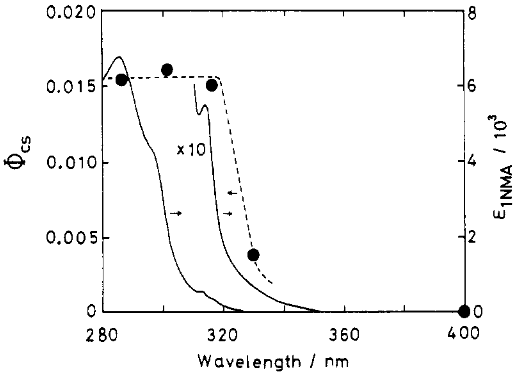

Figure 6. UV spectrum of P1NMA in benzene solution and (●) action spectrum of quantum yield for main-chain scission Φ_{cs}. The extinction coefficient ϵ is given based on the equivalent molarity of 1NMA monomer unit.

scission, those of the successive 1NMA sequences (1NMA–1NMA, 1NMA–1NMA–1NMA, etc.) exert an inhibiting effect on the main-chain scission due to intramolecular excimer formation.

Effect of the Irradiation Wavelength on the Quantum Yield for Main-Chain Scission. Figure 6 shows the action spectrum of the quantum yield for the main-chain scission of P1NMA in deaerated benzene solution (1 g dm^{-3}). The UV absorption band of P1NMA in the wavelength region above 280 nm is assigned to the π–π^* transition of the 1-naphthyl chromophore by reference to naphthalene. The Φ_{cs} value was constant (ca. 1.5 × 10^{-2} scissions per absorbed quantum) regardless of the wavelength used to irradiate the 1-naphthyl chromophore. The UV irradiation at >330 nm was not effective to induce the main-chain scission of P1NMA. These results indicate that the main-chain scission of 1NMA-containing polymers occurs via the electronically excited state of 1-naphthyl chromophores.

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Studies of the Antenna Effect in Polymer Molecules. 1. Singlet Electronic Energy Transfer in Poly[(9-phenanthryl)methyl methacrylate] and Its Copolymers

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ABSTRACT: Poly[(9-phenanthryl)methyl methacrylate] (poly(PhMMA)) and its copolymers with varying contents of (9-anthryl)methyl methacrylate (AMMA) and methyl methacrylate (MMA) were synthesized. The efficiency of intrachain singlet electronic energy transfer in fluid solutions from phenanthrene to anthracene was measured as a function of the mole fraction of anthracene, f_{AMMA}. A transfer efficiency of 70% was obtained for the copolymer with 1.3 mol % AMMA content. Fluorescence depolarization measurements on the phenanthrene emission at liquid nitrogen temperature in both the homopolymer and its copolymers give evidence for substantial singlet energy migration among the phenanthrene chromophores.

Introduction

The utilization of sunlight in photosynthesis requires efficient absorption and transfer of photon energy to localized reaction centers. In green plants, it is generally accepted that singlet energy migration occurs between 200 and 300 molecules of chlorophyll *a* in the primary process of plant photosynthesis.[1,2] Typically, the efficiency is estimated to be from 75% to 95%[3,4] for transfer from the so-called "antenna" pigments to the reaction centers.

The recent discovery that energy transfer processes in man-made polymers can mimic similar effects in natural chloroplasts has produced considerable interest in this field.[5-8] Polymers with intrachain transfer efficiencies comparable to those of green plant photosystems have been reported,[9,10] and singlet energy migration is believed to be partially responsible for the high efficiency.

This paper reports the synthesis and the energy transport properties of a new monomer, (9-phenanthryl)methyl

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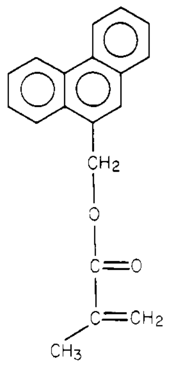
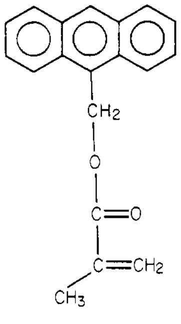
methacrylate (PhMMA), and photophysical studies of its homopolymer and copolymers with (9-anthryl)methyl methacrylate (AMMA) and methyl methacrylate (MMA).



