(32) M. R. Philpott, *J. Chem. Phys.*, **63**, 485 (1975).
(33) H. C. Wolf, *Adv. At. Mol. Phys.*, **3**, 119 (1967).
(34) A. A. Kazzaz and A. B. Zahlan, *Phys. Rev.*, **124**, 90 (1961).
(35) J. B. Birks, *Proc. Phys. Soc., London*, **79**, 494 (1962).
(36) G. E. Johnson, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20**(1), 403 (1979).
(37) S. Tazuke and F. Banba, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2463 (1976).
(38) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1971.
(39) Th. Förster, *Discuss. Faraday Soc.*, **27**, 7 (1959).
(40) M. Yokota and O. Tanimoto, *J. Phys. Soc. Jpn.*, **22**, 779 (1967).

Interpretation of the Fluorescence Decay Curves of Some Naphthalene-Containing Polymers

D. A. Holden, P. Y.-K. Wang, and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.

Received October 9, 1979

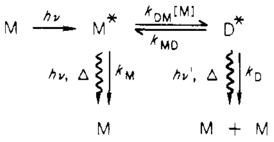
ABSTRACT: Fluorescence decay curves of both the free chromophore and the excimer have been recorded for a number of polymers whose repeating units contain the naphthalene chromophore. Monomer decays in poly(1-naphthylmethyl methacrylate) and poly[2-(1-naphthyl)ethyl methacrylate] were nonsingle exponential in fluid solution at 25 °C, with the long lifetimes τ_2 corresponding closely to the decay times of model compounds in the same solvent. Excimer decay times were not equal to monomer τ_2 values. Similar decay curves were recorded when naphthalene polymers were dispersed in polystyrene or poly(methyl methacrylate) matrices. It is proposed that the long-lived monomer emission in these polymers is not produced by thermal dissociation of the polymeric excimer but results from singlet naphthalene unable to form an excimer within the excited state lifetime.

The study of excimer formation in polymers bearing aromatic chromophores is presently an area of considerable activity.[1] Particularly interesting is the fact that under certain conditions of polymer mobility the dominant excimer-forming process is by electronic energy transfer between chromophores on the polymer to a suitable trap site.[1,2] Such polymers can function as chromophore aggregates intermediate in order between molecular crystals and dilute solutions of small molecules and in this way bear more than superficial resemblance to the chlorophyll aggregates which play an energy-gathering role in plant photosynthesis.[3]

Early studies of excimer fluorescence in polymers concentrated on the effects of solvent, temperature, and polymer structure on the steady-state fluorescence spectra. With the development of improved methods of measurement of nanosecond fluorescence lifetimes,[4,5] transient measurements have been applied to analysis of the kinetics of excimer formation.[6-15]

In all studies of homopolymers of naphthalene-containing monomers, the fluorescence decay function of the monomeric chromophore was not a single exponential[8,11,14,15] but could be represented adequately by a sum of two exponential decays. Because it generates decay laws of this functional form, the starting point for the interpretation of excimer kinetics in polymeric systems usually is a mechanism incorporating formation and subsequent dissociation of an excimer, as shown in Scheme I.[16]

Scheme I



In Scheme I, M* and D* represent the photoexcited free chromophore, or monomer, and the excimer, respectively. The fluorescence response functions of monomer and excimer have the forms shown in eq 1 and 2.[17] The relation

$$I_{FM}(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) \quad (1)$$

$$I_{FD}(t) = A_3[-\exp(-\lambda_1 t) + \exp(-\lambda_2 t)] \quad (2)$$

between λ_1 and λ_2 and the individual rate constants of Scheme I is complex:

