

# High Temperature Stable Photopatternable Copolymers: Synthesis, Optical Properties, and Photopatterning Process Studies

NOBUHIRO KAWATSUKI,<sup>1,\*</sup> RIKUJI WATANABE,<sup>2</sup> TOSHIAKI TOKUHARA,<sup>2</sup> MASAO UETSUKI,<sup>2</sup> SHIRO NAGATA,<sup>1</sup> and HIDEJIRO ICHIMURA<sup>2</sup>

<sup>1</sup>Central Research Laboratories, Kuraray Co., Ltd., 2045-1 Sakazu, Kurashiki 710 and <sup>2</sup>Technical Research Center, Kuraray Co., Ltd., 1620 Sakazu, Kurashiki 710, Japan

## SYNOPSIS

Photopatternable copolymers and photopatterning processes for high temperature stable optical elements have been studied. The photopatternable copolymers were synthesized from methyl methacrylate and methacrylic ester comprising a nonconjugate carbon-carbon double bond side chain and epoxy side chain. Their optical properties were investigated on film samples doped with *m*-benzoylbenzophenone (BBP). After irradiating with UV light, insoluble polymer was formed in a high yield at higher temperature, resulting in changes in thickness and refractive index, which were precisely controlled by the exposure energy of UV light. The two step photopatterning processes were carried out by means of UV irradiations with and without a photomask bearing a grating pattern followed by removal of unreacted BBP to draw an optical pattern on the polymer material with cross-linking. Further photoreaction was also performed to cure the polymer by exposure with a high energy UV lamp containing shorter wavelength light after the patterning process. By a combination of the patterning process and the postcuring process, an optical grating fabricated from these copolymers showed a heat stability up to 160°C. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Because of the great potential of organic polymer materials for integrated optics and photonics, a lot of functionalized polymeric materials have been studied.<sup>1</sup> Optical patterning is often useful for fabricating waveguides and/or grating elements. Usually, the wet process of the UV lithography procedures required to develop a UV-patterned photoresist. To fabricate a patterned structure on the materials directly, Chandross et al.<sup>2</sup> proposed a photolocking process in which a photochemical reaction was used to fix a dopant in a polymer film with a lower refractive index and the unreacted dopant was then removed by heating. The photolocking has been studied on methacrylate (MA) copolymers doped

with photoreactive dopants.<sup>3-7</sup> The advantage of this method is that the optically patterned structure can be directly formed on a polymer material by a photoreaction with UV irradiation. We developed a photoreactive polymer composite composed of copolymers of methyl methacrylate (MMA) and a methacrylic ester comprised of a carbon-carbon double bond doped with an aromatic ketone.<sup>6,7</sup> Film thickness and refractive index can be changed with UV irradiation followed by removal of the unreacted aromatic ketone. The photoreaction was applied to fabricate optical phase gratings and they showed heat stability up to 85°C.<sup>7</sup>

In the semiconductor industry, optical elements are sometimes put in a high temperature atmosphere such as in the production of a thin inorganic film coating or in an assembling process. In the case of organic optical elements, the structure of the optical pattern tends to deform at a high temperature because of their mobility above the glass-transition

\* To whom correspondence should be addressed.

temperature ( $T_g$ ). Optical elements fabricated from our materials<sup>7</sup> did not have enough heat stability for these processes at 150°C. Higher temperature stable photopatternable organic materials are required in practical use.

One of the factors for hardness of a polymer is attributed to a cross-linking of the material, so that higher  $T_g$  and less mobility of the material could be expected. Photochemical reaction is effective for cross-linking as well as changing in optical properties if the reaction undergoes not only between a polymer and a dopant but also between polymers. The patterning process of photoreactive materials should be designed to achieve a cross-linked structure for a whole patterned area.

This article describes new photopatternable optical materials and a new patterning process of those with UV lights to accomplish a high temperature stable patterned structure. The materials consist of MA copolymers comprising carbon-carbon double bond and epoxy side chain, and *m*-benzoylbenzophenone (BBP). Glycidyl methacrylate (GMA) have been copolymerized to the copolymer previously reported<sup>7</sup> to achieve higher cross-linking. Insoluble polymer was formed by irradiating UV light and its amount was changed with the reaction temperature. Optical properties of the materials and optical patterning processes comprising a few irradiation steps have been studied. Optical phase grating made from a new copolymer doped with BBP and a new process showed a high temperature stability at 160°C for several hours without a change in optical properties and structure.

## EXPERIMENTAL

### Materials

MMA, GMA, and methacryloyl chloride were used after distillation to remove the reaction inhibitor. Geraniol was supplied by Kuraray Co., Ltd. and used without further purification. BBP was synthesized as described previously.<sup>8</sup> All other solvents and chemicals were commercially available and used as received.

### Monomer Synthesis

#### 2-Butenyl MA (1a)

Under nitrogen atmosphere, a mixture of 28.0 g (0.389 mol) of 2-butenol, 39.2 g of triethylamine, 20 mg of 2,6-di-*t*-butyl-4-methyl-phenol (inhibitor), and 300 mL of dry ether was cooled to 5°C. Meth-

acryloyl chloride, 40.6 g (0.4 mol), was added dropwise with stirring. The reaction mixture was stirred for 2 h at 0°C and kept overnight at room temperature. After adding 300 mL of ether into the reaction mixture, the solution was poured into 300 mL of water and extracted with diethyl ether (3 × 100 mL). The combined ether extracts were washed with saturated aqueous sodium chloride (300 mL) and water (300 mL) and dried over sodium bicarbonate. The solvent was removed at reduced pressure and the raw product was distilled under vacuum. Finally the product was further purified by column chromatography over silica gel using dichloromethane as eluent.

YIELD: 24 g (45%); b.p. 70–72°C/22–24 mmHg. <sup>1</sup>H-NMR: (CDCl<sub>3</sub>): δ (ppm) = 1.70 (brs, 3H), 1.94 (s, 3H), 4.54 (brs, 2H), 5.51 (brs, 1H), 6.10 (brs, 1H), 5.58–5.80 (m, 2H). IR (neat): 1718 (C=O), 970 (C=C) cm<sup>-1</sup>.

#### 2-Methyl-2-Butenyl MA (1b)

**1b** was synthesized by the same procedure as **1a** from 91.4 g (1.02 mol) of 2-methyl-2-butenol and 107 g (1.02 mol) of methacryloyl chloride. The raw product was purified by distillation followed by column chromatography over silica gel using dichloromethane as eluent.

