Macromolecules **1986,** *19,* 585-588

Emission Quenching in the Dispersion of Carbazole-Containing Polymer Latex

Tokuji Miyashita, Masayuki Ohsawa, and Minoru Matsuda*

Chemical Research Institute of Nonaqueous Solutions, Tohoku University, Katahira 2-1-1, Sendai, 980 Japan. *Received June 5, 1985*

ABSTRACT: Very fine polymer latex particles consisting of sodium *p*-styrenesulfonate, dodecyl methacrylate, and a very small amount of vinylcarbazole were prepared. The quenching of photoexcited carbazole, which is covalently attached to the polymer latex as an emission probe, by pyridinium and viologen cations was studied from measurements of the steady-state emission intensities. The quenching becomes more effective in more dilute latex concentrations. This is due to the migration of cation quenchers into the anionic latex particles. In the quenching by viologens with various alkyl chain lengths, the quenching efficiency increased with increasing alkyl chain length. The Stern–Volmer plots showed a saturation phenomenon, which could be analyzed by a mechanism considering the equilibrium between the quenchers associated with the latex particle and the quenching sites in the latex particle.

Introduction

The photochemistry in the organized assemblies consisting of charged interfaces such as micelle,[1] microemulsion,[2] vesicle,[3] and polyelectrolyte[4] has been extensively investigated. Especially, the photoinduced electron-transfer reactions in such assemblies are receiving much attention in relation to solar energy conversion. Recently, interfacial systems using inorganic colloidal particles such as colloidal clay[5] and colloidal semiconductor[6] have been examined as other microheterogeneous systems without conventional surfactant compounds. It is interesting to examine the photochemical reactions on the surface of polymer latices that are known to form stable dispersions in aqueous solutions.[7] The catalytic reactions on the reactive surface of polymer latices[8] or biological applications, such as immunological microsphere[9] have been reported previously, and recently Winnik and coworkers have reported interesting work on the quenching of the probe covalently attached to polymer colloids in nonaqueous dispersion systems.[10]

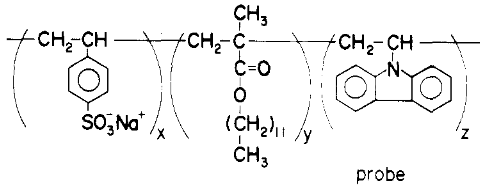
We prepared very fine polymer latex particles consisting of sodium *p*-styrenesulfonate (hydrophilic part), dodecyl methacrylate (hydrophobic part), and a very small amount of vinylcarbazole (fluorescence probe). Through the quenching reactions of the emission probe in the polymer latex solutions by various organic cations, we investigate the properties of the interface of the polymer latex as a reaction field for photoinduced electron transfer. An interpretation of the quenching mechanism in latex dispersion systems is described in this paper.

Experimental Section

Materials. Commercially available sodium *p*-styrenesulfonate (NaSS) (Tokyo Kasei) was purified by recrystallization from ethanol–water mixed solvent. Dodecyl methacrylate (DMA) (Tokyo Kasei) was treated with 5% NaOH solution to remove the inhibitor and dried over anhydrous sodium sulfate. *N*-Vinylcarbazole (VCZ) (Nakarai Chemicals) was recrystallized from ethanol. The preparation of viologens and pyridinium (Py^+) quenchers has been described elsewhere.[1c]

Preparation of Polymer Latex Particles. Terpolymerization of NaSS (2 g), DMA (0.57 mL), and VCZ (0.13 g) was carried out with 2,2′-azobis(isobutyronitrile) (AIBN) initiator in dimethylformamide (DMF)–water mixed solvent. The polymerization solution was poured into a large quantity of acetone solvent and centrifuged. The supernatant was drained and then the precipitate was rinsed with acetone several times to remove DMA, VCZ, and AIBN. It was then dispersed in water and the stable dispersion of polymer latex particles was obtained after filtration with a 5-μm membrane filter to remove macroaggregates. Finally, the polymer latex was purified by ion exchanging with cation (Dowex 50w-X8) and anion (Amberlite IRA-400) exchange resins, followed by ultrafiltration (Toyo ultrafilter UK-200). The composition of the polymer latex was determined by elemental analysis. The concentration of latex particles in solution was calculated from dry weight.

