Methacrylate Homo- and Copolymers Containing Photosensitive Abietate Group: Their High Thermal Stability, Unique Photocrosslinking Behavior, Transparency, and Photolithographic Application

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The monomer methacryloyloxyethyl abietate (**2**) was synthesized by a simple two-step reaction starting from abietic acid. The homopolymerization of **2** and its copolymerization with MMA using AIBN as an initiator provided high-molecular-weight polymers **3**−**6** ($10 \times 10^3 < M_n < 70 \times 10^3$) in high yields. These polymers were well-dissolved in organic solvents. The glass-transition temperatures, T_g, of all polymers were higher than 130 °C, much higher than that of PMMA. No melting points, T_m, were observed. Their decomposition temperatures were very high, as $T_{5\ wt\ \%\ loss} > 300$ °C. These results indicate that these polymers are thermally stable and glassy at room temperature. The absorption bands due to the conjugated carbon−carbon double bonds within the abietate group significantly decreased with an increase in the exposure doses. Normalized absorbance as a function of UV exposure doses nonlinearly changed because of the occurrence of a certain threshold at 1.0 J/cm^2 in all polymers. Solvent extraction experiment revealed that interchain crosslinking effectively occurred even in copolymers with relatively low amounts of the abietate group. The polymer films showed a clear transparency of more than 90%. Photolithography of the polymer films provided high-resolution pattern images.

Introduction

Abietic acid is the major constituent of resin acid that makes up the major portion of rosin.[1] Resin acid has been extensively used in paper sizing, printing inks, adhesives, glues, synthetic rubber, and dentistry. This naturally occurring compound undergoes a photodimerization reaction.[2−5] Recently, we synthesized polystyrene derivatives containing an abietate group. It could be verified that the polymers readily underwent a crosslinking reaction by UV irradiation.[6,7]

Photolithographic patterning technology has made significant contributions to the microelectronics industry.[8−10] Photolithography is generally based on photocrosslinking reactions of polymeric photoresists. Resist materials need to be highly transparent in a visible region in order to be used as display device materials.

A pure, atactic poly(methyl methacrylate) (PMMA) can easily be obtained by radical polymerization. PMMA is an amorphous plastic with a high surface brilliance, clear transparency, and high refractive index. PMMA has good mechanical strength, chemical resistance, and extremely good weather resistance. Because of its light weight, dimensional stability, heat resistance, and processability, in addition to its excellent optical properties and weather resistance, PMMA has many profound and diverse uses in a variety of practical applications.[11,12]

On the basis of these facts, we synthesized photocrosslinkable methacrylate homo- and copolymers containing abietate groups. The polymers were highly soluble and thermally stable. Polymer films easily underwent a crosslinking reaction by UV irradiation and maintained clear transparency in visible regions. Highly resolved pattern images were obtained using the polymer films.

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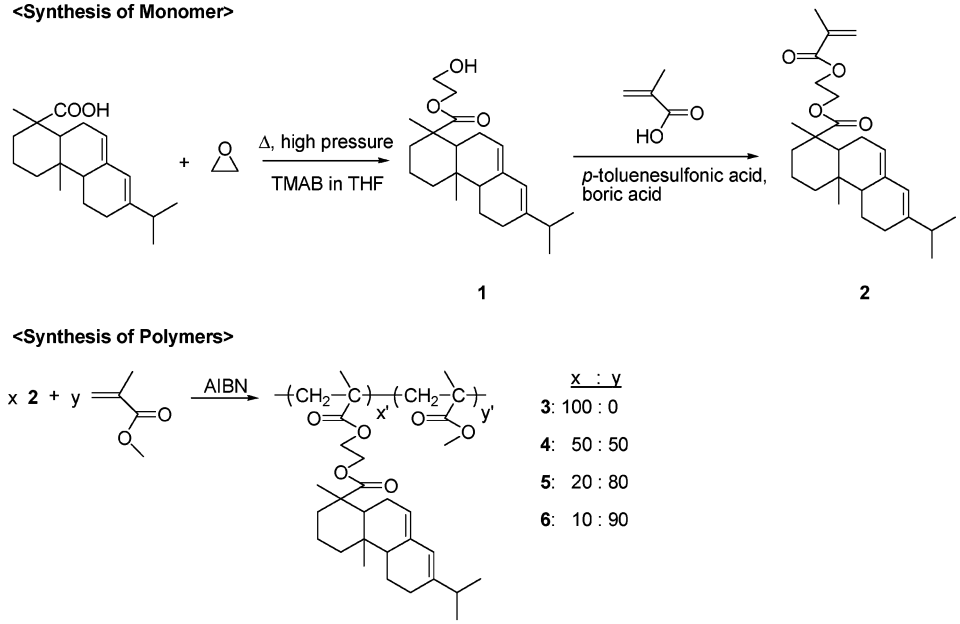
Table 1. Results of the Polymerization of 2-MMA[a]

