Photo-Cross-Linkable Polymers with Thermally Degradable Property

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Polymers having both epoxy moieties and thermally cleavable tertiary ester moieties in the side chain were synthesized and characterized. On UV irradiation, polymer films containing photoacid generators (PAG) such as 9-fluorenilideneimino *p*-toluenesulfonate (FITS) and triphenylsulfonium triflate (TPST) became insoluble in tetrahydrofuran. The insoluble fraction of the irradiated films was increased by postexposure-baking at 90 °C if FITS was used as a PAG. When the cross-linked polymer films were baked at 160−180 °C, they became soluble in methanol. The effective baking temperature was dependent on the type of PAG used and on the polymer structure. Thermal degradation of the photochemically induced network polymers was studied by FT−IR spectroscopy, TGA analysis, and film thickness changes.

Introduction

Polymers which become insoluble in solvents on UV irradiation are used as photosensitive materials such as photoresists, printing plates, inks, coatings, and photocurable adhesives.[1] Since photochemically cross-linked polymers are insoluble and infusible networks, scratching or chemical treatments with strong acid or base must be applied to remove these networks from substrates. However, cross-linked polymers are difficult or impossible to thoroughly remove without damaging underlying materials.

Recently, some thermosets which are thermally or chemically degradable under a given condition have been reported. Tesoro and Sastri reported epoxy resins containing disulfide linkages which could be cleaved by treatment with triphenylphosphine to generate thiols.[2,3] Epoxy resins having acetal linkages were studied by Buchwalter et al.[4] Since acetal linkages can be easily decomposed, the cured resins could be dissolved in acid-containing organic solvents. Ober et al.[5] synthesized and characterized a series of epoxides with primary, secondary, or tertiary ester linkages. They reported that the epoxy thermosets containing tertiary ester linkages underwent network breakdown upon heating. The networks of the cured epoxy resins which have tertiary esters were broken down at a lower temperature (∼220 °C) than those with primary or secondary esters. The thermosets cured from the epoxides had an advantage of being thermally decomposable at relatively modest temperatures without introduction of a catalyst into the system. Diacrylate and dimethacrylate monomers containing thermally cleavable tertiary ester linkages were synthesized, and the networks obtained by photopolymerization were observed to decompose on heating (180 ∼ 200 °C) to form partially dehydrated poly(acrylic acid) or poly(methacrylic acid) and volatile alkenes.[6] Decomposed products were soluble in basic solutions and could be removed by a simple thermal treatment followed by washing with a basic solution. Wong et al.[7] reported the synthesis and characterization of a series of epoxy compounds which contained thermally cleavable carbamate linkages. The cured samples of the formulations from these diepoxides started to decompose at relatively lower temperatures (200 ∼ 300 °C) as compared with 350 °C for the cured sample of the commercial cycloaliphatic epoxide. Endo et al. reported reusable polymers obtained from bicyclic ortho esters and spiro ortho esters.[8] These polymers can be converted to monomers by depolymerization. Polymers having bicyclo ortho ester moieties in the side chain were also reported.[9] Cross-linking of the polymers was done with BF_3·OEt_2, and de-cross-linking of the cross-linked polymers was performed by trifluoroacetic acid to generate the starting linear polymers.

In this paper, we report the synthesis and characterization of photo-cross-linkable polymers bearing thermally degradable property. The concept of the present system is shown in Figure 1. On irradiation, network formation takes place by the photoinduced-acid-cata-

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(1) Fouassier, J. P.; Rabek, J. F. *Radiation Curing in Polymer Science and Technology*; Elsevier Applied Science: New York, 1993.
(2) Tesero, G. C.; Sastri, V. *J. Appl. Polym. Sci.* **1990**, *39*, 1425.
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(5) Yang, S.; Chen, J.-S.; Korner, H.; Breiner, T.; Ober, C. K. *Chem. Mater.* **1998**, *10*, 1475.
(6) Ogino, K.; Chen, J.-S.; Ober, C. K. *Chem. Mater.* **1998**, *10*, 3833.
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(8) Hitomi, M.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2823.
(9) Hitomi, M.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1999**, *200*, 1268.

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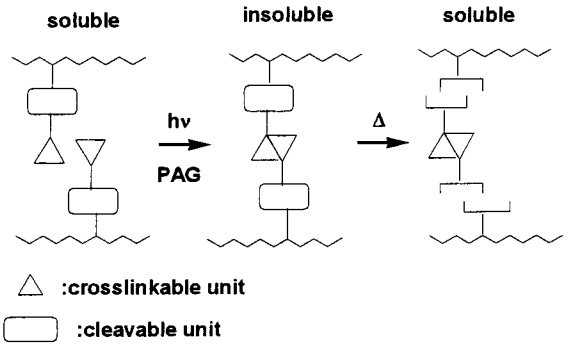
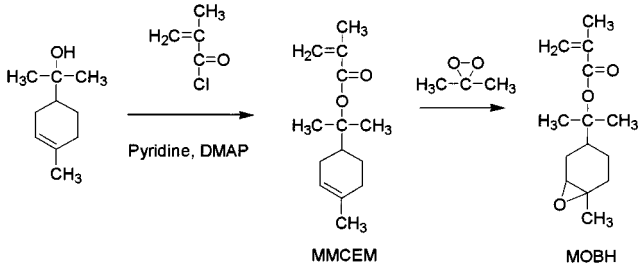


Figure 1. Concept of photo-cross-linkable polymers having thermally degradable property.

