on a Pt minigrid sheet.[1,10] These electrochemically switchable films composed of lipids or polypeptides are interesting as a new type of synthetic signal-receptive membrane and as a synaptic model membrane in which a nerve impulse (electric signal) initiates the rapid release of a chemical intermediary such as acetylcholine.

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Registry No. PFcAc, 35443-50-6; NQ_2, 97732-71-3; NS^-, 130-14-3; NS^{2-}, 1655-29-4; NS^{3-}, 5182-30-9; NA^+, 25251-63-2; NA^{2+}, 91606-37-0.

References and Notes

(1) For part 8, see: Okahata, Y.; En-na, G. *J. Chem. Soc., Perkin Trans. 2*, in press.
(2) Preliminary report: Okahata, Y.; Takenouchi, K. *J. Chem. Soc., Chem. Commun.* **1986**, 558.
(3) For a review: Okahata, Y. *Acc. Chem. Res.* **1986**, *19*, 57. *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser: New York, 1987; Vol. 2, Chapter 6.5.
(4) Okahata, Y.; Hachiya, S.; Ariga, K.; Seki, T. *J. Am. Chem. Soc.* **1986**, *108*, 2863.
(5) Okahata, Y.; Seki, T.; Ariga, K. *J. Am. Chem. Soc.* **1988**, *110*, 2495.
(6) Okahata, Y.; Ariga, K.; Nakahara, H.; Fukuda, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1069.
(7) Okahata, Y.; Ariga, K.; Shimizu, O. *Langmuir* **1986**, *2*, 538.
(8) Okahata, Y.; Taguchi, K.; Seki, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1122.
(9) Okahata, Y.; Fujita, S.; Izuka, N. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 751.
(10) Okahata, Y.; En-na, G.; Taguchi, K.; Seki, T. *J. Am. Chem. Soc.* **1985**, *107*, 5300. Okahata, Y.; En-na, G. *J. Phys. Chem.* **1988**, *92*, 4546.
(11) Okahata, Y.; Nakamura, G.; Noguchi, H. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1317.
(12) Maeda, M.; Kimura, M.; Hareyama, Y.; Inoue, S. *J. Am. Chem. Soc.* **1984**, *106*, 250. Higuchi, S.; Mozawa, T.; Maeda, M.; Inoue, S. *Macromolecules* **1986**, *19*, 2263.
(13) Chung, D.; Higuchi, S.; Maeda, M.; Inoue, S. *J. Am. Chem. Soc.* **1986**, *108*, 5823.
(14) Kinoshita, T.; Yamashita, T.; Iwata, T.; Takizawa, A.; Tsujita, Y. *J. Macromol. Sci., Phys.* **1983**, *B22*, 1.
(15) Kinoshita, T.; Sato, M.; Takizawa, A.; Tsujita, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 929; *Macromolecules* **1986**, *19*, 51.
(16) Takizawa, A.; Sato, M.; Kinoshita, T.; Tsujita, Y. *Chem. Lett.* **1984**, 1963.
(17) Takizawa, A.; Kinoshita, T.; Ohtani, A.; Tsujita, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 665.
(18) Kinoshita, T.; Sato, M.; Takizawa, A.; Tsujita, Y. *J. Am. Chem. Soc.* **1986**, *108*, 6399.
(19) Kinoshita, T.; Iwata, T.; Takizawa, A.; Tsujita, Y. *Colloid Polym. Sci.* **1983**, *261*, 933.
(20) Okahata, Y.; Iizuka, N.; Nakamura, G.; Seki, T. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1591.
(21) Lindsay, J. K.; Hauser, C. R. *J. Org. Chem.* **1957**, *22*, 355.
(22) Watanabe, J.; Ono, H.; Uematsu, I.; Abe, A. *Macromolecules* **1985**, *18*, 2141.
(23) Traverso, O.; Scandole, F. *Inorg. Chim. Acta* **1970**, *4*, 493.
(24) Sederel, W. L.; Bantjes, A.; Feijen, J. *Biopolymers* **1980**, *19*, 1603.
(25) Sandek, V.; Stokvava, S.; Schmidt, P. *Biopolymers* **1982**, *21*, 1011.
(26) Ambrose, E. J. *J. Chem. Soc.* **1950**, 3239.
(27) Watanabe, J.; Fukuda, Y.; Gehani, R.; Uematsu, I. *Macromolecules* **1984**, *17*, 1004.
(28) Watanabe, J.; Ono, H. *Macromolecules* **1986**, *19*, 1079.
(29) Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6139.
(30) Burgmayer, P.; Murray, R. W. *J. Phys. Chem.* **1984**, *88*, 2515.
(31) Shinohara, H.; Aizawa, M.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1986**, 87; *Chem. Lett.* **1985**, 179.
(32) Aizawa, M.; Watanabe, S.; Shinohara, H.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1985**, 264.
(33) Shimizu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1415.
(34) Iyoda, T.; Ohtani, A.; Shimizu, T. *Chem. Lett.* **1986**, 687.
(35) Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1984**, 106, 6861.
(36) Miller, L. L.; Zhou, Q. X. *Macromolecules* **1987**, *20*, 1594.

Excimer Kinetics in Copolymers Containing Isolated Pairs of Chromophores

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ABSTRACT: Side-chain cyclization in polymers was studied by observing the kinetics of excimer formation and decay in copolymers containing approximately 1% of bis[ω-(1-naphthyl)alkyl] esters of fumaric or itaconic acids. In the fumarate copolymer series the relative intensity of excimer fluorescence decreased with increasing number of CH_2 groups between the naphthalene chromophore and the ester linkage. Only 20–40% of starting conformations cyclized to give excimer during the singlet lifetime, with a rate constant of 5×10^7 to 5×10^8 s^{-1}, depending on solvent and temperature. The remainder decayed with the same lifetime as a monomeric model compound. In the itaconate ester copolymers the fraction of cyclizing monomer species was considerably smaller, but the rate of cyclization was comparable to that observed for the fumarate copolymers. Studies on a variety of bichromophoric model compounds showed that the geometry at the central C–C bond has a pronounced effect on the fraction of chromophore pairs capable of reaching the excimer configuration.

Introduction

The reaction between groups attached to a polymer chain is an important class of physical phenomenon, with relevance to chain branching, ring formation, and intramolecular catalysis.[1,2] Photophysical studies on model polymers can provide fundamental information on such intrachain reactions, provided the model system is carefully designed. An example is the use of excimer and exciplex formation by Winnik and co-workers to study the rates of end-to-end chain cyclization in polymers.[3] In order to create a well-defined model system the University of Toronto group had to achieve quantitative labeling of both ends of monodisperse polymers with chromophoric groups.