YIELD: 56.6 g (36%); b.p. 55–59°C/3–6 mmHg. <sup>1</sup>H-NMR: (CDCl<sub>3</sub>): δ (ppm) = 1.70 (brs, 3H), 1.92 (s, 6H), 4.55–4.70 (m, 2H), 5.24–5.50 (m, 2H), 6.08 (brs, 1H). IR (neat): 1712 (C=O), 970 (C=C) cm<sup>-1</sup>.

#### 2-Methyl-2-Propenyl MA (1c)

**1c** was also synthesized by the same procedure as **1a** from 2-methyl-2-propene-1-ol and methacryloyl chloride. The raw product was purified by column chromatography over silica gel using a mixture of hexane and ethyl acetate (19 : 1) as eluent.

YIELD: 35%; viscous oil. <sup>1</sup>H-NMR: (CDCl<sub>3</sub>): δ (ppm) = 1.76 (brs, 3H), 1.95 (s, 3H), 4.56 (brs, 2H), 4.92 (brs, 1H), 4.99 (brs, 1H), 5.56 (brs, 1H), 6.62 (brs, 1H). IR (neat): 1715 (C=O), 965 (C=C) cm<sup>-1</sup>.

#### Geranyl MA (1d)

**1d** was also synthesized by the same procedure as **1a** from 31 g (0.201 mol) of geraniol and 20 g (0.191 mol) of methacryloyl chloride. The raw product was purified by column chromatography over silica gel (hexane : ethyl acetate = 5 : 1 as eluent).

YIELD: 15.9 g (37.5%); viscous oil.  $^1\text{H-NMR}$  : ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) = 1.58 (s, 3H), 1.62 (s, 3H), 1.68 (s, 3H), 1.90 (s, 3H), 2.00–2.11 (m, 4H), 4.64 (brs, 2H), 5.06 and 5.35 (s, 2H), 5.51 (s, 1H), 6.09 (s, 2H). IR (neat): 1718 (C=O), 970 (C=C)  $\text{cm}^{-1}$ .

### Polymer Synthesis

The copolymers **2**, **3a–3f**, **4a**, **4b**, **5a**, and **5b** (Fig. 1) were obtained by a free radical solution polymerization in dioxane with azobisisobutyronitrile (AIBN) as an initiator. The concentration of monomers was 30–40% (w/v) and the [monomers]/[AIBN] molar ratio was about 1000. Monomer feed ratio, yield, and copolymer composition are summarized in Table I. Poly(methyl methacrylate) (PMMA) and copolymer of MMA-co-GMA (1/1 : mol/mol) were also synthesized from MMA by the same procedure and the number average of molecular weight was about 300,000. As an example for

the general copolymerization procedure the synthesis of copolymer **3b** is described as follows.

### Copolymer 3b

Fifteen point zero grams (0.107 mol) of 2-butenyl MA **1a**, 32.0 g (0.32 mol) of MMA, and 47 mg of AIBN were dissolved in 135 mL of dioxane. The reaction mixture was treated with a gentle stream of nitrogen. After sealing, the mixture was heated to 52°C for 24 h. The resulting homogeneous viscous solution was cooled and added dropwise into 400 mL of methanol to precipitate the polymer. After two additional precipitations from dichloromethane solution into methanol, the copolymer was extracted under reflux with methanol for 1 day. The polymer was dried at room temperature under vacuum for 48 h.

YIELD: 25 g (53 wt %).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$  (ppm) = 0.81 (brs), 0.98 (brs), 1.1–1.4 (m), 1.6–1.9 (m), 3.60 (brs,  $\text{OCH}_3$ ), 4.42 (brs,

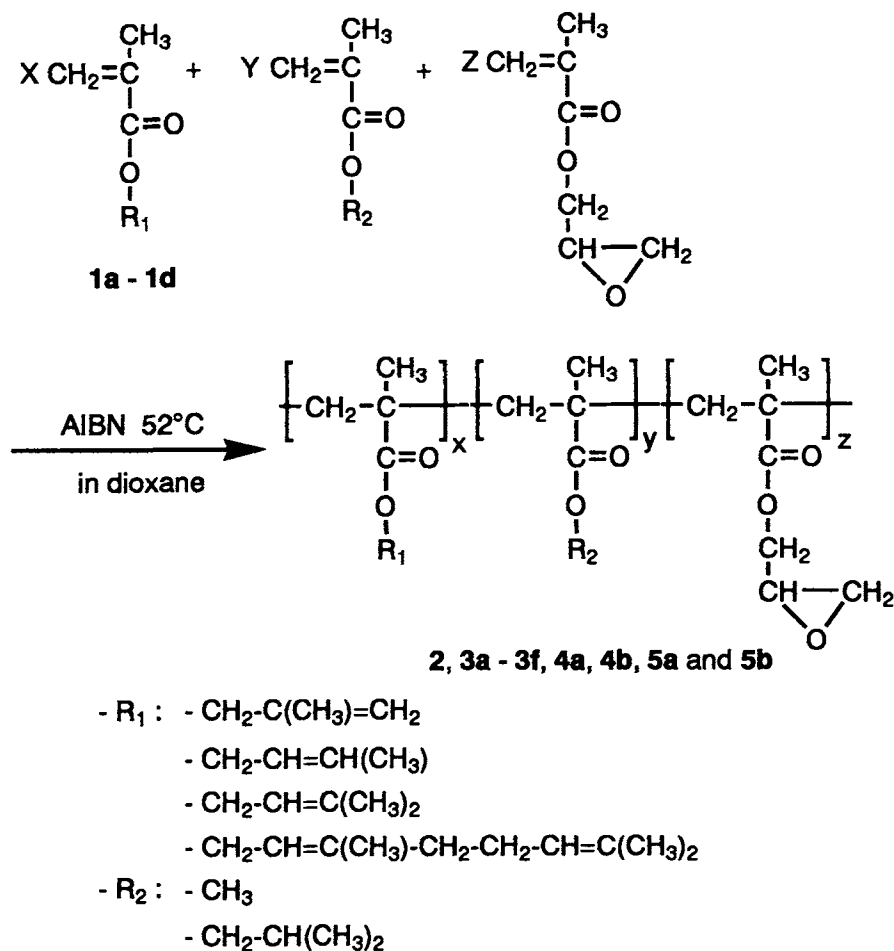


Figure 1 Synthesized photoreactive methacrylate copolymers.