Chart I



$x : y : z \approx 2.6 : 1 : <0.1$

Measurements. The polymer latex was deaerated by N_2 bubbling for at least 1 h. Fluorescence intensity was measured by Shimadzu RF 503A spectrofluorophotometer. An average diameter of the polymer latex particles was determined from the electron micrograph with Hitachi H-300 electron microscope. Flash photolysis for the detection of transient viologen radical cation was carried out by a flash (pulse width: 10 μs) with an energy of 145 J from xenon-filled flash lamps. Wavelengths from 320 nm to 440 nm were used for carbazole excitation with cut-off filters (D-25 and UV-32, Toshiba).

Results and Discussion

Polymer Latex Particles. The dispersion of the polymer latex having the composition shown in Chart I was very stable against even centrifugation at 40000*g*. The composition implies that this polymer latex contains highly charged particles. A more hydrophilic polymer with a greater *p*-styrenesulfonate content was dissolved into water homogeneously, and polymers richer in DMA did not give stable latex dispersion solutions. The diameter of the polymer latex particles with the composition shown in Chart I was calculated to be about 750 Å from the electron micrograph (Figure 1).

Fluorescence Quenching in the Latex Solutions. The fluorescence and the excitation spectra of the carbazole covalently attached to the polymer latex are shown in Figure 2. The structured fluorescence characteristic of monomeric *N*-alkylcarbazole with a strong (0,0) band at about 350 nm[11] is observed, and excimer emission around 430 nm has no appreciable intensity, indicating that the carbazole chromophores are isolated from each other in polymer latex.[12]

The fluorescence from the excited carbazole was quenched by various viologen (methyl (MV^{2+}), ethyl (EV^{2+}), butyl (BV^{2+}), and hexyl (HV^{2+}) substituents) and pyridinium cations. The formation of methylviologen radical cation with the absorption maximum at 605 nm was confirmed by the flash photolysis study, suggesting that

0024-9297/86/2219-0585$01.50/0

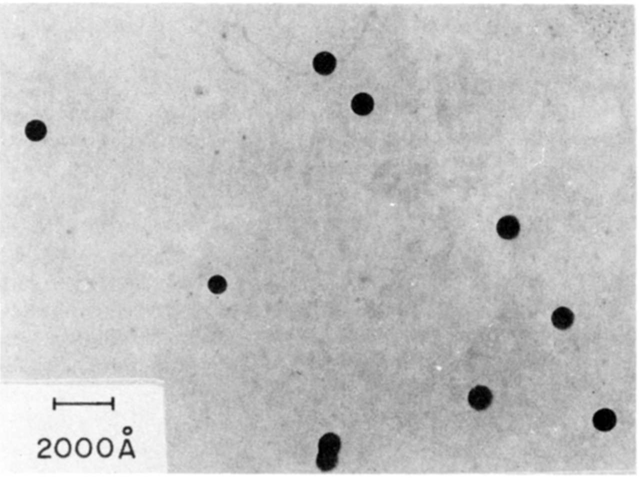


Figure 1. Electron micrograph of polymer latex particles.

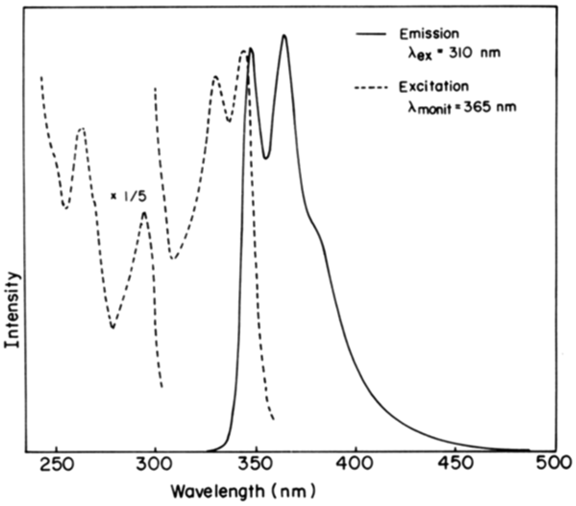
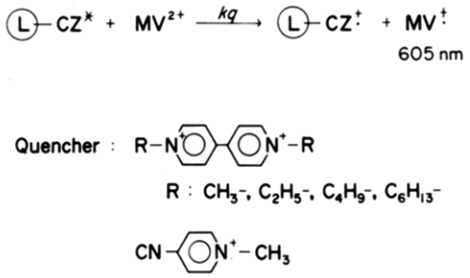


Figure 2. Emission and excitation spectra of carbazole covalently attached to the polymer latex.

