2) T0.01N(2), (3) T0.1N(2), and (4) T1N(2). (b) Emission spectra of the same polymers as in (a) with $\lambda_{ex} = 350$ nm.

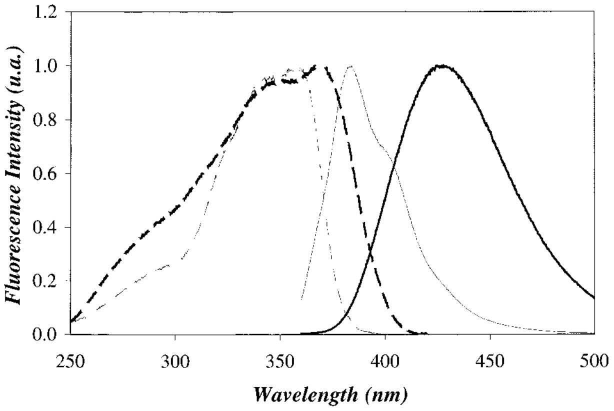

Figure 5. Excitation spectra of T1N(2) (- - -) and PEN (bold - - -) with $\lambda_{em} = 430$ nm and emission spectra of T1N(2) (—) and PEN (bold —) with $\lambda_{ex} = 350$ nm.

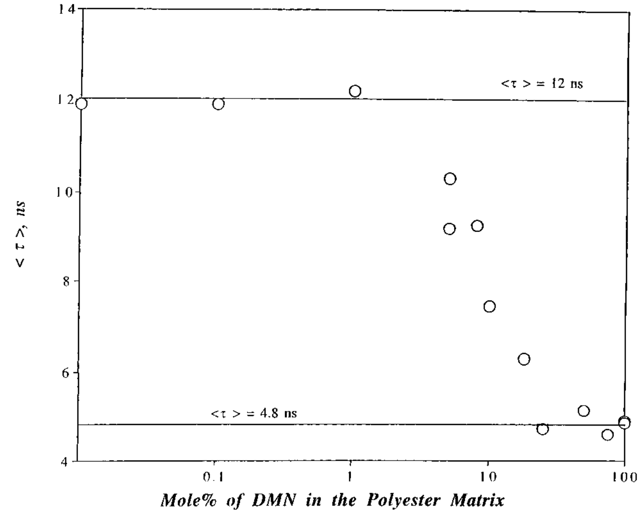

Figure 6. Average decay time of the DMN monomer in the copolymer matrices with $\lambda_{ex} = 350$ nm and $\lambda_{em} = 365$ or 380 nm.

least possible interference. The fluorescence decays of the monomer and the dimer were fitted with three exponentials, and the following approach was applied. The DMN dimer exhibited a very strong contribution with a decay time around 26.5 ns. To correct for potential dimer fluorescence leaking into the monomer fluorescence decay, the third decay time τ_3 was fixed to equal 26.5 ns. As the DMN concentration increased, the contribution from the third exponential was found to increase as a result of increased DMN dimer formation. At low DMN contents (DMN mol % $\leq$ 1 mol %), a short decay was observed. It seemed to arise from the PET matrix, which was found to emit fluorescence with a very short decay time of 1.2 ns, when excited at 350 nm. The emission of the PET matrix was taken into account by fixing the first decay time τ_1 to the lifetime of PET ($\tau = 1.2$ ns as measured on our SPC setup). Consequently, the second decay time τ_2 was attributed to the lifetime of the DMN monomer. A lifetime τ_2 of 12 ns was obtained. For DMN contents larger than 1 mol %, the contribution of 1.2 ns was inexistent as was expected with the decrease in the content of PET in the powders. For these higher DMN contents, the first lifetime was allowed to float, and the contributions from the first and second exponentials were attributed to the DMN monomer. For all polymer samples, the second exponential yielded a decay time τ_2 in the neighborhood of 12 ns. This was attributed to the emission of unquenched DMN monomers.