**Table I Monomer Feed Ratio, Yield, and Copolymer Composition of Copolymers**

No.	Copolymer <sup>a</sup> X - Y - Z	Feed Ratio (mol %)			Yield (%)	Composition (mol %) <sup>b</sup>		
		X	Y	Z		x	y	z
2	MAMA-MMA	52.0	48.0	—	36	52.8	47.2	—
3a	BMA-MMA	50.0	50.0	—	26	48.2	51.8	—
3b	BMA-MMA	25.1	74.9	—	52	24.1	75.9	—
3c	BMA-MMA	4.8	95.2	—	57	8.7	91.3	—
3d	BMA-iBuMA	25.5	74.5	—	66	24.5	75.5	—
3e	BMA-MMA-GMA	25.0	37.5	37.5	47	24.3	37.1	38.6
3f	BMA-MMA-GMA	24.9	50.2	24.9	48	24.4	49.1	26.5
4a	PMA-MMA	56.5	43.5	—	53	55.1	44.9	—
4b	PMA-MMA	30.8	69.2	—	50	27.5	72.5	—
5a	GeMA-MMA	58.5	41.5	—	44	54.7	45.3	—
5b	GeMA-MMA	26.5	73.5	—	44	23.2	76.8	—

<sup>a</sup> Feed monomers: MAMA, 2-methyl-2-propene-1-ol, MMA, methyl methacrylate; BMA, 2-butenyl methacrylate; iBuMA, isobutyl methacrylate; GMA, glycidyl methacrylate; PMA, 3-methyl-2-butenyl methacrylate; GeMA, geranyl methacrylate.

<sup>b</sup> Copolymerization ratio, determined by NMR.

O—CH<sub>2</sub>—CH=CHCH<sub>3</sub>), 5.57 (brs, O—CH<sub>2</sub>—CH=CHCH<sub>3</sub>), 5.78 (brs, O—CH<sub>2</sub>—CH=CHCH<sub>3</sub>). IR (film on NaCl): 1730 (ester C=O), 1149, 967 (*trans* C=C) cm<sup>-1</sup>.

### Characterizations

Differential scanning calorimetry (DSC) data were obtained on a Mettler DSC 30 using a heating rate of 10°C/min. The molecular weight and its distribution were measured by using tetrahydrofuran as eluent on a Waters 150-C gel-permeation chromatography (GPC) system calibrated with polystyrene standards. NMR spectra of the samples dissolved in deuterated chloroform were measured with a JEOL GX-500 NMR spectrometer operating at 500 and 125 MHz. IR spectra were measured on a JEOL JMS-DX 300 spectrometer. Copolymer composition was determined from relative intensities of NMR signals of monomeric units.

Refractive indices of thin film samples were measured by a prism coupling method at a wavelength of 632.8 nm on a quartz substrate. Film thickness and surface structure were measured on a Rank-Taylor-Hobson Talystep on the basis of a styru contact method.

### Film Preparation

Thin films were prepared from a solution of approximately 10 wt % of a polymer or a polymer doped with BBP dissolved in benzene or toluene. The solution was filtered through a 0.2-μm Teflon filter,

and then spin-coated at 900–1000 rpm on a substrate. Quartz substrates were used for measuring refractive index and thickness of the polymer film. IR spectra were measured with thin film samples spin-coated on a potassium bromide plate.

### Irradiation Apparatus

A 400-W high pressure mercury lamp (Toshiba) with a Pyrex filter in a temperature controlled bath was used for preparative photolysis. For evaluating optical and physical properties, photoreactive films were irradiated with a Canon PLA-521 mask aligner equipped with a high pressure mercury lamp with cut filters for IR and deep UV (< 300 nm) wavelength lights. Light intensity of this apparatus is 25 mW/cm<sup>2</sup> at 365 nm. This apparatus was also used for fabricating an optical patterning on the film. A high pressure mercury lamp without any filters using a Toshiba Toscore-1000, which contains deep UV wavelength of 254 nm as well as UV wavelength, with a dose rate of 30–60 mW/cm<sup>2</sup> at 365 nm, was also used for postcuring of the film.

### Preparative Photolysis of Film

The irradiation procedure was as follows: a solution containing 200 mg of polymer and 120 mg of BBP in ~ 1 mL of methylene chloride was poured onto a quartz plate. A transparent film was formed after evaporation of the solvent. After baking at 80°C for 40 min to remove the solvent completely, the film was irradiated for 2 h at various temperatures

through a Pyrex filter under a nitrogen atmosphere. Thorough washing of the irradiated film with warm methylene chloride ( $\sim 100$  mL total) left an insoluble polymer, which was collected by filtration. The methylene chloride washings were concentrated under reduced pressure and a soluble polymer was corrected by reprecipitation from methylene chloride solution to methanol. Combined organic solutions were evaporated under reduced pressure and the residue was subjected to preparative thin layer chromatography (TLC) (silica gel methylene chloride as eluent).

It was confirmed that the insoluble polymers isolated above were not contaminated with methylene chloride soluble substances. Thus, the isolated insoluble polymer was refluxed in methylene chloride

#### Film coating process

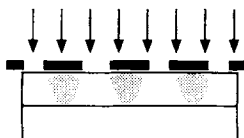
- Copolymer/dopant spin-coating. thickness: 1–3  $\mu\text{m}$ .
- Prebaking, 60–80  $^{\circ}\text{C}$  40 min.



(a)

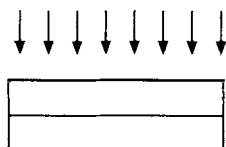
#### Patterning process

- UV light irradiation through a photomask (on PLA-521)



(b)

- UV light irradiation without the photomask



(c)

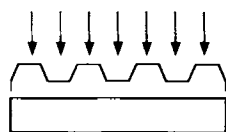
#### Post-curing process

- Heating to remove unreacted BBP



(d)

- Post-curing without any masks. (on Toscore-1000)



(e)

**Figure 2** Optical patterning process for fabricating optical elements from the photoreactive copolymers. (a) Toluene solution of copolymer/*m*-benzoylbenzophenone (BBP) was spin coated on a washed substrate (thickness; 1–3  $\mu\text{m}$ ), and prebaking at 60–80  $^{\circ}\text{C}$  for 40 min; (b) optical patterning through a photomask; (c) additional UV irradiation without the photomask; (d) optical pattern development by removing unreacted BBP by sublimation at 105  $^{\circ}\text{C}$  under 0.2 mmHg for 20 h; (e) postcuring irradiation without photomasks on Toscore-1000.

