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Studies of the Antenna Effect in Polymer Molecules. 4. Energy Migration and Transfer in 2-Naphthyl Methacrylate–Aryl Vinyl Ketone Copolymers

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ABSTRACT: The low-temperature luminescence of poly(2-naphthyl methacrylate) (P2NMA) in 2-methyltetrahydrofuran glasses was compared with those of small-molecule model compounds and two 2-naphthyl methacrylate–aryl vinyl ketone copolymers. Phosphorescence spectra of photodegraded P2NMA confirm that the low-energy triplet traps in the degraded polymer consist of bound acylnaphthol chromophores, formed by a photo-Fries reaction of the naphthyl ester. Copolymerized aromatic ketones quench the naphthalene singlet and are themselves quenched by triplet energy transfer back to the naphthalene chromophore. Studies of fluorescence depolarization and delayed fluorescence show that both singlet and triplet energy migrate between the naphthalene chromophores of P2NMA, although the range of singlet energy migration in this polymer is relatively small.

Introduction

Recent studies of the photophysics of chromophores bound to polymers have revealed that these systems are often far more complex than corresponding small-molecule systems.[1-7] It has even been suggested that the use of kinetic schemes involving rate constants to analyze photoprocesses in polymers may be an oversimplification.[7-9] On the time scale of fluorescence a polymer represents a highly heterogeneous system, since it contains a distribution of chromophore environments, interchromophore separations, and rates of approach between chromophores. Processes such as excimer formation, for example, are described not by a single rate constant but by a distribution of rates, which may not even be centered around a single "average" value.

In view of this complexity, the goal of the experimentalist is to create well-defined polymer systems containing as few variables as possible. For this reason we recently investigated singlet electronic energy migration and transfer in polymers dissolved in low-temperature glasses.[10,11] Under these conditions chromophore diffusion is suppressed and excimer fluorescence is not observed, so that the kinetics of energy transfer to low-lying traps were simplified.

Several publications have described the luminescence behavior of the poly(naphthyl acrylates) and methacrylates.[12-18] We recently demonstrated that these polymers have substantial photoreactivity,[18] a further complication in studying their photophysics. The elimination of this photoreactivity is an additional benefit of performing experiments on low-temperature glasses.

This article presents the results of an investigation of the photophysics of poly(2-naphthyl methacrylate) (P2NMA) and its copolymers with vinyl aromatic ketones. Luminescence measurements were performed on 2-methyltetrahydrofuran glasses at 77 K, in an effort to simplify the kinetics. In the first section, the use of luminescence to identify the photodegradation products of P2NMA is described. The use of luminescence spectroscopy to study polymer degradation has been demonstrated by Allen and McKellar[19] in experiments with a naphthalene-containing polyester.[20] Model compound spectra are necessary to achieve reliable identification of the emitting species. The second half of this publication shows the effects of singlet and triplet energy migration and transfer in the photophysics of P2NMA at 77 K. The advantage of using a ketone as a low-energy trap, instead of anthracene[21,22] or anthraquinone[23] chromophores, is that the low absorption coefficient of the ketone greatly reduces the radius of one-step Förster transfer from naphthalene to the trap. Once the range of direct transfer to the trap is decreased, the magnitude of the contribution from singlet energy migration between naphthalene chromophores becomes apparent.

Table I
Properties of the Polymer Samples

sample	% ketone in monomer mixture	% ketone in polymer	% conversion	$10^{-4} \times \overline{M}_n$[a]
P2NMA-1	0	0	67	8.6
P2NMA-2	0	0	43	60.3
P2NMA-PIPK	6	4.4	40	12.8
P2NMA-PVK	50	54	32	43.8

[a] By membrane osmometry.

Experimental Section

Materials. The preparation and purification of P2NMA and a copolymer of 2-naphthyl methacrylate with phenyl isopropenyl ketone (PIPK) was described previously.[18] P2NMA was also prepared by the monomer purification procedure of Pasch and Webber,[14] and the two samples gave identical spectra and fluorescence lifetimes. A copolymer of 2-naphthyl methacrylate with phenyl vinyl ketone (PVK) was prepared following the method for the other ketone copolymer.[18] Its composition was determined from its UV absorption spectrum in THF using the extinction coefficient of poly(PVK) ($\epsilon = 85\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ at 325 nm). Molecular weights were determined by membrane osmometry in THF or dioxane. Table I lists the compositions and properties of the polymer samples used in this study. P2NMA was photodegraded by irradiation of a deoxygenated benzene solution containing 0.02 M naphthalene chromophores through a Corning 7-54 filter (280–400-nm band-pass) with light from a high-pressure Hg lamp. The degraded polymer was recovered by precipitation into methanol.