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

where

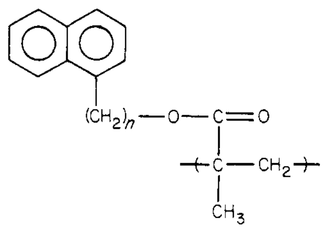
$$X = k_M + k_{DM}[M] \quad (4)$$

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

The mechanism presented in Scheme I applies rigorously only to small molecules such as pyrene[17] or 1-ethylnaphthalene in fluid solution, where excimers are formed by mutual diffusion of two chromophores. In bichromophoric compounds and polymers, excimer sites are created by a sequence of bond rotations, so that excimer formation is the result of several processes. Kinetics in a polymer system are further complicated by energy transfer. Nevertheless, decays of the type shown in eq 1 and 2 are observed for 1,3-dicarbazolylpropane,[18] poly(*N*-vinylcarbazole)[6] (PVCz), poly(1-vinylnaphthalene)[11] (P1VN), and poly(1-naphthyl methacrylate)[14] (PNMA), so that it is generally assumed that excimer dissociation takes place in polymers at room temperature.

Fluorescence decay measurements on poly(1-naphthylmethyl methacrylate) (PNMMA) and poly[2-(1-naphthyl)ethyl methacrylate] (PNEMA) and their model

0024-9297/80/2213-0295$01.00/0



n = 1, PNMMA
n = 2, PNEMA

compounds are described in this publication. These polymers differ from the compounds commonly studied in that adjacent chromophores are separated by more than three intervening atoms. They show substantial excimer emission, whereas the corresponding model compound dimers do not.[19] The present experiments show that Scheme I does not apply to the kinetics of excimer formation in these polymers. Moreover, because P1VN exhibits strikingly similar behavior, the interpretation of previous results in the field of polymeric excimers may require some revision.

Experimental Section

1-Naphthylmethyl methacrylate (NMMA) was obtained by the Schotten–Baumann condensation of 1-naphthalenemethanol with methacryloyl chloride in the presence of triethylamine, as described elsewhere.[3]

2-(1-Naphthyl)ethyl methacrylate (NEMA) was prepared from 2-(1-naphthyl)ethanol, following the method for NMMA.[3]

Polymers were prepared by AIBN-initiated radical polymerization at 60 °C in degassed benzene. Benzene was twice fractionated from P_2O_5. The polymers were purified by repeated precipitation from benzene into ethanol and showed no traces of impurities in their UV absorption or fluorescence excitation spectra. The molecular weights of PNMMA and PNEMA were 4.1×10^5 and 3.4×10^5, respectively, measured by membrane osmometry in toluene. P1VN was available from a previous study.[9]

The model compounds 1-naphthylmethyl pivalate (NMP) and 2-(1-naphthyl)ethyl pivalate (NEP) were prepared from the corresponding alcohols and pivaloyl (2,2-dimethylpropanoyl) chloride, following the method for NMMA, except that it was possible to reflux the reaction mixture overnight to increase the yield. The esters were twice chromatographed on alumina, eluting with cyclohexane, and were obtained as colorless oils. NMP: IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H, 3CH_3), 5.43 (s, 2 H, ArCH_2O), 7.0–8.0 (m, 7 H, ArH); UV (Cary 14-UV, THF) 316 nm (153 M^{-1} cm^{-1}), 312.5 (312), 291.5 (4490), 280 (6670), 271 (5630). NEP: IR (neat) 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H, 3CH_3), 3.32 (t, 2 H, ArCH_2), 4.37 (t, 2 H, CH_2O), 7.1–8.1 (m, 7 H, ArH).

Poly(methyl methacrylate) (PMMA) (Fisher) and polystyrene (PS) prepared by emulsion polymerization[20] were purified by two reprecipitations from benzene into a large volume of methanol. Films containing 0.5 wt % of naphthalene polymer in PMMA or PS were prepared by slow evaporation of mixed solutions in benzene on a distilled water surface. The films were dried in vacuo over P_2O_5.

Steady-state fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter and are shown corrected for the wavelength dependence of the detector response.[3] Fluorescence quantum yields were determined by the method described previously, using carefully purified α-naphthol as the standard.[3,21] Tetrahydrofuran was refluxed over $LiAlH_4$ and distilled under nitrogen. Toluene was twice fractionated from P_2O_5.

