

Functional Monomers and Polymers CLXVIII. Syntheses and Photoreactions of Poly(methacrylate)s Containing Thymine Bases

Minoo JALILI MOGHADDAM, Shigeo HOZUMI, Yoshiaki INAKI, and Kiichi TAKEMOTO

Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

(Received August 15, 1988)

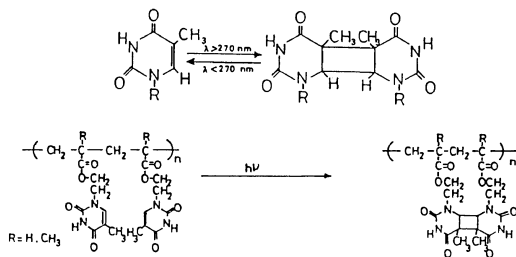
ABSTRACT: Poly(methacrylate)s having thymine derivatives were studied for photodimerizations of thymine units in solution and in the film state, and photolithographic sensitivity tests for their applicability to negative type photoresists. In these homopolymers and copolymers, thymine bases were attached to the polymer chain at positions N¹ or N³. Among these polymers, the alternate copolymer indicated the highest photosensitivity. The results are discussed from the viewpoint of intra- and/or intermolecular photodimerization and the quantum yields in solution and in the film state.

KEY WORDS Deep UV Photoresist / Negative Type Photoresist / Poly(methacrylate) / Thymine Base Derivative / Photosensitivity / Quantum Yield / Intermolecular Photodimerization / Intramolecular Photodimerization / Photo-crosslinking /

The photolithographic process is one of the most essential steps or probably the key process in microelectronics fabrication technology. Therefore researches on inventing new materials for photolithographic processes with high sensitivity, good resolution and dry etch resistance, has received much attention in these years.^{1,2} We have studied photoresists for deep-UV region and synthesized various polymers containing pyrimidine bases pendant to the polymer chain.³⁻⁷ It is well known that pyrimidine bases undergo photodimerization by exposure of the UV light above 270 nm, and also readily reverse to their monomers by UV light at shorter wavelengths (Scheme 1). Among the synthesized polymers, copolymers of methacrylates containing thymine or 6-cyano-uracil with butadiene exhibit high sensitivity and excellent resolution characteristics

as negative type photoresists.⁷ The photolyses of these polymers upon UV irradiation above 270 nm cause intramolecular or intermolecular dimerization of the pyrimidine bases competitively, where the intramolecular self association of the pyrimidine bases is an important factor for photodimerization of these polymers.⁵

In order to obtain photoresists with excel-



Scheme 1.

† Part CLXVII of the series: M. Miyata, T. Tsuzuki, K. Takemoto, and M. Kamachi, *Polym. J.*, **20**, 711 (1988).

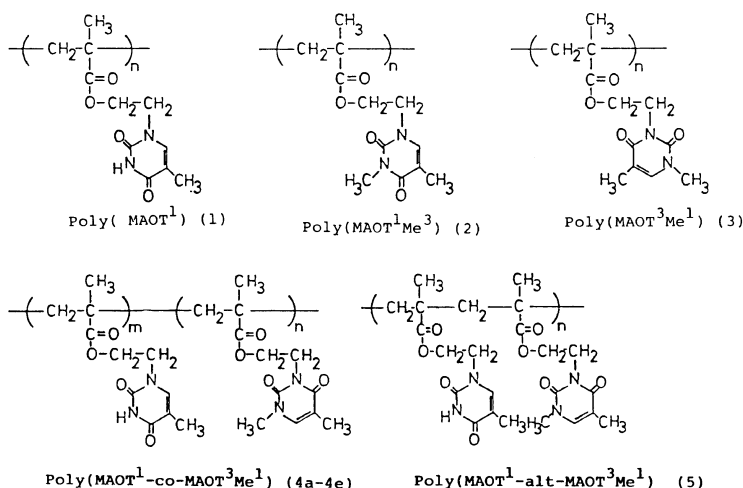


Figure 1. Synthetic poly(methacrylate)s containing thymine units in the side chain.

lent resolution and high sensitivity, it is necessary to suppress intramolecular reactions and enhance the intermolecular photodimerization of pyrimidine bases for effective photocrosslinking of the polymer chains. In the present paper, poly(methacrylate)s having various thymine derivatives were prepared based on molecular models (Figure 1). Homopolymers have thymine bases at position N¹ [poly(MAOT¹); (1, 2)] and N³ [poly(MAOT³Me¹); (3).] The copolymers were random (4a–4e) [poly(MAOT^{1-co}MAOT³Me¹)] and alternate (5) [poly(MAOT^{1-alt}MAOT³Me¹)] copolymers composed of monomers of MAOT¹ and MAOT³Me¹. The photoreactions and the lithographic properties of these polymers were studied and the results are discussed from the viewpoint of intermolecular or intramolecular photodimerization.

