Photo-cross-linkable Polymers Having Degradable Properties on Heating

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Photo-cross-linkable polymers having degradable properties on heating were described. Copolymers of esters or salts of *p*-styrenesulfonic acid with a novel monomer having both an epoxy moiety and a tertiary ester moiety were synthesized and characterized. Polymer films containing a photoacid generator became insoluble in organic solvents on UV irradiation. The insoluble fraction of the irradiated films was increased by post-exposure-baking at relatively low temperatures (40−100 °C). When the cross-linked polymer films were baked at 120−200 °C, they became soluble in water. The effective bake temperature was dependent on the polymer structure. Thermal degradation of the cross-linked polymers was studied by TGA analysis and in situ FT-IR spectroscopy.

Introduction

Recently, much attention has been paid to recovery or recycling of polymeric materials due to environmental regulations and interests in environmentally friendly materials. Especially, the recycling of thermosets, which are widely used as adhesives, printing plates, and matrixes for composite materials, is one of the most challenging target. The intractability of cured thermosets is based on their highly cross-linked three-dimensional networks. However, if the network bonds are cleaved through chemical reactions or physical treatments, the thermosets become easy to recover or recycle. From this point of view, some thermosets which are thermally or chemically degradable under a given condition have been designed and reported.[1−15] Tesoro and Sastri reported epoxy resins containing disulfide linkages which could be cleaved by treatment with triphenylphosphine to generate thiols.[1,2] Epoxy resins having acetal linkages were studied by Buchwalter and

Kosber.[3] The cured resins could be dissolved in acid-containing organic solvents due to hydrolysis of acetal linkages. Ober and our research group reported cross-linkable compounds having primary, secondary,[4] or tertiary ester linkages[4−9] applicable to the materials having degradable properties upon heating. The networks of the cured resins which have tertiary esters were broken down at lower temperature (~220 °C) than those with primary or secondary esters. Wong and co-workers reported the synthesis and characterization of a series of epoxy compounds which contained thermally cleavable carbonate[10] or carbamate[11] linkages. Malik and Clarson[12,13] reported the synthesis of resins having sterically hindered urea linkages. Endo and co-workers reported reusable polymers obtained from bicyclic ortho esters[14] and spiro ortho esters.[14,15] These polymers can be converted to monomers by depolymerization by treatment with trifluoroacetic acid.

We previously reported the photo-cross-linking systems having redissolution properties in solvents. Homopolymer of 1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]-hept-3-yl)ethyl methacrylate (MOBH), which has both an epoxy moiety and a tertiary ester linkage in a molecule, and its copolymers with *tert*-butyl methacrylate and *p-tert*-butoxystyrene were prepared.[7] Photo-cross-linking of the polymers was carried out by irradiation at 254 nm in the presence of photoacid generator. The cross-linked polymers were thermally decomposed at 150−200 °C. The decomposition occurred on the tertiary ester linkages. The thermally decomposed polymers were soluble in methanol or aqueous alkaline solution. Water is the most environmentally friendly solvent compared with methanol or aqueous alkaline solution.

From this point of view, we have studied the photo-cross-linkable polymers that can be dissolved away with water after use. In a previous communication,[9] we reported the preliminary results on the photo-cross-linkable polymers based on *p*-styrenesulfonic acid esters

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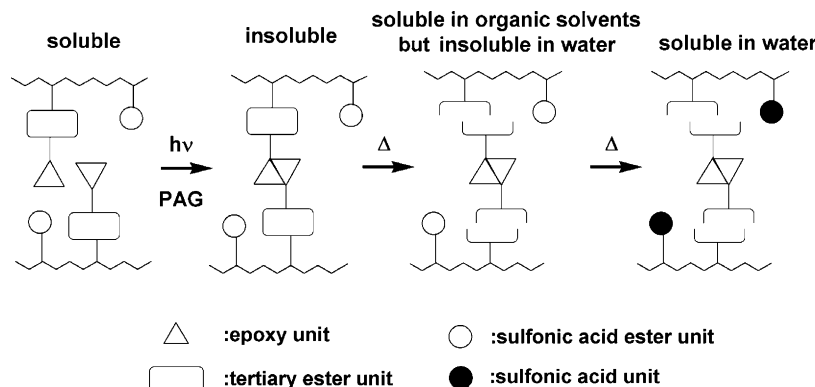(15) Hitomi, M.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1999**, *200*, 1268.

△ :epoxy unit   ○ :sulfonic acid ester unit

▭ :tertiary ester unit   ● :sulfonic acid unit

Figure 1. Concept of photo-cross-linkable polymers with redissolution properties.

and MOBH. The photochemically cross-linked polymers became soluble in water on baking. Figure 1 shows the design concept of the photo-cross-linkable polymers having redissolution properties in water. In this study we have extended the previous work. Some esters or salts of *p*-styrenesulfonic acid were copolymerized with MOBH. The photo-cross-linking of the polymers and thermal degradation of the cross-linked polymers have been investigated in detail.