The model compounds 2-naphthyl pivalate, 2-naphthyl isobutyrate, 1-aceto-2-naphthol, and 6-aceto-2-naphthol were available from previous experiments.[18] Di-2-naphthyl pentanedioate was prepared by condensation of glutaryl dichloride with sodium 2-naphthoxide in H_2O. It was purified by column chromatography on alumina, eluting with benzene, and was recrystallized twice from benzene to give colorless needles: mp 129.5–130.5 °C; NMR ($CDCl_3$) δ 2.3 (m, 2 H), 2.85 (t, 4 H), 7.1–8.0 (m, 14 H). 1,1′-Binaphthalene-2,2′-diol was prepared by the method of Fatiadi[24] and recrystallized from 2:1:1 H_2O–

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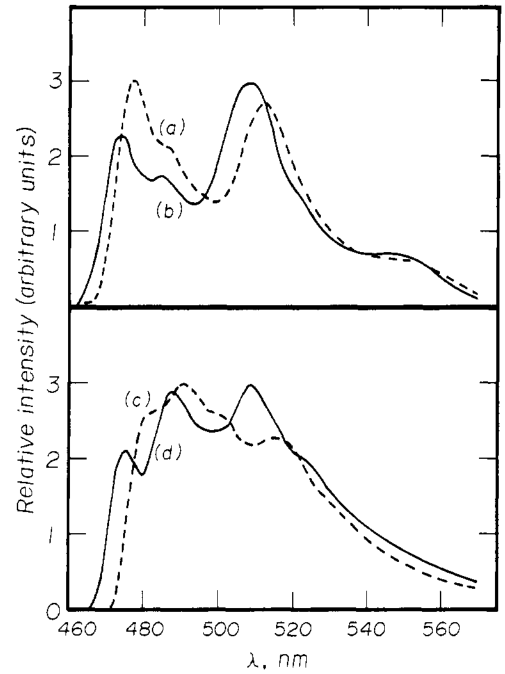


Figure 1. Phosphorescence spectra of solutions in 2-methyltetrahydrofuran at 77 K on 280-nm excitation: (a) P2NMA; (b) 2-naphthyl isobutyrates; (c) photodegraded P2NMA; (d) 6-aceto-2-naphthol.

methanol–acetone to give pale yellow crystals: mp 215–216 °C; UV (THF) $\lambda = 336$ nm ($\epsilon = 8030\ M^{-1}\ cm^{-1}$), 323 (6040), 289 (8040). 2-Methyltetrahydrofuran was purified by a literature method.[14]

Luminescence Methods. The fluorescence, phosphorescence, and delayed fluorescence spectra of polymers and model compounds were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorometer and are shown uncorrected for the wavelength dependence of the detector response. All solutions were prepared in freshly purified 2-methyltetrahydrofuran and were saturated with oxygen-free nitrogen. Each solution was used for only a single experiment, in order to avoid contamination by the luminescence from photoproducts.[14] Delayed luminescence and polarization measurements were performed with accessories provided with the instrument. Polarizations were corrected for grating-induced anisotropy by the method of Azumi and McGlynn.[25] Precautions were taking during polarization measurements to avoid interference from sample birefringence and delayed fluorescence.[11] The excitation and emission spectral bandwidths were 6 and 2 nm, respectively, for the total emission spectra, 10 and 5 nm for the weaker delayed emission, and 5 and 8 nm for polarization measurements, where delayed fluorescence was to be avoided.

Fluorescence decays were measured by single photon counting as described in previous publications.[10,11] Samples were excited at 280 nm through an interference filter; 337-nm emission was viewed at right angles to the excitation pulse through a monochromator.