Scheme I



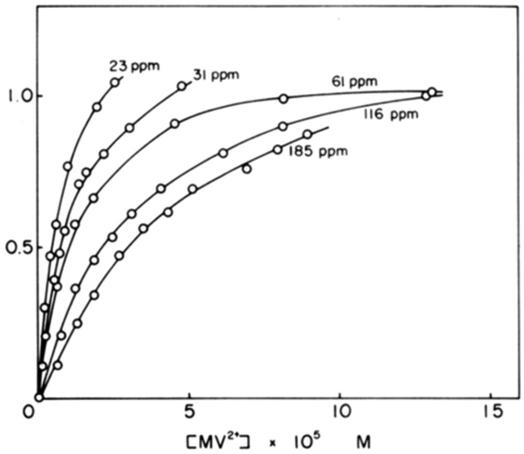


Figure 3. Plots of the ratios of fluorescence intensities against methylviologen concentrations in various latex concentrations.

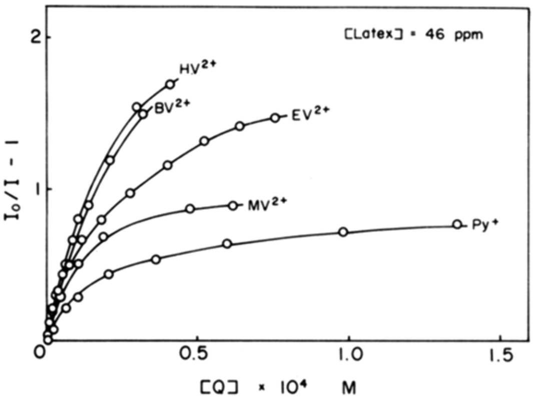


Figure 4. Difference in quenching efficiencies among various quenchers in 46 ppm polymer latex solution.

the quenching proceeds by the electron-transfer mechanism shown in (Scheme I). We could not detect clearly the transient absorption around 780 nm[2a,13] due to carbazole radical cation (absorption was small). This may be attributed to rapid electron transfer from neighboring anionic groups or some decomposition processes.[2a] The redox potential of the excited carbazole (E_{cz^+/cz^*}) can be estimated to be about −2.74 V (vs. SCE)[14] on the bases of singlet excitation energy (ΔE_{ex})[15] and the redox potential of carbazole ($E_{cz^+/cz}$).[16] The redox potential obtained means that the electron-transfer reaction from the excited carbazole to viologens (E_{redox} = −0.44 V vs. SCE) or pyridinium (E_{redox} = −0.6 V vs. SCE)[1d] is an exothermic and very favorable process.[17] The plots of the ratios of fluorescence intensities in the absence and the presence of methylviologen quencher (I_0/I) in various latex concentrations are shown in Figure 3. The plots deviated downward gradually from straight lines and approached saturation values. Apparently the quenching is different from conventional Stern–Volmer behavior in a homogeneous system and also from quenching in micellar and polyelectrolyte solutions, where upward curves are obtained.[1a,4a] Figure 3 shows that the efficiency of quenching increases with decreasing latex concentration. Viologen compounds in sodium dodecyl sulfate (SDS) micellar solution were found to be associated to micelle totally.[1c,18] Since the viologen cation quencher is expected to be associated with the anionic charged latex particles due to electrostatic and/or hydrophobic interactions, the effective quenching in dilute latex solutions can be explained by an increase in the number of quencher molecules per latex particle (concentration effect).