	feed (mole fraction)			product[b] (mole fraction)				
polymer	[**2**]	[MMA]	yield (%)	[**2**]	[MMA]	η^c (dL/g)	$M_n{}^d \times 10^3$	$M_w/M_n{}^d$
3	1.0	0.0	74	1.0	0.0	0.33	11.3	1.56
4	0.5	0.5	72	0.45	0.55	0.40	33.1	1.56
5	0.2	0.8	79	0.18	0.82	0.43	58.4	1.68
6	0.1	0.9	70	0.09	0.91	0.48	67.2	1.78

[a] Polymerized in DMF at 65 °C for 24 h. [b] Measured by ^{1}H NMR analysis. [c] Intrinsic viscosities, measured in chloroform at 25 °C with a Ubbelohde viscometer. [d] Measured in THF by GPC.

Scheme 1. Syntheses of Methacrylate Homo- and Copolymers Containing Abietate Group



Results and Discussion

Scheme 1 shows the synthetic procedure of methacrylate polymers containing an abietate group. Hydroxyethyl abietate, **1**, was synthesized by a high-pressure reaction of abietic acid with ethylene oxide. The condensation reaction of **1** with methacrylic acid provided the monomer (methacryloyloxyethyl abietate, **2**) with an appearance of gummy liquid in a yield of 68%. Abietic acid is extremely bulky and brittle by itself, and hence, abietic acid-containing polymers might be brittle if its molecules are not carefully designed. Thus, the reason why we incorporated an ethylene spacer into the pedant group of the monomer is for the proper flexibility of the expected polymer product. The results of the ^{1}H NMR and IR spectra of these compounds are shown in the Experimental Section. The radical polymerization of **2** and its copolymerization with MMA provided white solids.

Table 1 describes the results for the homopolymerzaiton of **2** and its copolymerization with MMA. Although **2** has a highly bulky abietate group, the homopolymerization of **2** using AIBN as an initiator provided polymer **3** with a high number-average molecular weight (M_n) of 11.3×10^3 in a yield of 74%. Also, the copolymerization of **2** with MMA (feed mole ratios of 50:50, 20:80, and 10:90) afforded high-molecular-weight copolymers **4**−**6** ($30 \times 10^3 < M_n < 70 \times 10^3$) in high yields. Moreover, all showed excellent solubility regarding organic solvents such as chloroform, THF, acetone, DMF, benzene, and toluene. The fraction mole ratios of **2** to the MMA unit in copolymers, which were calculated from the results of ^{1}H NMR, were 45:55, 18:82, and 9:91, close to the feed mole ratios. This is reasonable because the polymer yields were virtually quantitative. The M_n values and intrinsic viscosity increased with an increase in the feed ratio of MMA because of the steric hindrance of the bulky abietate group.

Figure 1 shows the ^{1}H NMR spectra of **3**−**6**. The homopolymer, **3**, shows peaks at 4.1 and 4.2 ppm (peak *c*) because of the ethylene group. On the other hand, copolymers **4**−**6** exhibit characteristic peaks at 3.6 ppm (peak *d*) because of the methyl group of MMA unit, in addition to the ethylene peaks. The mole fractions of **2** to the MMA unit in copolymers, as mentioned above, were estimated from the integral ratios of peaks *c* and *d*.

Figure 2 shows the DSC thermograms of polymers **3**−**6**. Glass-transition temperatures (T_g) of **3**−**6** are seen at relatively high temperatures of 150, 146, 138, and 134 °C, respectively, which are much higher than that (about 105 °C)[11,12] of PMMA. The T_g decreases with an increase in the content of MMA. This is due to the fact that the pendent abietate group is highly rigid. On the other hand, these polymers never show exothermic peaks due to melting points (T_m). Actually, the polymers are glassy at room temperature and appeared to be highly transparent in visible regions. This could be observed by the naked eye.