A related problem which has received little attention in the literature is the process of side-chain cyclization,[4] illustrated in Figure 1. We define side-chain cyclization

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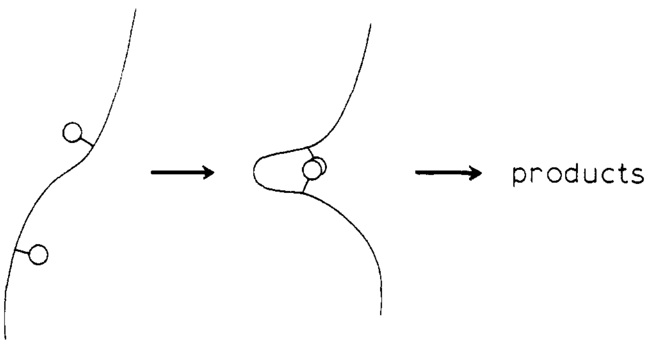
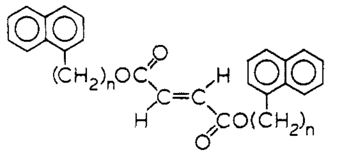


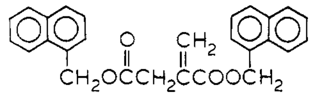
Figure 1. Conceptual illustration of side-chain cyclization in a polymer chain.

as the reaction between groups in two short pendant chains, such that the number of bonds separating the reacting groups is small relative to the total chain length. The chief problem in studying side-chain cyclization by a photophysical method is the difficulty of synthesizing well-defined model polymers. Side-chain cyclization is involved in excimer formation between adjacent chromophores in poly(vinylarenes) such as poly(*N*-vinylcarbazole) or poly(2-vinylnaphthalene).[5,6] These homopolymers, although readily synthesized, are highly complex systems, because the high chromophore density along the main chain allows singlet electronic energy migration to compete with bond rotation as a mechanism for population of the cyclized (excimer) configuration. In very dilute copolymers with a nonchromophoric monomer unit, energy migration is negligible, but the statistical nature of copolymerization prevents chromophores from being separated by a well-defined number of bonds. This is the case in the work of Cuniberti and co-workers, for example, who studied poly(vinyl acetate) labeled with low mole fractions of pyrenyl groups.[7,8] In other systems studied by Tazuke and co-workers, polycondensation was used to ensure that the two interacting groups were separated by a known number of bonds.[9,10] In both the carbazole/dialkyl terephthalate and pyrene/dimethylaniline exciplex systems, however, incorporation of these chromophores into a polymer led to appreciable ground-state association, so that the photophysical probe perturbed the ground-state conformations of the polymer.

In the present publication we describe the results of a photophysical investigation of side-chain cyclization in polymers containing adjacent pairs of naphthalene chromophores. Side-chain cyclization is indicated by formation of excimers between the two naphthalene groups, a process which was studied by steady-state and time-resolved fluorescence spectroscopy. The model polymers were obtained by free-radical copolymerization of minute amounts of bis[(1-naphthyl)alkyl] esters of fumaric acid and itaconic acid 1 and 2 with large excesses of the diluting monomers vinyl acetate and methyl methacrylate. In these copolymers the adjacent naphthalene groups are separated by 8–12 atoms but are separated from other pairs of chromophores by an average of 200 or more bonds. Comparison of the fumarate and itaconate ester series indicated a large effect of chain placement on the ground-state conformational distribution in polymers. In order to rule out the possibility of interaction between naphthalene chromophores in different monomer units, copolymers containing the singly tagged fumarate units 3 were also investigated. Finally, studies on model compounds were also used to probe the conformational requirements for excimer formation in the 1-naphthyl series. These model compounds included the conformationally free bis(1-naphthylmethyl) succinate (**4a**), and the conformationally hindered meso diester **4b** and *trans*- and *cis*-cyclohexanedicarboxylates **5a** and **5b**. Other still more conformationally restricted model compounds included the cyclobutanedicarboxylate **6** and the norbornenyl derivative **7**.



1a: n = 1
1b: n = 2
1c: n = 3



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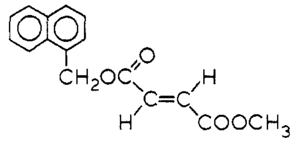

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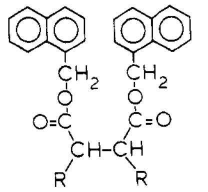
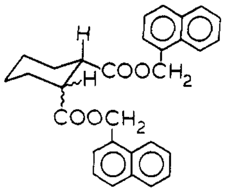
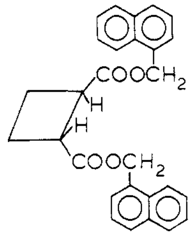


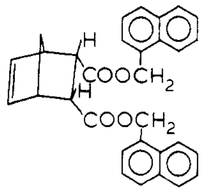
4a: R=H
4b: R=CH$_3$ (meso)



5a: trans
5b: cis



6



7

Experimental Section

The preparations of bis(1-naphthylmethyl) fumarate (**1a**), bis[2-(1-naphthyl)ethyl] fumarate (**1b**), bis[3-(1-naphthyl)propyl] fumarate (**1c**), methyl 1-naphthylmethyl fumarate (**3**), bis(1-naphthylmethyl) succinate (**4a**), and *meso*-bis(1-naphthylmethyl) 2,3-dimethylsuccinate (**4b**) were described in previous publications.[4,11]

Bis(1-naphthylmethyl) Itaconate (2). Freshly distilled itaconyl chloride (2.11 g) was added under N$_2$ to a stirred solution of 4.0 g of 1-naphthylmethanol in 25 mL of dry CH$_2$Cl$_2$, and then a solution of 3.06 g of *N*,*N*-dimethylaniline in 15 mL of dry CH$_2$Cl$_2$ was added dropwise over 30 min. After standing overnight the solution was refluxed for 1 h. The solution was extracted with 0.5 M HCl and concentrated aqueous NaCl and dried over Na$_2$SO$_4$. The product was chromatographed over neutral alumina, eluting

Table I
Properties of Copolymers from Fumarate and Itaconate Ester Monomers

copolymer	mol % naphthalene-containing monomer	$10^{-5}M_n$	M_w/M_n
VAc-*co*-**1a**	0.82	1.38	1.2
VAc-*co*-**1b**	0.92	1.17	1.6
VAc-*co*-**1c**	0.98	1.40	1.3
VAc-*co*-**3**-*co*-dimethylfumarate	1.03	1.63	1.4
MMA-*co*-**2**	0.34	3.27	
styrene-*co*-**2**	1.14	1.24	

with CH_2Cl_2. A colorless viscous oil was obtained: IR 1731, 1642, 1600, 1512 cm^{-1}; NMR ($CDCl_3$) δ 3.37 (s, 2 H), 5.44 (s, 2 H), 5.53 (s, 2 H), 5.65 (d, 1 H), 6.31 (unresolved d, 1 H), 7.3–8.0 (m, 14 H); UV (CH_2Cl_2) λ_{max} 316 nm (ϵ 784 M^{-1} cm^{-1}), 296 (11 030), 285 (15 700), 275 (13 000).