The difference in the quenching efficiency among various quenchers (viologens with various alkyl chain lengths and pyridinium) is exhibited in Figure 4. The viologen dication quenchers were more effective than the pyridinium monocation quencher. In the viologens, the quenching efficiency increases with increasing alkyl chain length. *n*-Hexylviologen was observed to be the most effective quencher in this work. Previously, in the quenching of photoexcited ruthenium complexes, we reported that the quenching efficiencies (the rate constants of quenching) of viologens do not vary with alkyl chain lengths in homogeneous solution (acetonitrile) as expected from the equality of redox potentials.[1c] Moreover, it is very interesting that the change in the quenching efficiencies by alkyl chain length was the reverse order compared with the results in the quenching of ruthenium complexes in SDS micellar solution where the efficiency decreases in the order methyl > ethyl > propyl > butyl > hexyl.[1c] The quenching reaction in SDS micellar solution proceeds on the surface region (Stern layer) of the micelle, and the surface diffusion of viologens is important process for the quenching. As the alkyl chain length increases from methyl to hexyl, the viologens are bound more tightly to the micelle due to hydrophobic interaction and the quenching efficiency decreases by the suppression of the surface diffusion of viologens. On the other hand, for the quenching of the carbazole in the latex particles, the viologen must enter the more hydrophobic region; that is, the incorporation of viologen into the latex particles by the electrostatic and/or hydrophobic interactions is important in the quenching of the latex solutions. As a result, the viologens with longer alkyl chains become effective quenchers. However, further systematic studies may be necessary to clarify the difference in the quenchings between latex solutions and micellar solutions.

Mechanism of the Quenching by Viologens. The saturation curves in the Stern–Volmer plots shown in Figures 3 and 4 mean that there is a limitation of the number of carbazole to be quenched. Similar saturation phenomena have been often encountered in the catalytic reactions in polymer or latex solutions, including some equilibrium processes (e.g., adsorption or some complexations).[7,8] Similar downward-curving Stern–Volmer plots have been reported in the quenching reaction in protein solutions, where the accessibility of quenchers on the surface of proteins is restricted.[19]

We consider the equilibrium (eq 1) between the viologens associated on the surface of the latex particle (Q_i (mol/particle)) and the quenching sites (S (mol/particle)) in the inner and/or more hydrophobic part of the latex particle. The viologens on the quenching sites (Q_s

$$Q_i + S \overset{K}{\rightleftharpoons} Q_s \qquad K\ (\text{mole/particle})^{-1} \tag{1}$$

(mole/particle)) can quench the fluorescence of carbazole chromophore. Since the ratio of fluorescence in the absence and the presence of quencher in latex solution can be expressed by the ratio of the quantum yields in each latex particle, we consider the quenching in each latex particle. The concentration (number) of the viologens in the quenching sites ($[Q_s]$ (mole/particle)) is given by the following:

$$[Q_s] = K[S][Q_i]/(1 + K[Q_i]) \tag{2}$$

$[Q_i]$ (mole/particle) is calculated from the added concentration of viologen ($[Q]_0$ (mol/L)) and the number of latex particles ($[L]/W$ (particle/L)) as follows:

$$[Q_i] = [Q]_0W/[L] \tag{3}$$

where [L] is the concentration of latex particle (g/L) and W is the weight of latex particle (g/particle); it is assumed that all viologens are associated with the latex particle. This assumption is supported by the results in Figure 3 and expected from the high anionic charge of this latex. The results in SDS micellar solution,[1c] where these viologens are totally solubilized in the micelle, and the association constants, measured as 10^6 M^{-1}, support this assumption. In the presence of viologen, the intensity of fluorescence decreases with $[Q_s]$ according to the Stern–Volmer equation, and the relative ratio of fluorescence intensities is expressed as follows:

$$I_0/I = 1 + K_{sv}[Q_s] = 1 + K_{sv}KW[S][Q]_0/([L] + KW[Q]_0) \tag{4}$$

$$(I_0/I - 1)^{-1} = \left(\frac{[L]}{K_{sv}KW[S]}\right)[Q]_0^{-1} + \frac{1}{K_{sv}[S]} \tag{5}$$

$$\text{slope} = (K_{sv}KW[S])^{-1}[L] \tag{6}$$

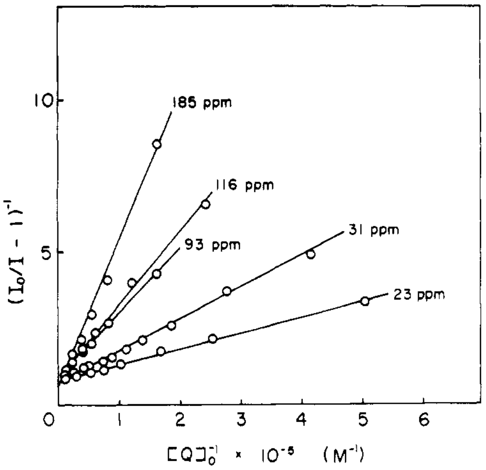


Figure 5. Double-reciprocal plots of fluorescence intensities with quencher concentrations (eq 5, see text).

