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Effects of Polymer Structure on Singlet Energy Migration in Poly(2-naphthylalkyl methacrylates)

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ABSTRACT: The effects of the pendant group structure on intramolecular singlet energy migration and excimer formation in poly(2-naphthylmethyl methacrylate) (PNMMA), poly[1-(2-naphthyl)ethyl methacrylate] (P-1-NEMA), poly[2-(2-naphthyl)ethyl methacrylate] (P-2-NEMA), and poly[3-(2-naphthyl)propyl methacrylate] (P-3-NPMA) were examined by fluorescence quenching experiments in deaerated 2-methyltetrahydrofuran. Introduction of steric hindrance near the naphthalene chromophore (P-1-NEMA) or of a polymethylene bridge between the polymer main chain and the naphthalene chromophore (P-2-NEMA and P-3-NPMA) was found to reduce excimer formation but retard energy migration as well, suggesting that more specific chromophore arrangement along the polymer chain is desirable for selective promotion of energy migration and suppression of excimer formation. In film, these polymers exhibited little monomer emission; extensive emission from excimer (PNMMA, P-2-NEMA, and P-3-NPMA) or that from a second-excimer-like trap (P-1-NEMA) indicates efficient trapping of excitation energy at these trap sites. The formation of the higher energy trap in P-1-NEMA film is discussed in terms of the conformational constraints, i.e., increased chromophore separation and chain rigidity, imposed by the pendant group structure.

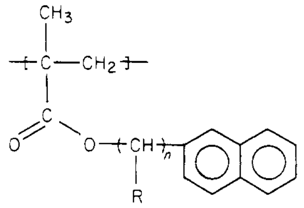
Introduction

Most vinyl polymers have random-coil conformations in solution but possess the characteristic of an imperfect one-dimensional organic crystal: light energy can migrate, in an exciton-like manner, through the chromophores attached to the polymer backbone.[1-3] One can thus take advantage of this in harvesting and transferring light energy to the energy acceptor, or to the reaction center, copolymerized at appropriate intervals or adsorbed onto the polymer by hydrophobic, electrostatic, or hydrogen-bonding interaction. As micelles and vesicles have recently been studied as reaction systems for photochemical reactions simulating the initial stages of photosynthesis,[4-6] polymers have the potential of being similarly exploited.

Chromophore aggregates in general, however, easily undergo concentration quenching often involving formation of an excimer between excited and nearby ground-state chromophores, which acts as an energy trap and thereby suppresses energy migration.[7-10] As in micelles and vesicles, mutual chromophore separation, orientation, and mobility are apparently important in controlling the photophysics of vinyl aromatic polymers. For example, Fox et al. report that practically no energy migration nor excimer formation occurs in alternating copolymers such as poly(2-naphthyl methacrylate-*alt*-styrene), suggesting that chromophores separated by more than one monomer residue are virtually isolated from one another.[11] Even with homopolymers such as poly(1-naphthylmethyl methacrylate), partial chromophore isolation due to steric causes has been suggested by Guillet et al.[12] Phillips et al. similarly discuss chromophore isolation in homopolymers in solution, but evaluating the preexponential factors of the triple-exponential fitting of the decay data, they suggest that chromophore isolation is not as important in poly(2-vinylnaphthalene) as in poly(1-vinylnaphthalene) or in poly(1-naphthyl methacrylate).[13,14]

We have previously observed that introduction of steric hindrance (e.g., poly(2-*tert*-butyl-6-vinylnaphthalene)) or introduction of a polymethylene bridge between the polymer main chain and the naphthalene chromophore (e.g., poly[3-(2-naphthyl)propyl methacrylate]) markedly suppresses excimer-forming interactions among the naphthalene chromophores.[15,16] These studies as well as those by other workers[12-14] prompted us to examine the effect of the polymer structure on energy migration and excimer formation in poly(2-naphthylalkyl methacrylates) with varying pendant group structure; quenching experiments on steady-state fluorescence, apart from the more sophisticated transient decay measurements, were found to provide pertinent information on the structural dependence of energy migration and excimer formation in these methacrylate polymers.

The emission characteristics of the films prepared from these polymers are also discussed in relation to the polymer conformation imposed by the pendant group structure.