PhMMA



AMMA

Experimental Section

Methacryloyl chloride was prepared by fractionally distilling a mixture of 30 mL of methacrylic acid (Eastman) and 90 mL of benzoyl chloride (Eastman) quickly over a 25-cm column. The distillate was then redistilled over 0.5 g of hydroquinone. Only the middle third of the distillate was kept; boiling range, 93–95 °C.

(9-Phenanthryl)methyl Methacrylate. (9-Phenanthryl)methanol was prepared by $NaBH_4$ reduction of 10 g of phenanthrene-9-carboxaldehyde (Aldrich) in 250 mL of refluxing methanol. After 3.5 h, the solution was cooled and diluted with warm water. The white crystals precipitated were then filtered and recrystallized with benzene (Fisher). The colorless needlelike crystals (mp 153.5–154.0 °C) were then dried overnight in vacuo. The methacrylate ester was prepared by dropwise addition of 2 equiv of methacryloyl chloride to a solution of 6 g of (phenanthryl)methanol, 12 mL of dry Et_3N, and 10 mL of dry THF at 0 °C. After the solution was stirred for 1 h the THF solvent was removed in a Rotovap and 50 mL of water was added to dissolve the amine salt. The product was then extracted with diethyl ether, and the ethereal solution was washed repeatedly with aqueous HCl, Na_2SO_4, H_2O, and saturated NaCl solution and then dried over $NaHCO_3$. After the ether was removed, the crude product was chromatographed on alumina with benzene as the eluting solvent. The product was then collected as the second band off the column and subsequently recrystallized several times from spectral grade *n*-pentane (Caledon). The product was a white crystalline solid: IR (Nujol) 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.95 (s, 3 H, CH_3), 5.5 (s, 1 H, =CH), 5.7 (s, 2 H, $COArH_2$), 6.15 (s, 1 H, =CH), 7.5–9.0 (m, 9 H, aromatic ring H).

(9-Phenanthryl)methyl Pivalate (PhMP). One equivalent of pivaloyl chloride was used to synthesize the ester using the same technique for preparing PhMMA. The crude product was purified by column chromatography followed by recrystallization from *n*-pentane; NMR ($CDCl_3$) δ 1.25 (s, 9 H, CH_3), 5.6 (s, 2 H, CH_2), 7.5–9.0 (m, 9 H, aromatic ring H).

(9-Anthryl)methyl Methacrylate. This monomer was prepared by reaction of (9-anthryl)methanol with methacryloyl chloride.

Polymers were prepared by AIBN-initiated free radical polymerization in degassed benzene (Fisher spectral grade) at 55 °C for 3 h. They were purified by multiple reprecipitations from chloroform into methanol, washed thoroughly with methanol and with *n*-pentane, and dried in vacuo over P_2O_5.

Tetrahydrofuran (THF) (Caledon, spectral grade) and 2-methyltetrahydrofuran (2MTHF) (MCB) were refluxed over $LiAlH_4$ for several hours and then fractionally distilled.

Steady-state fluorescence spectra were recorded with a Hitachi MPF-2A spectrophotometer with phototube response corrected. Quantum yields were determined with 1-naphthol and 9-methylanthracene as standards. Efficiencies of energy transfer, χ, from phenanthrene to anthracene were determined from copolymer fluorescence spectra according to[9]

$$\Phi_{Ph} I_A / \Phi_A I_{Ph} = \chi/(1 - \chi) \tag{1}$$

Here, Φ_{Ph} and Φ_A are the fluorescence quantum yields of poly(PhMMA) homopolymer and of the bound anthracene chromophore on direct excitation, respectively. I_A/I_{Ph} is the ratio of area under the anthracene and phenanthrene emissions.