Results and Discussion

Characterization of the Photodegradation Products of P2NMA. Figure 1 compares the phosphorescence spectra of P2NMA in 2-methyltetrahydrofuran at 77 K before and after irradiation in nitrogenated benzene solution for 2.5 h. Reprecipitation of the degraded polymer had no effect on its spectrum, a result which shows that the phosphorescent products are chemically bound to the polymer chain. Also included in Figure 1 are the spectra of the model compounds 2-naphthyl isobutyrate and 6-aceto-2-naphthol. It is evident that 280-nm excitation of the degraded polymer produces phosphorescence from unreacted 2-naphthyl ester chromophores and from 6-acyl-2-naphthol degradation products.

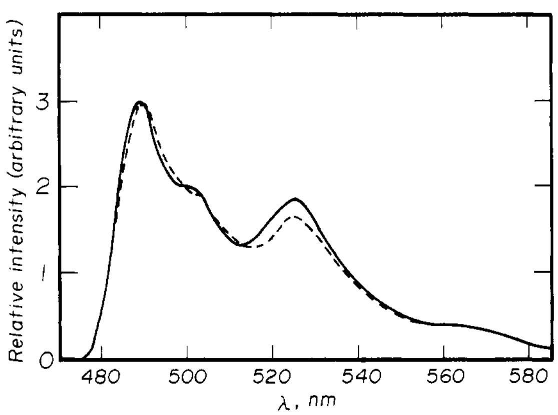


Figure 2. Phosphorescence spectra of solutions in 2-methyltetrahydrofuran at 77 K on 350-nm excitation: (- - -) photodegraded P2NMA; (—) 1-aceto-2-naphthol.

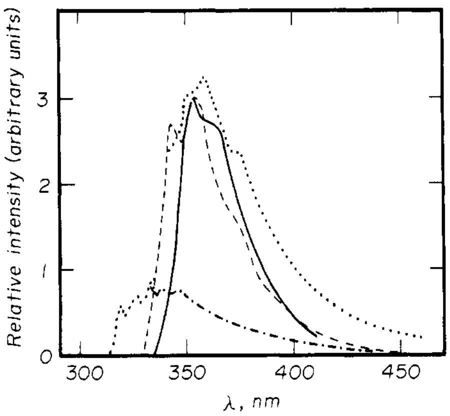


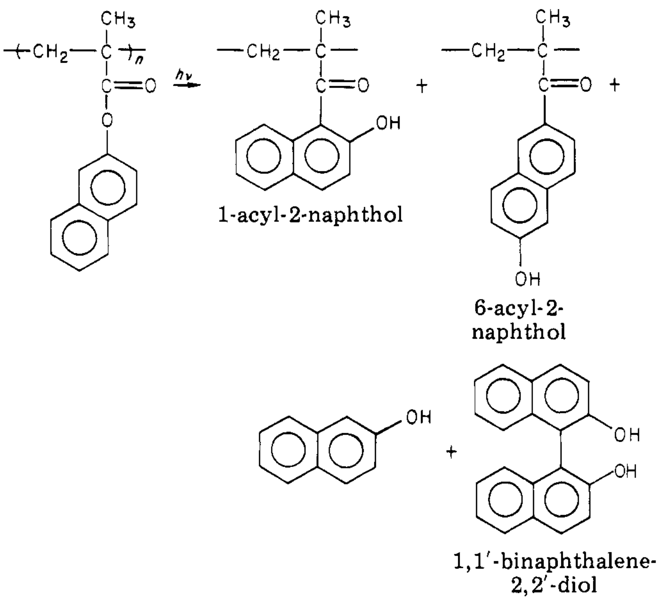
Figure 3. Fluorescence spectra of solutions in 2-methyltetrahydrofuran at 77 K on 280-nm excitation: (···) photodegraded P2NMA; (-·-) reprecipitated photodegraded P2NMA; (- - -) 2-naphthol; (—) 1,1′-binaphthalene-2,2′-diol.

When the degraded polymer is excited in the 350-nm region, a completely different phosphorescence spectrum results, illustrated in Figure 2. As comparison with the spectrum of 1-aceto-2-naphthol shows, this new emission is produced by excitation of 1-acyl-2-naphthol photolysis products.