R = H, n = 1: PNMA
R = H, n = 2: P-2-NEMA
R = H, n = 3: P-3-NPMA
R = CH_3, n = 1: P-1-NEMA

Experimental Section

Materials. The monomer precursors, i.e., 2-naphthylmethanol, 1-(2-naphthyl)ethanol, 2-(2-naphthyl)ethanol, and 3-(2-naphthyl)propanol, were synthesized according to methods reported in the literature.[17] The monomer and the monomeric model compounds were prepared from the above alcohols and methacryl or acetyl chloride and purified by recrystallization from *n*-hexane or by vacuum distillation, their structures being confirmed by ^{1}H NMR spectroscopy: 2-naphthylmethyl methacrylate (NMMA), mp 64–65.5 °C; 2-naphthylmethyl acetate (NMAc), mp 49.5–51.5 °C; 1-(2-naphthyl)ethyl methacrylate (1-NEMA), mp 49–50 °C; 1-(2-naphthyl)ethyl acetate (1-NEAc), bp 108–110 °C (0.35 mmHg); 2-(2-naphthyl)ethyl methacrylate (2-NEMA), 108–110 °C (0.2 mmHg); 2-(2-naphthyl)ethyl acetate (2-NEAc), bp 101–103 °C (0.2 mmHg); 3-(2-naphthyl)propyl methacrylate (3-NPMA), bp 134–137 °C (0.15 mmHg); 3-(2-naphthyl)propyl acetate (3-NPAc), bp 117–119 °C (0.2 mmHg).

Polymerization. Homopolymerization and copolymerization with methyl methacrylate (MMA) were carried out in benzene at 60 °C, using azobis(isobutyronitrile) as a radical initiator. The polymers precipitated in *n*-hexane were subsequently purified by repeated precipitation from benzene into *n*-hexane. The

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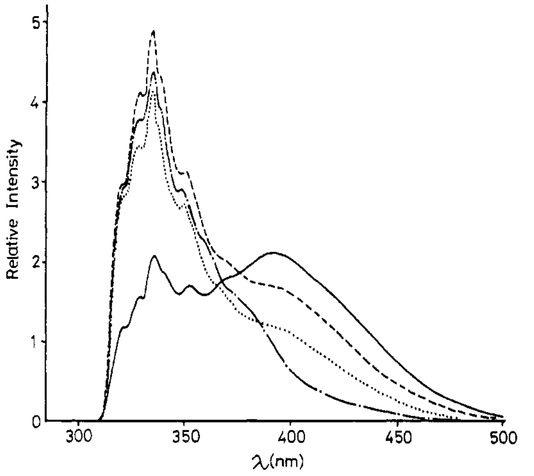

Figure 1. Fluorescence spectra of homopolymers in 2-methyltetrahydrofuran at 20 °C. Excitation wavelength: 304 nm (optical density, 0.16). (—) PNMMA; (-·-) P-1-NEMA; (---) P-2-NEMA; (···) P-3-NPMA.

compositions of the copolymers were determined from the 317-nm absorption of the 2-naphthylalkyl methacrylate residue in 2-methyltetrahydrofuran using the molar extinction coefficient of the corresponding monomeric model. The mole percent contents of 2-naphthylalkyl methacrylate in the copolymers were found to be similar to those in the polymerization feed (3–4%). The number-average molecular weights of the polymers were determined at 37 °C with a Hewlett-Packard high-speed membrane osmometer Model 501 with a Sartorius SM 11539 as a membrane and toluene as solvent.

Measurements. Fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrometer, with 2-methyltetrahydrofuran as solvent. The solvent was fractionally distilled from lithium aluminum hydride just before use in fluorescence measurements. Nitrogen gas was bubbled to remove oxygen dissolved in the solvent. All solutions were prepared to have an optical density of 0.16 at the excitation wavelength (304 nm). Identical excitation and recording conditions were employed for all the samples. (Biacetyl, used as a quencher, was purified by fractional distillation.)

The film samples were prepared by solvent casting from benzene (ca. 5 wt % in polymer concentration) on a quartz plate, followed by drying in vacuo to constant weights. The emission spectra of the films were taken using front-side illumunation with excitation at 304 nm.