**Table II** Weight-Averaged  $M_w$  and Number-Averaged  $M_n$  Molecular Weight, Glass-Transition Temperature ( $T_g$ ), and Refractive Index of Copolymers

No.	Molecular Weight <sup>a</sup>			$T_g^b$ ( $^{\circ}\text{C}$ )	Refractive Index <sup>c</sup>
	$M_w$	$M_n$	$M_w/M_n$		
<b>2</b>	NM	NM	—	79.9	1.500
<b>3a</b>	746,000	355,000	2.10	NM	1.499
<b>3b</b>	456,300	278,500	1.63	92.9	1.498
<b>3c</b>	513,500	241,300	2.13	110.2	NM
<b>3d</b>	870,000	398,000	2.19	54.1	1.486
<b>3e</b>	756,000	344,000	2.20	74.2	1.505
<b>3f</b>	724,800	354,800	2.04	81.3	1.505
<b>4a</b>	632,500	273,200	2.32	56.8	1.499
<b>4b</b>	523,600	233,300	2.24	78.9	1.497
<b>5a</b>	728,000	325,000	2.24	NM	1.508
<b>5b</b>	756,000	353,000	2.14	55.4	1.503

NM, not measured.

<sup>a</sup> Determined by GPC, polystyrene standards, tetrahydrofuran as eluent.

<sup>b</sup> Determined by DSC, second run at heating rate 10  $^{\circ}\text{C}/\text{min}$ .

<sup>c</sup> Measured at 632.8 nm.

overnight. No contaminants were detectable in the methylene chloride layer by high-performance liquid chromatography (HPLC).

#### Optical Properties Measurements

A transparent polymer film doped with 37.5–44.4 wt % of BBP on a quartz substrate was irradiated with a Canon PLA-521 mask aligner for 0–15 min. After the exposure, unreacted BBP was removed by sublimation at 105  $^{\circ}\text{C}$  for 20 h under vacuum of 0.2 mmHg. Thickness and refractive index change of the exposed and unexposed region was then measured, respectively.

#### Fabrication Process of Optical Elements

The typical fabrication process for the optically patterned elements such as a phase grating is shown in Figure 2(a–e). Films used for this experiment were 0.1–3.0  $\mu\text{m}$  thick and formed on a washed glass substrate. After the film was heated at 80  $^{\circ}\text{C}$  for 40 min to remove a solvent, it was irradiated for 2–15 min through a photomask with a grating pattern on a Canon PLA-521 mask aligner. After the first UV irradiation, the film was irradiated again for 0–2 min without photomask to react the unexposed region of the first irradiation step. The sample was then heated at 105  $^{\circ}\text{C}$  for 20 h under vacuum of 0.2 mmHg to allow the unreacted BBP to sublime. Thereby an

**Table III Yields (mg) of Products from Preparative Photolysis of Copolymer 3b and PMMA Doped with *m*-Benzoylbenzophenone (BBP) at Various Temperatures**

Polymer <sup>a</sup>	Reaction Temp. (°C)	Insoluble Polym. (mg)	Recovered Polym. (mg)	Recovered BBP (mg) <sup>b</sup>	Pinacol (mg) <sup>b</sup>
3b	7	170	62	82	< 1
	20	199	40	72	< 1
	40	205	12	75	< 1
	55	242	1	64	1
	70	239	< 1	75	1
	85	241	< 1	63	2
PMMA	20	2.5	180	89	3
	70	3.5	178	78	2.6

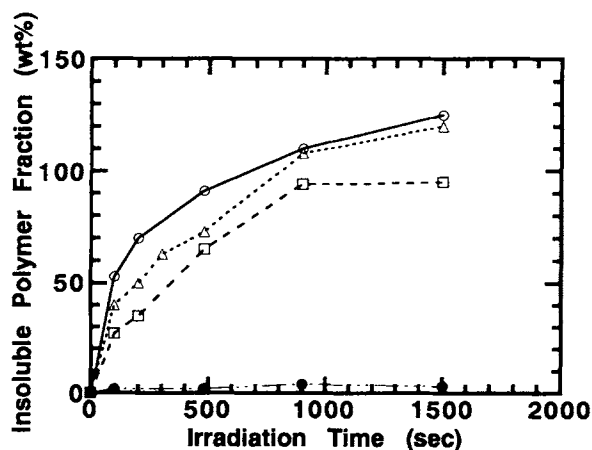
<sup>a</sup> A film, which was prepared by evaporation of solvent from methylene chloride solution of polymer, 200 mg, and BBP, 120 mg, was irradiated under nitrogen.

<sup>b</sup> Isolated by preparative TLC.

optical phase grating was fabricated. A postcuring process after the patterning process with a Toscore-1000 was performed to the sample without photo-masks for 7–17 min for a further photoreaction.

### IR Spectra Monitoring

A thin film containing 44.4 wt % BBP in polymer composite on a potassium bromide plate with a thickness of about 0.5 mm was irradiated with a Canon PLA-521 mask aligner and a Toshiba Toscore-1000 UV lamp apparatus. IR-spectrum was



**Figure 3** Insoluble polymer fraction in the film of *m*-benzoylbenzophenone (BBP) and photoreactive copolymers 3a–3c and PMMA as a function of irradiation time. The content of BBP in the film was 33.3 wt %. (○) 3a; (△) 3b; (□) 3c; (●) PMMA.

monitored at each step of the fabrication process of a phase grating as shown in Figure 2(a–e).

### Durability Measurements

Durability of diffraction efficiency was measured before and after heating for 7 h at 160°C on the phase gratings made from photoreactive copolymers.