Bis(1-naphthylmethyl) *trans*-1,2-Cyclobutanedicarboxylate (6). This compound was prepared following the method for the itaconate ester **2** and obtained as a very pale yellow viscous oil: IR (neat) 1731, 1600, 1512 cm^{-1}; NMR ($CDCl_3$) δ 2.09–2.20 (m, 4 H), 3.37–3.59 (m, 2 H), 5.59 (s, 4 H), 7.3–8.3 (m, 14 H); UV (CH_2Cl_2) λ_{max} 316 nm (ϵ 560 M^{-1} cm^{-1}), 295 (9700), 285 (14 000), 275 (12 400).

Bis(1-naphthylmethyl) *trans*-1,2-Cyclohexanedicarboxylate (5a). *trans*-Cyclohexane-1,2-dicarboxylic anhydride (Aldrich, 0.437 g), 1-naphthylmethanol (0.985 g, 2.2 equiv), and 50 mg of *p*-toluenesulfonic acid were refluxed in benzene (40 mL) and the benzene–water azeotrope was removed in a DeanStark trap. After removal of the solvent the reaction mixture was held at 180 °C for 2 h. The crude oil was chromatographed on silica gel, eluting with 5–50% v/v EtOAc/hexane. The product was recovered as a very viscous oil and was purified by Kugelrohr distillation (bp 329–333 °C (0.2 mmHg)) and further column chromatography. IR (neat) 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.10–1.44 (m, 4 H, 2 C_4H and 2 C_5H), 1.65–1.75 (m, 2 H, C_3H and C_6H), 1.97–2.14 (m, 2 H, C_3H and C_6H), 2.60–2.80 (m, 2 H, C_1H and C_2H), 5.35 (d, J = 12.5 Hz, 2 H, OCH_2), 5.50 (d, J = 12.5 Hz, 2 H, OCH_2), 7.35–7.95 (m, 14 H, Ar H); MS, m/z 452 (M$^+$, rel intensity 2), 157 (100), 142 (31), 141 (60).

Bis(1-naphthylmethyl) *cis*-1,2-Cyclohexanedicarboxylate (5b). The cis diester was prepared from *cis*-hexahydrophthalic anhydride following the procedure for compound **5a**. The product, obtained in 28% yield after column chromatography and Kugelrohr distillation, was a colorless viscous oil, bp 340–344 °C (0.4 mm Hg): IR (neat) 1728 cm^{-1}; NMR ($CDCl_3$) δ 1.24–1.57 (m, 4 H, 2 C_4H and 2 C_5H), 1.63–1.83 (m, 2 H, C_3H and C_6H), 1.94–2.15 (m, 2 H, C_3H and C_6H), 2.80–2.93 (m, 2 H, C_1H and C_2H), 5.33 (d, J = 12.5 Hz, 2 H, OCH_2 AB pattern), 5.46 (d, J = 12.5 Hz, 2 H, OCH_2 AB pattern), 7.35–7.95 (m, 14 H, Ar H); MS, m/z 452 (M$^+$, rel intensity 4), 158 (100), 142 (49), 141 (90).

Bis(1-naphthylmethyl) *cis*-5-Norbornene-*endo*-2,3-dicarboxylate (7). The norbornenyl diester was prepared from *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride following the procedure for compound **5a**. The product obtained after column chromatography was a colorless viscous oil in 27% yield: IR (neat) 1733 cm^{-1}; NMR ($CDCl_3$) δ 1.24 (br d, J = 8.6 Hz, 1 H, bridging CH_2 H anti to olefin), 1.41 (br d, J = 8.6 Hz, 1 H, bridging CH_2 H syn to olefin), 3.30 (br m, 2 H, CHCO), 3.12 (br m, 2 H, bridgehead CH), 5.27 (d, J = 12.4 Hz, 2 H, OCHAr), 5.51 (d, J = 12.4 Hz, 2 H, OCHAr), 6.23 (br m, 2 H, CH=CH), 7.36–7.93 (m, 14 H, Ar H); MS, m/z 462 (M$^+$, rel intensity 3), 303 (M$^+$ – $ArCH_2OH$, 5), 157 (25), 142 (50), 141 (100).

Copolymers were prepared by AIBN-initiated free-radical polymerization. In a typical polymerization 5 mL of purified vinyl acetate, 10 mg of the naphthalene-containing monomer, and 5 mg of recrystallized AIBN were degassed thoroughly and polymerized at 60 °C for 4 h. The polymer was purified by four reprecipitations from benzene into cyclohexane. Polymer compositions were determined by UV spectroscopy on a Cary 118 instrument, with the corresponding monomers used as reference compounds. Number-average molecular weights were determined by membrane osmometry in toluene. Polydispersities were estimated from size-exclusion chromatography with 2-butanone as the eluting solvent. Table I lists data for the copolymer samples used in this study.

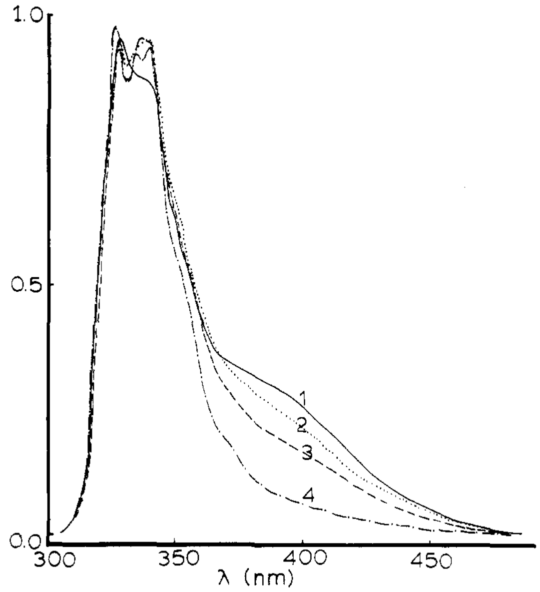


Figure 2. Steady-state fluorescence spectra of vinyl acetate copolymers of naphthylalkyl fumarate esters in methanol at 6 °C, λ_{ex} = 280 nm: (1) VAc-*co*-0.82% **1a**; (2) VAc-*co*-0.92% **1b**; (3) VAc-*co*-0.98% **1c**; (4) VAc-*co*-1.03% **3**-*co*-dimethylfumarate.

Fluorescence Measurements.[4,11] Steady-state fluorescence spectra were recorded with a Perkin-Elmer MPF-2A instrument with a thermostated sample holder. A 1-cm square quartz fluorescence cell with a 10-cm stem was used for all measurements, and sample solutions were deoxygenated with high-purity nitrogen. Fluorescence decays were measured by time-correlated single photon counting on a PRA International System 2000 instrument. In order to increase the excitation intensity when excimer decays were recorded at 430 nm, deuterium was used as the flashlamp gas. Fluorescence decays were analyzed by iterative reconvolution, and plots of the weighted residuals and the autocorrelation function of the residuals were used to judge the quality of the analysis.

