Photodegradation of 1-Naphthyl Methacrylate–Butyl Methacrylate Copolymers in Benzene Solution

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ABSTRACT: The photodegradation behavior of the copolymers of 1-naphthyl methacrylate (1NMA) with butyl methacrylate (BMA) in benzene solution has been investigated under deaerated conditions at room temperature. Irradiation in the 285–330-nm wavelength region led to main-chain cleavage in poly(1NMA) and poly(1NMA-*co*-BMA) accompanied by the evolution of carbon monoxide, whereas no chemical change was observed in the case of poly(BMA). The apparent rate constant for the main-chain scission of poly(1NMA-*co*-BMA) in benzene solutions (1 g dm^{-3}) increased with increasing 1NMA content up to 12.5 mol %. At this point the maximum value of 5.96×10^{-6} min^{-1} was obtained. Further increases in 1NMA content depressed the apparent rate for main-chain scission. The quantum yield for main-chain scission decreased monotonously with the increase in 1NMA content to attain its minimum value of 1.5×10^{-2} scissions per absorbed quantum for poly(1NMA).

Homopolymers of alkyl methacrylates such as methyl methacrylate (MMA),[1,2] butyl methacrylate (BMA),[3] and *tert*-butyl methacrylate (*t*-BMA)[4] have been well characterized with respect to thermal and photochemical degradation in solution as well as in the solid state. Considerable attention has also been given to the degradation behavior of various copolymers containing alkyl methacrylate monomer units. The major processes involved in the degradation of alkyl methacrylate polymers have been demonstrated to be decomposition of side-chain ester groups, main-chain carbon–carbon bond scission, and depolymerization. These processes are significantly affected by the structure of the alkyl group in the ester linkage. However, little is known about the degradation behavior of aryl methacrylate polymers.[5,6]

In this paper, the photodegradation characteristics of 1-naphthyl methacrylate (1NMA) homopolymer and copolymers with BMA in deaerated benzene solutions are reported. The main purpose of this work is to clarify the influence of the copolymer composition on the quantum yiled for main-chain scission occurring in poly(1NMA-*co*-BMA).

Experimental Section

Materials. Butyl methacrylate (BMA) was commercially available. 1-Naphthyl methacrylate (1NMA) was prepared according to the conventional method from methacryloyl chloride and 1-naphthol.[7] These monomers were purified by distillation under reduced pressure in an atmosphere of nitrogen immediately before use.

1-Naphthyl isobutyrate (1NIB) was prepared from isobutyryl chloride and 1-naphthol in a manner analogous to 1NMA. 1NIB thus prepared was purified by fractional distillation under reduced pressure in an atmosphere of nitrogen (1.7 kPa, 160–162 °C).

Commercial 2,2′-azobis(isobutyronitrile) (AIBN) and diacetyl (DAc) were used without further purification. Spectroscopic grade benzene was used as received.

Polymerization. 1NMA homopolymers for the determination of the Mark–Houwink parameters were prepared by bulk polymerization using AIBN as an initiator under various conditions. Radical copolymerizations of 1NMA with BMA were carried out in bulk (15 g) using AIBN (1 wt %) at 70 °C under deaerated conditions. The conversion in each of the copolymerizations did not exceed 10%. The homo- and copolymers were purifed by three precipitations from a benzene solution (2.5–2.8 wt %, 60 cm^3) into methanol (1 dm^3) and dried under reduced pressure in the dark.

Oligomerization. Photosensitized radical oligomerization of 1NMA (0.5 mol dm^{-3}) was carried out in deaerated benzene solution, using DAc (0.5 mol dm^{-3}) as a sensitizer. The light source was a 500-W xenon lamp (Ushio UXL-500D) and a cutoff glass filter (Toshiba VY-42) was used to selectively irradiate DAc. The number-average molecular weight of 1NMA oligomer was estimated to be 850–4300 from GPC measurements.