Results and Discussion

Fluorescence Spectra. The absorption spectra of the homopolymers in 2-methyltetrahydrofuran are quite similar to those of the copolymers and monomeric model compounds, indicating the absence of ground-state interactions between the neighboring naphthalene chromophores. The fluorescence spectra of the homopolymers and copolymers in deaerated 2-methyltetrahydrofuran are shown in Figures 1 and 2. The copolymers with 3–4 mol % of the naphthalene residue gave only the emission from the conventional excited naphthalene (monomer), whose shape and intensity are nearly identical with those of the corresponding monomeric model; the naphthalene chromophores in the copolymers are thus sufficiently isolated and do not interact with one another. The homopolymers, on the other hand, gave additional broad structureless emission around 400 nm from excited naphthalene dimer (excimer) formed between the neighboring naphthalene chromophores; the intensity of excimer emission relative to that of monomer emission decreases markedly on going from PNMMA to the other homopolymers.

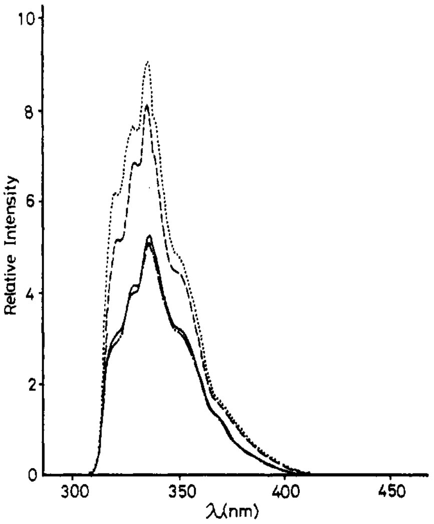

Figure 2. Fluorescence spectra of copolymers in 2-methyltetrahydrofuran at 20 °C. Excitation wavelength: 304 nm (optical density, 0.16). (—) PNMMA-*co*-MMA; (-·-) P-1-NEMA-*co*-MMA; (---) P-2-NEMA-*co*-MMA; (···) P-3-NPMA-*co*-MMA.

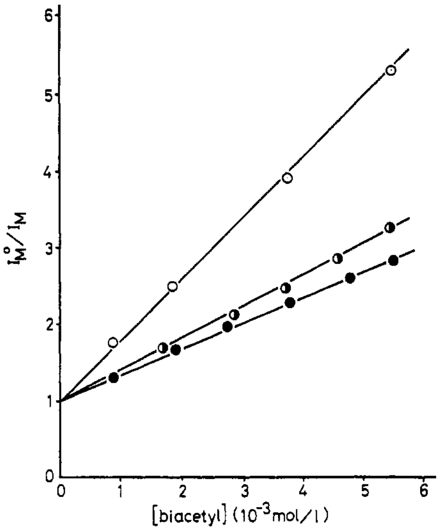

Figure 3. Plot of monomer emission intensity ratio $I_M{}^0/I_M$ against quencher concentration. $I_M{}^0$, emission intensity in the absence of quencher; I_M, emission intensity in the presence of quencher. (●) P-3-NPMA; (◑) P-3-NPMA-*co*-MMA; (○) 3-NPAc.

As seen in Figure 2, the intensity of the monomer emission I_M from the copolymer or that from the monomeric model measured under identical conditions decreases in the order of decreasing polymethylene chain length: P-3-NPMA-*co*-MMA > P-2-NEMA-*co*-MMA > PNMMA-*co*-MMA ≈ P-1-NEMA-*co*-MMA. Similar reduction of the monomer emission intensity has been reported on going from 3-phenylpropyl to 2-phenylethyl and to phenylmethyl esters.[19] The observed decrease in the monomer emission intensity suggests that the shorter polymethylene chain promotes through-space and/or through-bond interactions between the ester group and the excited naphthalene monomer, leading to acceleration of the nonradiative decay of the latter. Similar monomer emission intensities observed with PNMMA-*co*-MMA and P-1-NEMA-*co*-MMA suggest that the methyl group introduced near the naphthalene chromophore does not impose significant steric effects on the above interaction.

Fluorescence Quenching. As shown in Figure 3, the Stern–Volmer plot of monomer emission quenching by biacetyl gave straight lines both for the polymers and for the monomeric models. (I_M and $I_M{}^0$ here denote the monomer emission intensity measured at 336 nm in the presence and in the absence of biacetyl, respectively.) When PNMMA's of varying molecular weights, i.e., $\bar{M}_n$ =

Table I
Stern–Volmer Quenching Constants K_Q and Excited Monomer Lifetimes τ_M of Monomeric Models

sample	K_Q, L·mol^{-1}	τ_M,[a] ns	I_M^{rel}[b]
NMAc	474	30	1
1-NEAc	440	28	0.98
2-NEAc	788	49	1.64
3-NPAc	809	51	1.81

[a] Obtained from $K_Q = k_{QM}\tau_M$ and $k_{QM} = 1.6 \times 10^{10}$ L·mol^{-1}·s^{-1}. [b] Relative monomer emission intensities measured at 336 nm.