EXPERIMENTAL

Materials

Monomer Synthesis

1-(2-Hydroxyethyl)thymine (10). Methacrylonitrile (75 ml, 0.89 mol) was added to ethanolamine (54 ml; 0.89 mol), cooled in an ice bath. The mixture was stirred at room temperature for 4 h, and then refluxed for 4 h to

give the viscous oily product, 3-(2-hydroxyethylamino)-2-methyl-propionitrile (6).

The obtained 6 dissolved in 7 *N* hydrochloric acid (150 ml) was added to 260 ml cool aqueous solution of potassium cyanate (89 g). The resulting solution was stirred at room temperature for 12 h, and then evaporated to dryness. The residue was extracted with ethanol, and the solvent was evaporated to give the oily product, 1-(2-hydroxyethyl)-1-(2-cyanopropyl)urea (7).

An aqueous solution of 7 in methanolic hydrochloric acid (water; 400 ml, methanol; 400 ml, 35% hydrochloric acid; 140 ml) was refluxed for 5 h, and the solvent was evaporated to dryness. The solid residue was extracted with ethanol, and the solvent was evaporated to give 5,6-dihydro-1-(2-hydroxyethyl)thymine (8), which was crystallized by cooling, yield; 80% (120 g).

Compound 8 (86 g; 0.5 mol) was dissolved in acetic acid (250 ml), and bromine (80 g; 0.5 mol) in acetic acid (120 ml) was added dropwise to the solution under reflux. After evolution of HBr gas (7 h), sodium acetate (123 g; 1.5 mol) was added to the reaction mixture, and refluxed for additional 5 h. The solvent was removed under reduced pressure to dryness. The residual solid was then extract-

ed with ethyl acetate, and the extract was evaporated to dryness. Recrystallization from ethanol gave **9** in 80% yield (80 g). The obtained (**9**) was hydrolyzed with 120 ml of 12 *N* hydrochloric acid in 500 ml of methanol, under reflux. After 3 h, the solvent was removed under reduced pressure and the residue was crystallized from ethanol to give white crystals, 1-(2-hydroxyethyl)thymine (**10**), identified by IR and NMR spectra in the literature.³

1-Methyl-thymine (11). This compound was synthesized by the same method as that described for compound **10**, except that methylamine was used as the starting material instead of ethanolamine.

1-Methyl-3-(2-hydroxyethyl)thymine (12). Compound **11** (7 g; 0.05 mol) was dissolved in 200 ml dimethylformamide (DMF) under reflux, and ethylene carbonate (4.72 g, 0.05 mmol dissolved in 15 ml of DMF) was added dropwise to the solution. The reaction was continued until the system was degassed under reflux (about 2 h). The solvent was then removed under reduced pressure and the residue was crystallized from ethanol to obtain **12** in 92.6% yield (8.53 g); mp 174–175°C. IR (KBr, cm^{-1}): 3375, 3050, 3000, 2970, 1695, 1680, 1660, 1635, 1475, 1450, 1420, 1350, 1260, 1200, 1145, 1066, 950, 765, 675, and 645. ¹H NMR (60 MHz, in dimethyl sulfoxide (DMSO)-*d*₆ at 25°C, ppm): 1.82 (s, 3H), 3.29 (s, 3H), 3.57 (t, 2H), 3.97 (t, 2H), 4.75 (t, 1H), and 7.55 (s, 1H).

Anal. Calcd. for C₈H₁₂O₃N₂: C, 52.17%; H, 6.57%; N, 15.21%. Found: C, 52.23%; H, 6.60%; N, 15.21%.

1-Methyl-3-(2-methacryloyloxyethyl)thymine (13) (MAOT³Me¹). Methacrylic anhydride (3.0 ml, 0.024 mol) was added to a solution of **12** (3.68 g, 0.02 mol) in pyridine (20 ml), and the solution was stirred for 60 h at room temperature. Pyridine was removed under reduced pressure, and the oily residue was dissolved in a saturated aqueous solution of sodium bicarbonate to remove excess methacrylic anhydride. After extraction with diethyl ether and evaporation of the solvent, the re-

sidue was crystallized from cyclohexane to obtain **13** in 48% yield (2.43 g); mp 69–70°C. IR (KBr, cm^{-1}): 3150, 2960, 2780, 1690, 1660, 1470, 1440, 1410, 1350, 1300, 1280, 1260, 1230, 1150, 1130, 1010, 950, 870, and 750. ¹H NMR (60 MHz, in DMSO-*d*₆ at 25°C, ppm): 1.82 (s, 6H), 3.22 (s, 3H), 4.1–4.3 (m, 4H), 5.67 (s, 1H), 5.92 (s, 1H), and 7.55 (s, 1H).

Anal. Calcd. for C₁₂H₁₆O₄N₂: C, 57.14%; H, 6.39%; N, 11.11%. Found: C, 57.14%, H, 6.39%; N, 11.01%.

Polymer Synthesis

Poly[1-methacryloyloxyethylthymine]; *Poly(MAOT¹) (1)*. Poly(MAOT¹) (**1**) was prepared by free radical polymerization of the corresponding monomer according to the literature.³ The molecular weight of the polymer was determined by gel permeation chromatography (GPC) to be 246000.