UV Irradiation. The benzene solution was deaerated in a finger glass tube attached to an optical flat quartz cell (1-cm path length) by repeated freeze–pump–thaw cycles under reduced pressure (<2 mPa). The deaerated, magnetically stirred polymer solution was irradiated with monochromatic light from a Jasco CT-25N monochromator and a 500-W high-pressure mercury arc (Philips SP-500W). The intensity of the monochromatic light was determined by the simultaneous use of both a thermopile and a potassium ferrioxalate actinometer.[8] The deaerated solutions of 1NMA oligomer and 1NIB were irradiated with a Philips SP-500W high-pressure mercury arc and an Ushio UXL-500D xenon lamp, respectively, equipped with a cutoff glass filter (Toshiba UV-27).

Product Analysis. The volatile products liberated during the UV irradiation were confirmed by gas–liquid chromatography (GLC), using a Shimadzu GC-6A gas chromatograph (column: molecular sieve 13X (40–60 mesh) or 20% sebaconitrile on Chromosorb P, 3 m × 3 mm). The liquid and solid products obtained after evaporation of the benzene were subjected to IR measurement on a Jasco DS-403G spectrophotometer and ^{1}H NMR measurement on a JEOL PMX-60 spectrometer. All chemical shifts are reported in parts per million downfield of tetramethylsilane. UV absorption spectra were recorded on a Shimadzu UV-200S spectrophotometer.

Molecular Weight Measurement. The intrinsic viscosity ($[\eta]$) of the polymer in tetrahydrofuran (THF) was determined at 40 °C by extrapolation to zero polymer concentration in a dilution series of viscosity measurements. Gel permeation chromatography (GPC) was performed with a Toyo Soda HLC-802UR high-speed liquid chromatograph (column: TSK-Gel GMH_6 and $G2000H_6$, 0.6 m × 7.5 mm, eluted with THF at a flow rate of 1 cm^3 min^{-1} at 40 °C). The universal calibration curve correlating the hydrodynamic volume of the polymer with the molecular weight (M), log $[\eta]M$ vs. elution volume (V), was prepared with polystyrene standards (Toyo Soda, $\bar{M}_n/10^5$ = 12.4, 4.07, 1.04, 0.441, 0.169) in THF at 40 °C.[9,10] The molecular weight calibration curve, log M vs. V, for poly(1NMA) was obtained from the universal calibration curve with the Mark–Houwink K and a values (see Table II), which was subsequently converted to the relationship of log (degree of polymerization) (P_n) vs. V. The number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$) of the 1NMA-containing polymers were computed from the GPC chromatogram based on the calibration curve of log P_n vs. V.

Polymer Characterization. Table I summarizes the properties of 1NMA homopolymers prepared to determine the constants K and a in the Mark–Houwink equation

$$[\eta] = KM^a \quad (1)$$

The $[\eta]$ value observed for a polymer with a definite molecular weight distribution is correlated to the GPC data by

$$[\eta] = K^{1/(1+a)}\sum W_iJ_i^{a/(1+a)} \quad (2)$$

where W_i is the weight fraction obtained from the GPC chromatogram and J_i is equivalent to $[\eta]_iM_i$ in the universal calibration

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Table I
Properties of the Poly(1NMA)

	polymerization[a]		viscosity data[b]		GPC data[c]			
polymer	AIBN/ wt %	temp/ °C	$[\eta]$/dm^3 g^{-1}	$\bar{M}_v/10^5$	$\bar{M}_n/10^5$	$\bar{M}_w/10^5$	$\bar{M}_{GPC}/10^5$	$\bar{M}_v/10^5$
P1NMA-1	0.5	60	0.103	5.67	2.24	6.38	5.01	5.69
P1NMA-2	1.0	70	0.144	9.10	2.96	10.8	5.01	9.11
P1NMA-3	1.0	70	0.0579	2.51	0.880	3.14	1.53	2.52
P1NMA-4	1.5	80	0.0805	4.00	1.63	4.58	2.87	4.02

[a] In bulk, under deaerated conditions except for P1NMA-3. [b] $[\eta]$ in THF at 40 °C; $\bar{M}_v$ was evaluated by $8.7 \times 10^{-6} M^{0.708}$. [c] $\bar{M}_{GPC}$ was derived from the peak of the GPC chromatogram.