Scheme 1



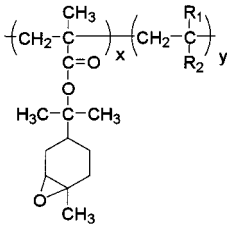
lyzed reactions of the cross-linkable moieties. A thermal treatment of the cross-linked polymers induces the cleavage of the network linkages. On the basis of this concept, we have synthesized polymers bearing both an epoxy moiety and a tertiary ester linkage in the side chain. These polymers are important as a photo-cross-linkable material which can be removed by baking after use.

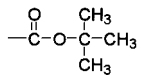
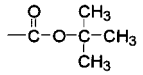
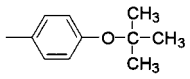
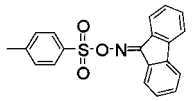
Experimental Section

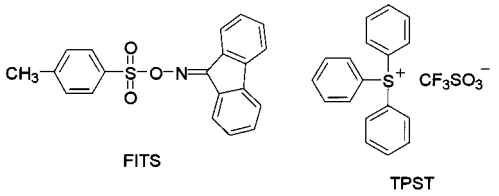
Materials. Benzene, *N*,*N*-dimethylformamide (DMF), dichloromethane, methyl methacrylate, *tert*-butyl methacrylate (TBMA), and p-*tert*-butoxystyrene (tBOSt) were purchased and distilled over CaH_2 before use. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Oxone (potassium peroxymonosulfate) was purchased from Aldrich. 9-Fluorenilideneimino *p*-toluenesulfonate (FITS)[10,11] and 9-fluorenilideneimino *p*-styrenesulfonate (FIS)[10] were prepared according to the method described elsewhere. Triphenylsulfonium triflate (TPST)[11] was obtained from Midori Kagaku and was used without further purification.

1-Methyl-1-(4-methyl-cyclohex-3-enyl)ethyl Methacrylate (MMCEM). MMCEM was synthesized by the reaction of methacryloyl chloride with α-terpineol (Scheme 1). To a cold (<5 °C) solution of α-terpineol (34.8 g, 0.226 mol) and 4-(dimethylamino)pyridine (DMAP) (2.7 g, 0.0221 mol) in anhydrous pyridine (31 mL) was slowly added a solution of 24.0 g (0.230 mol) of methacryloyl chloride in 110 mL of anhydrous dichloromethane. The mixture was stirred at ambient temperature for 40 h and then was thoroughly washed with 2N H_2SO_4. The organic phase was separated and washed with saturated sodium bicarbonate solution and then with water. The organic layer was dried over anhydrous $MgSO_4$. The product was purified by column chromatography; yield 25.6 g (51.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (s, 1H, CH_2=C), 5.39 (s, 1H, CH_2=C), 5.30 (s, 1H, −C*H*=C−), 1.83 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.41 (d, 6H, 2CH_3), 1.20−2.10 (m, 11H, C*H*, CH_2).

Scheme 2



polymer	R_1	R_2	composition x	composition y
PMOBH	—	—	100	0
P(MOBH(14)-TBMA)	CH_3		14	86
P(MOBH(32)-TBMA)	CH_3		32	68
P(MOBH-tBOSt)	H		15	85
P(MOBH-FIS)	H		97.4	2.6



1-Methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl Methacrylate (MOBH). MOBH was obtained by epoxidation[12] of MMCEM (see Scheme 1). Into a three-necked round-bottom flask fitted with an efficient magnetic stirrer, a Claisen adapter, two addition funnels, and a pH meter electrode were placed MMCEM (25.6 g, 0.115 mol), dichloromethane (160 mL), acetone(190 mL, 2.64 mol), phosphate buffer (pH = 7.4, 630 mL), and 18-crown-6 (1.26 g, 0.00477 mol). The flask was cooled to 0−5 °C using an ice−water bath. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (107 g, 0.174 mol) in 390 mL of water was added dropwise over the course of 2 h. At the same time, a solution of KOH (40 g, 0.713 mol) in 190 mL of water was also added dropwise to keep the reaction mixture at pH 7.1 ∼ 7.5. After the addition of oxone, the reaction mixture was stirred at 5 °C for an additional 4 h. The resulting mixture was filtered and extracted with three 80-mL aliquots of dichloromethane, and the combined organic layers were washed with water and dried over anhydrous $MgSO_4$. After removal of the solvents on a rotary evaporator, the oily residue was subjected to column chromatography to obtain the pure product; yield 14.3 g (52.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (s, 1H, CH_2=C), 5.40 (s, 1H, CH_2=C), 2.95 (d, 1H, epoxy *H*COC), 1.83 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.25 (d, 6H, 2CH_3), 1.20−2.10 (m, 7H, C*H*, CH_2).