2.0×10^5, 1.0×10^5, and 0.24×10^5, were employed, no significant changes in the intensities of monomer and excimer emission nor in the slope of the Stern–Volmer plot K_Q were observed; we may thus neglect the molecular weight dependence in the molecular weight range employed in the present study, i.e., $\bar{M}_n \geq 2.4 \times 10^4$, or $\bar{P}_n$ (degree of polymerization) ≥ 100. Similar results as to the molecular weight independence of the rate parameters have been obtained by Ishii et al. for polystyrene with $\bar{P}_n > 100$.[1]

The straightness of the Stern–Volmer plot observed for the homopolymers suggests that excimers formed in these methacrylate polymers do not dissociate significantly back to excited- and ground-state naphthalene pairs. Excimer/monomer equilibrium, such as that suggested by Birks for small molecules,[18] apparently does not hold in these and other vinyl polymers with pendant aromatic groups.[2,8,20] It is also suggested that chromophore isolation, proposed by Guillet et al. to explain the decay behavior of monomer emission from poly(1-naphthylmethyl methacrylate),[12] does not occur significantly with these polymers. In fact, Phillips et al. suggest, by fitting a triple-exponential function to the fluorescence decay curves, that both excimer dissociation and chromophore isolation are probably not as important in poly(2-vinylnaphthalene) as in poly(1-vinylnaphthalene) or in poly(1-naphthyl methacrylate).[13] We may thus rationalize our observation and those made by others[12,13] by assuming that 2-naphthyl chromophores situated as nearest neighbors along the polymer chain are generally not geometrically isolated from one another due to the influence of the geometry of the chromophore with respect to the polymer backbone and that excimers formed between them are stable and do not dissociate appreciably within the excimer lifetime. The above assumption needs to be tested rigorously, but it is consistent with the lack of solvent effect on excimer formation in poly(2-naphthyl methacrylate) as opposed to that in poly(1-naphthyl methacrylate);[10,11] the nonnearest chromophore interactions appear not to compete with the facile nearest-neighbor interactions in the former polymer.[21]

We may then put $K_Q = k_{QM}\tau_M$, where k_{QM} and τ_M denote the second-order rate constant of excited monomer quenching by biacetyl and the lifetime of the excited naphthalene monomer, respectively.[1] The K_Q values of the monomeric models and those of the polymers are given in Tables I and II.

The rate constant k_{QM} of the diffusion-controlled quenching process between the monomeric model and biacetyl is given as

$$k_{QM} = 4\pi N'(D_M + D_B)pR(1 + pR\{(D_M + D_B)\tau_M\}^{-1/2}) \quad (1)$$

where N' is Avogadro's number divided by 1000, D_M and D_B are the diffusion coefficient of the monomeric model and that of biacetyl, respectively, p is the quenching probability per molecular encounter, and R is the interaction radius. The transient term $pR\{(D_M + D_B)\tau_M\}^{-1/2}$ can be neglected here since its contribution to the overall quenching is expected to be less than 5% under the present conditions, where neither $D_M + D_B$ nor τ_M is very small. From the solvent viscosity dependence of k_{QM} reported by Birks et al. for quenching of naphthalene fluorescence by biacetyl[23] and the data of Sandros on quenching of naphthalene and triphenylene fluorescence,[24] we estimated k_{QM} to be 1.6×10^{10} L·mol^{-1}·s^{-1} in 2-methyltetrahydrofuran ($\eta = 0.49$ cP, 20 °C). Using this value and K_Q, we estimated the monomer lifetime of each monomeric model (Table I). (In the last column of Table I are listed the relative intensities of monomer emission from the monomeric models, which agree reasonably well with the ratios of the monomer lifetimes obtained above (within ±3%), suggesting that the radiative lifetime τ_{FM} is roughly common to the model compounds: $\tau_{FM} = \tau_M/\phi_{FM}$ = constant and thus $\tau_M \propto I_M$.) The monomer lifetimes of the copolymers and homopolymers were then estimated from the relative monomer emission intensities and the monomer lifetimes of the corresponding monomeric models assuming $\tau_M/(\tau_M)_{\mathrm{model}} = I_M/(I_M)_{\mathrm{model}}$ (Table II).