Poly[1-methacryloyloxyethyl-3-methylthymine]; *Poly(MAOT¹Me³) (2)*. Poly(MAOT¹Me³) (**2**) was prepared by methylation of poly(MAOT¹) (**1**) with methyl iodide in DMSO and potassium carbonate at room temperature for 24 h, by the same method as in the literature.¹¹

Poly[1-methyl-3-(2-methacryloyloxyethyl)thymine]; *Poly(MAOT³Me¹) (3)*. Monomer **13** (0.25 g, 0.1 mol l⁻¹) and AIBN (0.0016 g, 0.01 mol l⁻¹) were dissolved in 10 ml DMF, and radical polymerization was carried out for 24 h at 60°C. After the reaction, the solution was precipitated in methanol to obtain polymer (**3**) in 87% yield (0.22 g). The molecular weight of the polymer obtained by GPC was found to be 146000. IR (KBr, cm^{-1}): 2920, 1700, 1640, 1460, 1360, 1270, 1160, 1030, and 780. ¹H NMR (100 MHz, in DMSO-*d*₆, 150°C, ppm): 0.7 (s, 3H), 1.8 (s, 3H), 1.6–2.0 (m, 2H), 3.3 (s, 3H), 4.2 (s, 4H), and 7.4 (s, 1H).

Anal. Calcd. for C₁₂H₁₆O₄N₂: C, 57.14%; H, 6.39%; N, 11.11%. Found: C, 56.57%; H, 6.45%; N, 11.01%.

Poly[MAOT¹-co-MAOT³Me¹](4a–4e). Copolymers of MAOT¹ and MAOT³Me¹ were

Table I. Copolymerization of MAOT¹ with MAOT³Me¹

MAOT ¹ in monomer/%	Conversion/% ^a	MAOT ¹ in polymer/%
80	89	82
70	93	78
60	87	66
50	83	54
40	86	44

^a In DMF at 60°C for 24 h; [MAOT¹ + MAOT³Me¹] = 0.1 mol l⁻¹, [AIBN] = 0.01 mol l⁻¹.

prepared by the radical polymerization of various ratios of these monomers according to the method mentioned in the synthesis of poly(MAOT³Me¹) (in DMF, [MAOT¹ + MAOT³Me¹] = 0.1 mol l⁻¹, [AIBN] = 0.01 mol l⁻¹, 60°C, 24 h). The copolymers were obtained by precipitation in excess acetone. The conversions of the monomers are given in Table I. The molecular weight of the copolymer with composition of MAOT¹-MAOT³Me¹ (66:34) was 524000.

Poly[methacrylic acid-alt-MAOT³Me¹] (15). Polymethacrylic anhydride (**14**) was prepared according to the method in the literature.¹³ The molecular weight of the polymer obtained was about 95000. This polymer was then dissolved in a DMF-pyridine mixture (5 ml), and **12** (12.8 g, 0.07 mol) was added to this solution, and stirred for 3 days at 60°C. After the reaction, the solvent was distilled off under reduced pressure, and the residue was thoroughly washed with acetone and filtered to obtain polymer (**15**) in 34% yield (0.81 g). IR (KBr, cm⁻¹): 3400, 2950, 1720, 1620, 1450, 1390, 1350, 1260, 1140, 1020, and 780.

Poly[MAOT¹-alt-MAOT³Me¹] (5). To **15** (0.33 g, 0.001 mol) in 3 ml DMF, 1,2-*O*-ethanothymine¹⁰ (**16**) (0.25 g, 0.001 mol) was added and the reaction mixture was stirred at 80°C for 5 h. After the reaction, the mixture was poured into excess ethanol to obtain polymer (**5**) as a precipitant in 91% yield (0.41 g), IR (KBr, cm⁻¹): 3440, 2900, 1700, 1660, 1640,

1470, 1360, 1260, 1030, and 780. ¹H NMR (100 MHz, in DMSO-*d*₆ at 150°C, ppm): 0.6—1.4 (m, 6H), 1.8 (s, 10H), 3.3 (s, 3H), 4.0 (s, 2H), 4.2 (s, 6H), 7.4 (s, 2H), and 11.3 (s, 1H).