Fluorescence decays and time-resolved spectra were measured by single photon counting as described elsewhere.[9,10,21] For measurements on polymer films, the rejection of 280 nm scattered light at 330 nm was further enhanced by placing a Corning 7-51 filter (310–410-nm band-pass) in front of the Stop photomultiplier tube, in addition to the Jarrell-Ash monochromator. Fluorescence decays were analyzed by iterative reconvolution, shown recently to be the technique of choice for the extraction of decay times from real data.[22]

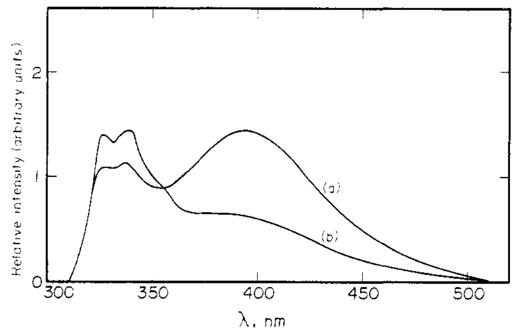


Figure 1. Fluorescence spectra in deoxygenated THF, λ_{ex} = 280 nm: (a) PNMMA, (b) PNEMA.

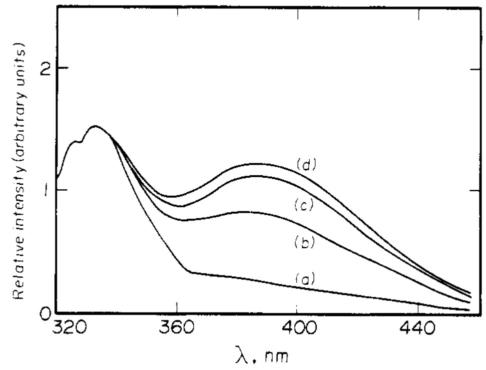


Figure 2. Time-resolved fluorescence spectrum of PNMMA in deoxygenated THF at 25 °C, λ_{ex} = 280 nm. Lower and upper time settings in ns from maximum of the exciting pulse are (a) 0.0–2.3, (b) 10.2–13.0, (c) 24.9–27.4, and (d) 102.4–116.9.

Results and Discussion

Both PNMMA and PNEMA show intramolecular excimer emission in dilute fluid solution at room temperature, as shown in Figure 1. The ratio of monomer to excimer emission I_M/I_D is higher for PNEMA than for PNMMA, reflecting the greater average interchromophore distance in PNEMA. As reported earlier for PNMA,[2] the proportion of excimer emission increases on dilution of the THF solution with either polar or nonpolar nonsolvents. In these polymers as well, the intensity of excimer emission increases in a chain-contracting solvent mixture.

The time-resolved fluorescence spectrum of PNMMA in THF is illustrated in Figure 2. Immediately following excitation of the naphthalene chromophore, monomer emission predominates. Over the first 10 ns from the maximum of the exciting pulse, a rapid growing in of the excimer band occurs. At longer times, the value of I_M/I_D continues to decrease, but at a much slower rate. At no time does I_M/I_D reach a constant value, although it should if the mechanism proposed in Scheme I is valid.

Better time resolution is obtained from fluorescence decay measurements on the two emitting species. Typical monomer and excimer decay curves are shown in Figure 3. Two features are readily apparent: the monomer (curve a) and excimer (curve b) decays are definitely not described by a single exponential, as required by an excimer dissociation mechanism, but the slopes of the two decay curves at long time differ by an amount far larger than the experimental error which is of the order of 2 ns. Table I lists values of the long lifetimes $\tau_2 = \lambda_2^{-1}$ obtained by fitting monomer and excimer curves to functions of the type shown in eq 2 and 3. The fluorescence lifetimes of the model compounds are included for comparison. It must be stressed that these decay times all fall in the regime

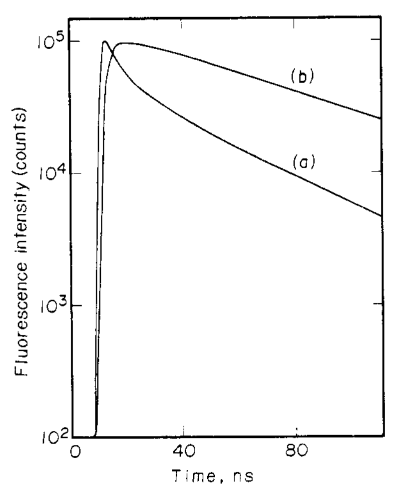


Figure 3. (a) Monomer and (b) excimer decays of PNMMA in deoxygenated toluene at 25 °C on excitation at 280 nm.