In Figure 4 is shown the relationship between the Stern–Volmer constants K_Q and the monomer lifetimes τ_M estimated from the relative monomer emission intensities and the monomer lifetime of NMAc, i.e., 30 ns. Good straight lines obtained indicate that the monomeric models and the copolymers respectively have common k_{QM}; the slope for the latter being nearly half that for the former indicates that the diffusion of the polymer-bound naphthalene chromophore is negligible compared with that of biacetyl; i.e., $D_M \simeq 0$. It also suggests that steric effects of the polymer segments are not significant and that no preferential adsorption of biacetyl onto polymer occurs in the 2-methyltetrahydrofuran solutions.

The k_{QM} values of the homopolymers and copolymers obtained from $k_{QM} = K_Q/\tau_M$ are listed in Table II.

Table II
Quenching of Monomer Emission by Biacetyl

sample[a]	$\bar{M}_n \times 10^{-5}$ [b]	K_Q, L·mol^{-1}	$\tilde{\tau}_M$,[c] ns	$10^{-10}k_{QM}$, L·mol^{-1}·s^{-1}
PNMMA-*co*-MMA (0.04)	1.5	228	30	0.75
PNMMA	2.0	225	12	1.81
P-1-NEMA-*co*-MMA (0.03)	1.4	252	29	0.86
P-1-NEMA	0.5	304	25	1.23
P-2-NEMA-*co*-MMA (0.04)	2.0	345	49	0.71
P-2-NEMA	3.6	344	30	1.17
P-3-NPMA-*co*-MMA (0.03)	1.5	408	48	0.86
P-3-NPMA	0.6	345	23	1.47

[a] The number in parentheses indicates the mole fraction of the naphthalene residue in the copolymer. [b] Determined osmometrically at 37 °C with toluene as solvent. [c] Obtained from monomer emission quantum yield relative to that of corresponding monomeric model.

Table III
Parameters for Energy Migration in Homopolymers

sample	$10^6\Lambda$, cm^2 s^{-1}	r_s, Å	$10^{-10}k_{mig}$, s^{-1}	$\bar{N}$	$\bar{N}^{1/2}$	$\bar{L}$, Å	$10^{-7}k_{DM}$, s^{-1}
PNMMA	34	3.6	5.2	650	25	92	4.8
P-1-NEMA	11	4.8	0.95	235	15	74	0.65
P-2-NEMA	15	4.5	1.5	440	21	95	1.4
P-3-NPMA	17	4.3	1.8	420	20	93	2.2

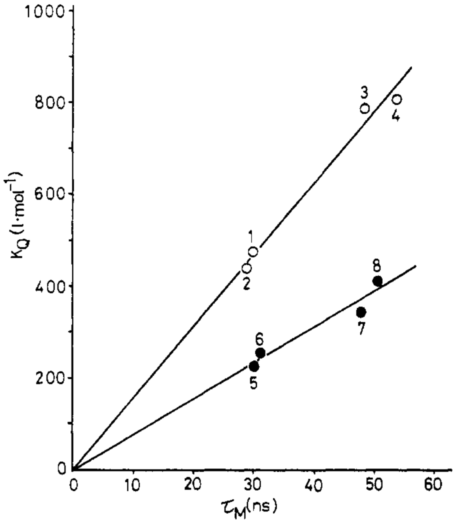

Figure 4. Plot of Stern-Volmer quenching constant K_Q against excited monomer lifetime τ_M: (1) NMAc; (2) 1-NEAc; (3) 2-NEAc; (4) 3-NPAc; (5) PNMMA-*co*-MMA; (6) P-1-NEMA-*co*-MMA; (7) P-2-NEMA-*co*-MMA; (8) P-3-NPMA-*co*-MMA.

