Photocrosslinkable Polymers with Redissolution Property

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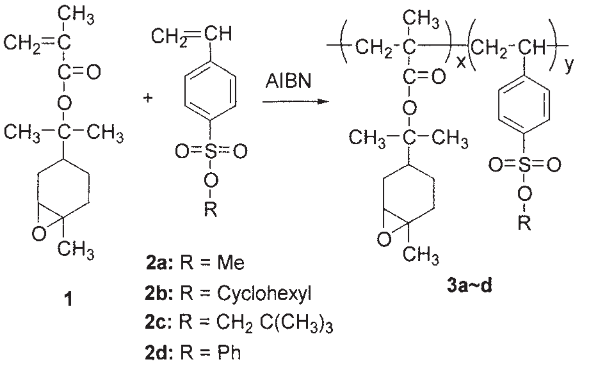
Polymers having both thermally degradable epoxy-containing moieties and sulfonic acid ester moieties in the side chain were prepared and characterized. On UV irradiation the polymer films containing photoacid generators became insoluble. The crosslinked polymer films became soluble in water after bake treatment at 120–200 °C.

Polymers which become insoluble in solvents on UV irradiation are used as photosensitive materials such as photoresists, printing plates, inks, coatings, and photocurable adhesives. Since photochemically crosslinked 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, crosslinked polymers are difficult or impossible to remove thoroughly without damaging underlying materials. Recently, some thermosets which are thermally or chemically degradable under a given condition have been reported.[1–7] These thermosets consist of crosslinkable moieties such as epoxy or radically polymerizable vinyl units and thermally degradable units such as tertiary ester, acetal, disulfide or spiro ortho ester units. In our previous work,[8] photocrosslinkable polymers having thermally degradable properties were synthesized and characterized. The photocrosslinked polymer dissolved in methanol, THF, and aqueous alkaline after thermal treatment. In this paper we report a new category of photocrosslinkable polymers which are thermally degradable. The photochemically crosslinked polymers become soluble in water when heated.

1-Methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl methacrylate (**1**), methyl styrenesulfonate (**2a**), cyclohexyl styrenesulfonate (**2b**),[9] neopentyl styrenesulfonate (**2c**),[10] and phenyl styrenesulfonate (**2d**) were prepared according to the literatures. 9-Fluorenylideneimino p-toluenesulfonate (FITS)[11] was used as a photoacid generator.

Polymers **3a**, **3b**, and **3d** were prepared by the photopolymerization using 2,2′-azobisisobutyronitrile (AIBN) in DMF at 30 °C to prevent gelation during polymerization. Irradiation ($\lambda > 390$ nm) was carried out using a medium-pressure mercury lamp (Toshiba SHL-100UV). The polymer **3c** was obtained by the conventional polymerization using AIBN in DMF at 55 °C. The resulting polymers were purified by reprecipitation from chloroform/methanol or THF/hexane. The fraction of **1** incorporated into the polymers was determined from ^{1}H NMR spectra. Polymerization conditions and polymer properties are summarized in Table 1. Polymers **3b–d** were colorless with high molecular weights. Polymer **3a** became insoluble during purification.

Table 1. Polymerization conditions and polymer properties[a]

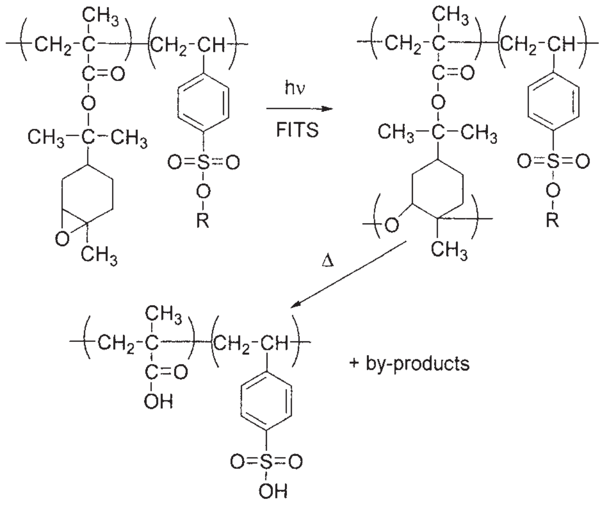


	Monomer in feed/mmol					Polym.	Yield	Mn[b]	Fraction/%	
Polymer	**1**	**2a**	**2b**	**2c**	**2d**	time/h	/%	$\times 10^{-4}$	x	y
3a	0.72	0.72				28	7.8[c]	-[d]	-[d]	-[d]
3b	3.1		3.1			7.5	47	9.1	42	58
3c	2.1			2.1		9	33	9.5	38	62
3d	2.4				2.4	11	17	15	28	72

[a] [Total monomer] = 4~8 M, [AIBN] = 1.5~1.7 mol% to total monomers.
[b] Number average molecular weight from GPC measurements.
[c] Crude yield. [d] Not measured.