Results and Discussion

Fluorescence of Fumarate Ester Copolymers. Figure 2 shows the steady-state fluorescence spectra of vinyl acetate copolymers with approximately 1 mol % of 1-naphthylalkyl fumarate monomers. The solvent is methanol, a Θ-solvent for poly(vinyl acetate) at 6 °C. In addition to the structured naphthalene emission with maxima at 326 and 337 nm, each spectrum shows a weak, broad emission band centered around 390 nm, which corresponds to emission from the naphthalene excimer. The relative intensity of the excimer emission band decreases with increasing number of bonds between adjacent chromophores in the series of copolymers from **1a** to **1b** to **1c**. Excimer emission is absent in the terpolymer containing methyl 1-naphthylmethyl fumarate, where there is only a single chromophore per monomer unit. This result indicates that there is no interference in these copolymer systems from cyclization across large loops of 200 bonds in the chain.

More detailed mechanistic and kinetic information is provided by fluorescence decay measurements. Parts a and b of Figure 3 show typical decays of the naphthalene monomer emission at 340 nm and the excimer emission at 420 nm. These decays were analyzed satisfactorily by a sum and a difference of exponentials, respectively (eq 1).

$$I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \tag{1}$$

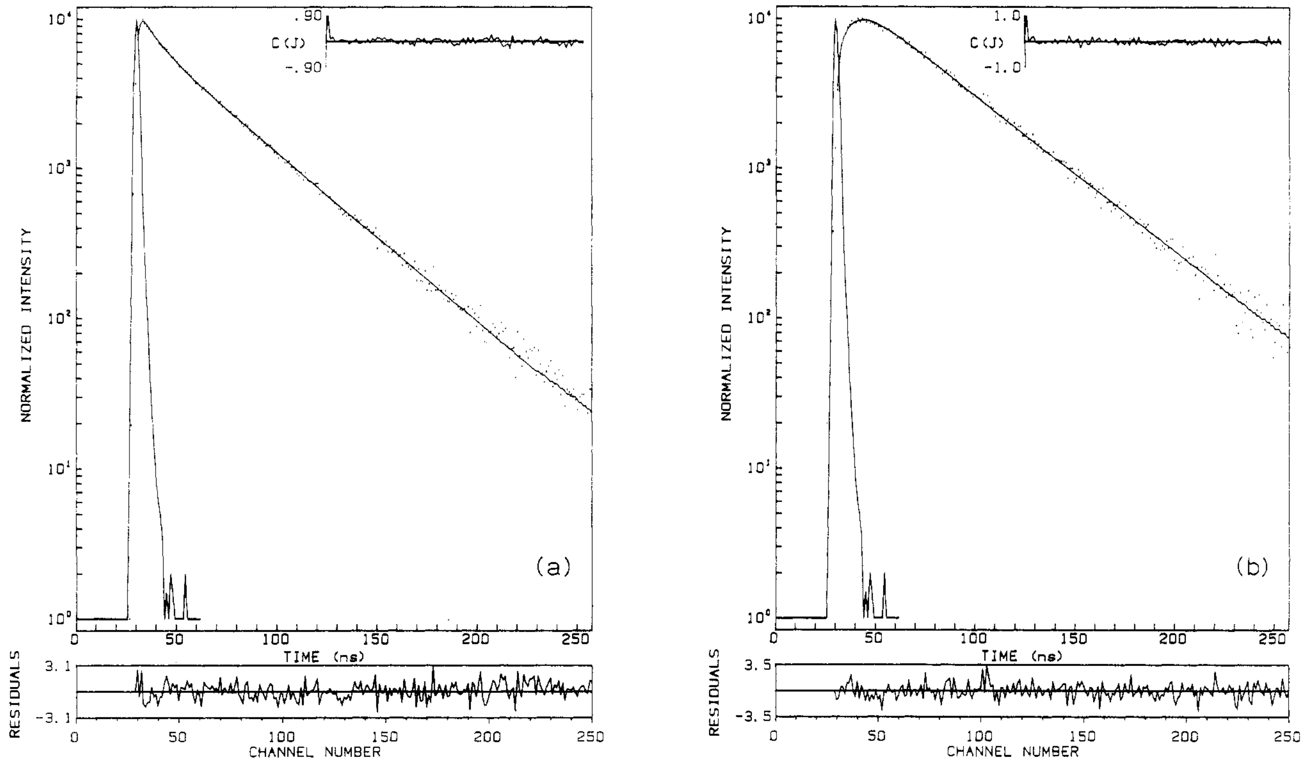


Figure 3. Fluorescence decays of poly((vinyl acetate)-*co*-0.82% **1a**) in nitrogenated toluene at 25 °C on excitation at 292 nm. (a) λ_{em} = 340 nm; fitting function $I(t) = 0.311 \exp(-t/8.42 \text{ ns}) + 0.689 \exp(-t/37.7 \text{ ns})$; $\chi_R^2 = 1.12$; (b) λ_{em} = 420 nm, fitting function $I(t) = -0.412 \exp(-t/8.0 \text{ ns}) + 0.588 \exp(-t/40.9 \text{ ns})$, $\chi_R^2 = 1.09$. *C*(*j*) is the autocorrelation function of the weighted residuals.

For the excimer decays it was necessary to relax the condition $A_1 = -A_2$ in order to obtain optimum fits. In a first report on the naphthylmethyl fumarate copolymers the observation of $A_1 < A_2$ for the excimer decays, where A_2 is the preexponential factor for the long-lived component, was attributed to a small amount of static excimer formation.[4] As a result the excimer fluorescence decay would correspond to eq 2. The relationship between the

$$I_f(t) = A_a \exp(-t/\tau_2) + A_b[-\exp(-t/\tau_1) + \exp(-t/\tau_2)] \quad (2)$$

preexponential factors of eq 1 and 2 would then be $A_1 = A_b$ and $A_2 = A_a + A_b$. While this may be true for the naphthylmethyl fumarate copolymers, which show the most intense excimer emission, the extent of excimer formation in copolymers of the naphthylethyl and naphthylpropyl homologues was so much smaller that it was difficult to differentiate the above situation from a simple overlap of excimer and monomer emission spectra at 430 nm. Because of the possibility of spectral overlap in the region where the 430-nm decays were collected, cyclization rate constants were obtained exclusively from analysis of the monomer decay curves. Nevertheless the 430-nm decays continued to be of use, because the presence of a component at 430 nm with a negative preexponential factor was used together with the ratio of steady-state fluorescence intensities at 326 and 430 nm to indicate the presence of measureable excimer emission.

Concern has been raised by De Schryver and co-workers about the extent of overlap of monomer and excimer emission spectra at short wavelengths.[12] To establish whether such overlap interfered with our analysis of monomer decays recorded at 340 nm, we examined published spectra which consisted almost exclusively of naphthalene excimer emission. These were the fluorescence spectrum of poly(2-isopropenylnaphthalene) (PIPN) film[13] and the time-resolved spectrum of poly(2-vinylnaphthalene) (P2VN) recorded at long times after excitation.[12] The ratio of the intensity at 340 nm to the maximum intensity at 390 nm was 0.068 for PIPN and 0.06 for P2VN. The average was used to determine the contribution of excimer emission to the total emission intensity at 340 nm. For the spectrum of the bis(1-naphthylmethyl) fumarate copolymer in methanol at 6 °C, which shows the most intense excimer emission, the contribution of the excimer to the total intensity at 340 nm is 1.5%. This contribution is an upper limit, since it is likely that the literature spectra of PIPN and P2VN still contain weak contributions from monomer emission at 340 nm. This analysis establishes the validity of analyzing monomer decays recorded at 340 nm for systems with low extents of excimer formation.