Experimental Section

Materials. *N,N*-Dimethylformamide (DMF) and pyridine were distilled over CaH_2 before use. 2,2′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. 9-Fluorenilideneimino *p*-toluenesulfonate (FITS) was prepared according to the method described elsewhere.[16] Sodium *p*-styrenesulfonate (SSNa), thionyl chloride, and solvents were purchased from Tokyo Kasei (Japan) and used as received. *p*-Styrenesulfonyl chloride was prepared by the reaction of thionyl chloride with SSNa as described elsewere.[17] 1-Methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl methacrylate (MOBH),[7] cyclohexyl *p*-styrenesulfonate (CHSS),[17] and 2,2-dimethylpropyl *p*-styrenesulfonate (NPSS)[18] were prepared as reported.

Methyl *p*-Styrenesulfonate (MSS). Methanol (0.802 mL, 2.22×10^{-2} mol) was mixed with pyridine (10.0 mL, 1.11×10^{-1} mol) and cooled to −20 °C. *p*-Styrenesulfonyl chloride (5.0 g, 2.22×10^{-2} mol) was added dropwise to the solution and kept at −20 °C for 1 h. The mixture was thoroughly washed with 2 N HCl. 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 (silica gel; eluent: chloroform); colorless liquid; yield 0.99 g (24%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.78 (d, 2H, phenyl), 7.50 (d, 2H, phenyl), 6.68 (dd, 1H, $CH_2=CH-$), 5.86 (s, 1H, $CH_2=CH-$), 5.38 (s, 1H, $CH_2=CH-$), 3.68 (s, 3H, $-O-CH_3$). bp 60−62 °C (0.005 mmHg).[19]

Phenyl *p*-Styrenesulfonate (PhSS). To a cold (<5 °C) solution of phenol (2.13 g, 2.22×10^{-2} mol) in anhydrous pyridine (10 mL) was slowly added 5.0 g (2.22×10^{-2} mol) of *p*-styrenesulfonyl chloride. The mixture was stirred at ambient temperature for 24 h and then thoroughly washed with 2 N HCl. The organic phase was separated and washed with saturated sodium bicarbonate solution and then with water. The product was purified by column chromatography (silica gel;

eluent: chloroform); colorless liquid; yield 0.87 g (15%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.69 (d, 2H, phenyl), 7.50 (d, 2H, phenyl), 7.19−7.30 (m, 5H, phenyl), 6.72 (dd, 1H, $CH_2=CH-$), 5.95 (s, 1H, $CH_2=CH-$), 5.75 (s, 1H, $CH_2=CH-$). Anal. Calcd for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65. Found: C, 64.48; H, 4.57.

Tetra-*n*-butylammonium *p*-Styrenesulfonate (TBASS). An aqueous solution (40 mL) of SSNa (6.45 g, 3.2×10^{-2} mol) was mixed with an aqueous solution (10 mL) of an equivalent mole of silver nitrate (5.38 g) (3.2×10^{-2} mol) in water. The white solid precipitated was separated by centrifugation and dried under vacuum: yield 6.75 g. The solid (6.75 g) was dissolved in acetonitrile (150 mL), and tetra-*n*-butylammonium chloride (6.44 g, 2.3×10^{-2} mol) was added to the solution. The mixture was stirred at 50 °C for 2 h and filtered. The filtrate was evaporated to dryness. TBASS was obtained as a white solid; yield 8.7 g (77%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.72 (d, 2H, phenyl), 7.22 (d, 2H, phenyl), 6.57 (dd, 1H, $CH_2=CH-$), 5.61 (s, 1H, $CH_2=CH-$), 5.14 (s, 1H, $CH_2=CH-$), 3.10 (t, 8H, $-N-CH_2-$), 1.44 (m, 8H, $-N-CH_2-CH_2-$), 1.27 (m, 8H, $-CH_2-CH_3$), 0.83 (t, 3H, $-CH_2-CH_3$). FAB-MS (*m/z*): 425 ([M]$^+$), 426 ([M + 1]$^+$).

Polymerization. Poly(MOBH-*co*-MSS) (P(MOBH-MSS)), poly(MOBH-*co*-CHSS) (P(MOBH−CHSS)), and poly(MOBH-*co*-PhSS) (P(MOBH−PhSS)) were prepared by radical copolymerization 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). Poly(MOBH-*co*-TBASS) (P(MOBH-TBASS) was prepared by the same procedure using acetonitrile as a solvent. Poly(MOBH-*co*-NPSS) (P(MOBH−NPSS)) was obtained by conventional copolymerization using AIBN in DMF at 55 °C. The resulting polymers were purified by reprecipitation from chloroform/methanol or THF/hexane. The molar ratios of the monomers incorporated into the polymers were determined from ^{1}H NMR spectra. The structures of the polymers and the photoacid generator FITS are shown in Scheme 1. Polymerization conditions and polymer properties are summarized in Table 1. Elemental analysis data for typical copolymers are as follows: Anal. Calcd for poly(MOBH$_{42}$-*co*-CHSS$_{58}$): C, 66.05; H, 8.01. Found: C, 65.95; H, 8.07. Anal. Calcd for poly(MOBH$_{38}$-*co*-NPSS$_{62}$): C, 64.73; H, 7.92. Found: C, 65.02, H, 8.01.