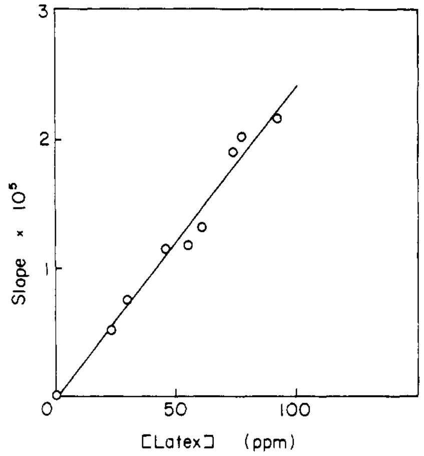


Figure 6. Plots of eq 6 (see text).

Table I
Quenching Efficiencies ($K_{sv}KW[S]$) and Maximal Fractions (f) of Quenched Carbazole by Various Quenchers

	quencher				
parameter	Py^+	MV^{2+}	EV^{2+}	BV^{2+}	HV^{2+}
$K_{sv}KW[S] \times 10^{-3}$	1.81	4.25	4.72	6.16	6.54
f	0.49	0.53	0.60	0.73	

The double-reciprocal plots of $(I_0/I - 1)^{-1}$ vs. $[Q]^{-1}$ from eq 5 in the case of methylviologen quencher are shown in Figure 5. Good linear relationships were obtained and their slopes increased with the latex concentrations (Figure 6). The linearity shown in Figure 6 is expected from eq 5. The quenching data in Stern–Volmer plots can be interpreted successfully by eq 3 or 4 as described above, indicating that the above mechanism for the quenching in the latex solution considering the equilibrium between quencher associated to latex particle and the quenching sites is reasonable. The reciprocal of the slope in Figure 6 gives $K_{sv}KW[S]$, the ratio of which is related to the quenching efficiency. The comparison of these values with various quenchers is shown in Table I, together with the maximal fraction of quenched carbazole (f) that can be obtained from the simulation of the Stern–Volmer plots by eq 3. The difference between monocation (Py^+) and dication (MV^{2+}) is larger than that among the viologens. It appears that the electrostatic effect on quenching in the polymer latex is more important than the hydrophobic effect. On the other hand, the maximal fraction of quenched carbazole is influenced by alkyl chain length in viologens (Figure 4 and Table I). The maximal fraction may depend on the extent to which the quencher can penetrate into the core of the polymer latex particles. This is related to water penetration and hydrophobic interaction. In HV^{2+} or BV^{2+} quencher, about 80% of the carbazole units were quenched. Those viologens can diffuse deeply into the latex particles by displacements of the hydrated or penetrated water due to hydrophobic interaction. We can therefore propose that this polymer latex is porous and flexible (not hard) within the latex beads.

Acknowledgment. T.M. thanks the Ministry of Education, Science, and Culture of Japan for the Grant-in-Aid for Encouragement of Young Scientist.

Registry No. (NaSS)·(DMA)·(VCZ) (copolymer), 99966-50-4; Py^+, 13441-45-7; MV^{2+}, 4685-14-7; EV^{2+}, 46713-38-6; BV^{2+}, 47082-19-9; HV^{2+}, 47369-13-1.

References and Notes

(1) (a) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543. (b) Thomas, J. K.; Almgren, M. "Solution Chemistry of Surfactants"; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 2, p 559. (c) Miyashita, T.; Murakata, T.; Matsuda, M. *J. Phys. Chem.* **1983**, *87*, 4529. (d) Miyashita, T.; Murakata, T.; Yamaguchi, Y.; Matsuda, M. *J. Phys. Chem.* **1985**, *89*, 497.

(2) (a) Yamaguchi, Y.; Miyashita, T.; Matsuda, M. *J. Phys. Chem.* **1981**, *85*, 1369. (b) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 3188. (c) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4279.

(3) (a) Tunuli, M. S.; Fendler, J. N. *J. Am. Chem. Soc.* **1981**, *103*, 2507. (b) Nomura, T.; Escabi-Perez, J. R.; Sunamoto, J.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1484.