Energy Migration. The transient term being neglected, the rate constant for the quenching process involving both molecular diffusion and energy migration is given as

$$k_{QM} = 4\pi N'(D_M + D_B + \Lambda)pR \qquad (2)$$

where Λ is the energy migration coefficient having the same dimension as the diffusion coefficients. Assuming pR to be common to the homopolymer and the corresponding copolymer and putting $D_M = \Lambda = 0$ for the copolymer and $D_M = 0$ for the homopolymer, we have Λ for the homopolymer as

$$\Lambda = \{(k_{QM})_{homo}/(k_{QM})_{co} - 1\}D_B \qquad (3)$$

where homo and co denote homopolymer and copolymer, respectively. From the Stokes-Einstein relationship $D = kT/4\pi\eta r$,[25] where η is the solvent viscosity and r is the molecular radius of the diffusing species, D_B is estimated to be 24×10^{-6} cm^2·s^{-1} ($r_B = 2.7$ Å and $\eta = 0.49$ cP). The Λ values thus obtained are listed in Table III. Energy migration is found to decrease in the order PNMMA > P-3-NPMA ≥ P-2-NEMA > P-1-NEMA. PNMMA has a Λ value approximately 1.5 times as large as the diffusion coefficient of a low-molecular-weight species, while others have Λ only about half as large as that value.

If we assume that energy migration involves nearest-neighbor naphthalene chromophores along the polymer chain, we can evaluate the rate constant k_{mig} from the one-dimensional migration model:[18]

$$k_{mig} = 2\Lambda/r_s^2 \qquad (4)$$

where r_s is the mean separation of the nearest-neighbor chromophores. When energy migration is assumed to involve a series of random-walk steps, each occurring with a probability defined by the Förster expression,[18] we also have

$$k_{mig} = (R_0/r_s)^6/\tau_M \qquad (5)$$

where R_0 is the critical distance at which migration and deactivation of excitation energy proceed with equal probabilities; R_0 is given as a function of the refractive index of the solvent, the relative orientation of the donor and acceptor, the emission quantum yield of the donor, and the spectral overlap of the acceptor absorption and donor emission, the donor and acceptor being excited- and ground-state naphthalene chromophores, respectively. From eq 4 and 5, we have

$$r_s = \{(R_0^6/\tau_M)/2\Lambda\}^{1/4} \qquad (6)$$

R_0^6/τ_M is constant for a given donor/acceptor pair in a given solvent; its value for isothermal energy transfer between randomly oriented excited- and ground-state 2-alkylnaphthalene chromophores in tetrahydrofuran whose refractive index is similar to that of 2-methyltetrahydrofuran[26] is reported to be 1.2×10^{-34} cm^6·s^{-1}.[27] Using this value and the respective Λ, we estimated r_s for each homopolymer (Table III). Here we assumed random orientation of the nearest-neighbor chromophores as they are separated by ten bonds or more. This assumption, however, may not be valid particularly for PNMMA and P-1-NEMA, where steric repulsion among the adjacent naphthyl and/or methyl groups may disturb the random orientation of the chromophores; as a result, we may have either overestimated or underestimated r_s. The r_s values obtained, however, are reasonable when the syndiotactic polymer models are examined, suggesting that the migration model based on the Coulombic interaction between the nearest-neighbor chromophores is adequate for the energy migration through the pendant naphthalene chromophores. From the r_s values and eq 4, k_{mig} is evaluated and listed in Table III. The average number of energy hopping $\bar{N}$ during the monomer lifetime, $\bar{N} = k_{mig}\tau_M$, is also given in Table III. All these parameters indicate that energy migrates most efficiently in PNMMA. The mean migration length $\bar{L}$ traveled by the excitation energy during its lifetime, when evaluated from the one-dimensional random-walk model $\bar{L} = (2\Lambda\tau_M)^{1/2}$ ($=r_s\bar{N}^{1/2}$), however, indicates that excitation energy migrates over nearly equal distances in PNMMA, P-2-NEMA, and P-3-NPMA; the decrease in Λ is thus compensated by the increase in excitation lifetime.