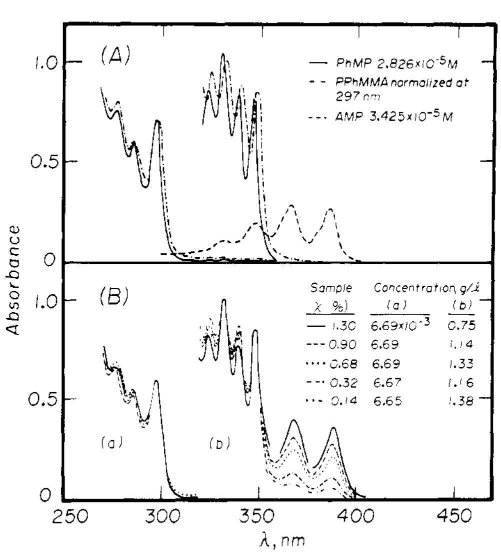


Figure 1. UV absorption spectra in deoxygenated THF at 25 °C. (A) Poly(PhMMA) and model compounds. (B) Poly(PhMMA-*co*-*x*% AMMA): (a) low concentrations; (b) high concentrations.

For low-temperature measurements, the sample cell was a 3-mm-diameter quartz tube. Samples were purged with dry nitrogen and then slowly immersed in liquid nitrogen in a quartz Dewar, a phosphorescence accessory to the spectrometer. The solvent used was a mixture of 2MTHF/THF (35/65 by volume) which forms a clear glass at 77 K.

The polarization *P* of the emission of glassy solutions was determined according to

$$P = (I_{\parallel} - I_{\perp}C)/(I_{\parallel} + I_{\perp}C) \tag{2}$$

where $I_{\parallel}$ and $I_{\perp}$ represent emission intensities with parallel and perpendicular orientation of the polarizers and the polarizer on the excitation side is oriented parallel to the ruling of the diffraction grating of the excitation monochromator. The factor *C* is a correction for the anisotropy induced by the diffraction grating and is given by $C = I_{\perp}'/I_{\parallel}'$. The primed quantities indicate that the excitation polarizer is oriented at right angles to the excitation diffraction grating.

Number-average molecular weights (M_n) of the polymers were determined by membrane osmometry. The copolymer compositions were determined by UV spectroscopy using poly(PhMMA) and (9-anthryl)methyl pivalate (AMP) as references.

Results and Discussion

Figure 1 shows the UV absorption spectra of poly(PhMMA), its copolymers with AMMA, and the model compounds (9-phenanthryl)methyl pivalate (PhMP) and AMP in THF solutions. The steady-state fluorescence spectrum of poly(PhMMA) in deoxygenated THF excited at 280 nm is shown in Figure 2. The polymer showed no low-energy broad-band excimer emission, in agreement with earlier concentration studies reported by Birks et al.[11]

The compositions of the copolymers of PhMMA with AMMA are listed in Table I. A typical fluorescence spectrum of a copolymer in deoxygenated THF at room temperature is shown in Figure 3. The emission of the polymer-bound AMMA is very similar to that of the model compound, AMP, excited at 366 nm, as is shown in the same figure. The absence of energy transfer in a mixed solution of PhMP (donor) and AMP (acceptor) at comparable bulk concentrations indicates that the emission of AMMA in the polymer arises entirely from the intrachain energy transfer from the PhMMA excited at 280 nm.

Table I also lists the energy transfer efficiencies of the copolymers at different AMMA compositions in deoxy-

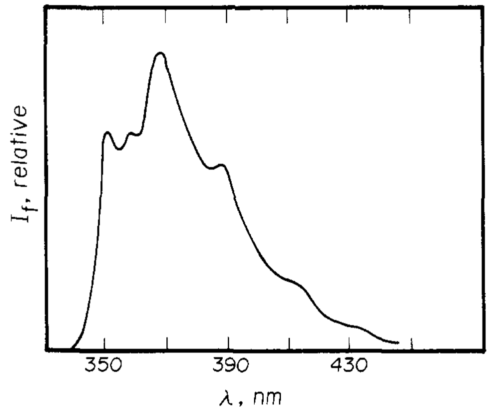


Figure 2. Steady-state fluorescence spectrum of poly(PhMMA) in deoxygenated THF at 25 °C, λ_{ex} = 280 nm.