Figure 3 shows the TGA curves of **3**−**6**. The TGA curves show a 5% weight loss at high temperatures ($T_{5\ wt\ \%\ loss}$) of

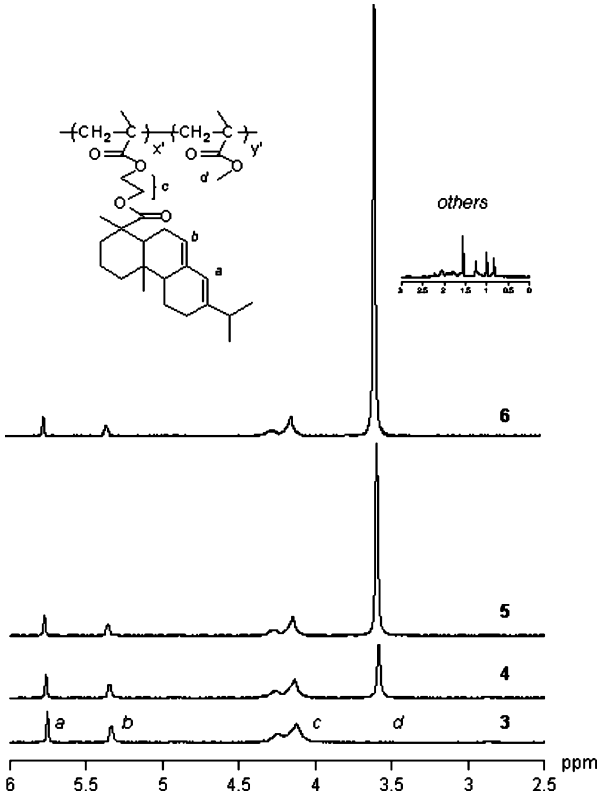


Figure 1. The ^{1}H NMR spectra of **3**−**6** in $CDCl_3$.

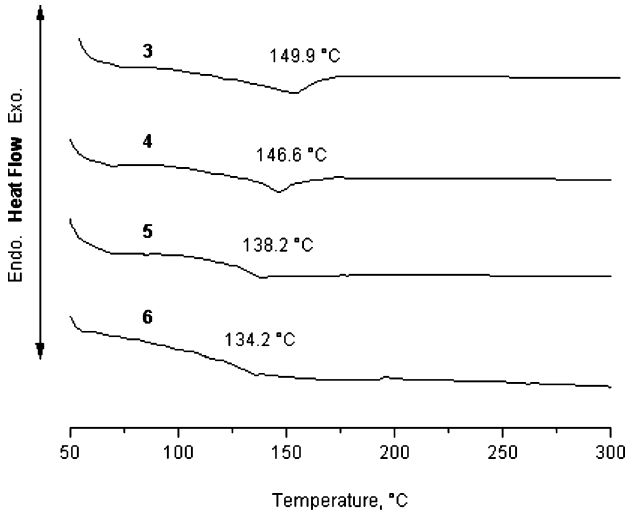


Figure 2. DSC thermograms of **3**−**6** recorded under nitrogen at a scan rate of 10 °C/min.

310, 320, 330, and 350 °C, respectively. The $T_{5\ wt\ \%\ loss}$ increased with an increase in the content of **2** in the copolymer. The higher the content of abietate group, the higher the thermal decomposition temperature became. This is because abietate group is rigid and thermally stable by itself, and hence, can protect main chains from heat.

Figure 4 shows the variation of the UV absorption spectra of **3** in film, with varying amounts of UV irradiation treatment conducted for different times. The three bands of the polymer in the range between 220 and 265 nm are due to the conjugated, carbon−carbon double bonds within the abietate group.[6,7] The absorption bands significantly decreased with an increase in exposure doses. This is due to the fact that the conjugated double bonds converted to a