From the preceding section it is evident that the decrease in monomer lifetime on going from the copolymer to the homopolymer is the result of an additional nonradiative decay process in the latter, i.e., excimer formation or self-quenching interaction. When the rate of excimer formation k_{DM} is evaluated from the difference of the reciprocal of the monomer lifetime between the homopolymer and copolymer (Table III)[28] and plotted against k_{mig}, we obtain a nearly linear relationship with a slope of ca. 10^3 (Figure 5): k_{DM} decreases almost linearly with k_{mig}. It is thus suggested that with the present series of polymers the structural dependence is nearly common to excimer

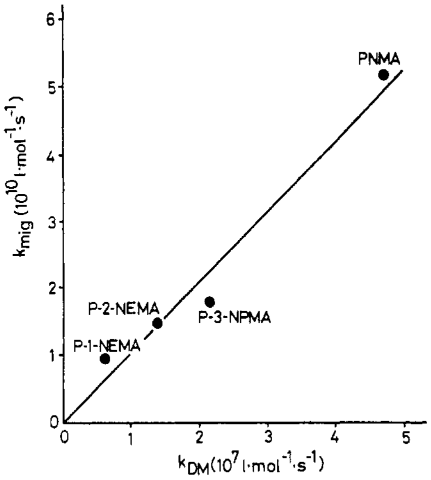

Figure 5. Plot of the rate constant of energy migration k_{mig} against that of excimer formation k_{DM}.

formation and energy migration: in each homopolymer the latter proceeds ca. 10^3 times faster than the former.

Excimers are mainly formed by bond rotations of the side group and polymer backbone to bring the excited and nearby ground-state chromophores to a sandwich-like arrangement within a distance of ca. 3.5 Å,[29] and thus the rate of its formation depends not only on the initial chromophore separation but also on the strain involved in attaining such arrangement.[30] Energy migration, on the other hand, depends mainly on the relative chromophore separation, if the assumption of random orientation holds, since each step of energy migration appears to proceed faster than the segmental movement of the polymer. The results obtained in the present study indicate then that in these methacrylate polymers the structural factor involved in excimer formation is directly related with that determining the chromophore separation. That is, suppressed excimer formation does not simply lead to larger energy migration, contrary to the expectation put forward by Webber et al.[31]

As shown in Table III, the average number of naphthalene chromophores traveled by a random-walk energy migration, $\bar{N}^{1/2}$, indicates that in PNMMA, for example, energy travels over ca. 25 naphthalene chromophores during its lifetime and thus reaches an energy acceptor efficiently if the latter is present in every 25 naphthalene chromophores along the polymer chain. This, we believe, shall be taken into account in using these and similar polymers for light-harvesting and -sensitizing systems for photochemical reactions.

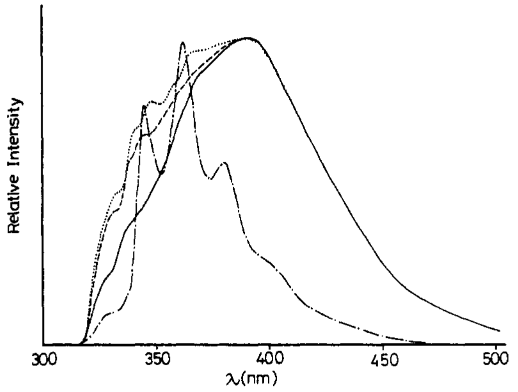

Figure 6. Fluorescence spectra of homopolymer films at 20 °C. Excitation wavelength: 304 nm. (—) PNMMA; (-·-) P-1-NEMA; (---) P-2-NEMA; (···) P-3-NPMA.