Table II
Determination of the Mark–Houwink Parameters *K* and *a* for the Poly(1NMA) in THF at 40 °C

combination	$K/10^{-6}$ dm^3 g^{-1}	*a*
P1NMA-1/P1NMA-2	8.87	0.706
P1NMA-1/P1NMA-3	8.86	0.706
P1NMA-1/P1NMA-4	8.50	0.709
P1NMA-2/P1NMA-3	8.78	0.703
P1NMA-2/P1NMA-4	8.78	0.707
P1NMA-3/P1NMA-4	8.44	0.710
	av 8.71 ± 0.17	av 0.708 ± 0.002

Table III
Properties of the Poly(1NMA-*co*-BMA)

	1NMA content/ mol %			
polymer	monomer	polymer[a]	$\bar{M}_n/10^4$ [b]	$\bar{M}_w/\bar{M}_n$ [b]
PBMA	0	0	6.02	2.01
CP1NB-1	1.4	3.2	6.19	2.01
CP1NB-2	3.4	7.3	6.39	1.98
CP1NB-3	6.9	12.5	5.92	2.10
CP1NB-4	10.6	14.6	5.56	2.31
CP1NB-5	14.3	16.4	5.68	2.06
CP1NB-6	30.0	28.5	6.33	2.21
CP1NB-7	40.1	36.4	6.01	2.13
CP1NB-8	71.1	56.4	9.54	2.31
CP1NB-9	90.0	84.9	7.52	1.83
P1NMA	100	100	6.98	2.40

[a] Determined by ^{1}H NMR. [b] Determined by GPC.

curve corresponding to a specified elution volume V_i.[11] Hence, from the viscosity and GPC data for the arbitrary set of 1NMA homopolymers listed in Table I, the self-consistent value of *a* can be computed by[11]

$$\frac{[\eta]_\alpha}{[\eta]_\beta} = \frac{\sum W_{i\alpha} J_i^{a/(1+a)}}{\sum W_{i\beta} J_i^{a/(1+a)}} \qquad (3)$$

Substituting the obtained *a* value in eq 2 provides the corresponding *K* value. Following the above procedure, the Mark–Houwink *K* and *a* values for the poly(1NMA) were determined to be (8.7 ± 0.2) × 10^{-6} dm^3 g^{-1} and 0.708 ± 0.002 in THF at 40 °C, respectively (Table II).[12] As shown in Table I, these values give excellent agreement between the viscosity-average molecular weight ($\bar{M}_v$) evaluated by the Mark–Houwink equation (eq 1) and that computed from the GPC chromatogram.[13]

Properties of the 1NMA–BMA copolymers are summarized in Table III. The copolymer composition was determined on the basis of ^{1}H NMR data; δ 3.7–4.5 (2 H, $CO_2CH_2C_3H_7$) and δ 6.3–8.3 (7 H, naphthalene ring) in benzene-d_6 solution.

Results and Discussion

Photochemical Reaction of Poly(1NMA-*co*-BMA). Neither the formation of gaseous products nor any structural changes in the polymer linkage were observed when BMA homopolymer (PBMA) in deaerated benzene solution at room temperature was irradiated with monochromatic light at 285 nm (2.62 × 10^{-5} einstein cm^{-2} min^{-1}). Although structural changes could not be detected by means of IR or ^{1}H NMR spectroscopy, the evolution of carbon monoxide was confirmed by GLC after the 285-nm irradiation of 1NMA homopolymer (P1NMA) and copolymer with BMA (CP1NB-3, Table III) in deaerated benzene or benzene-d_6 solution. The photoinduced CO evolution was also observed when the low molecular weight oligomer of 1NMA ($\bar{M}_n \simeq$ 850–4300) was irradiated with UV light at >270 nm. These results indicate that the electronically excited state of the 1-naphthyl chromophore in the side-chain ester linkage of 1NMA-containing polymers is responsible for the photoinduced CO evolution.

The IR spectrum of the 1NMA oligomer film after UV irradiation and evaporation of solvent (Figure 1) showed the appearance of an associated OH stretching band (3300–3500 cm^{-1}) and a CH bending band (890 cm^{-1}) that can be assigned to the vinylidene group (RR′C=CH$_2$). The formation of OH groups accompanying CO evolution suggests that the 1NMA oligomer undergoes photochemical decomposition of the side-chain ester group to give 1-naphthol. The formation of the vinylidene group may be due to scission of the main-chain carbon–carbon bond.