Table II
Analysis of Monomer and Excimer Fluorescence Decays of Bis(1-naphthylalkyl) Fumarate Copolymers with Vinyl Acetate

copolymer	λ_{em}, nm	A_1/A_2	τ_1; τ_2, ns	f_1	χ_R^2
P(VAc-*co*-0.82% **1a**)	340	0.451	8.4; 37.7	0.31	1.12
(toluene, 25 °C)	420	−0.701	8.0; 40.9		1.09
P(VAc-*co*-0.82% **1a**)	340	0.526	9.6; 31.1	0.41	1.04
(MeOH, 6 °C)	420	−0.538	4.2; 50.3		0.95
P(VAc-*co*-0.92% **1b**)	340	0.261	13.6; 62.1	0.21	1.11
(MeOH, 6 °C)	420	−0.608	16.1; 93.3		1.01
P(VAc-*co*-0.98% **1c**)	340	0.399	14.5; 61.3	0.29	1.04
(MeOH, 6 °C)	420	−0.597	16.5; 85.1		0.92

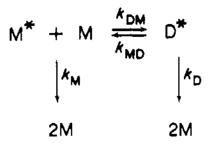
Table II lists representative decay parameters for three fumarate ester copolymers. Also included in Table II is the fraction f_1 of starting conformations which cyclize to the excimer configuration, given by

$$f_1 = A_1/(A_1 + A_2) \quad (3)$$

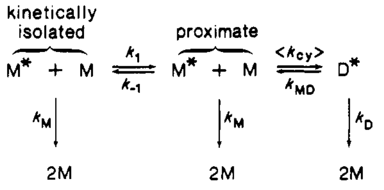
as well as values of the reduced χ-squared χ_R^2 of the weighted residuals. The maximum error in f_1 which can arise as a result of overlap with excimer emission at 340 nm is 5% of f_1.

In small-molecule excimer systems the Birks mechanism (Scheme I) is frequently used to interpret the decay ki-

Scheme I



Scheme II



netics.[14] In Scheme I M* and D* represent photoexcited free chromophore, or monomer, and excimer, respectively. Two key features of the Birks scheme for intramolecular excimer systems are that excimer formation is described by a homogeneous rate constant k_{DM}, and that biexponential monomer fluorescence decays originate from dissociation of the excimer to M* + M with a rate constant k_{MD}. Because monomer and excimer species are coupled in this way, the parameters τ_1 and τ_2 are the same for both fluorescence decays.

The data for the naphthylmethyl fumarate copolymer in toluene solution, shown in entry 1 of Table II, could conceivably be interpreted in terms of Scheme I, because the long lifetimes τ_2 of monomer and excimer fluorescence decays are the same within experimental error in this solvent. However, this is not the case for the naphthylpropyl fumarate copolymer in toluene, nor is it the case for the three copolymers in methanol solution, as shown in entries 2–4 of Table II, where τ_2 of the excimer decay is much longer than that of the monomer decay. Because the monomer and excimer τ_2 values were found to vary independently in different solvents, an alternative mechanism, shown in Scheme II, is proposed.[15] In Scheme II, the major fraction of ground-state conformations is sufficently far from the excimer configuration that no cyclization can occur during the excited-state lifetime. The magnitude of the rate constant k_1 is such that two distinct populations of monomer species exist in an experiment with a nanosecond time scale. In such a kinetic system f_1, the fraction of monomeric species which form excimer, is related to the ground-state equilibrium constant K_{cy} between proximate and isolated chromophores:

$$\frac{f_1}{1 - f_1} = \frac{k_1}{k_{-1}} = K_{cy} \qquad (4)$$

Provision is made in Scheme II for excimer dissociation, yet no evidence was found for this. We note the low extent of excimer dissociation in bichromophoric naphthalene systems at room temperature.[12,16] If only a small population of chromophore pairs cyclize to the excimer, and only a fraction of these excimers dissociate, the evidence for such dissociation—namely, an additional long-lived monomer decay component—is buried in the monomer decay of the kinetically isolated naphthalene chromophores.

Only a single excimer D* is proposed in Scheme II. This is because no evidence was found in these systems for multiple excimer species differing in emission spectra or decay times. In this respect these naphthalene-containing copolymers and model compounds differ from the $n = 3$ poly(vinylarenes), such as poly(*N*-vinylcarbazole), in which excimers formed at isotactic and syndiotactic diads have very different emission spectra and decay rates.[17-19] The explanation for the simpler behavior in our systems may lie in the greater number of bonds between the naphthalene chromophores, which results in smaller differences between the emission properties of the excimers at diastereomeric sites. As well, the itaconate copolymers and the model compounds, to be discussed in a later section, either do not show diastereomerism or, as in the case of compound **4b**, consist of a single diastereomer.

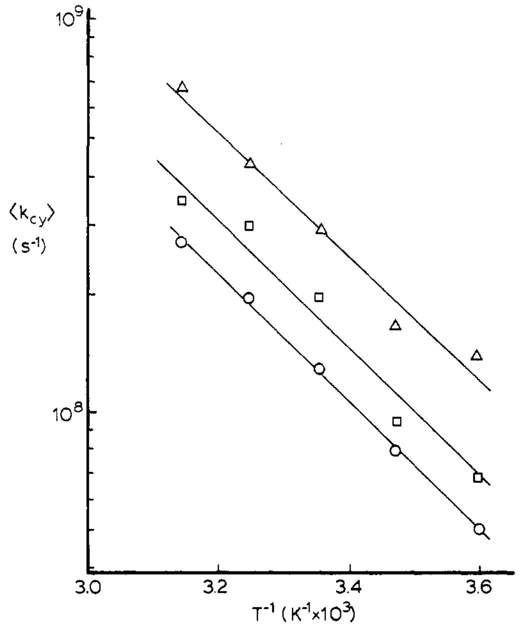


Figure 4. Temperature dependence of the rate constant $\langle k_{cy} \rangle$ for excimer formation in toluene by the cyclizing fraction of chromophore pairs: (○) poly((vinyl acetate)-*co*-0.82% **1a**); (□) poly((vinyl acetate)-*co*-0.92% **1b**); (△) poly((vinyl acetate)-*co*-0.98% **1c**).

In applying Scheme II to the fumarate copolymers we assumed that $k_{MD} \ll k_{DM}$, so that the two populations of monomeric chromophores decay with characteristic times

$$\tau_1 = (k_M + \langle k_{cy} \rangle)^{-1} \qquad (5)$$

and

$$\tau_2 = k_M^{-1} \qquad (6)$$

and the long decay time τ_2' of the excimer species is not necessarily equal to τ_2. Furthermore, in the low-temperature region where $k_{MD} \ll k_D$,

$$\tau_2' = k_D^{-1} \qquad (7)$$

where k_M and k_D are the sum of radiative and nonradiative rate constants for decay of monomer and excimer, respectively. In this mechanism, the monomer and excimer τ_2 values can coincide, and the fluorescence decay behavior can be superficially similar to that expected for the Birks scheme. This is what happens for the naphthylmethyl fumarate copolymer in toluene solution at 25 °C. In other solvents $\tau_2 \neq \tau_2'$ and Scheme II is clearly distinguishable from Scheme I.