Photochemical Reactions

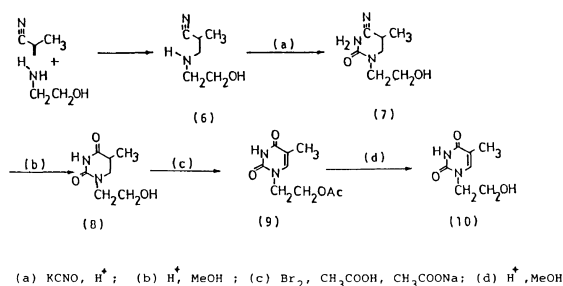
Photolyses of the polymers in solutions were carried out in a 10 mm quartz cell. All the samples were dissolved in DMSO and the concentration of the polymer solutions were adjusted at 1 × 10⁻⁴ mol l⁻¹ as the thymine unit. The photodimerization was followed by UV spectrophotometer at 270 nm. The light source was a monochromator adjusted at the wavelength 280 nm. The purified nitrogen gas was passed through the solution to displace the air before irradiation and light intensities were determined by potassium actinometry.⁶

Photolyses of the polymer films were carried out with a spectro-irradiator. Solutions of the polymers in DMF were cast on quartz substrates, and the solvents were rejected under vacuum for 1 day to obtain thin films of the polymers. The films were exposed to the irradiation of a 2 KW Xe-Arc lamp through a diffracting latticed window with a narrow wavelength range of UV light centered at 280 nm (268—292 nm).

For photosensitivity tests, DMF solutions of the polymers (10%, w/w) were spin coated on the aluminum substrates. The thickness of the films obtained, were about 0.3 μm. The polymer films were exposed to the irradiation of a UV light through the thin slit of a spectrophotograph by scanning up the aluminum substrates against the light slit, and then were developed in a DMF-*m*-xylene mixed solution under the same conditions (temperature and time).

Instrumentation

A JASCO SS-25 monochromator with a wavelength at 280 nm was used as the light source to determine the quantum yields of the resists in solution. Photolyses of the polymer films were carried out with using a Nihon


Scheme 2.

Bunko (CRM-FA) spectro-irradiator with a 2 KW Xe-Arc lamp as the light source. The ultraviolet spectra were measured with a Nihon-Bunko (UVIDEC-660) spectrophotometer.

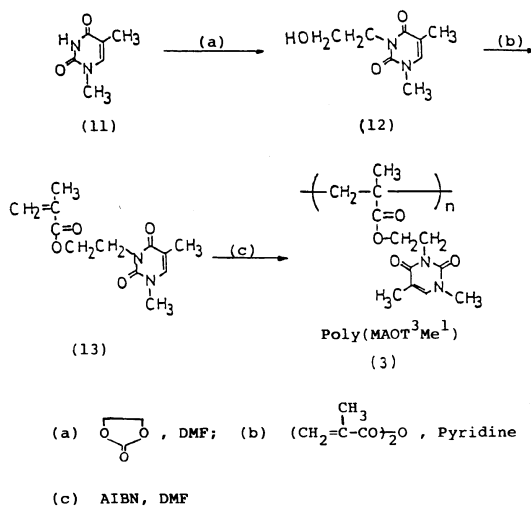
Measurement of the lithographic photosensitivity was made using a Nihon-Spectrophotograph (CT-40) with a 500 W Xe-short Arc lamp as deep UV light source. The polymer films on aluminum substrates were scanned up through the slit of the illuminating source by a continuous scanning mechanism. The resists were spin coated on the aluminum substrates by a Mikasa spinner (1H-D₂), and the thickness of the resists was measured using a Rank-Tieler Talystep profilometer.

The molecular weight distribution of the polymers was determined by gel permeation chromatography (GPC) using Toyo Soda HLC CP8000 with a thermostated column TSK gel G4000HT (Toyo Soda Co., $4 \times 10^3 - 4 \times 10^5 M_w$) and a UV detector operated at 270 nm with DMF as the eluent.

RESULTS AND DISCUSSION

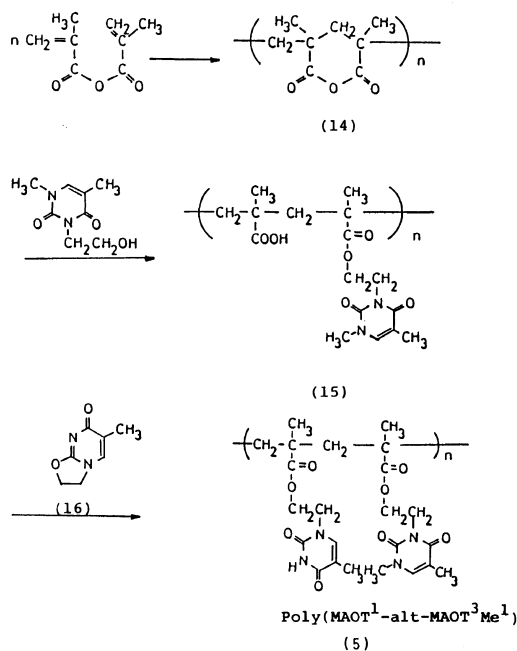
Material Synthesis

Hydroxyethyl derivatives of thymine were prepared starting with ethanolamine and methacrylonitrile according to a modified method for 1-alkyluracil as shown in Scheme 2.⁸ The methacrylate monomers were obtained by the reaction of the hydroxyethyl derivatives with methacrylic anhydride. Poly(methacrylate)s having various thymine derivatives


Scheme 3.

(Figure 1) were prepared according to Scheme 3.