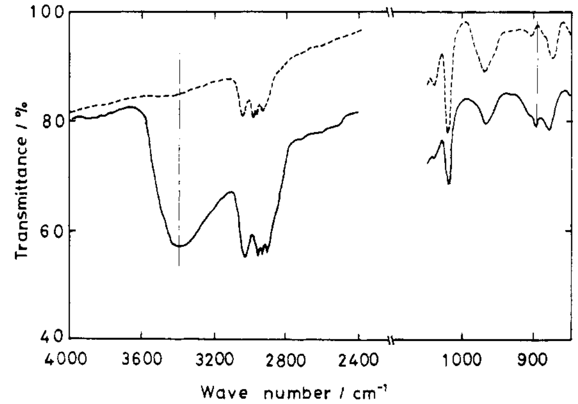
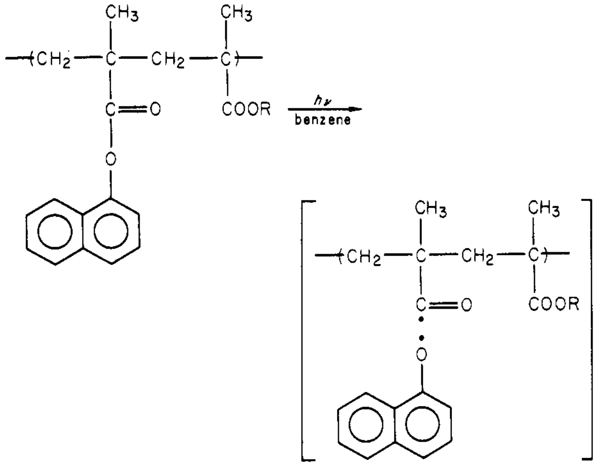


Figure 1. IR spectra of 1NMA oligomer (---) before and (—) after UV irradiation at >270 nm in deaerated benzene solution. The spectra were measured in film after evaporation of the benzene.

Recently, Guillet et al. reported the appearance of new UV absorption bands at 325 and 370 nm during the 280-nm irradiation of P1NMA in deaerated THF solution.[5] Guillet proposed that these bands are associated with a photo-Fries rearrangement of the side-chain ester groups.[5] In this work, however, the 285-nm irradiation of P1NMA in deaerated benzene solution was found to result in no UV spectral changes. This result is consistent with the report by Plank that nonpolar solvents do not favor the photo-Fries rearrangement of aryl esters.[14] While both the 1-naphthol formation with CO evolution and the Fries rearrangement are caused by photolysis of the side-chain ester groups, the former process is closely associated with the main-chain scission of 1NMA-containing polymers.

On the basis of the results presented above, a possible mechanism for the photodegradation of 1NMA-containing polymers can be given as follows: In the initial step, the decomposition of the ester linkage in the 1NMA monomer unit occurs via the electronically excited state of the 1-naphthyl group to form the 1-naphthoxy radical and polymer radical I.

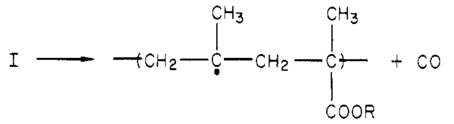


(4)

I

R = 1-naphthyl or butyl

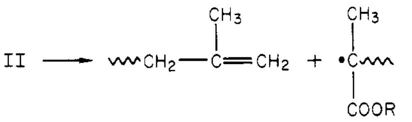
It is plausible that polymer radical I is unstable and will decompose to polymer radical II with CO evolution.



$$\mathrm{I} \longrightarrow -(CH_2-\dot{C}(CH_3)-CH_2-C(CH_3)(COOR))- + CO \quad (5)$$

II

In a subsequent step, β scission of the polymer radical II may occur to form the vinylidene group and polymer radical III.