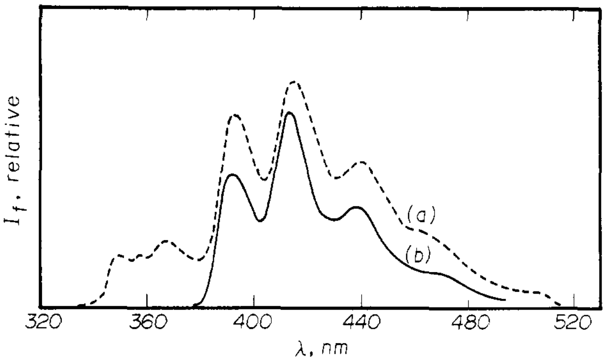


Figure 3. Steady-state fluorescence spectrum of (a) poly(PhMMA-*co*-0.68% AMMA) in deoxygenated THF at 25 °C, λ_{ex} = 280 nm, and (b) (9-anthryl)methyl pivalate in deoxygenated THF at 25 °C, λ_{ex} = 366 nm.

Table I
Quantum Efficiencies χ of Energy Transfer to Anthracene in Poly(PhMMA-*co*-AMMA) in Deoxygenated THF at 25 °C

monomer feed ratio $[M_A]/[M_{Ph}]$	f_{AMMA}, mol %	$\bar{M}_n \times 10^{-5}$ [a]	$\bar{N}_A$ [b]	χ, %
0	0	30	0	0
0.001	0.14	40	20	21.4
0.004	0.32	17	20	26.9
0.007	0.68	8	20	37.6
0.010	0.90	70	230	51.0
0.020	1.30	10	47	70.2

[a] Membrane osmometry. [b] Average number of anthracene units per chain.

genated THF solution. The efficiencies of transfer were found to be comparable to those for naphthalene-containing antenna polymers in the same solvent.[9,11]

Mixed 2MTHF/THF solvents form optically clear glass at 77 K. No sign of crystallization was detected in either glassy solutions of the polymers or their model compounds at this temperature. Even when all molecular diffusion is frozen out at this temperature, substantial energy transfer was observed, as shown in Figure 4. Structured phosphorescence from phenanthrene was detected in the dilute solutions of PhMP but was much reduced in intensity and is less structured in polymer solutions. Delayed fluorescence from the phenanthrene chromophore was also observed in the polymer solutions, indicating the presence of triplet energy migration, but the intensity was lower than that of the prompt fluorescence by at least a factor of 30. These results show that although migration of triplet energy occurs at 77 K, it does not interfere greatly with singlet transfer to anthracene.

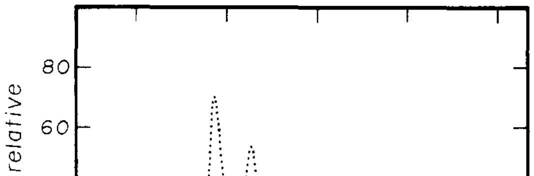


Figure 4. Fluorescence spectrum of poly(PhMMA) (curve a). Fluorescence spectra of poly(PhMMA-*co*-*x*% AMMA) in 2MTHF/THF glass at 77 K, λ_{ex} = 280 nm: (b) *x* = 0.32% AMMA, (c) *x* = 0.90% AMMA. Spectra uncorrected.

Table II
Fluorescence Depolarization Measurements at 77 K in Mixed 2MTHF/THF (35/65 by Volume) Solvent[a]

sample	P (±0.01)	P^{-1}
PhMP	0.10	10
poly(PhMMA)	0.00	∞
poly(PhMMA-*co*-AMMA)		
f_{AMMA} 0.14	0.018	56
0.32	0.005	200
0.68	0.008	125
0.90	0.00	∞
1.30	0.005	200

[a] λ_{ex} = 280 nm, λ_{em} = 366 nm.