Table I
Comparison of the Fluorescence Decay Times of Monomer and Excimer with Those of Model Compounds at 25 °C[a]

polymer	model compd	solvent	monomer τ_2, ns	excimer τ_2, ns	model τ, ns
PNMMA	NMP	THF	36 ± 2	48 ± 2	34 ± 1
PNMMA	NMP	toluene	40	63	39
PNEMA	NEP	THF	66	60	63
PNEMA	NEP	toluene	58	76	60

[a] λ_{ex} = 280 nm.

Table II
Total Fluorescence Quantum Yields ϕ_f of PNMMA and PNEMA and Their Model Compounds in THF at 25 °C[a]

polymer	ϕ_f	model	ϕ_f
PNMMA	0.092	NMP	0.066
PNEMA	0.12	NEP	0.084

[a] λ_{ex} = 280 nm.

where the accuracy of the single photon technique is greatest. The difference between monomer and excimer τ_2 values is genuine. On the other hand, the monomer τ_2 values are the same in all cases (within experimental error) as the decay times of the corresponding model compounds.

Table I also shows that in the case of PNEMA in THF the monomer τ_2 value is larger than the excimer τ_2 value. The possibility that differences in monomer and excimer decay times arise from impurities on the polymer chain which preferentially quench the free naphthalene chromophore must therefore be rejected. Porter has suggested that self-quenching occurs in naphthalene polymers,[23] leading to low apparent fluorescence quantum yields and to a decrease in the monomer lifetimes. He has pointed out the similarity to concentration quenching in chlorophyll-containing monolayers.[24] Table II lists the total emission quantum yields ϕ_f of PNMMA, PNEMA, and their model compounds. Since the polymers have slightly higher ϕ_f than their model compounds, one cannot invoke concentration self-quenching to explain the difference between monomer and excimer τ_2 values in these polymers.

It is therefore proposed that the slowly decaying component of monomer emission arises not by dissociation of the excimer but by the presence of singlet naphthalene in a configuration too far removed from that of the excimer to be quenched within its lifetime. These configurations could be isolated either by steric limitations, i.e., in terms of the number of bond rotations required to form an excimer, or by being outside the distance required for energy transfer to another naphthalene chromophore. These isolated chromophores fluoresce with the lifetime characteristic of a model compound in dilute solution, a lifetime which is coincidentally very close to the excimer decay time in some solvents. Similar behavior is exhibited by PVCz, but only at low temperature.[6]

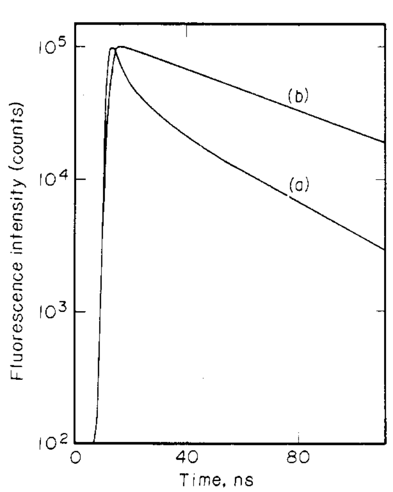


Figure 4. (a) Monomer and (b) excimer decays of PNMMA 0.5 wt % in polystyrene film in N_2 at 25 °C on excitation at 280 nm.