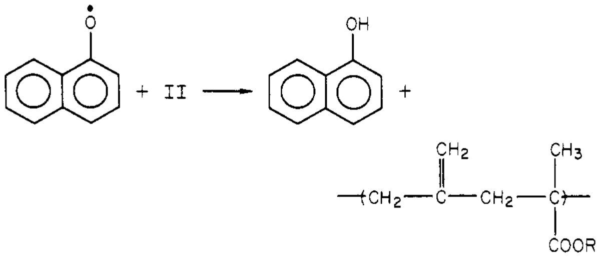


$$\mathrm{II} \longrightarrow \sim CH_2-C(CH_3)=CH_2 + \cdot C(CH_3)(COOR)\sim \quad (6)$$

III

Depolymerization from the polymer radical III appears to be minor under room-temperature UV irradiation in deaerated benzene solution, because the GPC chromatogram of the photoproducts after evaporation of the benzene showed the formation of a negligibly small amount of 1NMA monomer.

The abstraction of the labile β hydrogen from polymer radical II or III by 1-naphthoxy radical (disproportionation) accounts for the simultaneous formation of 1-naphthol and the vinylidene group.



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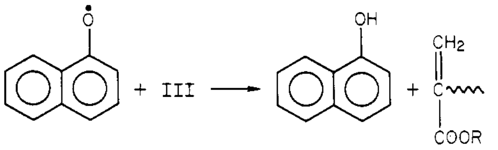
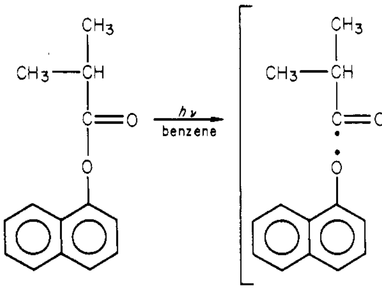


(8)

The possible recombination of the 1-naphthoxy radical with the polymer radical II or III to form an ether linkage could not be confirmed in this work.

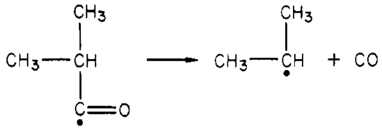
Photochemical Reaction of 1-Naphthyl Isobutyrate (1NIB). The photochemical behavior of 1NIB as a model compound for the 1NMA monomer unit in the 1NMA-containing polymers was also characterized. The GLC measurements showed that the deaerated solution of 1NIB in benzene evolves propane and propylene as well as CO after UV irradiation at >270 nm. The IR spectrum of the reaction mixture after UV irradiation showed nonassociated and associated OH stretching bands due to the formation of 1-naphthol at 3600 cm^{-1} and 3300–3500 cm^{-1}, respectively. Comparison of the ^{1}H NMR spectra of 1NIB in deaerated benzene-d_6 solution before and after UV irradiation indicated that the isopropyl group of 1NIB, 1.2 ppm (d, CH_3) and 2.7 ppm (septet, CH), decreases whereas the OH group of 1-naphthol, 5.4 ppm (s, OH), increases with irradiation time.

These results may lead to a mechanism for the photodecomposition of 1NIB as follows: Analogous to the photolyses of various organic esters,[15] 1NIB undergoes scission of the ester linkage through the UV absorption by the 1-naphthyl chromophore to form the 1-naphthoxy radical and isobutyryl radical.



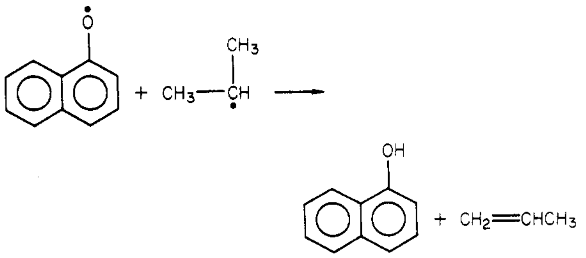
(9)

The CO evolution occurs by the decomposition of the unstable isobutyryl radical to give the isopropyl radical.



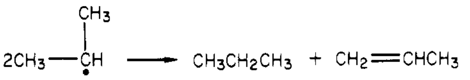
$$CH_3-CH(CH_3)-\dot{C}=O \longrightarrow CH_3-\dot{C}H(CH_3) + CO \quad (10)$$

The disproportionation of 1-naphthoxy radical with an isopropyl radical accounts for the formation of 1-naphthol and propylene.