**Table IV Photochemical Changes in Thickness ( $\Delta D$ ) and Refractive Index ( $\Delta N$ ) of Copolymers Doped with BBP**

Copolymer <sup>a</sup>	Refractive Index <sup>b</sup>		
	After Exposure	$\Delta N$ (%) <sup>c</sup>	$\Delta D$ (%) <sup>d</sup>
2	1.545	3.0	60
3a	1.548	3.2	80
3b	1.547	3.2	78
3d	NM	NM	70
3e	1.552	3.1	77
3f	1.551	3.1	75
4a	1.547	3.2	79
4b	1.546	3.2	68
5a	1.557	3.2	88
5b	1.552	3.2	85

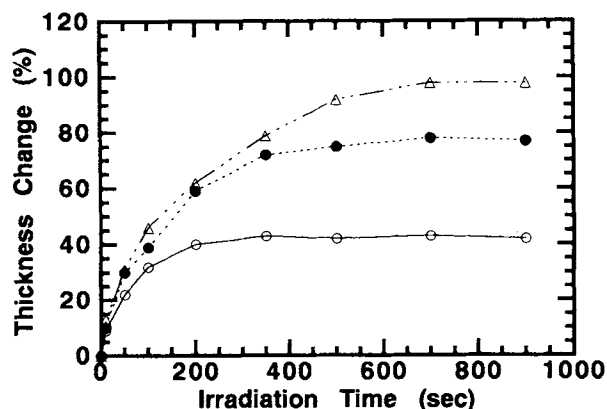
NM, Not measured. The film surface was not uniform because of phase separation between polymer and BBP.

<sup>a</sup> Copolymer/dopant = 1/0.8, film thickness before exposure 1.2–1.5  $\mu$ m. Unreacted BBP was removed by sublimation after exposure.

<sup>b</sup> Measured at 632.8 nm.

<sup>c</sup>  $(N_{\text{exposed}} - N_{\text{initial}})/N_{\text{initial}} \times 100$ .

<sup>d</sup>  $(D_{\text{exposed}} - D_{\text{initial}})/D_{\text{initial}} \times 100$ .



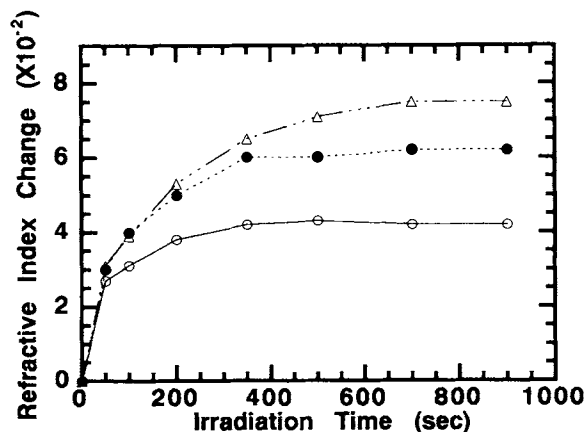
**Figure 4** Change in film thickness of copolymer **3f** doped with *m*-benzoylbenzophenone (BBP) as a function of irradiation time. The content of BBP in the film was (○) 33.3%; (●) 44.4%; (△) 52.4%.

Three gratings from different copolymers (**3b** and **3f**) with different fabrication processes were fabricated and measured.

## RESULTS AND DISCUSSION

### Polymer Synthesis

The methacrylate copolymers **2**, **3a–3f**, **4a**, **4b**, **5a**, and **5b**, studied are based on MMA, methacrylic ester comprising nonconjugate carbon–carbon double bonds, and GMA (Fig. 1). The copolymers were synthesized by a free radical polymerization using AIBN as an initiator. All synthesized copolymers were completely soluble in organic solvents such as



**Figure 5** Change in refractive index of copolymer **3f** doped with *m*-benzoylbenzophenone (BBP) as a function of irradiation time. The content of BBP in the film was (○) 33.3%; (●) 44.4%; (△) 52.4%.

**Table V** Molar Ratio of *m*-Benzoylbenzophenone (BBP) and 2-Butenyl Group of Copolymer **3f**

BBP (wt %) <sup>a</sup>	Dopant/Double Bond <sup>b</sup> (mol/mol)
33.3	0.865
44.4	1.385
52.4	1.904

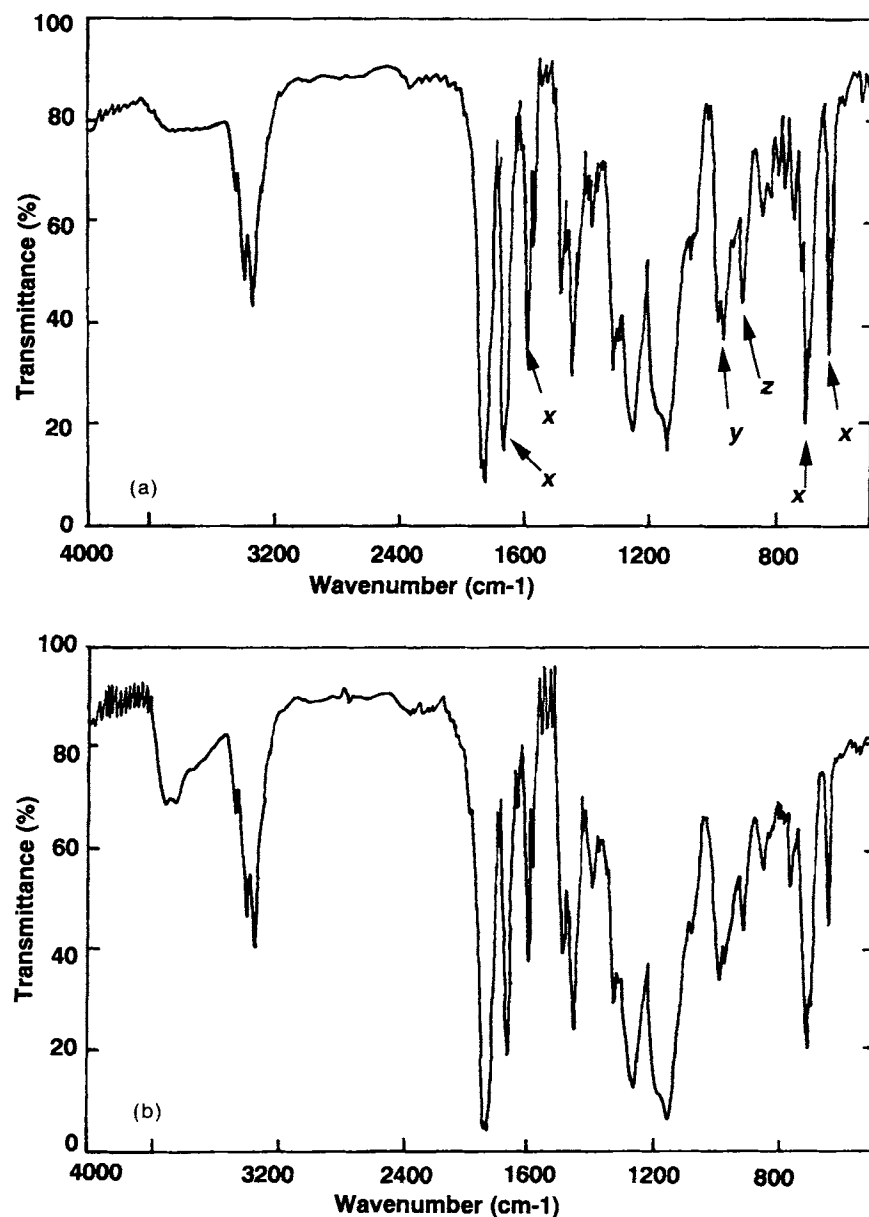
<sup>a</sup> Copolymer **3f** doped with *m*-benzoylbenzophenone (BBP).