Photo-cross-linking and Thermal De-cross-linking. All sample films were prepared on silicon wafers by spin-casting from solutions of cyclohexanone containing sample polymer and FITS. 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 FT-IR (1.9 μm) and in situ FT-IR (1.0 μm) measurements. Irradiation was performed at 254 nm in air using a low-pressure mercury lamp (USHIO ULO-6DQ) without a filter. The intensity of the light was measured with an Orc Light Measure UV-M02. Post-exposure-baking (PEB) treatment was carried out using a conventional hot plate. Insoluble fraction was determined by comparing the film thickness before and after dipping the samples into a solvent. Thickness of films was measured by interferometry using a Nanometrics Nanospec M3000.
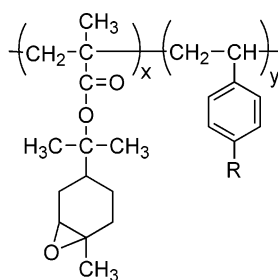
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Scheme 1

polymer	R
P(MOBH-MSS)	$-\overset{\displaystyle O}{\underset{\displaystyle O}{S}}-O-CH_3$
P(MOBH-CHSS)	$-\overset{\displaystyle O}{\underset{\displaystyle O}{S}}-O-$ cyclohexyl
P(MOBH-NPSS)	$-\overset{\displaystyle O}{\underset{\displaystyle O}{S}}-O-CH_2-C(CH_3)_3$
P(MOBH-PhSS)	$-\overset{\displaystyle O}{\underset{\displaystyle O}{S}}-O-$ phenyl
P(MOBH-TBASS)	$-\overset{\displaystyle O}{\underset{\displaystyle O}{S}}-O^-\ ^+N(C_4H_9)_4$

CH$_3$—phenyl—$\overset{\displaystyle O}{\underset{\displaystyle O}{S}}$—O—N=fluorenylidene

FITS

Thermolysis of TBASS. A solution of TBASS in diphenyl ether (33 wt %) was sealed into a glass capillary tube and heated at 220 °C for 5 h using an oil bath. ^{1}H NMR spectra of the sample were obtained using the external locking method using CDCl$_3$.

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. Elemental analysis was carried out using a Yanako CHN coder MT-3. A mass spectrum was measured using a Finnigan MAT MS spectrometer. UV–vis spectra were taken on a Shimadzu UV-2400 PC. FT-IR measurements were

carried out using a JASCO IR-410. In situ FT-IR measurements were carried out by using a Litho Tech Japan PAGA-100. Thermal decomposition behavior of films was investigated with a Shimadzu TGA 50 thermogravimetric analyzer (TGA) and a DSC 60 differential scanning calorimeter (DSC) under a nitrogen flow. Size exclusion chromatography (SEC) was carried out in tetrahydrofuran on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GM-NHR-$_H$ + GMNHR-$_N$; 8.0 mm i.d. × 30 cm each) and a differential refractometer JASCO RI1530. Number-average molecular weights (M_n) and molecular weight distribution (M_w/M_n) were estimated on the basis of a polystyrene calibration.

Results and Discussion

Synthesis of Polymers. We have prepared photo-cross-linkable polymers having water-soluble properties after thermal decomposition. We used novel monomer MOBH, which contained an epoxy unit as a cross-linking site and tertiary ester linkage as a thermally degradable moiety. A series of sulfonate esters, that is, MSS, CHSS, NPSS, and PhSS, were used as comonomers. TBASS was also employed as a comonomer. Copolymers of MOBH with MSS (P(MOBH-MSS)), MOBH with CHSS (P(MOBH−CHSS)), MOBH with PhSS (P(MOBH−PhSS)), and MOBH with TBASS (P(MOBH−TBASS)) were obtained by photopolymerization at 30 °C to prevent gel formation by conventional thermal polymerization at 60 °C. In the course of polymerization of MOBH at 60 °C using AIBN as an initiator, formation of insoluble fraction was sometimes observed.[7] Acetonitrile was used instead of DMF for the copolymerization of MOBH and TBASS because of the low solubility of P(MOBH-TBASS) in DMF. A copolymer of MOBH with NPSS (P(MOBH−NPSS)) was successfully synthesized by conventional radical polymerization at 50 °C. Polymerization conditions and characteristics of MOBH-containing polymers are summarized in Table 1. P(MOBH−MSS) became insoluble during purification due to low stability of methyl ester of *p*-styrenesulfonic acid. Contents of MOBH moiety were 28−42 mol % in P(MOBH−CHSS), P(MOBH−NPSS), and P(MOBH−PhSS) and 89 mol % in P(MOBH−TBASS). Glass transition temperatures (T_g) of the MOBH-containing polymers having CHSS, NPSS, and PhSS moieties were 107−122 °C, which were close to those of polystyrene and poly(methyl methacrylate). No T_g was observed for P(MOBH−TBASS) within the range of 20−150 °C. Number-average molecular weights of P(MOBH−CHSS), P(MOBH−NPSS), and P(MOBH−PhSS) were 9.1−15 × 10^4. SEC measurement of P(MOBH−TBASS) using a polystyrene-based column was not successful. Onset