Finally, brief comments are made on the emission characteristics of the films prepared from these methacrylate polymers. As shown in Figure 6, films of PNMMA, P-2-NEMA, and P-3-NPMA exhibited fluorescence mostly consisting of excimer emission.[32] As has been suggested for other aromatic polymers, excimers appear to be formed efficiently in film via intra- and/or intermolecular energy migration to naphthalene pairs suitably oriented for excimer formation, whose population is determined by the thermodynamic equilibrium of chain conformations at the temperature of film preparation.[33] In contrast with the other polymers, P-1-NEMA showed a remarkably different emission which appears in the wavelength region intermediate of monomer and excimer emissions. A similar emission has been observed by Frank et al. with poly(2-vinylnaphthalene) in a thermodynamically good polymer matrix, i.e., poly(isopropyl or *sec*-butyl methacrylate);[34] while admitting that the emission differs considerably from that from the excited monomer, they nevertheless assigned it to monomer fluorescence and concluded that extensive interpenetration of the guest and host polymer chains increases the chromophore separation and thereby suppresses excimer formation in a thermodynamically good host matrix. Irie et al. also observed a similar emission from poly(1- or 2-vinylnaphthalene) in a thermodynamically poor solvent, i.e., cyclohexane;[35] observing a new absorption band in the longer wavelength region and the mirror symmetry relationship between the absorption and emission spectra, they attributed the emission to that from a "second excimer" similar to that proposed by Johnson for poly(*N*-vinylcarbazole).[36] Johnson has suggested that stabilization of the second excimer in both excited and ground states comes from relatively long-distance charge resonace interactions of the partially eclipsed chromophores and rationalized its formation in poly(*N*-vinylcarbazole) in terms of the conformational restraints imposed by the stiff polymer chain having the bulky carbazole groups: since the binding energy of this species is expected to be low compared with that of excimer, strict geometric requirements need to be fulfilled for its formation and subsequent emission thereof prior to dissociation or conversion to the more stable conventional excimer. Irie et al. rationalized the formation of a second excimer in their system by assuming that the decrease of the interaction between the polymer chain and solvent and the increase of the interaction between aromatic side groups lead to rigid polymer conformation in a poor solvent. The fact that extensive second excimer emission and corresponding absorption ($\lambda_{max} \approx 340$ nm) were observed in the present study only with the film of P-1-NEMA thus provides strong evidence for the requirements of second excimer formation: the chromophores are to be separated, by steric or other causes, at distances longer than that for excimer formation and to be fixed in place, as in film, by the decreased chain mobility. The sites of second excimer formation may be either "ground-state" second excimer, which gives "excited" second excimer directly upon excitation or by energy transfer from nearby excited monomer, or its precursor, which forms second excimer by slightly shortening the interchromophore separation. The present case, we believe, is the first example of a film composed of a single polymer component that exhibits extensive second excimer emission.

Registry No. PNMMA, 71154-40-0; P-1-NEMA, 74976-97-9; P-2-NEMA, 71154-42-2; P-3-NPMA, 71154-44-4; NMAC, 35480-23-0; 1-NEAc, 32860-25-6; 2-NEAc, 83053-19-4; 3-NPAc, 27650-56-2; PNMMA-*co*-MMA, 74981-45-6; P-1-NEMA-*co*-MMA, 74976-98-0; P-2-NEMA-*co*-MMA, 83041-80-9; P-3-NPMA-*co*-

MMA, 83041-81-0; biacetyl, 431-03-8.

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Properties of Racemic and Optically Active Poly(α-methyl-α-ethyl-β-propiolactones)

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ABSTRACT: Optically active and racemic poly(α-methyl-α-ethyl-β-propiolactones) (PMEPL) were studied by calorimetry (crystallization and fusion), polarized microscopy, small-angle light scattering, X-ray diffraction, and static and dynamic mechanical methods. Optically active PMEPL's have higher equilibrium melting points, enthalpies of fusion, and crystallization rates than the racemic PMEPL's. They have lower solubilities, different crystal structures, but similar T_g's. PMEPL's of intermediate optical purities were also studied. The observed results are discussed in terms of the stereoregularity of PMEPL chains. They are compared to the properties of other poly(α,α-disubstituted-β-propiolactones).

Introduction

Racemic monomers may lead to optically active polymers via a stereoselective polymerization. For example, optically active polyoxiranes and polythiiranes were prepared in this fashion.[1-4] However, this method leads to poly(α-methyl-α-*n*-propyl-β-propiolactones) (PMPPL) of low optical purities[5,6] and the physical properties of the racemic and optically active PMPPL's were shown to be very similar.[7]

High optical purity polylactones, similar to the high optical purity polyamides prepared by Schmidt[8] from β-lactams containing one or two asymmetric centers, must then be prepared from lactone enantiomers. Schmidt showed that the optically active poly(β-amides) have higher melting points and lower solubilities than the corresponding racemic polymers. Similarly, D'Hondt and Lenz[9] and Carrière and Eisenbach[10] prepared poly(α-phenyl-α-ethyl-β-propiolactones) (PPEPL) having optical purities of 80 and 95%, respectively. They showed that optically active PPEPL's have a melting point of about 130 °C higher than the racemic PPEPL's.

More recently, we have prepared poly(α-methyl-α-ethyl-β-propiolactones)[11] (PMEPL) having optical purities of 99%. We have shown that the high optical purity PMEPL's have a higher melting point, T_f, and a higher enthalpy of fusion, ΔH_f, than the racemic one, in agreement with the previous examples. However, the increase in T_f and ΔH_f is not linear: T_f and ΔH_f remain constant

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