<sup>b</sup> Molar fraction of 2-butenyl group in copolymer **3f**.

benzene or chloroform, indicating that no cross-linking occurred during copolymerization. Polymerization was carried out at 52°C after purification of the monomers prior to mixing in order to prevent gelation of the reaction mixture, which took place above 60°C and even below 60°C without purifying the monomers by column chromatography before the polymerization reaction. The gelation occurred during the reaction when the monomer used was purified only by distillation, especially in copolymers **3a–3f** and highly concentrated comonomers **1a–1d**. A small amount of methacryloyl chloride could cause gelation and cross-linking of monomers. The results of GPC, DSC, and refractive index investigations of copolymers **2**, **3a–3f**, **4a**, **4b**, **5a**, and **5b** are summarized in Table II. The molecular weight and its distribution was measured by GPC calibrated with polystyrene standards. All copolymers showed a monomodal distribution. The number average molecular weights were on the order of 230,000–400,000 g/mol and the weight average molecular weights were on the order of 450,000–870,000 g/mol. All polymers were amorphous. The  $T_g$  varied with a copolymer composition dominated by the number of nonconjugate carbon–carbon double bond.  $T_g$  decreased with an increasing amount of the methacrylic ester of **1a–1d**. The copolymers were slightly higher in refractive index than PMMA ( $n = 1.485$  at 632.8 nm) with increasing content of comonomers **1a–1d**, suggesting the effect of the  $\pi$ -electron located on side chains of the comonomers.

### Photoreaction of Copolymers Doped with BBP

The photochemical reaction of copolymers **3b** or PMMA doped with BBP was studied in the solid film at various temperatures. The reaction was carried out at a composition of 37.5 wt % BBP doped in a polymer film. Product yields are summarized in Table III. In the case of copolymer **3b**, an insoluble polymer is a main product as previously reported.<sup>6</sup>



**Figure 6** IR spectra of the photoreacted polymer film formed on a KBr plate. Film before exposure contained 44.4 wt % of *m*-benzoylbenzophenone (BBP) in copolymer **3f**: (a) Before irradiation. *x* designates absorption of BBP; *y* absorption band of carbon-carbon double bond of 2-butenyl group of **3f**; *z* epoxy ring bond absorption of **3f**; (b) after irradiation for 10 J/cm<sup>2</sup> on a Canon PLA-521 mask aligner; (c) after removing unreacted BBP by heating at 105°C for 20 h under 0.2 mmHg; (d) Postcured sample irradiated for 17 min on a Toshiba Toscore-1000 UV lamp.

The yield of the insoluble polymer became larger above 55°C, whereas recovered copolymer **3b** decreased with raising a reaction temperature. A very small amount of pinacol was formed at lower temperature and the yield of recovered BBP decreased with increasing temperature. These results show that the photoreaction is influenced by the  $T_g$  of the

matrix.<sup>9</sup> Photoreaction is faster at the higher temperature because the  $T_g$  of the film is about 30–50°C by the effect of doped BBP as a plasticizer in the polymer matrix. A small amount of insoluble polymer was also formed in the case of PMMA. This shows that a hydrogen atom of PMMA was abstracted by an excited BBP to form a cross-linkage.