Table 1. Polymerization Conditions and Properties of Polymers

polymer	MOBH (mmol)	comonomer (mmol)	solvent (mL)	AIBN (mmol)	polymerization time (h)	yield (%)	$M_n^{\,j}$ × 10^{-4}	$M_w/M_n^{\,j}$	composition^{l,m} (mol %) x	y	$T_g^{\,n}$ (°C)	$T_d^{\,o}$ (°C)
P(MOBH−MSS)^a	0.72	0.72^c	0.15^h	0.019	28	7.8	k	k	k	k	k	185
P(MOBH−CHSS)^a	3.1	3.1^d	1.6^h	0.12	7.5	47	9.1	5.1	42	58	107	140
P(MOBH−NPSS)^b	2.1	2.1^e	1.5^h	0.063	9	33	9.5	5.4	38	62	122	174
P(MOBH−PhSS)^a	2.4	2.4^f	0.60^h	0.082	11	17	15	2.5	28	72	115	206
P(MOBH−TBASS)^a	2.1	0.52^g	0.72^i	0.044	41	18	k	k	89	11	k	214

^{a} Polymerization was carried out at 30 °C with UV irradiation. ^{b} Polymerization was carried out at 50 °C. ^{c} Methyl *p*-styrenesulfonate. ^{d} Cyclohexyl *p*-styrenesulfonate. ^{e} 2,2-Dimethylpropyl *p*-styrenesulfonate. ^{f} Phenyl *p*-styrenesulfonate. ^{g} Tetra-*n*-butylammonium *p*-styrenesulfonate. ^{h} *N,N*-Dimethylformamide. ^{i} Acetonitrile. ^{j} Determined by SEC (THF, polystyrene standards). ^{k} Not measured. ^{l} See Scheme 1. ^{m} Determined by ^{1}H NMR. ^{n} Glass transition temperature determined from DSC. ^{o} Onset temperature of decomposition determined from TGA.
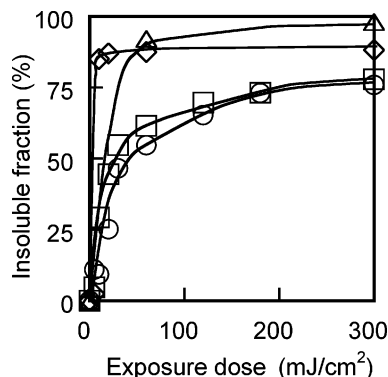
Figure 2. Effect of polymer structure on photoinduced insolubilization of P(MOBH−CHSS) (□), P(MOBH−NPSS) (○), P(MOBH−PhSS) (△), and P(MOBH−TBASS) (◇) films. Additive: 3.6 mol % FITS. Dissolution: tetrahydrofuran for 10 min except for P(MOBH−TBASS) (solvent: acetone).

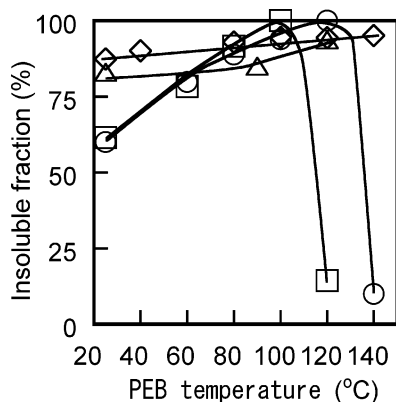**Figure 3.** Effect of PEB temperature on insoluble fraction of the irradiated P(MOBH−CHSS) (□), P(MOBH−NPSS) (○), P(MOBH−PhSS) (△), and P(MOBH−TBASS) (◇) films. Additive: 3.6 mol % FITS. Irradiation dose: 60 mJ/cm². Heating time: 10 min. Dissolution: tetrahydrofuran for 10 min except for P(MOBH−TBASS) (solvent: acetone).

temperatures (T_d) of thermal decomposition of P(MOBH−CHSS), P(MOBH−NPSS), P(MOBH−PhSS), and P(MOBH−TBASS) were 140, 174, 206, and 214 °C, respectively. This finding was consistent with the fact that sulfonate esters of primary alcohols are thermally more stable than those of secondary or tertiary alcohols.