The photolysis of P2NMA causes pronounced changes in the fluorescence spectrum of the polymer, as well as in its phosphorescence spectrum. Figure 3 compares the fluorescence spectra of photodegraded P2NMA and reprecipitated photodegraded P2NMA from which the small-molecule photoproducts have been removed. It is evident that the bulk of the new fluorescent species are small-molecule products removed by reprecipitation. On the strength of the correspondence between the new emission bands and those of two likely photoproducts, these small-molecule species are identified as 2-naphthol, which has a fluorescence maximum at 352 nm, and 1,1′-binaphthalene-2,2′-diol, with emission maxima at 353 and 360 nm. The source of the long-wavelength tail and the nature of the new fluorescent species which is not removed by reprecipitation have not yet been determined.

Scheme I summarizes the photochemical processes which occur on irradiation of poly(2-naphthyl methacrylate) in benzene solution. Phosphorescence spectra provide evidence in addition to the UV absorption spectra reported earlier[18] to show that the naphthyl ester groups of P2NMA undergo a photo-Fries rearrangement. These photo-Fries products are undoubtedly what caused the changes in the phosphorescence spectrum of P2NMA on long storage in solution reported by Pasch and Webber.[14] The binaphthol may be a secondary product formed in small amounts by the dimerization of 2-naphthoxy radicals.

Scheme I



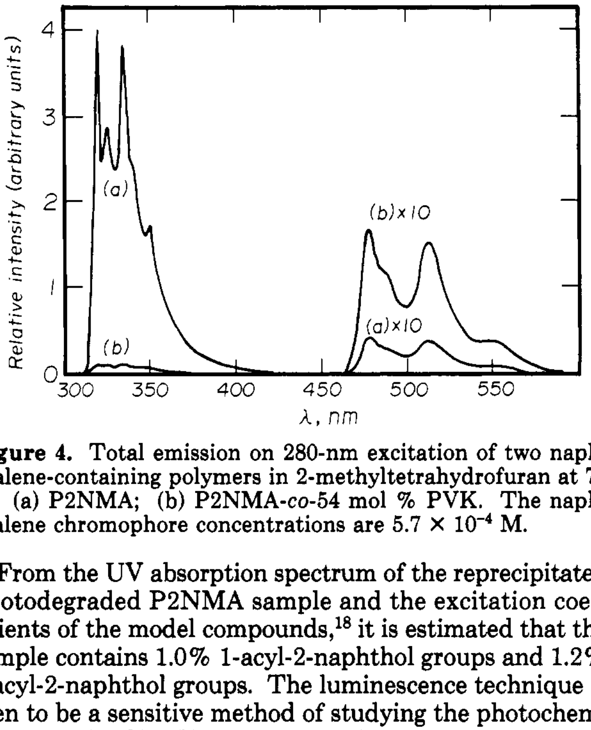


Figure 4. Total emission on 280-nm excitation of two naphthalene-containing polymers in 2-methyltetrahydrofuran at 77 K. (a) P2NMA; (b) P2NMA-*co*-54 mol % PVK. The naphthalene chromophore concentrations are 5.7×10^{-4} M.

From the UV absorption spectrum of the reprecipitated photodegraded P2NMA sample and the excitation coefficients of the model compounds,[18] it is estimated that the sample contains 1.0% 1-acyl-2-naphthol groups and 1.2% 6-acyl-2-naphthol groups. The luminescence technique is seen to be a sensitive method of studying the photochemistry of P2NMA. There are several reasons for this. The products have extinction coefficients of 10–30 times higher than those of the S_1 absorption band of P2NMA, which has $\epsilon = 320\ M^{-1}\ cm^{-1}$ at 317 nm. 2-Naphthol and 1,1′-binaphthalene-2,2′-diol fluoresce with quantum yields several times higher than P2NMA. The acylnaphthol products phosphoresce with much greater efficiency than P2NMA because of their higher quantum yield of singlet-to-triplet intersystem crossing. In addition, the photo-Fries products are excited by triplet energy migration and transfer from the 2-naphthyl ester chromophores, as the results of the following section show. An important consequence of the great sensitivity of these luminescence measurements is that they show that the unirradiated polymer is free of these photo-Fries impurities, which would have interfered with subsequent photophysical measurements.

Studies of Energy Transfer and Migration. Figure 4 compares the total emission spectrum of P2NMA in a 77 K 2-methyltetrahydrofuran glass on excitation at 280 nm with that of P2NMA–54 mol % PVK recorded under identical conditions. These spectra consist of naphthalene "monomer" fluorescence in the 320–380-nm region and naphthalene phosphorescence in the 470–540-nm region. Neither naphthalene excimer fluorescence nor ketone phosphorescence is observed on excitation of the naphthalene chromophore.[13] Figure 4 shows that the naphthalene fluorescence is quenched on copolymerization with the aromatic vinyl ketone monomer. The decrease in fluorescence intensity is matched by a corresponding increase in the naphthalene phosphorescence intensity.