Polymerization. Poly(MOBH) (PMOBH), poly(MOBH-*co*-TBMA) (P(MOBH(14)-TBMA) and P(MOBH(32)-TBMA)), and poly(MOBH-*co*-tBOSt) (P(MOBH-tBOSt)) were prepared by radical polymerization in degassed DMF solution at 30 °C using AIBN as an initiator with irradiation using a medium-pressure mercury lamp (Toshiba SHL-100UV) with a cutoff filter (Toshiba UV-35). Copolymerization of MOBH and FIS

(10) Shirai, M.; Kinoshita, H.; Tsunooka, M. *Eur. Polym. J.* **1992**, *28*, 379.

(11) FITS: mp: 160−162 °C. T_d: 225 °C (DSC), 261 °C (TGA). Quantum yield for the photochemical acid generation at 254 nm: 0.065 in PMMA film. TPST: mp: 132−134 °C. T_d: 330 °C. Quantum yield for the photochemical acid generation at 248 nm: 0.20 in novolac resin.[16]

(12) Crivello, J. V.; Liu, S. *Chem. Mater.* **1998**, *10*, 3724.

Table 1. Polymerization Conditions and Polymer Properties

polymer	monomer in feed: MOBH (mmol)	TBMA (mmol)	tBOSt (mmol)	FIS (mmol)	DMF (mL)	AIBN (mmol)	polymerization time (h)	yield (%)	$M_n^c \times 10^{-4}$	M_w/M_n^c	composition[d,e] (mol %): x	y	T_g^f (°C)	T_d^g (°C)
PMOBH[a]	10.5	0	0	0	4.0	0.18	2.5	44.0	5.1	2.2	100	0	117.5	216
P(MOBH(14)-TBMA)[a]	8.4	43.6	0	0	9.0	0.66	3.7	36.6	4.6	2.3	14	86	117.9	229
P(MOBH(32)-TBMA)[a]	2.1	4.01	0	0	0.50	0.22	1.0	40.9	9.3	2.6	32	68	117.3	218
P(MOBH-tBOSt)[a]	2.9	0	27.0	0	4.5	0.30	23.0	9.2	3.0	1.8	15	85	95.0	234
P(MOBH−FIS)[b]	3.4	0	0	0.083	2.6	0.32	8.5	56.6	6.2	2.7	97.4	2.6	131.2	203

[a] Polymerization was carried out at 30 °C with UV irradiation. [b] Polymerization was carried out at 50 °C. [c] Determined by GPC (THF, polystyrene standards). [d] See Scheme 2. [e] Determined by ^{1}H NMR. [f] Glass transition temperature determined from DSC. [g] Decomposition temperature determined from TGA.

was carried out by conventional radical polymerization in degassed DMF at 50 °C using AIBN as an initiator. The photopolymerization was not carried out because FIS weakly absorbed the irradiation light around 350 nm. The resulting polymers were purified by reprecipitation from chloroform/methanol. The fraction of the MOBH incorporated into the polymers was determined from the peak intensity of the ^{1}H NMR spectra. The structures of the polymers and photoacid generators are shown in Scheme 2. Polymerization conditions and properties of the polymers are summarized in Table 1.

Photo-Cross-Linking. All sample films were prepared on silicon wafers by spin casting from solutions of cyclohexanone/chloroform (1:1, v/v) containing sample polymer and photoacid generators. The sample films were dried on a hot plate at 120 °C for 2 min. The thickness of films was about 0.5 μm except for the sample films for the FT−IR measurements (1.9 μm). Irradiation was performed at 254 nm in air using a low-pressure mercury lamp (Ushio ULO-6DQ, 6 W) without a filter. The intensity of the light was measured with an Orc Light Measure UV-M02. Insoluble fraction was determined by comparing the film thickness before and after developments with tetrahydrofuran (THF). Thickness of films was measured by interferometry (Nanometrics Nanospec M3000).

Measurements. ^{1}H NMR spectra were observed at 400 MHz using a JEOL LA-400 or at 270 MHz using a JEOL GX-270 spectrometer. UV−vis spectra were taken on a Shimadzu UV-2400 PC. FT−IR measurements were carried out using a JASCO IR-410. Thermal decomposition behavior was investigated with a Rigaku TAS 100 thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) under nitrogen flow. Heating rate was 10 °C/min for both measurements. Size exclusion chromatography (SEC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex KF-806M + GMNHR-$_N$; 8.0 mm i.d. × 30 cm each) and a differential refractometer JASCO RI1530. The number-average molecular weight (M_n) and molecular weight dispersion (M_w/M_n) were estimated on the basis of a polystyrene calibration.

Results and Discussion

Synthesis of Polymers. On the basis of the concept shown in Figure 1, we have designed the polymers which have the following properties: (i) photo-cross-linkable, (ii) thermally cleavable at moderate temperatures (150−200 °C), and (iii) easy preparation. To satisfy these properties, we chose epoxy units as cross-linking sites and tertiary ester linkages as thermally degradable units. If we use these polymers in combination with photoacid generators, they can work as photo-cross-linkable polymers because ring-opening polymerization of the epoxy units is initiated by the photochemically generated acids. Tertiary esters are known to break down into carboxylic acid and alkene by thermal treatment at temperatures lower than primary esters.[13] Furthermore, the temperature of tertiary ester cleavage is lowered in the presence of strong acids.[13] α-Terpineol was employed as a precursor, which is a tertiary alcohol bearing a cycloalkene ring. The olefinic double bond of the cycloalkene ring can be converted to an epoxy moiety. MMCEM can be prepared by the reaction of methacryloyl chloride and α-terpineol in good yield (51%). By epoxidation of MMCEM,[12] the novel monomer MOBH bearing epoxy and tertiary ester groups was obtained in 52% yield. Synthetic procedures are summarized in Scheme 1.