Photo-cross-linking Properties. Polymer films containing a photoacid generator were irradiated at 254 nm and insoluble fraction was studied. FITS as a photoacid generator was photolyzed to generate *p*-toluenesulfonic acid. The photoinduced acid initiated cationic polymerization of epoxy units in the side chain to generate networks. Figure 2 shows the insolubilization properties of the polymers on irradiation at ambient temperature. The insoluble fraction was determined by comparing the thickness of the films before and after dipping into tetrahydrofuran except for the film of P(MOBH−TBASS). Acetone as a solvent was used for the P(MOBH−TBASS) film. The films of MOBH-containing polymers with 3.6 mol % of FITS showed a high efficiency of insolubilization on irradiation. The ring-opening reaction of the epoxy moiety is known to easily occur by strong acids. The reaction mechanism is shown in Scheme 2.

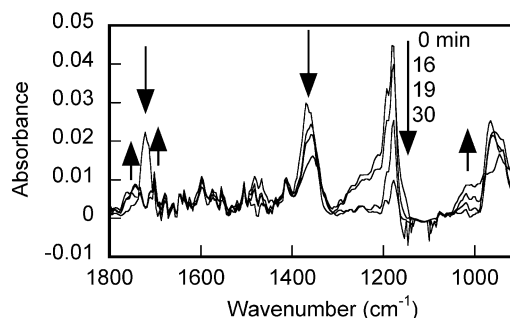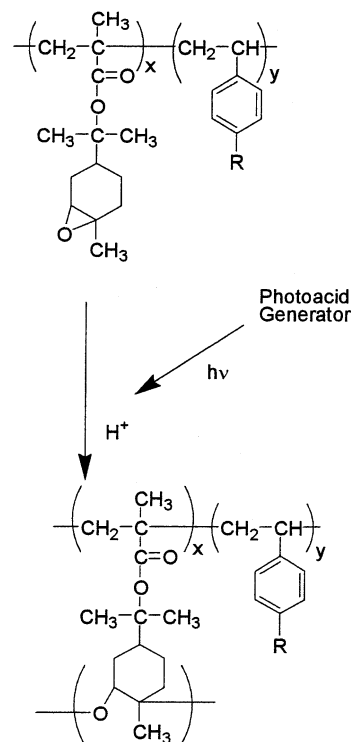The insoluble fraction of the present polymers was enhanced by PEB treatment at temperatures below T_d

Figure 4. In situ FT-IR spectra of the photo-cross-linked P(MOBH−NPSS) film containing 3.6 mol % FITS on baking at 150 °C. Film thickness: 1.0 μm. Irradiation dose: 60 mJ/cm².

Scheme 2

(Figure 3). The insoluble fraction of irradiated P(MOBH−PhSS) and P(MOBH−TBASS) films was increased with the baking temperature below 140 °C. No insolubilization was observed when the unirradiated films were baked under the same conditions. In contrast, the insoluble fraction of irradiated P(MOBH−CHSS) and P(MOBH−NPSS) showed a maximum value at 100 and 120 °C, respectively. The decrease of insoluble fraction on bake treatment at 120 °C for P(MOBH−CHSS) and 140 °C for P(MOBH−NPSS) was a result of thermal decomposition of each cross-linked polymer.

Thermal Degradation. The reaction mechanism of the thermal decomposition of the cross-linked polymers was studied by FT-IR spectroscopy. The spectral changes of the sample film were measured at a constant temperature using an in situ FT-IR system. The heating temperature was selected by referring to T_d of the polymers from TGA analysis. Figure 4 shows the in situ FT-IR spectral changes of irradiated P(MOBH−NPSS) films containing 3.6 mol % FITS when baked at 150 °C. The peak at 1720 cm^{-1} due to ester carbonyl observed for the unirradiated film rapidly disappeared and the
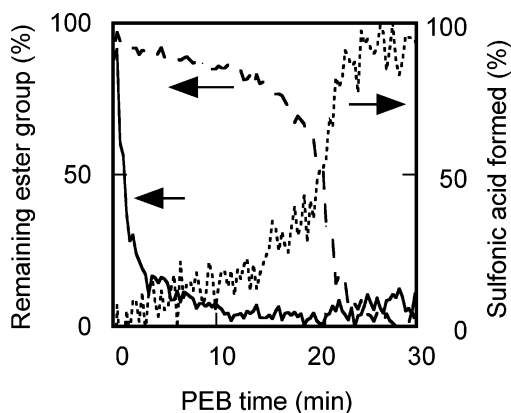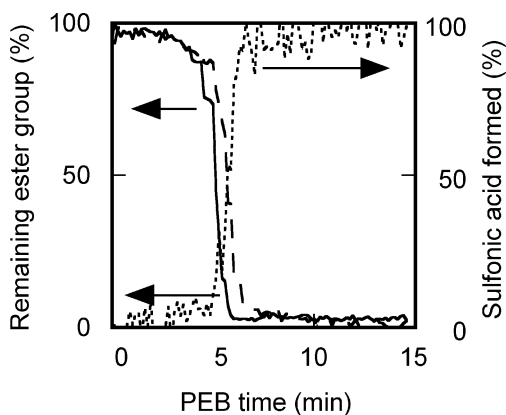
Figure 5. Thermolysis of the photo-cross-linked P(MOBH–NPSS) film containing 3.6 mol % FITS measured by in situ FT-IR spectroscopy. Irradiation dose: 60 mJ/cm². Heating temperature: 150 °C. Film thickness: 1.0 μm. Solid line: carboxylate group (1720 cm^{-1}). Broken line: sulfonate ester group (1178 cm^{-1}). Dotted line: sulfonic acid groups (1018 cm^{-1}).