In Figure 6, we plotted the average decay time $\langle\tau\rangle$ of the DMN monomer as a function of DMN content. For DMN contents smaller than 1 mol %, $\langle\tau\rangle$ is equal to τ_2 since τ_1 accounts for the PET contribution and τ_3 accounts for the DMN dimer contribution. For DMN contents larger than 1 mol % where no PET emission was detected, $\langle\tau\rangle$ is obtained with the two first decay times τ_1 and τ_2 and the two preexponential factors A_1 and A_2 according to eq 2.

$$\langle\tau\rangle = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2} \qquad (2)$$

τ_3 (which equals 26.5 ns) is not taken into account in eq 2 since it accounts for the contribution of the DMN dimer. Figure 6 shows that $\langle\tau\rangle$ exhibits a decrease from 12 ns (for DMN mol % $\leq$ 1 mol %) down to 4.8 ns (for DMN mol % $\geq$ 25 mol %). It is worth noting that the DMN concentration range over which this transition occurs coincides with those observed in Figure 3. The decrease in the DMN monomer average decay time with increased DMN content is due to enhanced quenching via energy transfer from the excited DMN monomer to the DMN ground-state dimers. This is supported by our steady-state fluorescence measurements (cf. Figure 5). On the other hand, the monomer average decay time $\langle\tau\rangle$ plateaus at high DMN contents. This indicates that no additional quenching of the DMN monomer is taking place with further increments in the DMN content. It seems that the polymer matrix is saturated with DMN

Table 1. Results of the Analysis of the Fluorescence Decays of the DMN Monomer in Various Polyester Matrices According to Eq 1[a]

DMN content (mol %)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	χ^2
0.01	0.37	1.2	0.62	11.8	0.01	26.5	1.33
0.1	0.14	1.2	0.84	12.3	0.02	26.5	1.41
1.0	0.11	1.2	0.88	12.4	0.02	26.5	1.33
5.0	0.28	4.7	0.69	12.5	0.03	26.5	1.04
8.0	0.50	5.5	0.47	13.3	0.03	26.5	1.16
10.0	0.49	3.5	0.46	11.8	0.05	26.5	1.24
18.0	0.58	3.3	0.32	11.7	0.09	26.5	1.19
25.0	0.61	2.2	0.29	10.1	0.10	26.5	1.38
50.0	0.57	2.5	0.26	11.0	0.17	26.5	1.37
75.0	0.62	2.3	0.24	10.7	0.14	26.5	1.08
100.0	0.63	2.2	0.24	11.9	0.14	26.5	1.04

[a] $\lambda_{ex} = 350$ nm and $\lambda_{em} = 365$ nm for samples having a DMN content smaller than 5 mol %, and $\lambda_{ex} = 350$ nm and $\lambda_{em} = 380$ nm for samples having a DMN monomer content larger than 5 mol %.

dimers, which cannot further inhibit the DMN monomer fluorescence. Since all spectroscopic properties that we monitored exhibit the same transition occurring over the same DMN concentration range (cf. Figures 2 and 6), progressive saturation of the polymer matrix with DMN dimers must be the underlying effect that controls these trends. The decay times and preexponential factors of the DMN monomer fluorescence decays are presented in Table 1.

The fluorescence decays of the excited DMN dimer were first fitted with a biexponential. The χ^2 were a little bit high (≤ 1.5), and the residuals indicated some slight distortions at longer times. All decays exhibited a short rise time and a long decay component of about 26.5 ns, which was attributed to the lifetime of the DMN dimer. However, this lifetime is relatively short when compared with other polymeric systems exhibiting naphthalene excimer fluorescence. Excimer lifetimes ranging from 44 up to 73 ns have been reported for poly(1-vinylnaphthalene), poly(naphthylmethyl methacrylate), and poly(2-(1-naphthyl)ethyl methacrylate).[9,23] T*X*N(2) copolymers have also been reported to exhibit a weak phosphorescence with a maximum at 456 nm when excited at 350 nm.[3] Thus, the longer-lived component that we observed at 480 nm could arise from a phosphorescent species as well. To account for the slight distortions observed at longer times, a third exponential was introduced to fit the decays, and its decay time was fixed arbitrarily in the analysis to equal 50 ns. This contribution was supposed to arise from a small population of low-energy dimer or a phosphorescent species whose lifetime is longer than 26.5 ns but could not be determined experimentally due to the weak signal. The χ^2 were only slightly improved, but the residuals and the autocorrelation function of the residuals were randomly distributed around zero, indicating a good fit. In all the dimer fluorescence decays, the second exponential was the main contributor to the decays with a decay time of about 26.5 ± 1.5 ns (cf. Figure 7). The contribution of the third exponential was very small ($A_3/A_2 \leq 0.04$). A rise time was detected in all polymer samples. The decay times and preexponential factors are listed in Table 2.