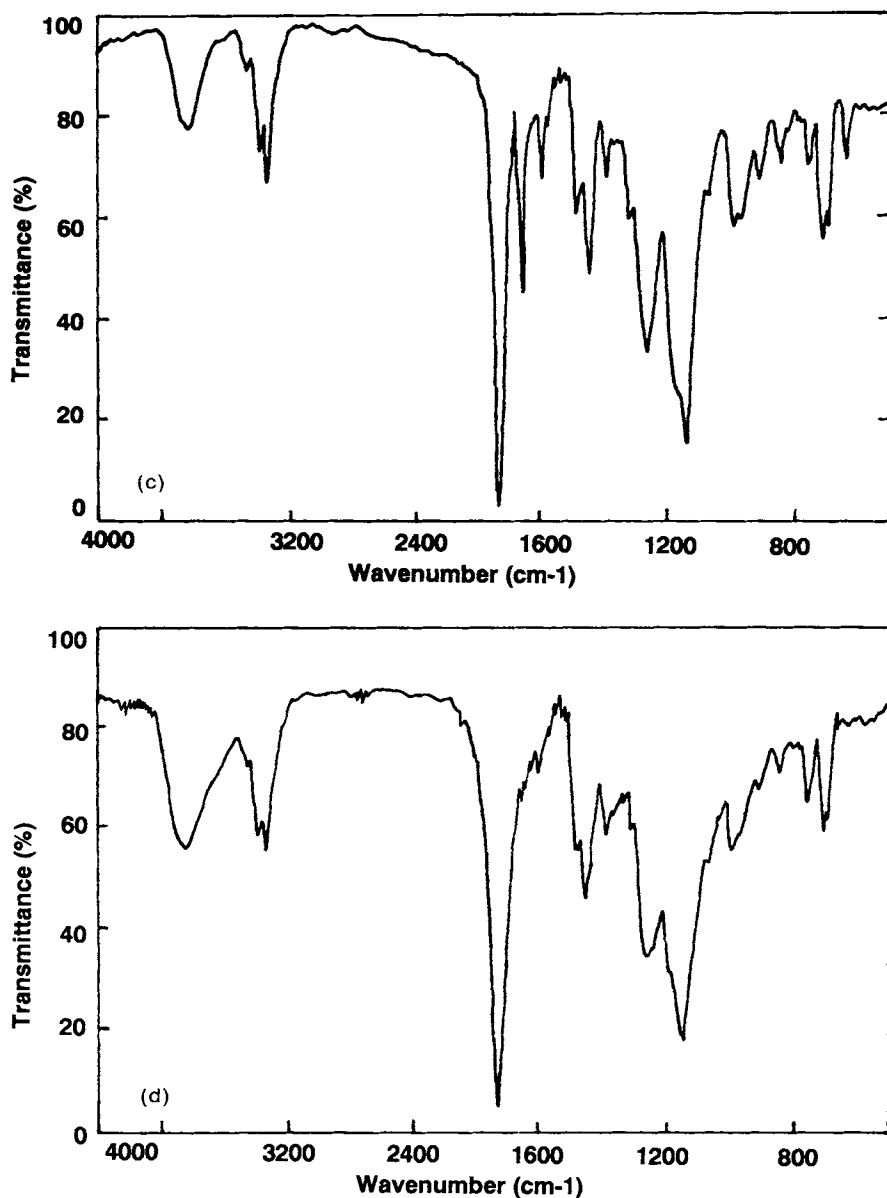


Figure 6 (Continued from the previous page)

This reaction was very slow compared to the reaction with the carbon-carbon double bond side chain. A little bit more insoluble polymer ( $\sim 10$  mg in the same reaction condition at  $20^\circ\text{C}$ ) than PMMA was formed when PMMA-co-GMA was used. This means that the hydrogen atom abstraction from the glycidyl group is slightly faster than that from MMA.

The photoreaction rate of different copolymers was monitored by measuring an insoluble fraction of photoreacted polymer film doped with BBP at various irradiation times. Figure 3 shows an insoluble polymer fraction of copolymers **3a**–**3c** and PMMA doped with 33.3 wt % of BBP as a function

of the irradiation time. Reaction is faster with increased molar ratio of photoreactive comonomer **1b** as a result of the concentration of the reaction site restricted in the polymer matrix film.<sup>10</sup>

#### Optical Properties of Photoreacted Copolymers

Copolymers used are composed of methacrylic ester with nonconjugate carbon-carbon double bonds that can photochemically react with BBP, resulting in a refractive index change as well as a thickness change after irradiating UV light.<sup>7</sup> Table IV shows photochemical changes in thickness and refractive index

of the photoreactive copolymer films doped with 44.4 wt % BBP. Each film was exposed about  $15 \text{ J/cm}^2$  (10 min) at 365 nm on a PLA-521 mask aligner. It can be seen that values of  $\Delta N$  and  $\Delta D$  were around 3% and 60–88%, respectively, and these values were slightly increased with increasing the portion of nonconjugate carbon–carbon double bonds in the copolymers. The effect of side chains, such as the methyl, isopropyl, or glycidyl group, might be very small because a hydrogen abstraction reaction by the excited BBP would be very slow compared to that of nonconjugate carbon–carbon double bonds containing side chain.  $\Delta N$  and  $\Delta D$  are more influenced by a proportion of BBP and an exposure time. Figures 4 and 5 show that the thickness and the refractive index of the copolymer **3f** were changed with the amount of BBP. Both  $\Delta N$  and  $\Delta D$  became larger with increasing the proportion of BBP or the exposure time. These phenomena suggest that the change of optical properties of the film can be regulated by adjusting the exposure energy and the content of BBP. Other copolymers showed similar results. With an increased proportion of BBP, the photoreaction was accelerated in the initial stage to be saturated earlier as shown in Figures 4 and 5, suggesting an increase in number of reaction sites. Table V shows the molar ratio of BBP and carbon–carbon double bond constituting the main reaction site in each case of Figures 4 and 5. Excess BBP to the carbon–carbon double bond could react slowly with other reaction sites such as the MMA monomer unit and the glycidyl side chain unit as a result of cross-linking.

### Optical Patterning Processes

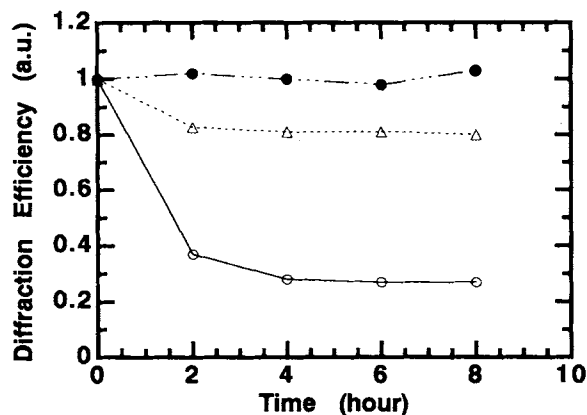
The optical patterning process for fabricating optical elements in this study is depicted in Figure 2. Photoreactive polymer, in general, needs high resolution to achieve a precise patterned optical element. The optical patterning should be carried out at a temperature lower than  $T_g$  because a high temperature above  $T_g$  might cause motion of the polymer matrix as a result of a low resolution in spite of high reactivity at the temperature above  $T_g$  as described previously. For this reason UV light with filters to cut IR and deep UV lights were used for a patterning process to keep the film temperature below its  $T_g$  during the photoreaction. After the first exposure step with a photomask [Fig. 2(b)], the film was irradiated without a photomask to react an unexposed portion at the first exposure step [Fig. 2(c)]. This step shows that the whole region of the film was photoreacted and cross-linked with different cross-linking density according to the optical pat-

tern. Sublimation of unreacted BBP revealed an optically patterned structure shown in Figure 2(d). If the cross-linking density of the whole exposed area was sufficient, the optical element could have a high temperature stability. In order to achieve the higher cross-linked structure of the film, the postcuring process shown in Figure 2(e) was also carried out in addition to the patterning process. The cross-link reaction could take place in the residual benzoyl group attached to the copolymer, olefinic side chain, and/or glycidyl group (**3e** and **3f**) by the postcuring. A strong energy UV light such as a Toscore-1000 was used to accelerate the reaction in the solid state. The optical pattern was not affected by IR heating.