In Scheme II the formation of excimer is described by a rate constant $\langle k_{cy} \rangle$. In a system as conformationally complex as these copolymers, there is no reason to suppose $\langle k_{cy} \rangle$ is a homogeneous rate constant; instead it merely represents an average rate constant for cyclization. The fluorescence decay data do not allow us to generate the detailed distribution function of k_{cy}, because there is no statistical need to propose more complex fitting functions to the decay curves than that of eq 1. Instead the average

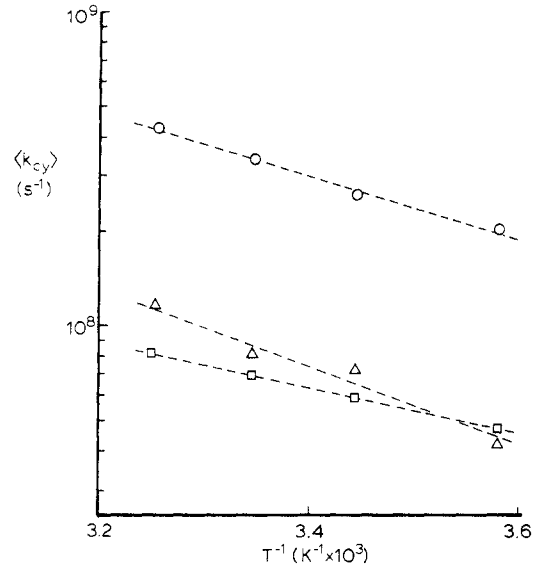


Figure 5. Rate constants $\langle k_{cy} \rangle$ for excimer formation by fumarate ester copolymers with vinyl acetate in Θ-solvent mixtures of methanol and ethanol: (○) poly(VAc-*co*-0.82% **1a**); (□) poly(VAc-*co*-0.92% **1b**); (△) poly(VAc-*co*-0.98% **1c**). The Θ-conditions are 6 °C, 100/0 v/v MeOH/EtOH; 17 °C, 80/20 v/v MeOH/EtOH; 26.5 °C, 60/40 v/v MeOH/EtOH; 34 °C, 50/50 v/v MeOH/EtOH.[20]

value $\langle k_{cy} \rangle$ is determined from the short lifetime of the monomer decay curve by using eq 8. Figure 4 shows the

$$\langle k_{cy} \rangle = 1/\tau_1 - k_M = 1/\tau_1 - 1/\tau_2 \qquad (8)$$

variation with temperature of $\langle k_{cy} \rangle$ for the naphthylalkyl fumarate copolymers in toluene. The temperature dependence of the three systems was the same within experimental error, with activation energies for $\langle k_{cy} \rangle$ of 32 ± 3 kJ mol^{-1}.

An interesting result of the fluorescence decay studies was that the rate constant for cyclization increased in the order **1a** < **1b** < **1c**. The rate of cyclization was highest for the copolymer with the greatest distance between the two naphthalene chromophores. The reason that the ratio I_D/I_M of excimer to monomer steady-state fluorescence intensities varied in the opposite order with chain length was that the fraction of excited monomers which proceeded to the excimer configuration decreased more rapidly in the order **1a** > **1b** > **1c**. In an effort to see whether this phenomenon reflected a unique effect of a good solvent on the distribution of ground-state conformations in these copolymers, the temperature dependence of $\langle k_{cy} \rangle$ was studied for solutions in methanol/ethanol mixtures whose compositions were varied to maintain Θ-solvent conditions for poly(vinyl acetate) at all temperatures.[20] Figure 5 shows the temperature dependence of $\langle k_{cy} \rangle$ for the three copolymers in Θ-solvents. The slope for ln $\langle k_{cy} \rangle$ versus T^{-1} has no direct relationship to an activation energy, because although the chain-expanding power of the mixed solvents remains constant, the viscosity is allowed to vary. In the series of Θ-solvents, the chain length dependence of $\langle k_{cy} \rangle$ is reversed, being highest for the naphthylmethyl fumarate copolymer and considerably lower for the other two copolymers.

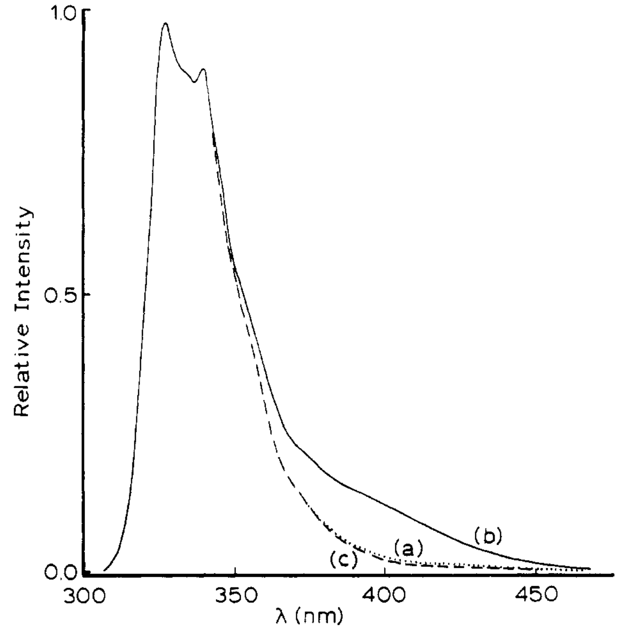


Figure 6. Fluorescence spectra of (a) poly((methyl methacrylate)-*co*-0.34% **2**), (b) dimethylsuccinate **4b**, and (c) succinate **4a** in deoxygenated toluene at 5 °C.

Table III
Analysis of Monomer and Excimer Fluorescence Decays of Bis(1-naphthylmethyl) Itaconate Copolymers in Toluene at 25 °C

copolymer	λ_{em}, nm	A_1/A_2	τ_1; τ_2, ns	f_1	χ_R^2
P(styrene-*co*-1.14% **2**)	337	0.075	6.2; 40.8	0.07	1.05
	430	−0.516	11.5; 45.6		1.07
P(MMA-*co*-0.34% **2**)	340	0.183	7.5; 42.3	0.16	1.09
	430	−0.459	13.2; 53.2		1.12

Comparison with Copolymers of Bis(1-naphthylmethyl) Itaconate (2). Figure 6 shows the fluorescence spectrum of poly(MMA-*co*-0.34% **2**) in nitrogenated toluene. The extent of excimer formation in this copolymer is an order of magnitude less than for the naphthylmethyl fumarate copolymer, even though the chromophores are separated by the same number of bonds. The relative intensity of the excimer fluorescence is almost too weak to measure in the steady-state spectrum. That excimer formation does indeed occur is shown by the fluorescence decay curve recorded at 430 nm, which grows in gradually, with a rise time of about 10 ns. Table III lists representative decay parameters for the emission at 340 and 430 nm. Both monomer and excimer decays are biexponential. The agreement between the monomer and excimer τ_1 values is poor, but this is attributed to the very small preexponential factor for the short-lived monomer decay component, which results in a large error for τ_1 measured at 340 nm. It is significant that values of $\langle k_{cy} \rangle$ calculated for the itaconate and fumarate copolymers are very similar, but the fraction f_1 of cyclizing ground-state conformations is much lower for the itaconate ester copolymer. The effect of the different mode of attachment of the side chains in the itaconate ester copolymer is not to decrease chromophore mobility but to decrease the fraction of ground-state conformations which can reach the excimer configuration during the 40-ns fluorescence lifetime.