(11)

Similarly, the disproportionation of isopropyl radicals with each other may give propane and propylene.



$$2CH_3-\dot{C}H(CH_3) \longrightarrow CH_3CH_2CH_3 + CH_2=CHCH_3 \quad (12)$$

It is apparent that the mechanism presented for the photodegradation of 1NMA-containing polymers is consistent with the above photochemical behavior of 1NIB.

Molecular Weight Change of Poly(1NMA-*co*-BMA). The $\bar{M}_n$ values of the 1NMA-containing polymers

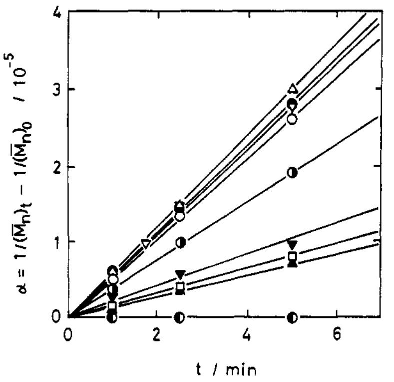


Figure 2. Degree of main-chain scission α vs. 285-nm irradiation time t: (◐) PBMA; (○) CP1NB-1; (●) CP1NB-2; (△) CP1NB-3; (▽) CP1NB-4; (◑) CP1NB-6; (▼) CP1NB-8; (▲) CP1NB-9; (□) P1NMA.

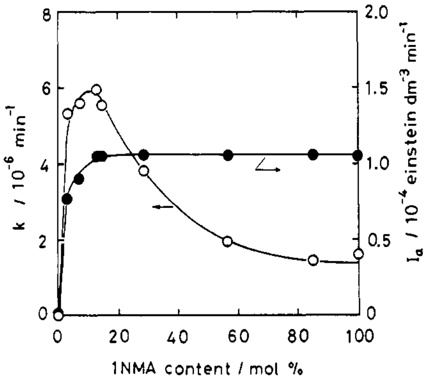


Figure 3. Variations of (○) apparent rate constant for main-chain scission k and (●) number of absorbed quanta I_a as a function of 1NMA content on 285-nm irradiation of poly(1NMA-*co*-BMA) in deaerated benzene solution.

decreased rapidly in deaerated benzene solutions (1 g dm^{-3}) with the 285-nm irradiation time. It should be noted that PBMA does not absorb light at 285 nm ($\epsilon = 0$) and undergoes no molecular weight change under these conditions.

As shown in Figure 2, a linear relationship between the degree of main-chain scission (α) and the 285-nm irradiation time (t) was found to hold for each of the 1NMA-containing polymer systems. This relationship can be represented by

$$\alpha = \frac{1}{(\bar{M}_n)_t} - \frac{1}{(\bar{M}_n)_0} = kt \qquad (13)$$

where $(\bar{M}_n)_0$ and $(\bar{M}_n)_t$ are the number-average molecular weights measured before and after UV irradiation, respectively, and k is the apparent rate constant for the main-chain scission. The k value for each polymer was derived from the slope of the straight line of the plot of eq 13 in Figure 2.

Figure 3 shows the variation of the k value as a function of the 1NMA content (X_N) in poly(1NMA-*co*-BMA). The k value increased rapidly with increasing X_N up to 12.5 mol % (CP1NB-3). At this point the maximum rate constant of 5.96 × 10^{-6} min^{-1} was obtained. In the region of X_N above 12.5 mol %, the main-chain scission was depressed with increasing X_N to attain the ultimate value of 1.62 × 10^{-6} min^{-1} at X_N = 100 mol % (P1NMA). Since the UV absorption of poly(1NMA-*co*-BMA) at 285 nm is due to the 1-naphthyl chromophore, the number of absorbed quanta (I_a) increases with increasing X_N up to 28.5 mol % (Figure 3). For the poly(1NMA-*co*-BMA) with X_N > 28.5 mol %, complete UV absorption occurs, leading to a constant I_a value of 1.05 × 10^{-4} einstein dm^{-3} min^{-1}.