When the conventional radical polymerization of MOBH was carried out at 50−60 °C, gel formation frequently occurred because of undesired reaction of the epoxy moiety in MOBH. Thus, homopolymer of MOBH was usually prepared by photopolymerization at 30 °C to prevent gel formation. Copolymers of MOBH with TBMA (P(MOBH(14)-TBMA) and P(MOBH(32)-TBMA)) and with tBOSt (P(MOBH-tBOSt)) were also prepared by the same way. Contents of the MOBH moiety in the copolymers of P(MOBH(14)-TBMA), P(MOBH(32)-TBMA), and (P(MOBH-tBOSt) were 14, 32, and 15 mol %, respectively. Glass transition temperatures (T_g) of these polymers were 95.0−117.9 °C which were close to that of poly(methyl methacrylate). Number-average molecular weights of the polymers were 3.0−9.3 × 10^4. Thermal decomposition temperatures (T_d: onset temperature) of the polymers were 216−234 °C. For the preparation of a copolymer of MOBH and FIS (P(MOBH−FIS)), we could not use the above method because the photolysis of FIS occurred during polymerization. However, P(MOBH−FIS) was successfully synthesized by conventional radical polymerization at 50 °C without gel formation. Polymerization conditions and properties of P(MOBH−FIS) are also summarized in Table 1. T_g for P(MOBH−FIS) was 131.2 °C which was higher than that for PMOBH. The incorporation of bulky FIS units increased the T_g value. P(MOBH−FIS) had a lower T_d value (203 °C) than PMOBH (216 °C). The PMOBH film with 3.6 mol % FITS gave the same TGA curve as that for P(MOBH−FIS). This suggests that the trace of acid generated by thermolysis of FITS or FIS units in P(MOBH−FIS) causes acid-catalyzed decomposition of tertiary ester linkages in the polymer at slightly lower temperature. Although the T_d value for FITS was 225 °C from the TGA measurement, it was confirmed from DSC measurement that FITS started to decompose at lower temperature (∼204 °C).

Photo-Cross-Linking Properties. Polymer films containing photoacid generators were irradiated at 254 nm, and insoluble fraction in THF was studied. FITS and TPST as photoacid generators were photolyzed to generate *p*-toluenesulfonic acid and trifluoromethane-

(13) Ito, H.; Ueda, M. *Macromolecules* **1988**, *21*, 1475.

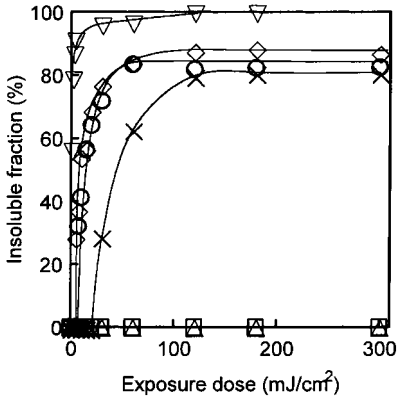
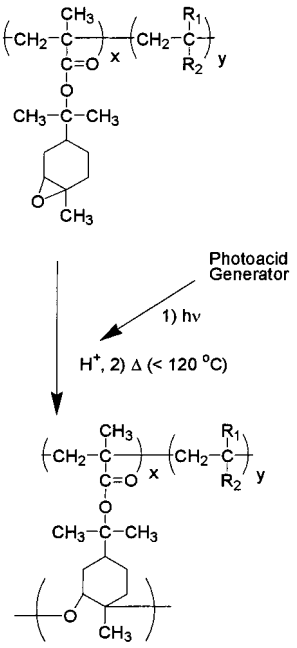


Figure 2. Effects of polymer structure and PAG on photoinduced insolubilization. Polymer film: (○) PMOBH with 3.6 mol % FITS, (△) P(MOBH(14)-TBMA) with 3.6 mol % FITS, (×) P(MOBH(32)-TBMA) with 3.6 mol % FITS, (□) P(MOBH-tBOSt) with 3.6 mol % FITS, (▽) PMOBH with 3.6 mol % TPST, and (◇) P(MOBH−FIS). Development was done with THF for 10 min, except PMOBH film with TPST (development for 2 min).