Table II
Relative Contributions from Prompt Fluorescence (I_F), Phosphorescence (I_p), and Delayed Fluorescence (I_{DF})[a]

sample	I_F(333 nm) / I_p(478 nm)	I_{DF}(333 nm) / I_p(478 nm)	χ,[b] %
P2NMA[c]	97	0.70	0
P2NMA-*co*-4.4 mol % PIPK	52	1.09	43
P2NMA-*co*-54 mol % PVK	0.60	<0.01	97
2-naphthyl pivalate	78	<0.01	0

[a] Solutions 5.7×10^{-4} M in naphthalene chromophores in 2-methyltetrahydrofuran at 77 K. Uncorrected intensities. [b] Extent of quenching of naphthalene fluorescence by copolymerized ketone. [c] Sample 1, Table I.

Table III
Fluorescence Polarization P of Some Naphthalene-Containing Compounds[a]

compound	P[b]
2-naphthyl pivalate	0.148
di-2-naphthyl pentanedioate	0.101
P2NMA[c]	0.023
P2NMA-*co*-4.4 mol % PIPK	0.030

[a] Solutions 5.7×10^{-4} M in chromophore concentration in 2-methyltetrahydrofuran at 77 K. [b] 300-nm excitation, 320-nm emission; estimated error ±0.01. [c] Sample 1, Table I.

Table II compares the relative intensities of fluorescence and phosphorescence of the three polymers with those of 2-naphthyl pivalate. Also listed are the relative contributions from delayed fluorescence and the efficiency χ of singlet energy transfer from naphthalene to ketone in the two copolymers. This energy transfer efficiency is 43% in the 4.4% PIPK copolymer and is almost complete in the 54% PVK copolymer, both at room temperature and at 77 K. Incorporation of ketone chromophores into the copolymer also affects the naphthalene delayed fluorescence intensity, but in a different way. At low ketone mole fractions the intensity of delayed fluorescence actually increases, despite the quenching effect of the ketone. At sufficiently high ketone contents this trend is reversed and the delayed fluorescence is quenched entirely.

The polarization P of the prompt naphthalene fluorescence was measured in 77 K 2-methyltetrahydrofuran glasses under conditions where delayed fluorescence constituted a negligible portion of the total emission. Representative values of P, calculated according to eq 1, are

$$P = (I_{\parallel} - GI_{\perp})/(I_{\parallel} + GI_{\perp}) \qquad (1)$$

found in Table III. In eq 1, $I_{\parallel}$ and $I_{\perp}$ are the relative fluorescence intensities with parallel and perpendicular orientation, respectively, of the excitation and emission polarizers, and G is the correction for grating-induced anisotropy.[25] The P values in Table III are only slightly

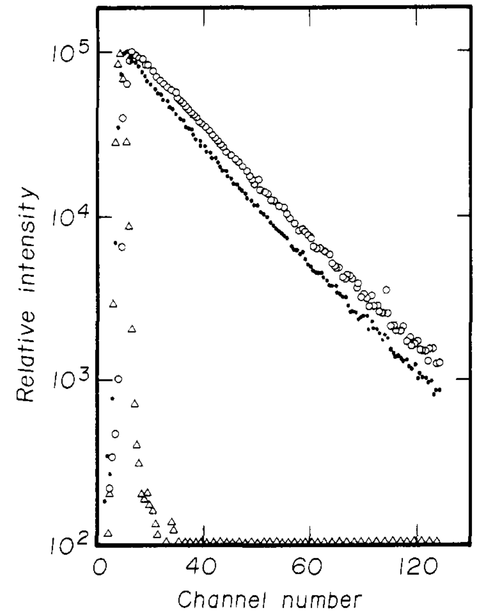


Figure 5. Fluorescence decays at 337 nm on 280-nm excitation of solutions in 2-methyltetrahydrofuran at 77 K. (○) P2NMA; (●) P2NMA-*co*-4.4 mol % PIPK; (△) excitation pulse profile.