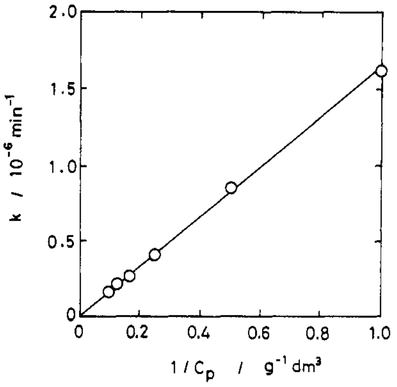


Figure 4. Apparent rate constant for main-chain scission k vs. reciprocal of P1NMA concentration C_p on 285-nm irradiation in deaerated benzene solution.

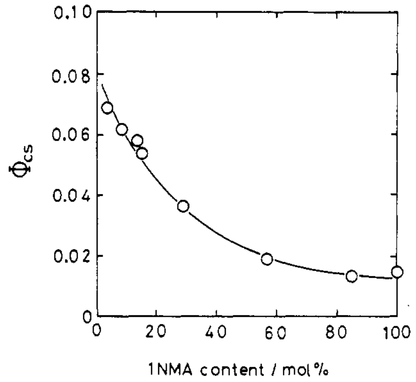


Figure 5. Variation of quantum yield for main-chain scission Φ_{cs} as a function of 1NMA content on 285-nm irradiation of poly(1NMA-*co*-BMA) in deaerated benzene solution.

The effect of polymer concentration (C_p) on the k value was determined for P1NMA in deaerated benzene solution under conditions of complete UV absorption. Under these conditions I_a is constant and independent of C_p. As shown in Figure 4, k is proportional to the reciprocal of C_p. This result is consistent with the general relationship given by[16]

$$k = \Phi_{cs} I_a / C_p \qquad (14)$$

where Φ_{cs} is the quantum yield for main-chain scission. The result shown in Figure 4 also indicates that the present systems are not affected by photochemical nonhomogeneity due to complete UV absorption.[17] Thus it seems that the main-chain scission proceeds uniformly over the reaction volume and complete UV absorption does not lead to serious errors in the evaluation of k.

The Φ_{cs} value for the 1NMA-containing polymer was calculated by eq 14 and is plotted against X_N in Figure 5.[18] It is apparent that the Φ_{cs} value decreases monotonously with X_N to attain its minimum (1.5 × 10^{-2} scissions per absorbed quantum) in the case of P1NMA. This minimum value agrees fairly well with the literature value in THF at 25 °C.[5] On the other hand, the maximum Φ_{cs} value should be obtained for a poly(1NMA-*co*-BMA) with an infinitely low 1NMA content. This can be estimated by extrapolation in Figure 5 to be ca. 8 × 10^{-2} scissions per absorbed quantum.

As will be reported in a subsequent paper,[19] the probability of intramolecular excimer formation between the adjacent 1-naphthyl chromophores increases with the increase in X_N. In view of the characteristics of the main-chain scission and the intramolecular excimer formation in the poly(1NMA-*co*-BMA), it follows that while the microstructure of the isolated 1NMA monomer unit (BMA–1NMA–BMA) is highly efficient toward main-chain

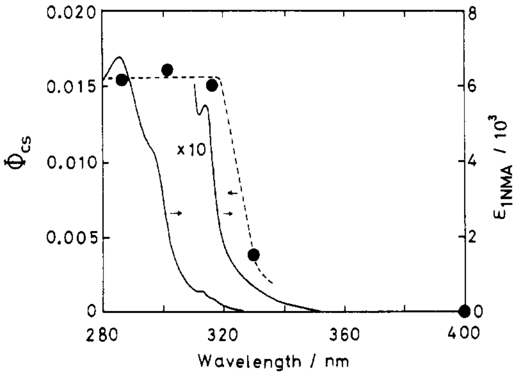


Figure 6. UV spectrum of P1NMA in benzene solution and (●) action spectrum of quantum yield for main-chain scission Φ_{cs}. The extinction coefficient ϵ is given based on the equivalent molarity of 1NMA monomer unit.

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 $\pi-\pi^*$ transition of the 1-naphthyl chromophore by reference to naphthalene. The Φ_{cs} value was constant (ca. 1.5 $\times$ 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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