Scheme 3



sulfonic acid, respectively. The FIS unit in P(MOBH−FIS) was also photolyzed to form *p*-styrenesulfonic acid moieties. The photoinduced acids initiated cationic polymerization of epoxy units in the side chain to generate networks (Scheme 3). Figure 2 shows the insolubilization properties of the polymers on irradiation at ambient temperature. P(MOBH−FIS) film and PMOBH film containing 3.6 mol % of FITS showed high efficiency of insolubilization. Effective insolubilization was also observed for P(MOBH(32)-TBMA). No significant insolubilization was observed for P(MOBH(14)-TBMA) and P(MOBH-tBOSt) because of low fractions of MOBH units (14 ∼ 15 mol %). The film of P(MOBH−FIS) showed almost the same insolubilization properties as the PMOBH film containing FITS. TPST was more effective for the insolubilization of PMOBH film compared to FITS. The ring-opening reaction of epoxy moiety is known to easily occur by strong acids. However, as for P(MOBH(14)-TBMA) and P(MOBH-tBOSt)

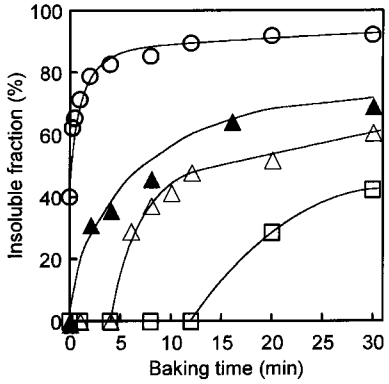


Figure 3. Effect of postexposure-baking treatment at 90 °C on insolubilization of the irradiated polymer films containing 3.6 mol % FITS. Polymer film: (○) PMOBH, (△) P(MOBH-(14)-TBMA), and (□) P(MOBH-tBOSt), (▲) P(MOBH(14)-TBMA) film containing 3.6 mol % TPST and PEB treatment at 60 °C. Irradiation dose: 60 mJ/cm^2 except for PMOBH (10 mJ/cm^2). Development was done with THF for 10 min.

films containing 3.6 mol % of TPST, photoinduced insolubilization was not observed at room temperature.

The insoluble fraction of the present polymers was increased by the postexposure-baking (PEB) treatment at 60−120 °C. The PEB treatment effect on the insolubilized fraction was increased with baking temperature. Figure 3 shows the PEB treatment effect on the enhancement of insolubilization at 90 °C. Sample films containing 3.6 mol % FITS were irradiated for a given period and followed by baking at 90 °C. After the irradiation at room temperature, the insoluble fractions for PMOBH film and the copolymer films (P(MOBH-(14)-TBMA) and P(MOBH-tBOSt)) were 40% and 0%, respectively. However, the insoluble fraction was increased with PEB treatment time though the enhancement for P(MOBH(14)-TBMA), and P(MOBH-tBOSt) was smaller than for PMOBH. A similar effect of PEB treatment was observed for P(MOBH−FIS). When FITS was replaced by TPST, the effect of PEB treatment at 60 °C on insolubilization was enhanced. No insolubilization was observed when unirradiated polymer films were baked at 90 °C for 30 min.

Thermal Degradation. It is known that *tert*-butyl esters of carboxylic acids thermally decompose to form carboxylic acids and isobutene.[13] The thermal decomposition temperature is lower if strong acids are present.[13] Figure 4 shows FT−IR spectral changes of PMOBH film containing 3.6 mol % FITS on irradiation. After irradiation of the film with a dose of 180 mJ/cm^2 at room temperature, no significant changes in the FT−IR spectrum were observed though the film became insoluble in THF. When the irradiated film was baked at 90 °C for 10 min, the FT−IR spectrum showed no significant changes except the slight decrease of the peak due to epoxy moieties at 846 cm^{-1} . When the irradiated film was baked at 160 °C for 10 min, the peak due to ester carbonyl at 1740 cm^{-1} observed for the unirradiated film shifted to 1715 cm^{-1} and the peak due to C−O−C at 1140 cm^{-1} disappeared (Figure 4c). Furthermore, a broad peak due to OH of carboxylic acid units appeared at 2500 ∼ 3500 cm^{-1}. This finding suggests that the cleavage of the tertiary ester moiety in PMOBH occurred to generate poly(methacrylic acid) as shown in Scheme 4. The peak due to the epoxy moiety

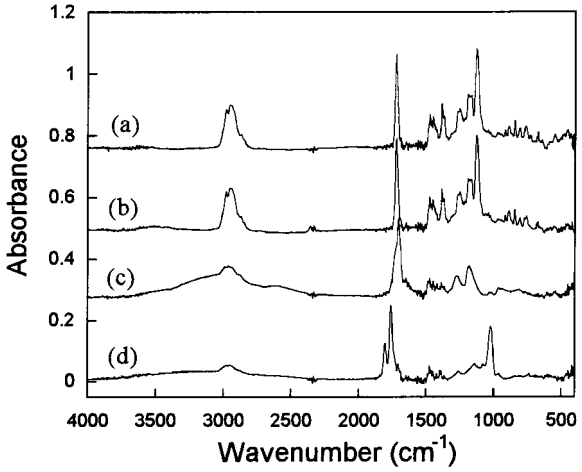
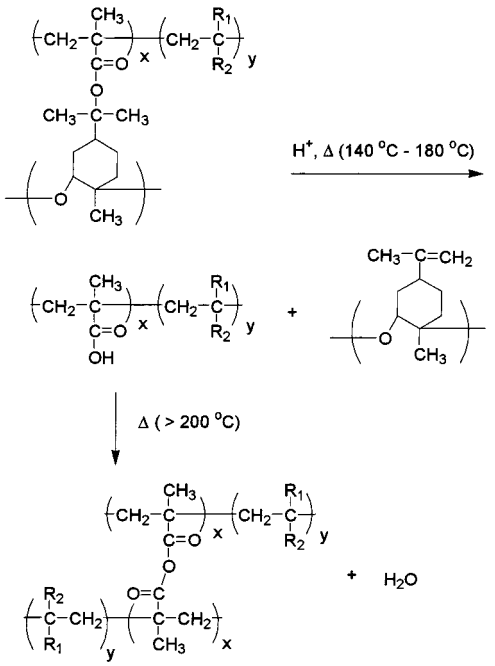


Figure 4. FT−IR spectra of PMOBH films containing 3.6 mol % FITS (a) before exposure, (b) after exposure (180 mJ/cm^2), (c) after postexposure-baking at 160 °C for 10 min, (d) after baking at 200 °C for 36 min for the sample shown by curve (c). Film thickness: 1.9 μm.