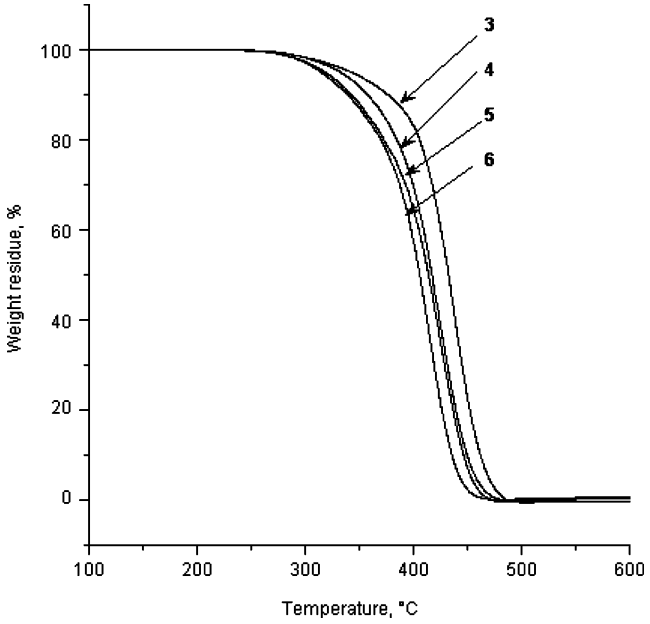


Figure 3. TGA thermograms of **3**−**6** recorded under nitrogen at a heating rate of 10 °C/min.

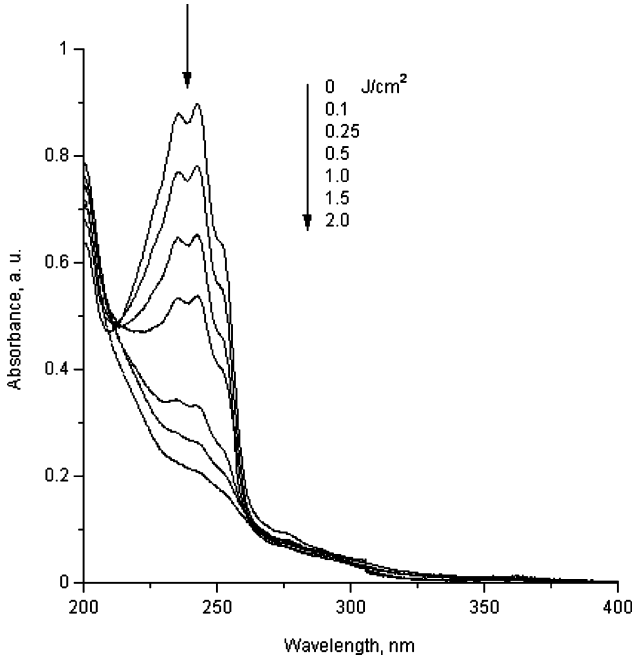


Figure 4. Variation of UV spectra of **3**, in film, with exposure doses.

saturated cyclic alkane through dimerization. Copolymers **4**−**6** showed similar behavior.

Figure 5 shows the normalized absorbance of **3**−**6** in film with varying exposure doses. The changes in absorbance occurred nonlinearly, and a certain threshold is seen at 1.0 J/cm^2 in all polymers. This can be correlated to the photocrosslinking behavior of the present polymers. This crosslinking behavior will be mentioned in detail later.

To investigate the relationship between the abietate group content of the polymers and the degree of photocrosslinking, we measured their insoluble fractions with different irradiation times. Figure 6 shows the plots of the insoluble fractions of **3**−**6** as functions of irradiation time. Because the photocrosslinking of polymers is based on photodimerization, the reaction should occur intermolecularly for effective

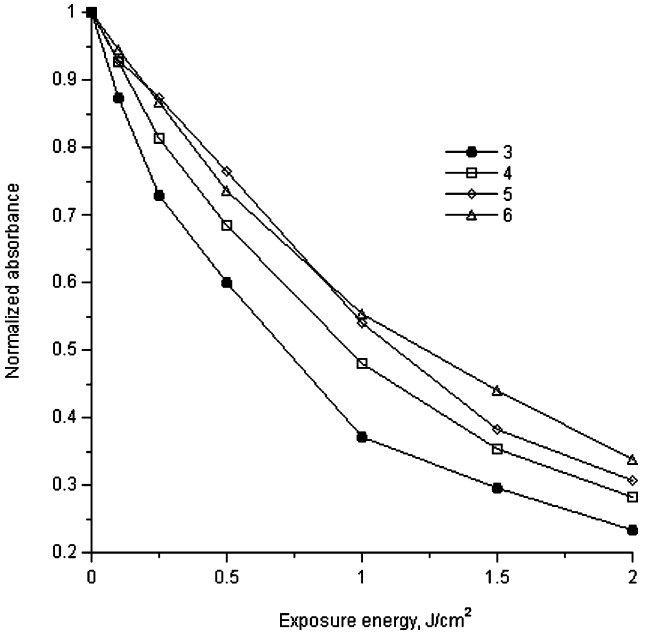


Figure 5. Normalized absorbances of **3**−**6**, in film, with exposure doses.