Table III
Compositions and Molecular Weights of Poly(PhMMA-*co*-MMA)

monomer feed ratio $[M_{PhMMA}]/[M_{MMA}]$	PhMMA, mol %	$\bar{M}_n \times 10^{-5}$
0.040	2.80	3.0
0.089	5.90	17.0
0.155	9.24	4.4
0.242	13.57	4.2
0.374	29.92	9.4

The polarization data at 77 K are shown in Table II. The donor fluorescence is essentially depolarized in all the poly(PhMMA-*co*-AMMA) samples as well as in the homopolymer. In view of the low delayed fluorescence intensities observed, its contribution to the total depolarization is negligible. The depolarization P^{-1} measured is therefore that arising from the prompt fluorescence of phenanthrene. On the other hand, the dilute glassy solution of the model compound PhMP shows a retention of the polarization observed at 365 nm (P^{-1} = 10.0 ± 0.5). The extensive depolarization in the phenanthrene chromophore emission from polymer solutions is strong evidence for the occurrence of singlet energy migration. This can be further tested by examining the P^{-1} values for a series of copolymers of PhMMA and MMA at varying PhMMA mole fraction, f_{AMMA}.

The composition and molecular weights of poly(PhMMA-*co*-MMA) samples are listed in Table III. The emission spectra of these copolymers at all compositions show only the structured emission characteristic of the phenanthrene group, which is substantially identical with that of both homopolymer and the model compound PhMP. The fluorescence depolarization P^{-1} obtained at 77 K at various f_{PhMMA} is summarized in Figure 5. A linear relationship was obtained between P^{-1} and f_{PhMMA} at low f_{PhMMA}. Extrapolating P^{-1} to the limit of f_{PhMMA} = 0 gives

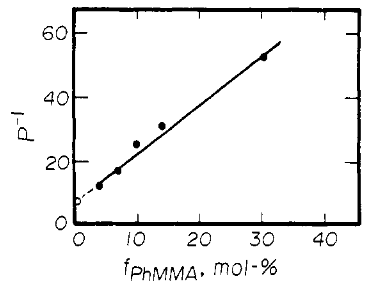


Figure 5. Fluorescence depolarization (P^{-1}) of poly(PhMMA-*co*-MMA) in 2MTHF/THF glass at 77 K. λ_{ex} = 280 nm, λ_{em} = 366 nm. The open circle is P^{-1} for the model compound PhMP.

$P^{-1}(f_{PhMMA} \rightarrow 0) = 8.0$, which is comparable to the value of 10 for the isolated PhMP chromophore under the same conditions. This composition dependence of P^{-1} is in accord with the concentration effect of depolarization proposed by Weber[12] and supplies further evidence for singlet energy migration in the polymers. Studies on other aromatic polymers have shown similar effects.[13-18] For example, in studies of 1-vinylnaphthalene or styrene copolymerized with methyl methacrylate, Reid and Soutar observed a linear correlation of monomer P^{-1} with $\bar{l}_M$, the mean sequence length of the fluorescent monomer units.[17,18] Similarly, a linear plot of P^{-1} vs. f_M, the mole fraction of the fluorescent monomer, was obtained for poly(acenaphthalene-*co*-methyl acrylate) and poly(acenaphthalene-*co*-methyl methacrylate).[19,20] The authors proposed that in the former case, the singlet energy migration was primarily along the polymer backbone through a pseudo-one-dimensional random walk. The energy migration in the latter case was considered to be a series of Förster transfers within the polymer coil rather than a down-chain hopping involving predominantly adjacent chromophores. In the phenanthrene-containing polymer systems studied here, the linear plot of P^{-1} against f_{PhMMA} was obtained at relatively low f_{PhMMA}, which could be explained in terms of a series of transfers from nonneighboring groups. The quality of the polarization measurements was not sufficiently good to draw more definite conclusions about the migration kinetics at higher PhMMA contents.

Conclusions

Through studies of homo- and copolymers containing bound anthracene traps, (phenanthryl)methyl methacrylate has been shown to be efficient in harvesting light photons. The observed depolarization of monomer fluorescence emission in polymers containing extended sequences of PhMMA units is strong evidence for the occurrence of singlet energy migration. The high efficiency of transfer is partially attributed to this process, which appears to occur both in fluid solutions at room temperature and also when the chromophores are rigidly frozen in hydrocarbon glasses at 77 K. The absence of excimer formation in these polymers permits more quantitative characterization of the extent of energy migration within the chain.

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