Table III
Fluorescence Decay Times of Naphthalene Monomer and Excimer in Polymer Matrices[a]

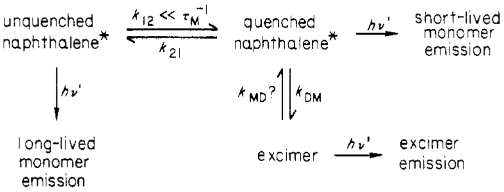
polymer	matrix	monomer[b] τ_2, ns	excimer[b] τ_2, ns
PNMMA	PS	35	55
PNMMA	PMMA	46	55
PNEMA	PS	40	73
PIVN	PS	42	52
PIVN	PMMA	47	53

[a] In nitrogen at 25.0 °C; λ_{ex} = 280 nm. [b] Error ±2 ns.

Excimer Formation in Solid Films. Further insight into the significance of fluorescence decays in polymers is obtained by studies of PNMMA, PNEMA, and P1VN dispersed in glassy polymer matrices. The conventional description of the process of excimer dissociation is that it proceeds by thermally activated bond rotation.[14] This process should therefore be suppressed when the polymer is dissolved in a rigid matrix, analogous to cooling the polymer to a low temperature. Significantly, PNMMA, PNEMA, and P1VN show both monomer and excimer emission when dispersed in PS or PMMA films. The differences observed in the ratio I_M/I_D in the two polymeric solvents are probably caused by differences in the chain expanding power of the matrix, as shown recently for poly(2-vinylnaphthalene) (P2VN) by Frank and Gashgari.[25] While these mixed films probably do not represent true solutions,[3] this does not affect interpretation of the results, as both phases are far below the glass transition at room temperature.

The fluorescence decays of PNMMA dispersed in polystyrene are shown in Figure 4, and the lifetimes are tabulated in Table III. All of the samples prepared exhibited similar behavior. Monomer decays are strikingly similar to those observed in fluid solution. The contribution from the long-lived component is just as prominent in films, where molecular motion is decreased, as it is in THF or toluene. Moreover, the same substantial differences in τ_2 values of monomer and excimer are observed in the solid phase (35 and 55 ns for the film sample of Figure 4). These studies reinforce our belief that the

Scheme II



long-time monomer emission in these polymers is produced by isolated unquenched chromophores and not by excimer dissociation.

In fluid solutions of small molecules, where quenching is by mass diffusion, there is no reservoir of chromophores which is unavailable for excimer formation. The reduced mobility of polymeric chromophore aggregates means that only a fraction of chromophore conformations can proceed to the excimer configuration in times on the order of the singlet lifetime.[26] Nonexponential monomer decay implies that the rate of interconversion of the two kinds of chromophores is slow relative to the rate of fluorescence. A conceptual mechanism incorporating this ground state preequilibrium is shown in Scheme II. Current results suggest that it applies at room temperature to naphthalene polymers whose chromophores are separated by more than three atoms in fluid solutions and to all naphthalene polymers in rigid matrices. No attempt is made in Scheme II to resolve excimer formation into all possible bond rotations and starting configurations[27] since in PNEMA they would be too numerous to list.

Nishijima et al.[28] and David et al.[29] have conducted thorough studies of the effect of temperature on I_M, I_D, and the ratio I_D/I_M in naphthalene-containing polymers. I_D/I_M of model compounds such as 2-ethylnaphthalene passes through a well-defined maximum at about −90 °C, followed by a decrease at higher temperature as excimer dissociation becomes competitive.[28] The corresponding polymer I_D/I_M maxima are shifted to considerably higher temperatures, to approximately room temperature in P2VN and poly(acenaphthylene). Polymers whose chromophores are separated by more than three atoms would be expected to lag still further behind their model compounds in approaching the "pseudoequilibrium" region described by Scheme I. Evidence for this conclusion lies in the fact that the model compound dimer bis(1-naphthylmethyl) pentanedioate does not show excimer emission at room temperature.[19] This compound therefore lags behind the P1VN dimer, 1,3-dinaphthylpropane, which at room temperature is well into the region of free interconversion of the various monomer configurations and excimer, as required by the mechanism of Scheme I. For these reasons, it is proposed that the nonexponentiality of monomer decays in polymers such as PNMMA is best interpreted by means of the "low temperature" type of mechanism illustrated in Scheme II.