Scheme 4



at 846 cm^{-1} disappeared after the bake treatment. Two pathways are possible to explain the disappearance of the peak due to epoxy units: (1) ring-opening reaction completely occurred; (2) the side-chain moiety degraded during baking treatment was vaporized. The second pathway was confirmed from TGA analysis of the film as will be discussed below. A new peak appeared at ca. 1800 cm^{-1} when the irradiated film was baked at 200 °C for 36 min (Figure 4d). This is due to the formation of carboxylic acid anhydride moieties (Scheme 4). It was reported that the dehydration reaction started almost simultaneously with the thermal decomposition of tertiary ester moieties in the side chain of the polymers.[6,13]

When P(MOBH(14)-TBMA) film containing 3.6 mol % FITS was irradiated and baked at 160 °C for 10 min, the film gave the same FT−IR spectrum as observed for the thermally degraded PMOBH film. This suggests that the thermal degradation of MOBH and TBMA units occurred simultaneously to generate poly(methacrylic acid). Furthermore, after the thermal treatment of the irradiated P(MOBH-tBOSt) film containing 3.6 mol % FITS, formation of poly(methacrylic acid-*co*-vinylphenol) was confirmed by FT−IR measurements. The peak at 1140 cm^{-1} due to C−O−C disappeared and the peak at 1240 cm^{-1} ascribed to phenolic C−O stretching newly appeared. Poly(*tert*-butoxystyrene) is known to thermally decompose to generate poly(vinylphenol) and isobutene at relatively low temperatures (∼100 °C) in the presence of strong acids.[14] Thermal degradation of the tertiary ester linkage in P(MOBH−FIS) was also observed after irradiation and then baking at 180 °C.

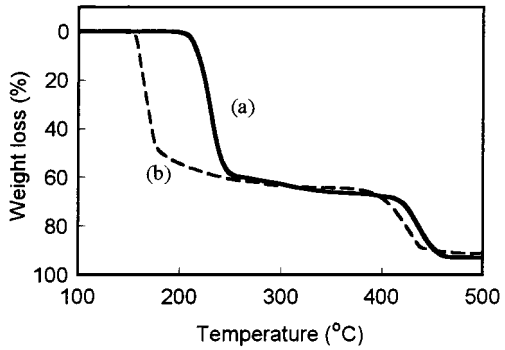


Figure 5. TGA curves of (a) PMOBH film and (b) PMOBH film containing 3.6 mol % FITS after irradiation with a dose of 300 mJ/cm^2. Heating rate: 10 °C/min under N_2 flow.

Figure 5 shows TGA curves of (a) PMOBH film and (b) irradiated PMOBH film containing 3.6 mol % of FITS. PMOBH started to decompose at ca. 220 °C to generate poly(methacrylic acid). The weight loss at 320 °C was 64% which was consistent with the weight of the ester moiety of MOBH units of PMOBH. However, FT−IR spectrum of the PMOBH baked at 320 °C showed the formation of anhydride. If anhydride was formed, the weight loss should be 68%. This disagreement may be due to the nonvolatile epoxy oligomers thermally formed from MOBH moiety. The PMOBH film containing *p*-toluenesulfonic acid generated photochemically started to decompose at ca. 150 °C. The weight loss for PMOBH films with and without acids was almost the same. The cross-linked PMOBH film could be thermally decomposed to poly(methacrylic acid) or poly(methacrylic acid) anhydride at lower temperatures than PMOBH in the absence of acid. P(MOBH-(14)-TBMA) started to decompose at ca. 230 °C to generate poly(methacrylic acid) in the absence of acids. The weight loss was 50%, which corresponded with the value estimated for the formation of poly(methacrylic acid) anhydride from P(MOBH(14)-TBMA). This suggests that the decomposition temperature of the *tert*-butyl ester linkages in TBMA units is almost the same as the tertiary ester linkages in MOBH units. P(MOBH-tBOSt) started to decompose at ca. 230 °C, and the second decomposition started at 270 °C because of the cleavage of the tertiary ether linkages in tBOSt units. However, in the presence of photoinduced acid, the decomposition of *tert*-butyl ether linkages and tertiary ester linkages in P(MOBH-tBOSt) occurred simulta-

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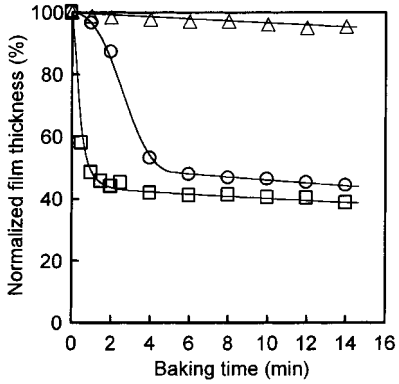

Figure 6. Effect of baking on the changes of thickness of the irradiated PMOBH films containing 3.6 mol % FITS. Baking temperature: (△) 140, (○) 160, and (□) 180 °C. Irradiation dose: 60 mJ/cm^2.