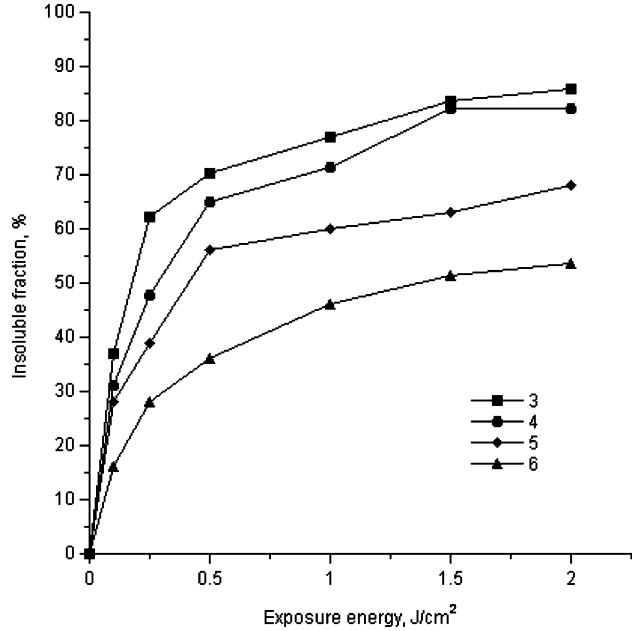


Figure 6. Insoluble fractions of **3**−**6**, in film, with exposure doses.

insolubilization rather than intramolecularly. The insoluble fractions of the polymers were not in proportion to abietate group contents. For example, the fractions reached about 68% for **3**, about 61% for **4**, about 57% for **5**, and about 50% for **6** at 0.5 J/cm^2, respectively. The insoluble fractions of copolymers **4**−**6** were fairly high in spite of the low abietate group contents, as compared to that of homopolymer **3** with 100% abietate group. This means that intermolecular dimerization effectively occurs even in a polymer with low abietate group content. Thus, it can be concluded that even low abietate group content in copolymers is sufficient for adequate insolubilization.

When display devices undergo a high-temperature treatment process, organic materials such as polymer photoresists are often unexpectedly discolored, thus leading to a decrease in visible region transparency. This could be fatal in practical

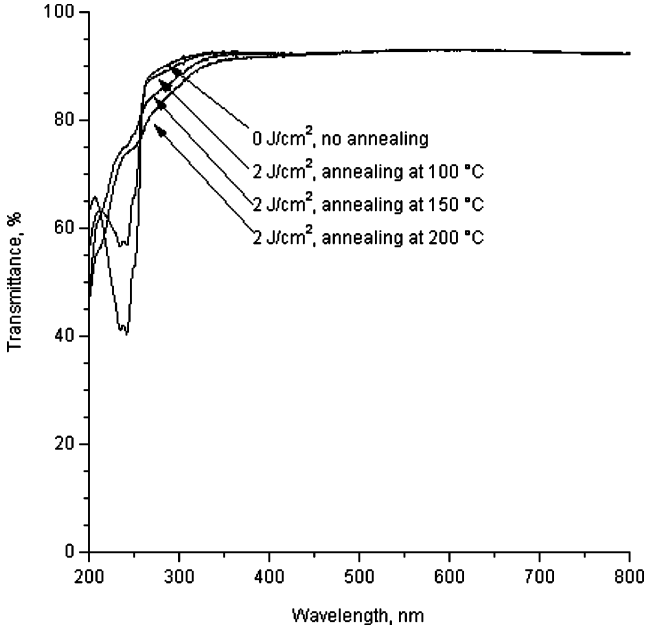


Figure 7. Transmittance spectra of **3**, in film, before and after the irradiation of 2 J/cm^2 and subsequent annealing for 30 min at different temperatures.

application. Thus, polymer photoresists are needed to maintain high transparency in visible regions after a thermal treatment process. Figure 7 exhibits the transparency of **3** in film treated with UV irradiation and subsequent annealing. The polymer film maintains a clear transparency of >90% in a visible region of >400 nm. This is comparable to those of PMMA (92%)[11,12] and inorganic glass (92%).[13,14] Other copolymer films, **4**−**6**, also showed a clear transparency of more than 90%. Thus, the present polymer used in our experiments is one of the most promising candidates as a negative photoresist because of its clear transparency and excellent photosensitivity.