Figure 6. Thermolysis of the photo-cross-linked P(MOBH–CHSS) film containing 3.6 mol % FITS measured by in situ FT-IR spectroscopy. Irradiation dose: 60 mJ/cm². Heating temperature: 120 °C. Film thickness: 1.0 μm. Solid line: carboxylate group (1720 cm^{-1}). Broken line: sulfonate ester group (1178 cm^{-1}). Dotted line: sulfonic acid groups (1018 cm^{-1}).

peak at 1710 cm^{-1} due to carboxylic acid appeared. The peak of C–O–C stretching (ca. 1150 cm^{-1}) was not measured because the peak overlapped with a strong peak due to Si–O–Si stretching of the silicon wafer used. After the film was heated for 15 min, the peak at 1178 cm^{-1} due to sulfonate ester started to decrease and the peak at 1018 cm^{-1} ascribed to sulfonic acid increased. Disappearance of carboxylate ester and sulfonate ester units, and appearance of sulfonic acid units in the cross-linked P(MOBH–NPSS), was followed using the peaks at 1730, 1140, and 1018 cm^{-1}, respectively (Figure 5). Carboxylate ester units decomposed to generate carboxylic acid within 3 min on heating at 150 °C. The decomposition of 2,2-dimethylpropyl sulfonate units suddenly occurred after heating at 150 °C for 17 min. It is known that sulfonate ester units show self-acceleration properties for the thermal decomposition.[18] Figure 6 shows the thermal decomposition of the cross-linked P(MOBH–CHSS) at 120 °C. In contrast to P(MOBH–NPSS), the decomposition of carboxylate ester units and sulfonate ester units occurred simultaneously at relatively low temperature. The thermolysis
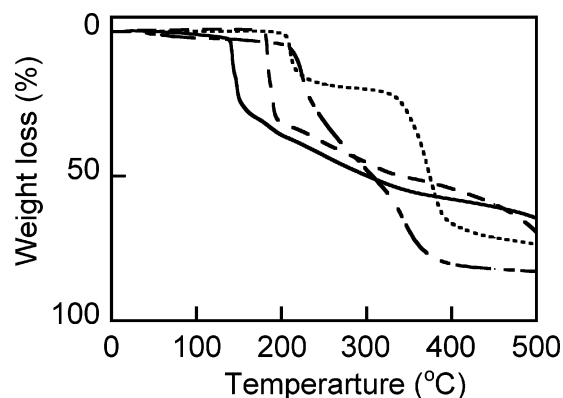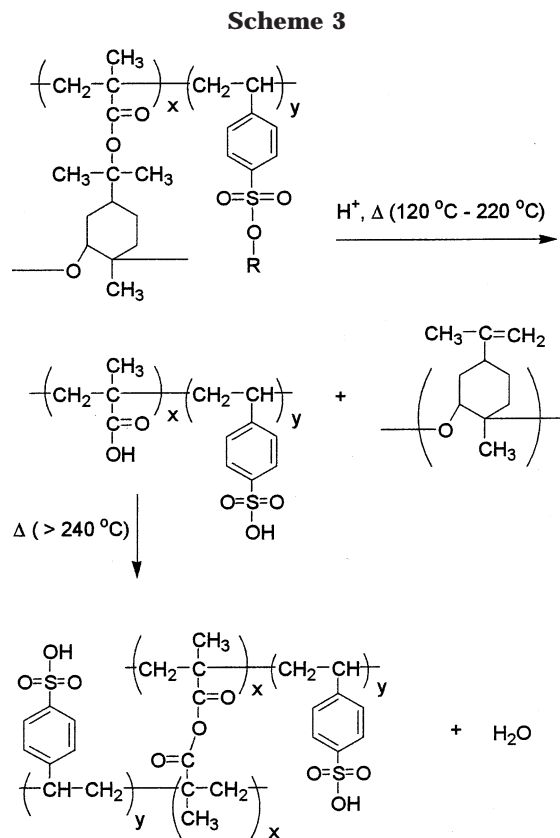

Figure 7. TGA curves of P(MOBH–CHSS) (–), P(MOBH–NPSS) (---), P(MOBH–PhSS) (···), and P(MOBH–TBASS) (-··-). Heating rate: 10 °C/min.

of PhSS and TBASS units was not observed at 160 °C, which was the highest baking temperature of our FT-IR system.