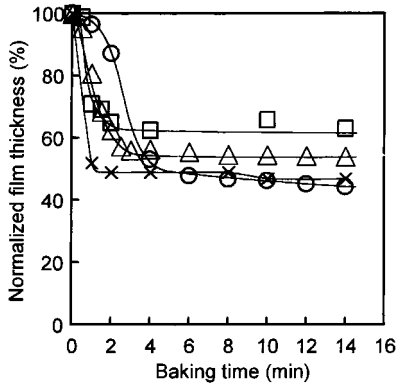

Figure 7. Decrease of thickness of the cross-linked PMOBH (○), P(MOBH(14)-TBMA) (△), P(MOBH(32)-TBMA) (×) and P(MOBH-tBOSt) (□) films containing 3.6 mol % FITS on baking at 160 °C. Irradiation dose to cross-link the polymer: 60 mJ/cm^2.

neously at 160 °C. This was confirmed by the finding that a TGA curve for P(MOBH-tBOSt) showed one-stage decomposition.

Figure 6 shows the decrease of thickness of PMOBH film containing FITS when irradiated and baked at given temperatures. Although, on baking at 140 °C, no significant decrease of film thickness was observed, decrease of the thickness (∼55%) was observed when baked at 160 and 180 °C for 14 min. This finding was consistent with the data from TGA analysis. The decrease of the film thickness on baking was dependent on polymer structure (Figure 7). The thickness decrease for PMOBH, P(MOBH(32)-TBMA), P(MOBH(14)-TBMA), and P(MOBH-tBOSt) was 55, 53, 50, and 40%, respectively. The decrease was due to the vaporization of alkenes produced by the acid-catalyzed thermolysis. This finding suggests that the chain length of the side-chain ether units obtained by the ring-opening reaction of epoxy moieties must be short.

Dissolution properties of the photochemically cross-linked PMOBH are shown in Figure 8. PMOBH film containing 3.6 mol % of FITS was irradiated and followed by baking at 140−180 °C. The film baked at 140 °C was not soluble in methanol. When baked at 160 or 180 °C, the cross-linked film became soluble in methanol. Longer bake treatment was necessary if baking temperature was low. Likely, the degraded polymer does not really dissolve but breaks off from a

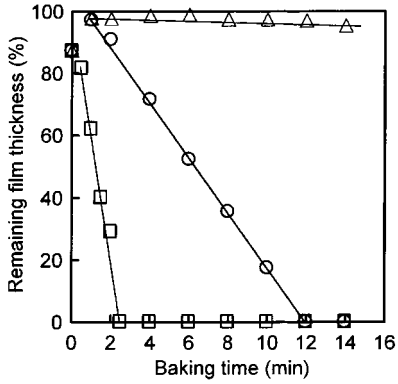

Figure 8. Dissolution properties of the thermally decomposed PMOBH films cross-linked by irradiation. Baking temperature: (△) 140, (○) 160, and (□) 180 °C. Irradiation dose to cross-link the polymer containing 3.6 mol % FITS: 60 mJ/cm^2. Development was done with methanol for 10 min.

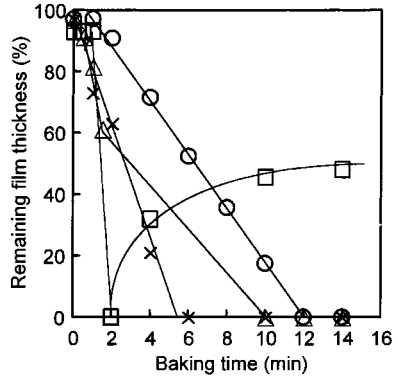

Figure 9. Dissolution properties of the cross-linked PMOBH (○), P(MOBH(14)-TBMA) (△), P(MOBH(32)-TBMA) (×), and P(MOBH-tBOSt) (□) films containing 3.6 mol % FITS on baking at 160 °C. Irradiated films were baked at 90 °C for 10 min before the bake treatment at 160 °C. Development was done with methanol for 10 min. Irradiation dose to cross-link the polymers: 60 mJ/cm^2.

substrate because of diminished mechanical and adhesive properties. The irradiated PMOBH film baked at 180 °C was dissolved in methanol and filtered with a membrane filter (pore size: 0.5μm). The filtrate was evaporated to dryness and almost 100% of the polymer was recovered. This finding suggests that the degraded polymer did not break off from a substrate. Furthermore, it was confirmed that the separated polymer was poly(methacrylic acid) by reference to the FT−IR and ^{1}H NMR spectra of the authentic poly(methacrylic acid). However, the dissolved polymer may have small amounts of anhydride groups which cannot be detected by the spectroscopic analysis.