Table IV
Long-Time Fluorescence Decay Times τ of P2NMA and P2NMA-*co*-4.4 mol % PIPK in 2-Methyltetrahydrofuran at 77 K[a]

polymer	τ, ns
P2NMA[b]	33.9
P2NMA-*co*-4.4 mol % PIPK	34.1

[a] Chromophore concentrations 10^{-3} M; λ_{ex} = 280 nm.
[b] Sample 2, Table I.

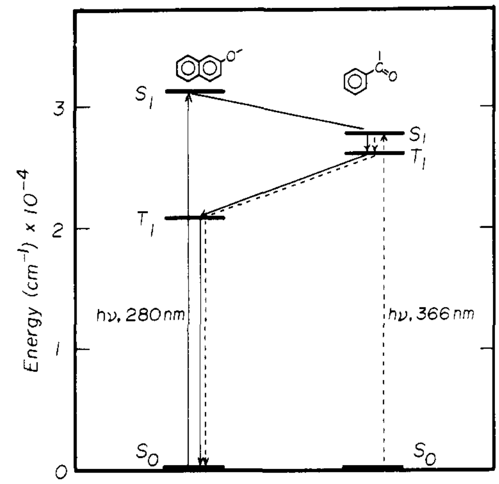


Figure 6. Energy level diagram for poly(2-naphthyl methacrylate–phenyl vinyl ketone). Also shown are the primary deactivation pathways on excitation of naphthalene at 280 nm (—) and on excitation of the aromatic ketone at 366 nm (- - -).

affected by changing the excitation and observation wavelengths throughout the $S_0 \rightarrow S_2$ absorption and $S_0 \leftarrow S_1$ emission bands. The polarization of a monomeric model compound is about 0.15, somewhat lower in a small-molecule dimer,[11,26] and close to zero in P2NMA and P2NMA–PIPK.

Figure 5 illustrates the decay of the fluorescence from P2NMA and P2NMA–PIPK in 2-methyltetrahydrofuran at 77 K. Table IV lists values of the decay times τ of these polymers, obtained by iterative reconvolution of the exponential tails of the decay curves. The decay of the homopolymer fluorescence is exponential, with a lifetime of 33.9 ± 0.5 ns.

The results of these and earlier energy-transfer experiments[18] are interpreted in terms of the energy level diagram shown in Figure 6. A key feature of the naphthalene–ketone copolymer system is that the naphthalene singlet and triplet levels lie above and below the ketone singlet and triplet levels, respectively. Absorption of light by the naphthalene group is followed by singlet energy transfer to the lower energy ketone group, as observed in a variety of other small-molecule and polymer experiments.[27-32] Rapid intersystem crossing populates the ketone triplet, which is then quenched by triplet energy transfer to the lower lying naphthalene triplet state.[13,33-37] Thus the effect of copolymerization of 2-naphthyl methacrylate with increasing amounts of a ketone-containing monomer is to increase the population of naphthalene triplet species per chain. If the polymer contains low concentrations of ketone groups, this effect manifests itself as an increase in the intensity of delayed fluorescence resulting from triplet–triplet annihilation. In the 54% PVK copolymer this increase is reversed, both because of near-quantitative quenching of delayed fluorescence by adjacent ketone groups and because of the absence of long 2-naphthyl methacrylate sequences through which triplet energy migration can occur.

The fluorescence polarization and delayed fluorescence measurements described earlier show that both singlet and triplet energy migrate between the naphthalene chromophores of P2NMA and result in increased efficiency of transfer to singlet and triplet traps. Depolarization of P2NMA fluorescence does not arise from scattered light or birefringent sample solutions, effects which would depolarize the emission from model compounds as well, nor is it a consequence of delayed fluorescence originating in triplet energy migration. A recent publication[38] has proposed that the depolarized fluorescence observed in polymers by several authors[39-46] arises from delayed fluorescence and that such experiments therefore do not constitute evidence for singlet energy migration. However, a simple quantum yield argument shows that delayed fluorescence can never have greater intensity than prompt fluorescence, so that the observed polarization could never be less than 50% of that of an isolated chromophore. As the present work has shown, the effects of delayed fluorescence can in practice be eliminated at low excitation intensities. Depolarization of polymer fluorescence under our experimental conditions, where the pendant chromophores are immobile, must be considered as evidence for singlet energy migration.