Radical polymerization and copolymerization of these monomers were carried out using AIBN as the initiator. Results of the copolymerization are summarized in Table I; the content of each unit was determined by ¹H NMR spectra. Poly(MAOT¹Me³) was obtained by methylation of poly(MAOT¹), according to the literature.¹¹ The alternate copolymer [poly(MAOT¹-*alt*-MAOT³Me¹)] was obtained by reaction of poly(methacrylic anhydride) with the hydroxyethyl derivative of thymine followed by reaction with another cyclic type of thymine derivative, as shown in Scheme 4.



Scheme 4.

Photolysis

Photoreaction of the Polymers in Solution. Photochemical reactions of the polymers in dilute solutions were studied to determine the quantum yields of the intramolecular photodimerization of the thymine units along the polymer chain. The quantum yields determined at the wavelength 280 nm for all polymers and copolymers are listed in Table II. The values of the molar extinction coefficients and hypochromicities of the polymers based on thymine monomers are also listed in the table.

The hypochromicity generally showed interactions between nucleic acid bases and their stacked conformation in the ground state; the greater the stacked conformation, the higher was the quantum yield. On the other hand, it was known that photodimerization occurs only intramolecularly in dilute solutions of polymers with pendant thymine bases.³ Therefore, the quantum yields obtained in Table II indicate the efficiency of the intramolecular photodimerization in each poly-

Table II. Molar extinction coefficients, quantum yields, and hypochromicities of the polymethacrylates with pendant thymine bases

Compound	ϵ^a	Φ_d^b	H/% ^c
Poly(MAOT ³ Me ¹)	8300	0.017	7.8
Poly(MAOT ¹)	7990	0.0095	11.2
Poly(MAOT ¹ Me ³)	—	0.012	—
Poly(MAOT ¹ - <i>co</i> -MAOT ³ Me ¹)			
(82 : 18)	9000	0.0038	0.0
(78 : 22)	9100	0.0046	1.1
(66 : 34)	8600	0.0044	4.4
(54 : 46)	8900	0.0065	1.1
(44 : 56)	9200	0.0096	2.2
Poly(MAOT ¹ - <i>alt</i> -MAOT ³ Me ¹)	7600	0.0059	15.5

^a Molar extinction coefficient at 272 nm in DMSO at 25°C.

^b Quantum yield in DMSO.

^c Hypochromicity relative to thymine monomer in DMSO at 25°C ($\epsilon_{\text{thymine}} = 9000$).

mer, and are related to the stacking of the thymine bases and reactivity of the stacked thymine bases for photodimerization.

The quantum yield values were plotted against the composition of copolymers as shown in Figure 2a. The oblique line shows hypothetical quantum yield for the mixture of homopolymers [poly(MAOT¹) and poly(MAOT³Me¹)], and the real curve represents the quantum yields of various copolymers of MAOT¹ and MAOT³Me¹. Poly(MAOT³Me¹) showed a higher quantum yield than poly(MAOT¹), which suggests that the sterical arrangement of thymine bases in poly(MAOT³Me¹) is more favorable for the photodimerization than that of poly(MAOT¹).

Molecular models indicated that the formation of the thymine photodimers are sterically difficult for the alternate copolymers of MAOT¹ and MAOT³Me¹ but favorable for the homopolymers. These considerations of molecular models may explain the lower quantum yield of the copolymer than those of homopolymers as shown in Figure 2a. The possibility of the adjacent existence of MAOT¹ and MAOT³Me¹ increased in random copoly-

mer of MAOT³Me¹ and MAOT¹, and hence the favorable stacking conformations of thymine units decreased in such a way that the photodimerization would occur sterically with difficulty. The alternate copolymer [poly-

(MAOT¹-*alt*-MAOT³Me¹)], in which MAOT¹ units and MAOT³Me¹ units exist certainly next to each other, showed lower quantum yields than the random copolymer of MAOT¹ and MAOT³Me¹. This is also evidence for the large strain in the polymer chains for photodimerization of the adjacent MAOT¹ and MAOT³Me¹ rather than MAOT¹ units or MAOT³Me¹ units.

Photoreaction in the Solid State. The rates of photodimerization of thymine units in the side chains of the poly(MAOT¹), poly(MAOT³Me¹), and poly(MAOT¹-*co*-MAOT³Me¹) (66/34) were measured in the solid state. Figure 3 shows the percent of thymine bases remaining in the polymer chain against irradiation energy at 280 nm. The formation of thymine dimer units was then confirmed by reversible photodissociation of thymine dimer units by irradiation of a narrow wavelength range of UV light centered at 249 nm, as shown in the same figure. The initial rate of the disappearance of thymine units, where there were very few isolated thymine bases grafted to the polymer chains,¹⁴ was ob-

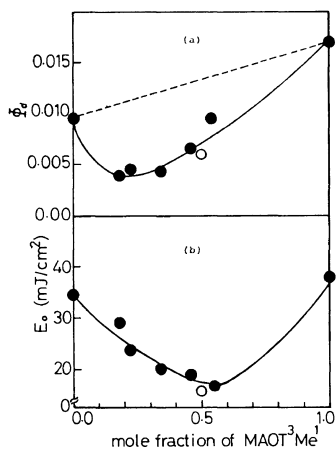


Figure 2. (a) Quantum yields for intramolecular photodimerization of homopolymers and copolymers: ○, poly(MAOT¹-*alt*-MAOT³Me¹). (b) The minimum required energy for remaining of homopolymers and copolymers: ○, poly(MAOT¹-*alt*-MAOT³Me¹).