Figure 9 shows the dissolution properties of the cross-linked P(MOBH(14)-TBMA), P(MOBH(32)-TBMA), P-(MOBH-tBOSt), and PMOBH. The irradiated films (exposure dose: 60 mJ/cm^2) were baked at 90 °C for 10 min and then baked at 160 °C. The cross-linked PMOBH, P(MOBH(32)-TBMA), and P(MOBH(14)-TBMA) became soluble in methanol after baking for 6−12 min. Although the cross-linked P(MOBH-tBOSt) became soluble after baking for 2 min, the dissolved fraction decreased when baked for a longer period than 2 min. This may be due to the formation of partial network by the esterification reactions between carboxylic acid and phenol units which were generated by the thermolysis

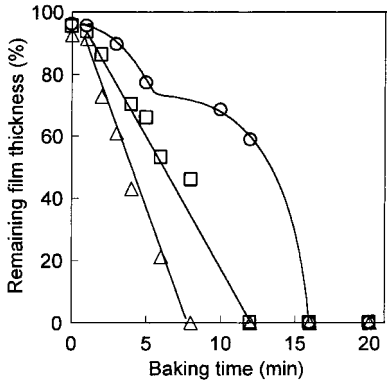

Figure 10. Dissolution properties of the cross-linked (△) PMOBH films containing 2.6 mol % FITS irradiated with a dose of 60 mJ/cm^2 and P(MOBH−FIS) films after irradiation with a dose of (○) 60 and (□) 450 mJ/cm^2 to cross-link the polymers. Baking temperature: 180 °C. Development was done with methanol for 10 min.

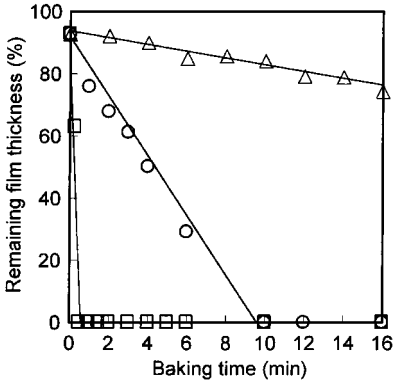

Figure 11. Dissolution properties of the cross-linked PMOBH films containing 3.6 mol % TPST. Baking temperature: (△) 70, (○) 90, and (□) 110 °C. Irradiation dose to cross-link the polymer: 60 mJ/cm^2. Development was done with methanol for 10 min.

of P(MOBH-tBOSt). Solubility changes of the cross-linked P(MOBH−FIS) by thermolysis were compared with that of cross-linked PMOBH containing 2.6 mol % FITS (Figure 10). From the decrease of absorbance at 250 nm in UV spectrum on irradiation at 60 mJ/cm^2, photolyzed fractions of FIS units in P(MOBH−FIS) and FITS in PMOBH film were calculated to be 83 and 87%, respectively. Thus, there are no big differences in the photoreactivity of FIS units in P(MOBH−FIS) and FITS in PMOBH film. The cross-linking properties of P-(MOBH−FIS) and PMOBH containing 2.6 mol % FITS were almost the same as shown in Figure 2. However, on bake treatment, the cross-linked PMOBH and cross-linked P(MOBH−FIS) showed a large difference in dissolution properties. On baking the P(MOBH−FIS) film exposed at 450 mJ/cm^2 to thoroughly photolyze FIS units, the dissolution curve was similar to that for the cross-linked PMOBH film containing FITS, except for the prolonged baking time to completely dissolve the film. However, the thermally induced dissolution profile for the P(MOBH−FIS) film irradiated at 60 mJ/cm^2 was different from the film exposed at 450 mJ/cm^2. The reduced dissolution fraction may be due to the partial cross-linking induced by the acid-catalyzed reaction of the unphotolyzed FIS units. Polymer films bearing FIS units have been reported to become insoluble in solvents because of the formation of sulfonic acid anhydride linkages at relatively low temperatures (∼80 °C) if acids are present in the film.[15]

Baking temperature to dissolve the cross-linked polymers was dependent on the photoacid generator used. Figure 11 shows the dissolution properties of the cross-linked PMOBH film containing 3.6 mol % of TPST. After baking at 90−110 °C for 0.5−10 min, it became soluble in methanol. When FITS was used as a photoacid generator, the baking at 160−180 °C for 3−12 min was necessary to completely dissolve the cross-linked PMOBH (see Figure 8). Thus, the baking temperature to thermally decompose the cross-linked polymers could be selected by changing photoacid generators.

Conclusions

We have synthesized a novel methacrylate monomer (MOBH) which has an epoxy moiety and a tertiary ester linkage in a molecule. Homopolymer of MOBH and copolymers of MOBH with *tert*-butyl methacrylate and with *tert*-butoxystyrene were obtained by the conventional radical photopolymerization. Polymer films containing photoacid generators (PAG) became insoluble in tetrahydrofuran on UV irradiation because of the photoinduced acid-catalyzed cross-linking reaction of epoxy units. De-cross-linking of the irradiated polymer films was performed by thermal treatment at 90−180 °C; the temperature was dependent on the type of PAG and polymer structure. It was confirmed that de-cross-linking occurred by the cleavage of tertiary ester linkages. The polymers can be applied to photo-cross-linkable materials for temporary use.

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