In a recent series of publications, Soutar and co-workers established a linear relationship between P^{-1} and l_n, the mean sequence length of fluorescent monomer units in random copolymers of a fluorescent monomer with an inert monomer such as methyl methacrylate.[44-46] Essentially complete depolarization was observed for copolymers whose l_n values were less than 10. The question arises whether there is an upper limit of chromophores over which the singlet energy can migrate within the chromophore fluorescence decay time. Depolarization measurements are insufficiently precise to detect energy migration over long distances, but a partial answer to this question is obtained through analysis of fluorescence decay curves of the type shown in Figure 5. If the distance over which one-step Förster transfer[47] occurs from naphthalene to the ketone is large relative to the distance covered by energy migration during the donor lifetime, then the decay $I_D(t)$ of excited donor is approximately given by Förster kinetics:[48]

$$I_D(t) = \text{constant} \times \exp[-(t/\tau_D)] \exp[-2C(t/\tau_D)^{1/2}] \quad (2)$$

In eq 2 τ_D is the donor fluorescence decay time in the absence of acceptor, and the parameter C describes the dependence of the transfer rate on the acceptor concentration. Under Förster kinetics the decay of the donor at long time following excitation is exponential, with a decay time τ_D. On the other hand, if the distance covered by energy migration is large relative to the radius of Förster transfer to the bound trap, then the donor decay is given by Stern–Volmer kinetics:

$$I_D(t) = \text{constant} \times \exp\{-[k_{DA}[A] + (1/\tau_D)]t\} \quad (3)$$

where [A] is the effective trap concentration and k_{DA} is a rate constant for energy transfer. Here, the donor decay is exponential with a shorter lifetime than is observed for an isolated donor. In Stern–Volmer kinetics a 43% reduction in the donor fluorescence intensity should correspond to a 43% reduction in its apparent decay time. Figure 5 shows no such reduction in the naphthalene decay time in the ketone-containing copolymer, only a minor deviation from exponentiality consistent with Förster kinetics. Thus it is proposed that the singlet energy migration which gives rise to fluorescence depolarization in P2NMA encompasses only a small number of chromophores, probably fewer than ten, since the fluorescence of P2NMA at 77 K still retains a measurable degree of polarization (Table III), in contrast with several other naphthalene-containing polymers.[41,44–46] Thus while the present experiments show that the extent of singlet energy migration in P2NMA is relatively low, this may not be true for all other naphthalene-containing polymers.

Conclusions

Luminescence studies of glassy solutions at 77 K were shown to be a useful technique for characterization of the photodegradation products of poly(2-naphthyl methacrylate). As a corollary, these experiments established that the undegraded polymer could be obtained free of such quenching impurities.

Both photodegradation and excimer formation are suppressed in P2NMA in low-temperature glasses. Nevertheless, the photophysics of the polymer remains complex. P2NMA shows both singlet and triplet energy migration, with the former occurring over a smaller range than the latter. The large difference in energy between the first excited singlet state and the triplet state of the naphthalene chromophore permits both singlet energy transfer to bound ketone traps and triplet energy transfer from these traps back to the naphthalene chromophore. This phenomenon was used to sensitize delayed fluorescence in P2NMA containing low mole fractions of a vinyl ketone comonomer.