(4) (a) Miyashita, T.; Matsuda, M. *Polym. Commun.* **1984**, *25*, 138. (b) Meisel, D.; Matheson, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6577.

(5) DellaGuardla, R. A.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 990.

(6) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376.

(7) Frank, A. J.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1979**, *83*, 716.

(8) (a) Suen, C-H.; Morawetz, H. *Macromolecules* **1984**, *17*, 1800. (b) Kitano, H.; Sun, Z.-H.; Ise, N. *Macromolecules* **1983**, *16*, 1306.

(9) Rembaum, A.; Chang, M.; Richards, G.; Li, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 609.

(10) Pekcan, O.; Winnik, M. A.; Croucher, M. D. *J. Colloid Interface Sci.* **1983**, *95*, 420. Pekcan, O.; Winnik, M. A.; Egan, L.; Croucher, M. D. *Macromolecules* **1983**, *16*, 699. Winnik, M. A.; Hua, M. H.; Hougham, B.; Williamson, B.; Croucher, M. D. *Macromolecules* **1984**, *17*, 262.

(11) Johnson, G. E. *J. Phys. Chem.* **1974**, *78*, 1512.

(12) Yokoyama, M.; Tamamura, T.; Atsumi, M.; Yoshimura, M.; Shirota, Y.; Mikawa, H. *Macromolecules* **1975**, *8*, 101.

(13) $E_{cz^+/cz^*} = E_{cz^+/cz} - \Delta E_{ex} = -2.74$ V.

(14) Taniguchi, Y.; Nishina, H.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1646.

(15) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(16) Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Nonaqueous System"; Marcel Dekker: New York, 1970.

(17) Rhem, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.

(18) Rodgers, M. A. J.; Becker, J. C. *J. Phys. Chem.* **1980**, *84*, 2762.

(19) Lakowicz, J. R. "Principles of Fluorescence Spectroscopy"; Plenum Press: New York, 1983; Chapter 9.

Fluorescence and Energy Migration in 2-Vinylnaphthalene Alternating and Random Copolymers with Methyl Methacrylate and Methacrylic Acid

Fenglian Bai,[†] C. H. Chang, and S. E. Webber*

Department of Chemistry and Center for Polymer Research, University of Texas at Austin, Austin, Texas 78712.

Received April 17, 1985

ABSTRACT: The fluorescence of alternating and random copolymers of 2-vinylnaphthalene with methyl methacrylate [P(2VN-*alt*-MMA) and P(2VN-*co*-MMA)] and methacrylic acid [P(2VN-*alt*-MA) and P(2VN-*co*-MA)] has been studied. The alternating copolymers have essentially no excimer fluorescence, unlike the random copolymers. The fluorescence decay of the alternating copolymers can be fit satisfactorily to a single exponential while the random copolymers require a three-exponential fitting function. The fluorescence quenching of these copolymers was compared with that of an excimer-free copolymer P(2VN-*co*-MMA) with ca. 3% naphthalene and a small-molecule model, 2-ethylnaphthalene. The energy migration distance (L_s) deduced from the former experiments showed that L_s for the alternating copolymers were approximately twice that of the random copolymers.

Introduction

Singlet energy migration in polymers with pendant aromatic groups has been studied extensively.[1-5] It is well-known that excimer formation can occur at adjacent chromophores[5] or non-nearest neighbors[6] and can act as a trap to terminate energy migration. Thus it is expected that changing the local concentration and/or mutual orientation of chromophores in the polymer coil will affect excimer formation with an concomitant change in energy migration rate. It has been reported by Nakahira et al.[1] that excimer formation in naphthyl polymers could be reduced by introducing bulky groups on the chromophore. However, in this case the energy-transfer rate was also reduced. In the present work, alternating naphthyl copolymers have been prepared in which the chromophores are separated equally and with sufficient chromophore separation to prevent excimer formation.

There are a few reports of photophysical studies of alternating copolymers in the literature. In 1974 Fox et al.[7] included an alternating copolymer of 2-vinylnaphthalene and methyl methacrylate in their studies and demonstrated that excimer formation was essentially eliminated. The present paper can be regarded as an extension of this earlier paper. In 1975 Wang and Morawetz[8] studied co-

---

[†] Permanent address: Institute of Chemistry, Academia Sinica, Beijing, China.

0024-9297/86/2219-0588$01.50/0