Acknowledgment. Thanks are extended to Mr. D. Ng and to Dr. M. A. Winnik for helpful discussions. We are grateful to the National Research Council of Canada for fellowship support (to D.A.H.) and to the Natural Sciences and Engineering Research Council of Canada for financial support of this research.

References and Notes

(1) W. Klöpffer in "Organic Molecular Photophysics", Vol. 1, J. B. Birks, Ed., Wiley-Interscience, New York, 1973.
(2) A. C. Somersall and J. E. Guillet, *J. Macromol. Sci., Rev. Macromol. Chem.*, **13**, 135 (1975).
(3) D. A. Holden and J. E. Guillet, *Macromolecules*, preceding paper in this issue.
(4) C. Lewis, W. R. Ware, L. J. Doemeny, and T. L. Nemzek, *Rev. Sci. Instrum.*, **44**, 107 (1973).
(5) V. J. Koester and R. M. Dowben, *Rev. Sci. Instrum.*, **49**, 1186 (1978).
(6) G. E. Johnson, *J. Chem. Phys.*, **62**, 4697 (1975).
(7) S. Ito, M. Yamamoto, and Y. Nishijima, *Rep. Prog. Polym. Phys. Jpn.*, **20**, 481 (1977).
(8) K. P. Ghiggino, R. D. Wright, and D. Phillips, *Chem. Phys. Lett.*, **53**, 552 (1978).
(9) C. E. Hoyle, T. L. Nemzek, A. Mar, and J. E. Guillet, *Macromolecules*, **11**, 429 (1978).
(10) C. E. Hoyle and J. E. Guillet, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 185 (1978).
(11) K. P. Ghiggino, R. D. Wright, and D. Phillips, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1499 (1978).
(12) K. P. Ghiggino, R. D. Wright, and D. Phillips, *Eur. Polym. J.*, **14**, 567 (1978).
(13) M. Keyanpour-Rad, A. Ledwith, A. Hallam, A. M. North, M. Breton, C. Hoyle, and J. E. Guillet, *Macromolecules*, **11**, 1114 (1978).
(14) J. S. Aspler and J. E. Guillet, *Macromolecules*, **12**, 1082 (1979).
(15) J. E. Guillet, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20** (1), 395 (1979).
(16) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1970.
(17) J. B. Birks, D. J. Dyson, and I. H. Munro, *Proc. R. Soc. London, Ser. A*, **275**, 575 (1963).
(18) G. E. Johnson, *J. Chem. Phys.*, **61**, 3002 (1974).
(19) D. A. Holden and J. E. Guillet, unpublished results.
(20) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry", Interscience, New York, 1961.
(21) J. S. Aspler, C. E. Hoyle, and J. E. Guillet, *Macromolecules*, **11**, 925 (1978).
(22) D. V. O'Connor, W. R. Ware, and J. C. Andre, *J. Phys. Chem.*, **83**, 1333 (1979).
(23) G. Porter, private communication.
(24) S. M. de B. Costa, J. R. Froines, J. Harris, R. M. Leblanc, B. H. Orger, and G. Porter, *Proc. R. Soc. London, Ser. A*, **326**, 503 (1972).
(25) C. W. Frank and M. A. Gashgari, *Macromolecules*, **12**, 163 (1979).
(26) M. Goldenberg, J. Emert, and H. Morawetz, *J. Am. Chem. Soc.*, **100**, 7171 (1978).
(27) Y. Nishijima and M. Yamamoto, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **20** (1), 391 (1979).
(28) Y. Nishijima, Y. Sasaki, M. Tsujisaki, and M. Yamamoto, *Rep. Prog. Polym. Phys. Jpn.*, **15**, 453 (1972).
(29) C. David, M. Piens, and G. Geuskens, *Eur. Polym. J.*, **8**, 1019 (1972).