Comparison with Small-Molecule Model Compounds. Figure 6 compares the fluorescence spectra of the bis(1-naphthylmethyl) esters of succinic and *meso*-2,3-dimethylsuccinic acid in ethanol at 5 °C. The succinate **4a** shows only monomer emission, whereas the dimethylsuccinate **4b** also shows very weak excimer emission. In an earlier publication it was stated that compound **4b** showed no measurable excimer emission in THF at 25 °C.[4] The reason for the apparent discrepancy is shown in Figure 7, which illustrates the temperature-dependence of the ratio I_D/I_M of the 420-nm emission to the 326-nm emission intensity. By 25 °C this ratio decreases to a value indistinguishable from that of the succinate ester **4a**. The

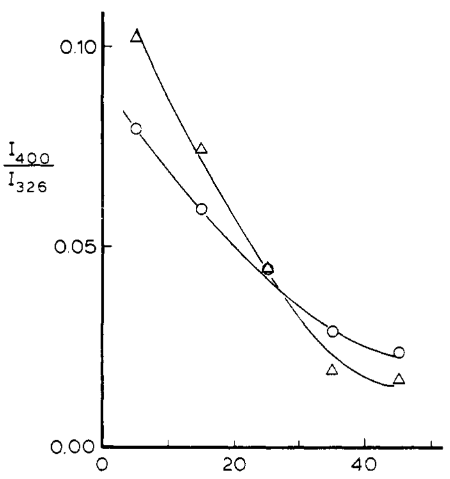


Figure 7. Variation of ratio of intensities of 400- and 326-nm emission for dimethylsuccinate **4b**: (○) solutions in toluene; (△) solutions in ethanol.

Table IV
Temperature Dependence of the Fluorescence Lifetime τ of Bis(1-naphthylmethyl) Succinate (4a)

	τ, ns			τ, ns	
T, °C	in toluene	in ethanol	T, °C	in toluene	in ethanol
5	42.0	42.2	35	39.0	35.4
15	40.5	40.2	45	37.9	33.3
25	39.9	37.4			

decrease in the ratio I_D/I_M could arise either from a more pronounced temperature-dependence for k_D than for k_M or from excimer dissociation at higher temperature.[5] Table IV lists the temperature dependence of the fluorescence lifetime of compound **4a**. The decrease in τ with temperature for compound **4a** cannot be attributed to a homogeneous intramolecular quenching process because the same temperature dependence is shown by compounds such as 1-naphthylmethyl acetate which contain a single chromophore. For compound **4a** k_M increases by factors of 1.1 and 1.26 in toluene and ethanol over a 40 °C range. In contrast to the modest temperature dependence of k_M indicated by the results of Table IV, k_D determined according to eq 7 for the copolymer of vinyl acetate with bis(1-naphthylmethyl) fumarate increases by a factor of 2.1 in alcohol solvent mixtures between 6 and 34 °C. In order to detect weak excimer emission more readily, fluorescence studies were conducted on ethanol solutions well below room temperature. Of the six model compounds studied, only compound **4b** and the *trans*- and *cis*-cyclohexanedicarboxylates **5a** and **5b** showed measurable excimer fluorescence in ethanol at 5 °C. Table V lists data from the analysis of the monomer and excimer decay curves of these compounds, as well as single-exponential decay times for the compounds which show no measurable excimer formation. The average rate constant $\langle k_{cy} \rangle$ for excimer formation is roughly four times higher for the model compounds than for the bis(1-naphthylmethyl) fumarate and itaconate copolymers. The fraction f_1 of cyclizing chromophore pairs is comparable for the three model compounds and the itaconate copolymers but significantly lower than for the fumarate copolymer.

All three of the model compounds which form excimers would be expected to have major proportions of ground-state conformations having approximately 60° dihedral angles around the central C–C bond. Rotation around this central bond is slow on the nanosecond timescale, as shown by the incomplete coalescence of the cyclohexyl ring H signals in the ^{1}H NMR spectra recorded at room temperature. The absence of excimer formation in the cyclobutane derivative **6** and the norbornenyl diester **7**, having dihedral angles of 120° and 0°, respectively, suggests that a strain-free central dihedral angle of 60° is necessary for the creation of a measurable cyclizing population.

Table V
Analysis of Fluorescence Decays of Small-Molecule Bis(1-naphthylmethyl) Esters in Ethanol at 5 °C

compd	λ_{em}	A_1/A_2	τ_1; τ_2, ns	f_1	χ_R^2
4a	340	0.000	42.2[a]	0.00	1.25
4b	340	0.136	2.4; 40.8	0.12	1.14
4b	412	−0.420	2.7; 40.8		1.00
5a	326	0.174	2.2; 39.7	0.15	1.11
5a	430	−0.834	0.9; 38.6		1.19
5b	325	0.139	3.5; 37.8	0.12	1.19
5b	430	−0.645	1.0; 35.1		1.26
6	330	0.000	40.5[a]	0.00	1.10
7	337	0.000	33.4[a]	0.00	1.16

[a] Single-exponential decay.

The results for the itaconate ester copolymers and the model compounds show that it is not possible to assign the kinetically isolated or proximate chromophore pairs to particular diastereomers or conformations at the central C–C bond. Even the cyclohexane derivatives, which on a nanosecond timescale have only a single conformation at this C–C bond, show kinetically inhomogeneous excimer formation. Instead the difference between the fumarate and itaconate copolymers lies in the degree to which the main chain blocks access of the chromophores to different regions of space.

Conclusions

In copolymers containing small amounts of 1-naphthylalkyl fumarates or itaconates we were able to study excimer kinetics without the complication of energy migration. Despite this major simplification, the kinetic behavior of these intramolecular excimer systems remained complex. In contrast to end-to-end cyclization of long chains,[3] side-chain cyclization to form medium-sized rings was kinetically inhomogeneous. The majority of ground-state conformations were unable to cyclize to the excimer configuration during monomer excited-state lifetimes of from 30 to 70 ns. That even such reduced systems still show complex excimer kinetics suggests that research aimed at using excimer fluorescence to probe other physical phenomena should proceed with caution. The kinetic inhomogeneity in these bis(1-naphthylalkyl) esters is also in contrast to excimer formation in compounds where the chromophores are separated by a smaller number of flexible bonds, such as the 1,3-diarylpropanes and many of the diastereomeric 2,4-diarylpentanes.[18-20]

The six model compounds and the two naphthylmethyl diester copolymers form a series in which all chromophores are separated by eight atoms and the only differences are in the substituents at the central C–C bond. This series of bichromophoric naphthalene derivatives nevertheless showed major differences in the fraction of cyclizing conformations and in the rate of excimer formation.