Figures 6(a–d) show IR spectra of the film of copolymer **3f** doped with 37.5 wt % BBP at each step of the patterning process. As shown in Figure 6(a), copolymer **3f** exhibited absorption bands  $1740 \text{ cm}^{-1}$  for C=O,  $970 \text{ cm}^{-1}$  for the carbon–carbon double bond of the 2-butenyl group, and  $910 \text{ cm}^{-1}$  for the epoxy ring of the glycidyl group, BBP exhibited those of  $1660 \text{ cm}^{-1}$  for C=O, 1600 and  $720 \text{ cm}^{-1}$ , and  $640 \text{ cm}^{-1}$  for the phenyl ring, respectively. After UV light irradiation of  $10 \text{ J/cm}^2$  at 365 nm with a Canon PLA-521 mask aligner, the absorption of carbon–carbon double bond at  $970 \text{ cm}^{-1}$ , epoxy group at  $910 \text{ cm}^{-1}$ , and carbonyl group of BBP at  $1660 \text{ cm}^{-1}$  was decreased, while other peaks changed a small amount [Fig. 6(b)]. After removing an unreacted BBP at  $105^\circ\text{C}$  for 20 h under 0.2 mmHg, the absorption of BBP and epoxy ring displayed a further decrease, although the carbonyl bond of BBP at  $1660 \text{ cm}^{-1}$  still remained [Fig. 6(c)]. These results indicate bonding of the phenyl carbonyl group to the polymer and a thermal ring-opening reaction of the epoxy group. The absorption intensities of the residual carbonyl group of BBP, carbon–carbon double bond, and epoxy group of the polymer film decreased in the course of the postcuring process as shown in Figure 6(d). This is a consequence of the further photoreaction occurring at the postcuring process with high energy UV light. The photoreacted film was very hard, brittle, and nonswellable in organic solvents. In addition, films of **2**, **3a–3f**, **4a**, **4b**, **5a**, and **5b** were cross-linked without BBP and became insoluble in organic solvents by a high energy UV light of a Toscore-1000 lamp generating deep UV light at 254 nm as a result of reaction of  $[2 + 2]$  by deep UV light.<sup>11</sup>

### Stabilities

A stability test was carried out with respect to phase grating samples made from photoreactive copolymers (**3b** and **3f**) with high diffraction efficiencies.



**Figure 7** Stability test of the phase gratings fabricated varying with copolymers and processes. Grating pitch was  $60\ \mu\text{m}$  and the copolymer was doped with 37.5 wt % *m*-benzoylbenzophenone (BBP). Each film was exposed with UV light with a photomask for 10 min and without it for 2 min. Ratio of the first order and the zero order diffraction efficiencies at wavelength 632.8 nm was monitored in the course of heating at  $160^\circ\text{C}$ . (○) Sample A, copolymer **3b** without postcuring. Initial diffraction efficiency ( $\eta$ ) was 173%. (△) Sample B, copolymer **3b** with postcuring for 7 min. Initial  $\eta$  was 164%. (●) Sample C, copolymer **3f** with postcuring for 7 min. Initial  $\eta$  was 165%.

To compare the effects of copolymers and the fabrication processes, three samples were prepared using photoreactive copolymers doped with 37.5 wt % BBP to form ca.  $3\text{-}\mu\text{m}$  thickness films before exposure. Sample A was irradiated 10 min with a photomask and successively irradiated 1 min without the photomask followed by removing unreacted BBP at  $105^\circ\text{C}$  for 20 h using copolymer **3b**. Sample B was fabricated in the same way as sample A and additional postcuring for 7 min. Sample C was fabricated from copolymer **3f** in the same way as sample B. It can be seen from Figure 7 that the grating sample B, was greater in heat stability than a sample A when the same copolymer **3b** was used. Because of higher cross-linking density of the glycidyl group, sample C showed much better heat stability than samples A and B.

## CONCLUSIONS

Photoreactive copolymers were synthesized from methacrylic esters comprising nonconjugate carbon-carbon double bond and epoxy ring. Photoreaction of the photoreactive film of copolymers doped with BBP resulted in formation of insoluble polymer and its reaction rate was faster at higher temperature

because of motion of the polymer matrix film. Insoluble polymer was formed even in the case of PMMA although the reaction was very slow. Optical properties of the photoreactive film after irradiation of UV light showed the film thickness change of  $\sim 100\%$  and the refractive index change of  $\sim 3.2\%$ , respectively, depending on the concentration of BBP and the exposure time.

The two step exposures in the patterning process with and without a photomask followed by removing unreacted BBP were performed to achieve cross-linking of the whole portion of the polymer material. After the patterning process, residual photoreactive moieties such as phenyl carbonyl groups of BBP attached to the polymer, carbon-carbon double bonds, and epoxy groups, can also photochemically react, resulting in a highly cross-linked pattern. With monitoring of IR spectra for each step in the exposure process, it was found that high cross-linking was caused by the photoreaction of residual reactive groups at postcuring. A phase grating fabricated from the photoreactive film followed by the postcuring showed a high temperature stability up to  $160^\circ\text{C}$ .

The authors thank Prof. Y. Ito of Kyoto University for his helpful comments and useful discussions.

## REFERENCES

1. L. A. Hornak, Ed., *Polymers for Lightwave and Integrated Optics*, MerceL Dekker, New York, 1992.
2. E. A. Chandross, C. A. Pryde, W. J. Tomlinson, and H. P. Weber, *Appl. Phys. Lett.*, **24**, 72 (1974).
3. W. J. Tomlinson, H. P. Weber, C. A. Pryde, and E. A. Chandross, *Appl. Phys. Lett.*, **26**, 303 (1975).
4. H. Franke, *Appl. Opt.*, **23**, 2729 (1984).
5. W. Driemeier and A. Brockmeyer, *Appl. Opt.*, **25**, 2960 (1986).
6. Y. Ito, Y. Aoki, T. Matsuura, N. Kawatsuki, and M. Uetsuki, *J. Appl. Polym. Sci.*, **42**, 409 (1991).
7. N. Kawatsuki and M. Uetsuki, *Appl. Opt.*, **29**, 210 (1990).
8. Y. Ito, N. Kawatsuki, B. J. Giri, M. Yoshida, and T. Matsuura, *Org. Chem.*, **50**, 2893 (1984).
9. E. Dan and J. E. Guillet, *Macromolecules*, **6**, 230 (1970).
10. P. L. Egerton, E. Pitts, and A. Reiser, *Macromolecules*, **14**, 95 (1981).
11. N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, New York, 1978.

Received November 15, 1993

Accepted January 27, 1994