Figure 8 shows photographic images of the **3** and **4** films patterned through photolithography. The photopattens are highly resolved with lines of 30 μm, a space of 30 μm, and a thickness of 2 μm. The resolution is considerably high relative to those of commercial photoresists with features of about 50−100 μm.

In conclusion, we successfully synthesized photocrosslinkable methacrylate-based polymers, **3**−**6**, containing an abietate group by the homopolymerization of the finely designed monomer, **2**, and its copolymerization with MMA. The T_g values of all polymers were higher than 130 °C, and much higher than that of PMMA. No T_m was observed. The decomposition temperatures were very high, as $T_{5\ wt\ \%\ loss}$ > 300 °C. Photocrosslinking nonlinearly occurred, and a certain threshold in the insoluble fractions could be seen at 0.5 J/cm^2 in all polymers. Polymer films showed a level of transparency of more than 90%. Highly resolved images were obtained from polymer films by photolithography. We expect that these polymers could be used in display device materials that require heat resistance, transparency, and photoresist properties.

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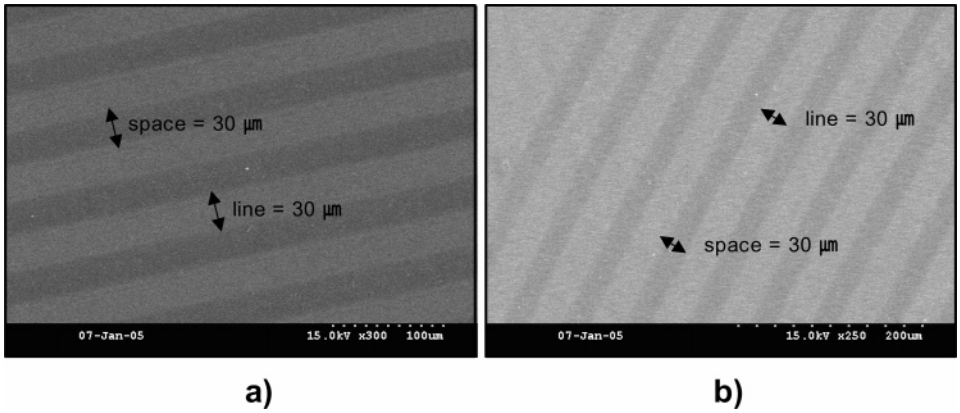

Figure 8. Scanning electron micrographs of developed patterns for (a) **3** and (b) **4**.

Experimental Section

Materials. Abietic acid was isolated from crude abietic acid (Aldrich, 70%) using diphenylamine.[15] Ethylene oxide (Korea Polyol Co.) and tetramethylammonium bromide (TMAB, Aldrich) were used as received. Methacrylic acid of reagent grade was distilled in the presence of calcium chloride under reduced pressure. Methyl methacrylate (MMA) of reagent grade was distilled in the presence of hydroquinone under reduced pressure. *N*,*N*-Dimethylformamide (DMF) was distilled in the presence of barium oxide under reduced pressure. Tetrahydrofuran (THF) and benzene were distilled in the presence of sodium. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. All other reagents were used as received.