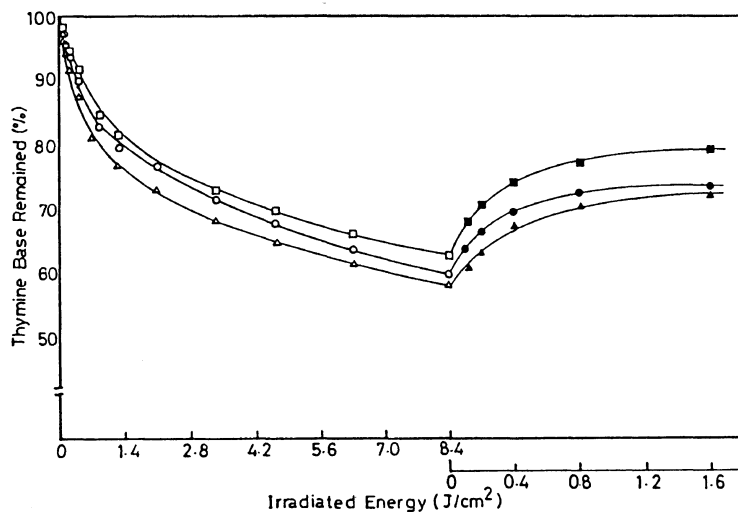


Figure 3. Photodimerization and photodissociation of thymine units and their photodimers in the side chains of the homopolymers and copolymers in the film state. Photodimerization reaction as a function of irradiated energy at 280 nm: □, poly(MAOT¹); ○, poly(MAOT³Me¹); △, poly(MAOT¹-*co*-MAOT³Me¹)(66:34). Photodissociation reaction as a function of irradiated energy at 249 nm: ■, poly(MAOT¹); ●, poly(MAOT³Me¹); ▲, poly(MAOT¹-*co*-MAOT³Me¹)(66:34).

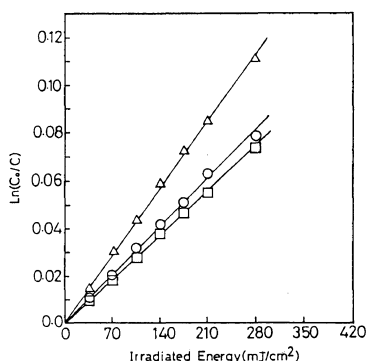


Figure 4. Initial photodimerization rate of thymine units in the side chain of the polymers and copolymers in the film state: \square , poly(MAOT¹); \circ , poly(MAOT³Me¹), \triangle , poly(MAOT¹-*co*-MAOT³Me¹)(66:34).

tained by plotting the $\ln C_0/C$ against irradiation energy at 280 nm as shown in Figure 4, where C_0 and C are the concentrations of thymine unit before and after irradiation of various doses, respectively.

The initial quantum yields of the polymers in the film state were obtained by using eq 1¹⁵

$$\phi_d = [1/(\sigma_a)(C_0)][\Delta C/\Delta L] \quad (1)$$

where σ_a is the absorption cross section of the polymer, ΔC is the change in thymine concentration, and ΔL is the increment of the light exposure. The quantum yields and maximum conversions for photodimerization reaction of these polymers are listed in Table III.

It was found that the quantum yields of the homopolymers in the film state were about 5–9 times of those in the solution. The high quantum yield in the film state suggests that the thymine bases fixed in the film state, and the possibility for intermolecular reaction increases. However, the stacking conformation of the thymine bases in the side chain of the homopolymers are favorable for the intramolecular photodimerization and hence intramolecular photodimerization should occur efficiently even in the film state.

Quantum yields of the copolymers were lower in solution (Figure 2a), and higher in the

Table III. Quantum yields and maximum photodimerization conversion of thymine bases in polymethacrylates with pendant thymine bases in the film state

Polymer	ϕ_d	Conv. _{max} /%
Poly(MAOT ¹)	0.086	40
Poly(MAOT ³ Me ¹)	0.080	37
Poly(MAOT ¹ - <i>co</i> -MAOT ³ Me ¹) (66:34)	0.159	42

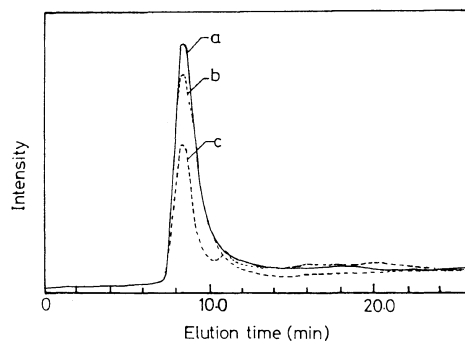


Figure 5. Gel permeation chromatograms of poly(MAOT¹-*co*-MAOT³Me¹)(66:34), in dilute solution exposed to the irradiation of UV light at 280 nm; (a), before irradiation, $M_n = 5.42 \times 10^5$, $M_w/M_n = 5.58$; (b, c), after exposure of 4.2 and 35 J cm^{-2} doses.

film state (Table III) than those of the homopolymers. This suggests that the intermolecular photodimerization of thymine bases occurs preferentially for copolymers in the film state.