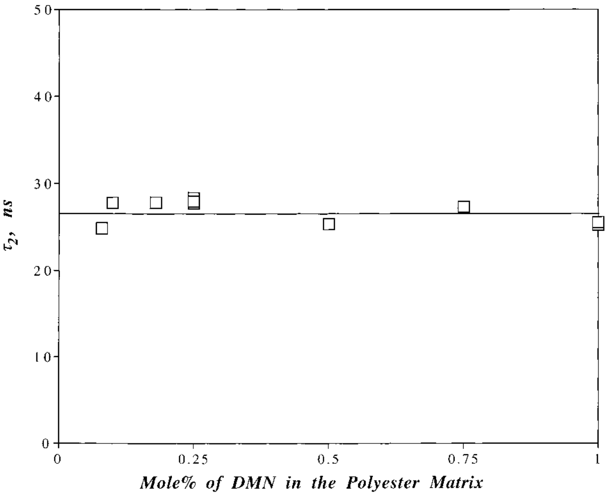

Figure 7. Second lifetime τ_2 of the excimer decays obtained with $\lambda_{ex} = 350$ nm and $\lambda_{em} = 480$ nm.

Table 2. Results of the Analysis of the Fluorescence Decays of the DMN Excimer in Various Polyester Matrices According to Eq 1[a]

DMN content (mol %)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	χ^2
8.0	−0.47	3.4	1.00	24.9	0.03	50.0	1.27
10.0	−0.52	4.7	1.00	27.5	0.00	50.0	1.34
18.0	−0.53	4.0	1.00	27.9	0.01	50.0	1.47
25.0	−0.42	3.4	1.00	27.8	0.01	50.0	1.43
50.0	−0.25	1.7	1.00	25.4	0.04	50.0	1.21
75.0	−0.25	2.8	1.00	27.4	0.01	50.0	1.29
100.0	−0.21	1.7	1.00	25.3	0.02	50.0	1.25

[a] $\lambda_{ex} = 350$ nm and $\lambda_{em} = 480$ nm.

In the case of solutions, excimer-forming systems in liquids exhibit a biexponential decay for the excimer decay with a rise time that reflects the rate of production of the excimer. A steep rise time indicates an important excimer formation. Ideally, the ratio of the preexponential factors equals −1.0, according to the conventional Birks'scheme.[14] If ground-state dimers are present, the ratio A_1/A_2 takes a value more positive than −1.0. The more positive the A_1/A_2 values, the more ground-state dimers are present.

The rise time observed in all solid-state samples indicates that not all ground-state dimers are formed upon excitation. Instead, the excitation of a ground-state dimer can result from the excitation of a ground-state DMN monomer, followed by energy migration between DMN monomers, energy transfer from the last excited DMN monomer to a first ground-state DMN dimer, energy migration between DMN dimers, and ending with emission from the last excited DMN dimer. This complicated excitation mechanism leads to delays, which result in the observed rise time. Figure 8 represents the rise time τ_1 and the preexponential factor A_1/A_2 of the polymer samples versus DMN content. Figure 8 exhibits the now familiar trend. A transition is observed as the DMN content increases. The rise time τ_1 decreases, and the A_1/A_2 ratio becomes more positive. For DMN contents larger than 50 mol %, the rise time and the A_1/A_2 ratio plateau. These results agree very well with our steady-state observations. Our steady-state fluorescence experiments indicate that increasing the DMN content in the polymer matrix creates more ground-state DMN dimers, which are the trap sites for the excited DMN monomers. These complexes can be excited directly at 350 nm (cf. Figure 5), and the ratio A_1/A_2 becomes more positive. As the number of traps increases, there is an increase in the rate of dimer