Monomer Synthesis. *Hydroxyethyl Abietate (**1**).* Abietic acid (6.0 g, 20 mmol) was dissolved in THF (15 mL), and then the solution, together with TMAB (153 mg, 1 mmol) and ethylene oxide (8.73 g, 200 mmol), were put into a high-pressure reactor and stirred for 4 h at 80 °C. The solution was filtered before the solvent evaporated. The crude mixture was washed several times by aq. NaOH at pH 9. The crude product was further purified by flash column chromatography (Merck, silica gel; eluent, 4:1 THF: hexane), in order to provide the desired product (yield 4.95 g, 72%), which is a highly viscous liquid. ^{1}H NMR (DMSO-d_6): δ 5.72 (1H, $(CH_3)_2CHC{=}CH$), 5.32 (1H, $>C{=}CH$), 4.74 (1H, $-OH$), 4.00 (2H, $COOCH_2$), 3.60 (2H, $-CH_2OH$), and 2.27−0.72 (27H, other protons). IR (KBr): 3520, 2930, 1730, 1635, 1450, 1390, 1270, 1240, 1250, 1090, 1029, 880, 698 cm^{-1}.

*Methacryloyloxyethyl Abietate (**2**).* A 300 mL round-bottomed flask was equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar and flushed with dry nitrogen. Benzene (30 mL), hydroquinone (200 mg), *p*-toluenesulfonic acid (400 mg), boric acid (100 mg), methacrylic acid (1.29 g, 15 mmol), and compound **1** (4.32 g, 12 mmol) were placed in the flask, and the mixture was refluxed with stirring for 72 h. The product was extracted with diethyl ether, washed with water, and dried over anhydrous sodium sulfate. Diethyl ether was evaporated, and the crude product was purified by flash column chromatography (eluent, 8:1 hexane:THF) in order to give the desired product (yield 3.51 g, 68%) which is a highly viscous liquid. ^{1}H NMR ($CDCl_3$): δ 6.10, 5.56 (2H, $-COO(CH_3)C{=}CH_2$), 5.75 (1H, $(CH_3)_2CHC{=}CH$), 5.32 (1H, $>C{=}CH$), 4.34 (2H, $H_2(CH_3)C{=}CCOOCH_2$), 4.29 (2H, $-COO\ CH_2CH_2OOC-$), and 2.32−0.79 (30H, other protons). IR (KBr): 2944, 1725, 1639, 1445, 1377, 1311, 1241, 1144, 1048, 937, 870, 689 cm^{-1}.

Synthesis of Polymers. An AIBN solution (4.7 mg, 29 μmol) was added to a solution of **2** (1.2 g, 2.9 mmol) or comonomers (**2** and MMA, 2.9 mmol in total) in DMF (5 mL) and then sealed at 25 °C under nitrogen. The solution was kept for 24 h at 65 °C. The polymerization mixture was poured into a large excess of methanol to precipitate polymer. The polymer was filtered with a sintered glass (G3) and dried under reduced pressure.

Measurements. The weight- and number-average molecular weights (M_w and M_n, respectively) of the polymers were measured in THF with a Waters Alliance V2000 gel permeation chromatograph (GPC). The ^{1}H NMR spectra were measured in $CDCl_3$ solution at 25 °C using a Bruker Advanced Digital 400 FT-NMR spectrometer. The IR and UV−visible spectra were measured using a JUSCO-IR 810 spectrometer (KBr pellet) and a Shimadzu Model 2401 spectrophotometer, respectively. The intrinsic viscosities of the polymers were measured in chloroform at 25 °C with an Ubbelohde viscometer. The measurements of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted with a Dupont 2000 differential scanning calorimeter and a Dupont 2100 thermal gravimetric analyzer, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min. The micrographs of the photopatterned polymer films were measured on a Hitachi S-570 scanning electron microscope (SEM) operating at an accelerating voltage of 20 kV.

Photoreaction. To investigate the photochemical reaction of the polymers, 2 wt % THF solutions were coated on to quartz plates by a spin coater (SC-300), dried at room temperature, and irradiated with a high-pressure mercury lamp (3 mW/cm^2) for accumulative times. Their UV spectra were measured with the same UV spectrophotometers described above.

Photocrosslinking. Two weight percent THF solutions of the polymers were coated on to thin glass plates by spin coating, dried at room temperature, and irradiated with the same lamp for different times. The insoluble fractions were measured by weight after samples were developed in THF for 10 min. The weights of the samples before and after extraction were measured on a METTLER TOLEDO AX205 analytic balance with readability up to 0.01 mg.

Photolithography. Two weight percent chloroform solutions of the polymers were coated on to an ITO glass by spin coating and dried at room temperature. The film was exposed to a UV light at an exposure dose of 5 J/cm^2, through photomask and then washed with a mixture solvent (1:9 water:acetone) three times and dried.

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