TGA analysis of the polymers gave useful information for the reaction mechanism of thermolysis of the polymers. In the case of P(MOBH–CHSS), the first weight loss was completed at 160 °C and the weight loss was 27%. The value was larger than the expected value for the thermolysis of P(MOBH–CHSS) to poly(MOBH–styrenesulfonic acid) (weight loss: 19%) and was smaller than the value for the transformation of P(MOBH–CHSS) into poly(methacrylic acid-*co*-styrenesulfonic acid) (weight loss: 44%). Thus, the decomposition of MOBH moieties and CHSS moieties occurred simultaneously. This was supported by the result of in situ FT-IR measurement. The disagreement of the weight loss may be due to the generation of nonvolatile materials during the thermolysis. A similar finding was observed for the thermolysis of P(MOBH–NPSS) (Figure 7). The first weight loss was 32%, which was larger than that expected for the formation of poly(MOBH–styrenesulfonic acid) (weight loss: 18%) and was smaller than that for the formation of poly(methacrylic acid–styrenesulfonic acid) (weight loss: 41%). P(MOBH–PhSS) showed 17% weight loss at 205–215 °C. The value corresponded to the weight loss for conversion of P(MOBH–PhSS) to poly(methacrylic acid–PhSS) (weight loss: 17%). Moreover, T_d of P(MOBH–PhSS) (206 °C) was almost the same as that of poly(MOBH) (216 °C).[7] The weight loss of P(MOBH–TBASS) started at 214 °C, which corresponded to the T_d of MOBH moiety in P(MOBH–TBASS) and continued to 360 °C. The total weight loss was 78%. This result suggested that the decomposition of MOBH moiety, TBASS moiety, and main chain scission occurred at 214–360 °C.

It is known that *tert*-butyl esters of carboxylic acids thermally decompose to form carboxylic acids and isobutene. The thermal decomposition temperature is lowered if strong acids are present.[20] TGA curves of P(MOBH–CHSS), P(MOBH–NPSS), P(MOBH–PhSS), and P(MOBH–TBASS) containing 3.6 mol % of *p*-toluenesulfonic acid were measured. Weight loss was observed at about 100 °C for P(MOBH–CHSS), P(MOBH–NPSS), and P(MOBH–PhSS). Acid-containing P(MOBH–TBASS) started to decompose at about

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

Scheme 3

Figure 8. Effect of polymer structure on redissolution properties of the photo-cross-linked P(MOBH−CHSS) (□), P(MOBH−NPSS) (○), P(MOBH−PhSS) (△), and P(MOBH−TBASS) (◇) films containing 3.6 mol % FITS on baking. Dissolution: water for 10 min. Baking time: 10 min. Irradiation dose: 60 mJ/cm^2.

Figure 9. Effect of baking time on redissolution of the photo-cross-linked P(MOBH−CHSS) films containing 3.6 mol % FITS. Baking temperature: (△) 100 °C, (○) 120 °C, and (□) 140 °C. Dissolution: water for 10 min. Irradiation dose: 60 mJ/cm^2.

150 °C. Thermal decomposition of poly(MOBH) started at about 150 °C in the presence of *p*-toluenesulfonic acid, which was ca. 50 °C lower than that for poly(MOBH) without acid.[7] At present, we cannot clearly explain the reason T_d of copolymers is lower than that of poly-(MOBH) in the presence of acid. The acid-catalyzed cleavage of the sulfonate ester units may participate in lowering the T_d values. Details are under investigation. When the COOH-containing polymers which were generated by thermolysis were baked at above 240 °C, dehydration of carboxylic acid units occurred to generate carboxylic anhydride units. This was confirmed by in situ FT-IR measurements. The reaction mechanism is shown in Scheme 3.