Scheme II, which describes inhomogeneous excimer kinetics in terms of slowly interconverting populations of monomer chromophores, was consistently useful in describing the photophysics of the copolymers. The existence of kinetically isolated chromophores is likely to be a widespread phenomenon in polymer photophysics. However, depending on the magnitude of k_1 and k_{-1}, there should be an entire spectrum of behavior described by Scheme II, from true kinetic isolation for small k_1 and k_{-1}

to a complex distribution of quenching rates for k_1 and k_{-1} on the order of k_{DM},[21] to collapse to Scheme I for values of k_1 and k_{-1} which are large relative to k_{DM}.

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Registry No. (**1a**)(VAc) (copolymer), 83561-73-3; (**1b**)(VAc) (copolymer), 110864-45-4; (**1c**)(VAc) (copolymer), 110864-46-5; **2**, 110864-47-6; (**2**)(MMA) (copolymer), 115797-69-8; (**2**)(styrene) (copolymer), 110864-48-7; (**3**)(VAc)(dimethyl furmarate) (copolymer), 115797-68-7; **4a**, 83561-76-6; **4b**, 83572-93-4; **5a**, 115826-84-1; **5b**, 115797-43-8; **6**, 115797-42-7; **7**, 115797-44-9; itaconyl chloride, 1931-60-8; 1-naphthylmethanol, 4780-79-4; *trans*-cyclohexane-1,2-dicarboxylic anhydride, 14166-21-3; *cis*-5-norbornene-*endo*-2,3-carboxylic anhydride, 129-64-6; *cis*-hexahydrophthalic anhydride, 13149-00-3.

References and Notes

(1) Winnik, M. A. *Chem. Rev.* **1981**, *81*, 491.
(2) Mita, I.; Horie, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1987**, *C27*, 91.
(3) Winnik, M. A. *Acc. Chem. Res.* **1985**, *18*, 73.
(4) Holden, D. A.; Guillet, J. E. *Macromolecules* **1982**, *15*, 1475.
(5) Holden, D. A.; Guillet, J. E. *Dev. Polym. Photochem.* **1980**, *1*, 27.
(6) Frank, C. W.; Semerak, S. N. *Adv. Polym. Sci.* **1984**, *54*, 31.
(7) Cuniberti, C.; Perico, A. *Eur. Polym. J.* **1980**, *16*, 887.
(8) Cuniberti, C.; Musi, L.; Perico, A. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 265.
(9) Tazuke, S.; Yuan, H. L. *Polym. J. (Tokyo)* **1982**, *14*, 215.
(10) Tazuke, S.; Yuan, H. L. *Macromolecules* **1984**, *17*, 1878.
(11) Holden, D. A.; Gray, J. B.; McEwan, I. *J. Org. Chem.* **1985**, *50*, 866.
(12) De Schryver, F. C.; Demeyer, K.; Van der Auweraer, M.; Quanten, E. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 93.
(13) Holden, D. A.; Corey, L.; Kovarova, J.; Guillet, J. E. *Macromolecules* **1986**, *19*, 1180.
(14) Birks, J. B.; Dyson, D. J.; Munro, I. H. *Proc. R. Soc. London, A* **1963**, *275*, 575.
(15) Holden, D. A.; Wang, P. Y.-K.; Guillet, J. E. *Macromolecules* **1980**, *13*, 295.
(16) Avouris, P.; Kordas, J.; El-Bayoumi, M. A. *Chem. Phys. Lett.* **1974**, *26*, 373.
(17) De Schryver, F. C.; Moens, L.; Van der Auweraer, M.; Boens, N.; Monnerie, L.; Bokobza, L. *Macromolecules* **1982**, *15*, 64.
(18) Collart, P.; Toppet, S.; De Schryver, F. C. *Macromolecules* **1987**, *20*, 1266.
(19) De Schryver, F. C.; Collart, P.; Goedeweeck, R.; Ruttens, F.; Lopez Arbelao, F.; Van der Auweraer, M. *ACS Symp. Ser.* **1987**, *No. 358*, 186.
(20) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; p IV-167.
(21) Ghiggino, K.; Roberts, A. J.; Phillips, D. *Adv. Polym. Sci.* **1981**, *40*, 69.

Intermolecular Excimer Kinetics of Methyl Pyrenebutyrate in Polystyrene/Toluene Mixtures[1]

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ABSTRACT: The kinetics of excimer formation are examined for methyl 4-(1-pyrene)butyrate (**1**) in polystyrene/toluene mixtures containing up to 50% polystyrene by weight. By virtue of a convolution analysis of the fluorescence decay data, we recover the transient component b of the diffusion-controlled excimer formation rate coefficient, $k_1(t) = a(1 + bt^{-1/2})$. The steady-state value a was obtained by using a normal Birks' analysis of the decay curves. From these values, the diffusion coefficient of **1** is obtained as a function of polymer concentration, c. The dependence of D on c fits the simple obstacle model for diffusion.

Introduction

Pyrene excimer formation, first observed by Förster and Kasper,[3] has become a classic reaction for studying the influence of environment on diffusion-controlled processes. For example, excimer formation from pyrene dissolved in lipid membranes has been used to monitor their fluidity changes.[4] Intramolecular excimer formation in chain molecules containing pyrene groups at both ends provides a means of studying molecular and macromolecular cyclization dynamics.[5]

Here we examine a different kind of problem. We are interested in the influence of inert polymeric additives on the rate of diffusion-controlled reactions in solution. The presence of the polymer as a solute has a large effect on the bulk solution viscosity but a much smaller effect on small molecule diffusion. This influence is expressed via a change in the microscopic friction coefficient which retards diffusion. In the "obstacle model",[6] the polymer chains serve as impediments along diffusion trajectories, and in the "free volume model",[7] they reduce the free volume accessible for molecular motion.

Our objective in these experiments is not to provide any kind of definitive test of these models. These models treat self-diffusion coefficients, D_s, which are accessible through pulsed gradient NMR measurements[8] and other methods.[9] Here, we are interested in diffusion-controlled reactions and, in particular, the transient term associated with the time evolution of the distribution function of the reactants. From this data, we can extract the mutual diffusion coefficient, D_m, of the reactants and the effective reactive distance, R', characterizing pyrene excimer formation. R' varies inversely with D_m (vide infra) and becomes equal to the intrinsic reactive distance in the limit of $D_m \rightarrow 0$. Adding unlabeled polymer is a convenient way of varying D_m for the reacting species while keeping the temperature constant.

These data become available through a novel method we developed for fluorescent decay curve analysis of two interrelated fluorescent states, here excimer and excited monomer. In this case, the two decay curves are connected