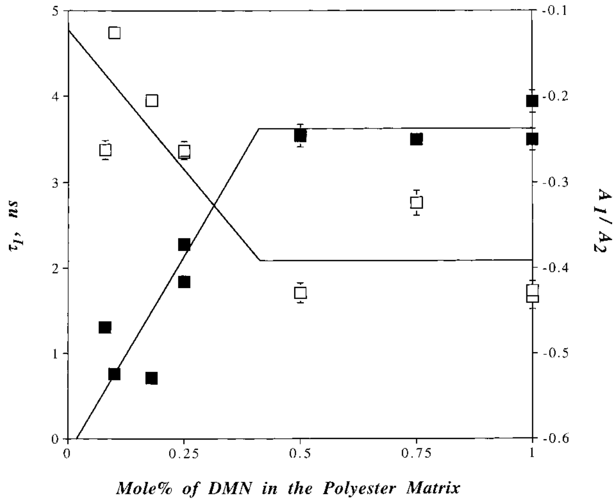

Figure 8. Rise time τ_1 (□) and A_1/A_2 ratio (■) of the excimer decays obtained with $\lambda_{ex} = 350$ nm and $\lambda_{em} = 480$ nm.

formation by energy transfer from an excited DMN monomer to a ground-state DMN dimer. In turn the dimer rise time shortens.

A fluorescence decay of PEN was also acquired with $\lambda_{ex} = 390$ nm and $\lambda_{em} = 480$ nm. At this excitation wavelength, the DMN monomer is not supposed to absorb as shown from our fluorescence excitation spectra (cf. Figure 3). Furthermore, UV absorption of DMN or PEN in dilute solution shows no absorption above 360 nm. No rise time was detected in this decay, indicating that DMN excimer is formed by direct excitation.

It might seem surprising a priori that our fluorescence decay measurements carried out on the PEN matrix probe the fluorescence emission of the excited DMN monomers at 380 nm, although no DMN monomer emission can be observed in the steady-state emission spectrum of PEN reported in Figure 1. Several factors contribute to explaining this phenomenon. At high DMN contents, the average decay time of the excited DMN monomer is 4.8 ns. The lifetime of the excited DMN dimer is 26.5 ns. Consequently, the excited DMN dimer could fluoresce 26.5/4.8 = 5.5 times more strongly than the DMN excited monomer (assuming the same radiative rate constant for both compounds). Furthermore, the quenching of many excited DMN monomers results in the creation of many excited DMN dimers which further strengthens the fluorescence exhibited by the excited DMN dimers. Thus, the DMN monomers are present, as probed by our time-resolved fluorescence measurements at 380 nm, but their fluorescence emission is dwarfed by that of the excited DMN dimers, as shown by our steady-state fluorescence measurements in Figure 1.

Conclusions

We have carried out fluorescence emission and excitation spectra and time-resolved fluorescence decays on TXN(2) copolymers. All our fluorescence measurements indicate that dimer formation occurs for DMN contents larger than 1 mol %. For DMN contents larger than 25 mol %, all the parameters that were monitored plateau (the position of the steady-state fluorescence peak maximum (Figures 1 and 2), the full width at half-maximum of the excitation spectra (Figures 2 and 3), the average decay time of the monomer (Figure 6), the rise time of the excimer decay, and the A_1/A_2 ratio in the dimer decay (Figure 8)). We take the leveling of these parameters as an indication that, for DMN contents larger than 25 mol %, the entire volume of the polymer matrix is then covered by the traps (the DMN ground-state dimers) and quenching of the DMN monomer is maximum. Adding more traps (DMN contents ≥25 mol %) results in no further increase in DMN monomer quenching.

The DMN monomer and dimer were found to exhibit a lifetime of 12 and 26.5 ns, respectively. Energy migration is believed to take place among DMN monomers or dimers, and energy transfer can occur between an excited DMN monomer and a ground-state dimer, but not between an excited DMN dimer and a ground-state monomer.

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