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References and Notes

(1) Johnson, G. E. *J. Chem. Phys.* **1975**, *62*, 4697.
(2) Rippen, G.; Kaufmann, G.; Klöpffer, W. *Chem. Phys.* **1980**, *52*, 165.
(3) Phillips, D.; Roberts, A. J.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 2401.
(4) Roberts, A. J.; Cureton, C. G.; Phillips, D. *Chem. Phys. Lett.* **1980**, *75*, 554.
(5) Phillips, D.; Roberts, A. J.; Soutar, I. *Eur. Polym. J.* **1981**, *17*, 101.
(6) Holden, D. A.; Wang, P. Y.-K.; Guillet, J. E. *Macromolecules* **1980**, *13*, 295.
(7) Holden, D. A.; Guillet, J. E. "Developments in Polymer Photochemistry. 1", Allen, N. S., Ed.; Applied Science Publishers: Barking, 1980.
(8) Burkhart, R. D.; Avilés, R. G.; Magrini, K. *Macromolecules* **1981**, *14*, 91.
(9) Egerton, P. L.; Pitts, E.; Reiser, A. *Macromolecules* **1981**, *14*, 95.
(10) Holden, D. A.; Rendall, W. A.; Guillet, J. E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 11.
(11) Holden, D. A.; Guillet, J. E. *Macromolecules* **1982**, *15*, 1475.
(12) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1973**, *6*, 218.
(13) Somersall, A. C.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1975**, *13*, 135.
(14) Pasch, N. F.; Webber, S. E. *Macromolecules* **1978**, *11*, 727.
(15) Hoyle, C. E.; Guillet, J. E. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 185.
(16) Abuin, E. A.; Lissi, E. A.; Gargallo, L.; Radic, D. *Eur. Polym. J.* **1979**, *15*, 373.
(17) Aspler, J. S.; Guillet, J. E. *Macromolecules* **1979**, *12*, 1082.
(18) Merle-Aubry, L.; Holden, D. A.; Merle, Y.; Guillet, J. E. *Macromolecules* **1980**, *13*, 1138.
(19) McKellar, J. F.; Allen, N. S. "Photochemistry of Man-Made Polymers"; Applied Science Publishers: London, 1979.
(20) Allen, N. S.; McKellar, J. F. *J. Appl. Polym. Sci.* **1978**, *22*, 2085.
(21) Aspler, J. S.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* **1978**, *11*, 925.
(22) Holden, D. A.; Guillet, J. E. *Macromolecules* **1980**, *13*, 289.
(23) Nakahira, T.; Shinomiya, E.; Fukumoto, T.; Iwabuchi, S.; Kojima, K. *Eur. Polym. J.* **1978**, *14*, 317.
(24) Fatiadi, A. J. *J. Res. Natl. Bur. Stand., Sect. A* **1968**, *72*, 39.
(25) Azumi, T.; McGlynn, S. P. *J. Chem. Phys.* **1962**, *57*, 2413.
(26) Johnson, G. E. *Macromolecules* **1980**, *13*, 145.
(27) Heskins, M.; Guillet, J. E. *Macromolecules* **1970**, *3*, 224.
(28) Wagner, P. J. *Mol. Photochem.* **1971**, *3*, 169.
(29) Somersall, A. C.; Guillet, J. E. *Macromolecules* **1972**, *5*, 410.
(30) Augustyniak, W. *J. Photochem.* **1980**, *13*, 99.
(31) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 1397.
(32) David, C.; Lempereur, M.; Geuskens, G. *Eur. Polym. J.* **1972**, *8*, 417.
(33) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 537.
(34) David, C.; Demarteau, W.; Geuskens, G. *Eur. Polym. J.* **1970**, *6*, 1405.
(35) Lukac, I.; Hrdlovic, P.; Manasek, Z.; Bellus, D. *J. Polym. Sci., Part A-1* **1971**, *9*, 69.
(36) Lukac, I.; Hrdlovic, P. *Eur. Polym. J.* **1975**, *11*, 767.
(37) Aikawa, M.; Takemura, T.; Baba, H.; Irie, M.; Hayashi, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3643.
(38) MacCallum, J. R. *Eur. Polym. J.* **1981**, *17*, 209.
(39) Schneider, F. *Z. Naturforsch., A* **1969**, *24A*, 863.
(40) Yokoyama, M.; Tamamura, T.; Atsumi, M.; Yoshimura, M.; Shirota, Y.; Mikawa, H. *Macromolecules* **1975**, *8*, 101.
(41) David, C.; Baeyens-Volant, D.; Geuskens, G. *Eur. Polym. J.* **1976**, *12*, 71.
(42) David, C.; Putman-de Lavareille, N.; Geuskens, G. *Eur. Polym. J.* **1977**, *13*, 15.
(43) David, C.; Baeyens-Volant, D.; Piens, M. *Eur. Polym. J.* **1980**, *16*, 413.
(44) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 153.
(45) Reid, R. F.; Soutar, I. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 231.
(46) McInally, I.; Reid, R. F.; Rutherford, H.; Soutar, I. *Eur. Polym. J.* **1979**, *15*, 723.
(47) Förster, Th. *Ann. Phys. (Leipzig)* **1948**, *2*, 55.
(48) Förster, Th. *Z. Naturforsch., A* **1949**, *4A*, 321.