GPC Study of the Polymers

The molecular weight changes by photodimerizations were measured by GPC. The chromatograms before and after photochemical reaction of poly(MAOT¹-*co*-MAOT³Me¹)(66:34) in DMF solution are shown in Figure 5. The molecular weight of this copolymer was higher than that of homopolymers (based on standard polystyrene), as shown in Figures 7 and 8. Figure 5 shows that the photodimerization of thymine units in solution is predominantly an intramolecular reaction, and no intermolecular photodimerization leading to an increase in molecular weight of the polymer

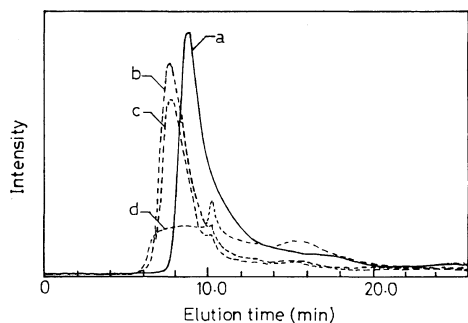


Figure 6. Gel permeation chromatograms of poly(MAOT¹-co-MAOT³Me¹) (66:34), in the film state exposed to the irradiation of UV light at 280 nm: (a), before irradiation; (b–d), after exposure of 0.42, 2.52, and 6.3 J cm⁻² doses.

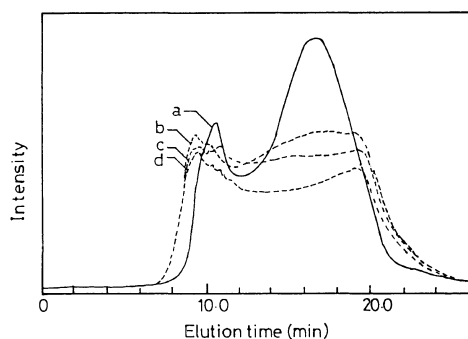


Figure 7. Gel permeation chromatograms of poly(MAOT¹), in the film state exposed to the irradiation of UV light at 280 nm: (a), before irradiation, $M_n = 2.46 \times 10^5$, $M_w/M_n = 3.5$; (b–d), after exposure of 0.84, 2.49, and 18.90 mJ cm⁻² dose.

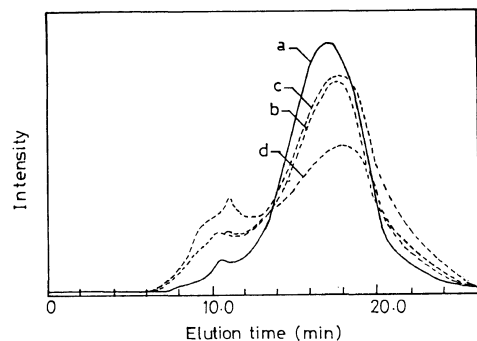


Figure 8. Gel permeation chromatograms of poly(MAOT³Me¹), in the film state exposed to the irradiation of UV light at 280 nm: (a), before irradiation, $M_n = 1.46 \times 10^5$, $M_w/M_n = 3.5$; (b–d), after exposure of 0.63, 2.52, and 18.90 J cm⁻² doses.

occurs. On the other hand, in the film state (Figure 6), an increase of molecular weight was observed due to the intermolecular photodimerization of thymine units to form photocrosslinking.

The photodimerization of homopolymers in the film state also caused increase in their molecular weights as shown in Figures 7 [poly(MAOT¹)] and 8[poly(MAOT³Me¹)]. These figures show that polymer chains with the same molecular weights as those before irradiation existed after irradiation. This suggests that the intramolecular and intermolecular reactions occurs simultaneously. However, Figure 6 for the copolymer showed a higher photo-crosslinking rate by intermolecular photodimerization. This indicates that poly(MAOT¹-co-MAOT³Me¹) can be a highly sensitive polymer as negative type photoresist.

Lithographic Photosensitivity and Its Relation to Quantum Yield

In order to apply thymine polymers to deep-UV photoresist for integrate circuit production, a primary photosensitivity evaluation was carried out. The photosensitivity evaluation of the various polymers was performed in the film state, and their relation to the quantum yields in solution and film state was considered. The photosensitivity range of each polymer, the maximal sensitive wavelength, and the gel dose (E_0) are listed in Table IV. The gel doses at the maximal wavelength are also plotted against copolymer composition as shown in Figure 2b.