Redissolution Properties. Redissolution properties of the cross-linked MOBH-containing polymers in water are shown in Figure 8. The cross-linked P(MOBH−CHSS), P(MOBH−NPSS), and P(MOBH-TBASS) films became soluble in water after baking at 120−220, 160−200, and 200−220 °C, respectively, and they became insoluble again if baked at above 220−260 °C due to the formation of carboxylic acid anhydride units as shown in Scheme 3. No dissolution in water was observed for the cross-linked P(MOBH−PhSS) film after baking at 80−240 °C. Cross-linked P(MOBH−PhSS), however, became soluble in methanol when baked at 140−200 °C for 10 min. Thus, in the case of P(MOBH−PhSS), de-cross-linking reaction of MOBH units occurred but PhSS units were thermally stable. Although, from TGA analysis, the acid-containing P(MOBH−TBASS) was shown to start to decompose at 150 °C, the complete redissolution of P(MOBH−TBASS) was observed when heated at above 200 °C in the presence of acids. This is quite different from the case of P(MOBH−CHSS), P(MOBH−NPSS), and P(MOBH−PhSS). Fur-
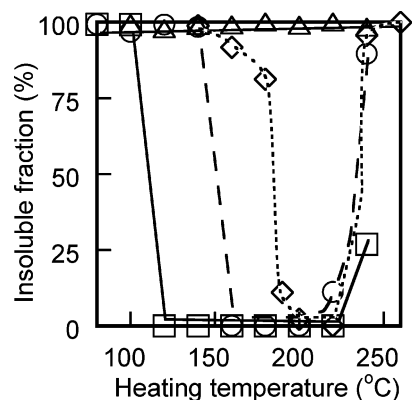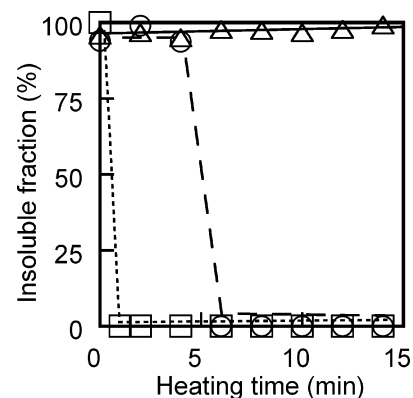
thermore, cross-linked P(MOBH−NPSS) and P(MOBH−PhSS) became soluble in methanol after the baking treatment at 140 °C for 10 min.

Figure 9 shows the relationship between the insoluble fraction of cross-linked P(MOBH−CHSS) and baking time. With the increase of baking temperature, the cross-linked P(MOBH−CHSS) became soluble in water after shorter baking treatment. Similar results were observed for P(MOBH−NPSS) and P(MOBH−TBASS).

The structure of the thermally decomposed polymers was checked by ^{1}H NMR measurements. The ^{1}H NMR spectrum of the cross-linked P(MOBH−CHSS) after baking treatment at 120 °C for 10 min was measured in D$_2$O. The peak at 3.4 ppm due to epoxy proton and 4.6 ppm due to methine proton adjacent to sulfonate esters in P(MOBH−CHSS) measured in CDCl$_3$ disappeared and a broad peak at 0.4−2.2 ppm due to main chain CH$_2$ and CH$_3$ and at 6.2−8.0 ppm due to aromatic protons were observed. This finding suggested the formation of poly(methacrylic acid-*co*-styrenesulfonic acid) by the thermal treatment of the cross-linked P(MOBH−CHSS). Decomposed P(MOBH−TBASS) gave a complicated spectrum. Thermolysis of tetra-*n*-butyl-ammonium *p*-toluenesulfonate (TBATS) was carried out as a model study. Figure 10 shows the ^{1}H NMR spectra of TBATS in diphenyl ether before (bottom) and
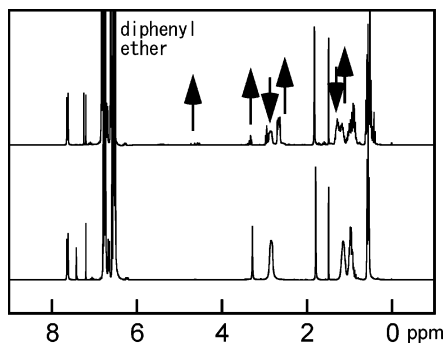
Figure 10. ^{1}H NMR spectra of TBATS (33 wt %) in diphenyl ether before (bottom) and after (top) heating at 220 °C for 5 h.

after (top) heating at 220 °C for 5 h. A decrease in the peak intensities of the methyl proton adjacent to nitrogen and the appearance of olefinic protons at 5.0–6.0 ppm were observed. Thus, Hoffmann-type decomposition of tetra-*n*-butylammonium unit in TBASS moieties was suggested.

When the cross-linked polymer films were baked at 120–200 °C, they became soluble in water and insoluble fractions also became zero. The cross-linked epoxy moieties did not remain in the baked film as insoluble parts. The cross-linked epoxy moieties contain tertiary ether moieties which are thermally decomposed in the presence of acid. Thus, the fragments from the cross-linked epoxy moieties can be vaporized during bake treatment. This was supported by the TGA study reported in a previous paper.[7]

Conclusions

We have designed and synthesized photo-cross-linkable polymers that can be rendered soluble in water. Copolymers of a novel monomer, MOBH, which has an epoxy moiety and a tertiary ester linkage in a molecule, and styrenesulfonates were photo-cross-linkable when irradiated in the presence of a photoacid generator. The photochemically cross-linked polymers became soluble in water if baked at a given temperature. Thermal decomposition of the tertiary ester linkage of the network generated linear polymers. Furthermore, the thermal decomposition of sulfonate ester units enhanced the solubility of the polymers in water. These photosensitive polymers were removable from substrates after use by baking and soaking in water. P(MOBH–NPSS) is the most useful in this application because of a relatively high baking temperature and wide temperature range of the baking treatment for redissolution. Thus, the polymer can be applied to environmentally friendly photo-cross-linkable materials.