Polymer films (ca. 0.5 μm) containing FITS were irradiated at 254 nm and insoluble fraction in THF was studied. FITS was photolyzed to generate *p*-toluenesulfonic acid. The photoinduced acid initiated the cationic polymerization of epoxy units in the side chain to form networks (Scheme 1). The **3b–d** films containing 3.6 mol% FITS became insoluble in THF after irradiation and the insoluble fraction increased by subsequent heating at relatively low temperatures (60–100 °C). Baking was carried out on hot plate in air. No insolubilization was observed when the unirradiated films were baked under the same conditions.

It is known that *tert*-butyl esters of carboxylic acids thermally decompose to form carboxylic acids and isobutene.[12] The thermal decomposition temperature is lowered if strong acids are present. It was reported that the **1** units incorporated in polymers were thermally decomposed to generate carboxylic acid units.[8] Figure 1 shows effect of baking temperature on the dissolution properties of the irradiated (60 mJ/cm^2) **3b–d** films containing 3.6 mol% FITS. When baked below 100 °C, the **3b–d** films were insoluble in water. The crosslinked **3b** and **3c** films became soluble in water after baking at 120–220 and 160–200 °C, respectively, and they were recrosslinked by baking at above 220–240 °C due to the formation of acid anhydride. No dissolution was observed for the crosslinked **3d** film after baking at 80–240 °C.



Scheme 1. Photocrosslinking and thermal decrosslinking of **3b** and **3c**.

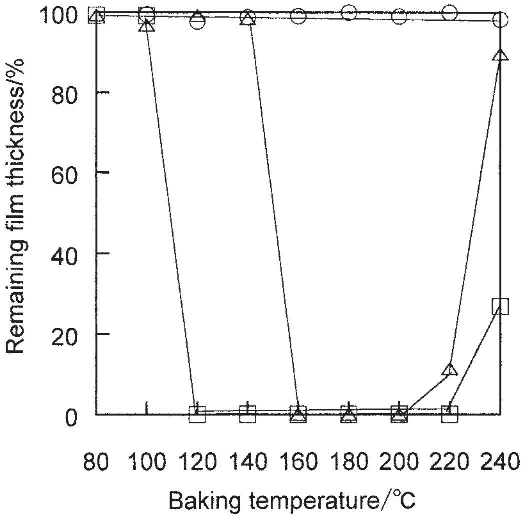


Figure 1. Dissolution properties of the crosslinked **3b** (□), **3c** (△) and **3d** (○) films after baking for 10 min.

The thermal degradation of **1** and **2b–d** units in the polymers was studied by in-situ FT-IR spectroscopy using Litho Tech PAGA-100. The spectral changes of the sample film were measured at constant temperature. When the crosslinked **3b** film was baked at 120 °C, the peaks at 1720 (carboxylic acid ester) and 1178 cm^{-1} (sulfonic acid ester) decreased and the peak at 1018 cm^{-1} (sulfonic acid) increased. The carboxylic acid ester moiety due to **1** and sulfonic acid ester unit due to **2b** decreased simultaneously. The increase of the peak at 1018 cm^{-1} corresponded to the decrease of the peak at 1178 cm^{-1}. When the crosslinked **3c** film was baked at 150 °C, the peak at 1720 cm^{-1} (carboxylic acid ester) decreased and then followed by the decrease of the paek at 1178 cm^{-1} (sulfonic acid ester). The increase of the peak at 1018 cm^{-1} (sulfonic acid) corresponded to the decrease of the peak at 1178 cm^{-1} as shown in Figure 2. The thermally generated sulfonic acid units may catalyze the polymerization of epoxy units and the thermolysis of carboxylic acid ester units. No thermolysis of **2d** units in the crosslinked **3d** was observed when baked at 240 °C. Thus, the generation of carboxylic acid units and sulfonic acid units was necessary to dissolve the crosslinked films into water. It was confirmed that the reinsolubilization of **3b** and **3c** after baking at higher temperatures was due to the formation of acid anhydride moieties. It was confirmed by FT-IR measurements.[8]

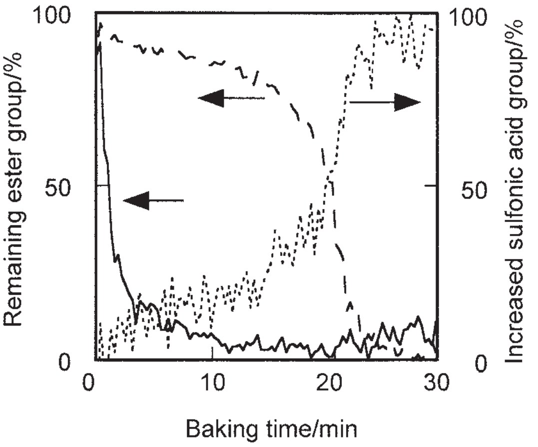


Figure 2. Thermolysis of the crosslinked **3c** film measured by in situ FT-IR spectroscopy. Exposure dose: 60 mJ/cm^2. Baking temperature: 150 °C. Solid line: carboxylate group (1720 cm^{-1}). Broken line: sulfonate ester group (1178 cm^{-1}). Dotted line: sulfonic acid group (1018 cm^{-1}).

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