A comparison of Figures 2a and 2b shows that the quantum yield in solution is related to photosensitivity in the film state. The copolymers which had lower quantum yield in the solution, showed higher photosensitivity than those of homopolymers. This finding was supported by comparing the quantum yields of the polymers in the film state (Table III) and GPC data. The copolymer of poly(MAOT¹-co-MAOT³Me¹) (66:34), which had a low quantum yield in solution (Figure 2a), the highest quantum yield in the film state (Table III) and

Table IV. Lithographic evaluations of polymethacrylates with pendant thymine bases

Polymer	λ/nm^a	$\lambda \text{ max}/\text{nm}^b$	$E_0/\text{mJ cm}^{-2c}$
Poly(MAOT ³ Me ¹)	230—305	280	38.0
Poly(MAOT ¹)	230—300	280	34.6
Poly(MAOT ¹ Me ³)	230—305	280	16.7
Poly(MAOT ¹ - <i>co</i> -MAOT ³ Me ¹) (82:18)	(78:22)	250—305	280
	(66:34)	230—305	280
	(54:46)	230—310	280
	(44:56)	230—310	280
		200—315	270
Poly(MAOT ¹ - <i>alt</i> -MAOT ³ Me ¹)	200—315	270	15.8

^a Photosensitive wavelength range.

^b Maximal photosensitive wavelength.

^c Minimum required energy for photo-crosslinking at the maximal wavelength.

high rate of crosslinking (Figure 6), showed higher photosensitivity than homopolymers (Table IV). Therefore, polymers with lower quantum yields of intramolecular photodimerization showed higher photosensitivity caused by intermolecular photodimerization. These results revealed that polymers of high photosensitivity can be obtained by suppression of intramolecular photodimerization and intensifying the intermolecular photodimerization.

However, the polymer composition of the lowest quantum yield in solution is not the same as that of the highest sensitivity in the film state. This is due to the fact that sensitivity is evaluated in this determination after development, and many factors interfere besides the photo-crosslinking reaction, such as the solubility of the polymer for film fabrication, adherence of the polymers solution to the substrates, molecular weights of the unirradiated polymers, and the choice of the developers. Therefore the polymer of the highest photosensitivity does not agree with the polymer of the lowest intramolecular quantum yield.

CONCLUSION

Poly(methacrylate)s with different sterical arrangements of thymine bases in their side chains were prepared and their photochemical

reactions were studied. Evaluation of lithographic photosensitivity of these polymers revealed the following: The alternate copolymer of MAOT¹ and MAOT³Me¹ was the most highly photosensitive polymer, and the photosensitivity of the copolymers increased with increasing content of adjacent MAOT¹-MAOT³Me¹ in the side chains of the copolymers. This indicates that polymers of high photosensitivity values can be obtained by suppression of intramolecular photodimerization and intensifying intermolecular photodimerization.

Acknowledgment. The authors express grateful acknowledgment to Japan Synthetic Rubber Co., for the photosensitivity evaluation of the thymine polymers.

REFERENCES

1. L. F. Thompson, C. G. Willson, and M. J. Bowden, "Introduction to Microlithography," ACS Symposium Series, 219, 1983.
2. L. F. Thompson, C. G. Willson, and J. M. J. Frechet, "Materials for Microlithography," ACS Symposium series, 266 1984.
3. Y. Kita, Y. Inaki, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 427 (1980).
4. Y. Kita, T. Uno, Y. Inaki, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 477 (1981).
5. Y. Kita, T. Uno, Y. Inaki, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 2347 (1981).

Syntheses and Photoreactions of Poly(methacrylate)s Containing Thymine Bases

6. Y. Inaki, S. Fukunaga, Y. Suda, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 119 (1985).
7. Y. Inaki, S. Fukunaga, K. Takemoto, and Y. Harita, *J. Polym. Sci., Polym. Chem. Ed.*, in contribution.
8. W. W. Zorbach and R. S. Tipson, "Synthetic Procedures in Nucleic Acid Chemistry," Vol. I, Academic Press, New York, N.Y., 1968, p 63.
9. W. W. Zorbach and R. S. Tipson, "Synthetic Procedures in Nucleic Acid Chemistry," Vol. I, Academic Press, New York, N.Y., 1968, p 109.
10. Y. Kita, H. Futagawa, Y. Inaki, and K. Takemoto, *Polym. Bull.*, **2**, 195 (1980).
11. S. B. Fang, Y. Inaki, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2455 (1984).
12. S. B. Fang, Y. Inaki, and K. Takemoto, *Polym. J.*, **17**, 443 (1985).
13. J. A. Moore, *Macromolecular Syntheses, Collective Vol.*, **1**, 41 (1977).
14. Y. Kita, T. Uno, Y. Inaki, and K. Takemoto, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1733 (1981).
15. G. J. Fisher and H. E. Johns, "Photochemistry and Photobiology of Nucleic Acids," Vol. I, S. Y. Wang, Ed., Academic Press, New York, 1976, p. 234.