

# Novel thermally degradable diepoxy crosslinkers containing sulfonate ester groups for photo-crosslinking

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Received 3 March 2004; received in revised form 13 April 2004; accepted 13 April 2004

## Abstract

New diepoxy crosslinkers (Cr-1, Cr-2 and Cr-3) containing thermally degradable sulfonate ester linkages were synthesized and characterized. From FT-IR and UV spectroscopic experiments, it was confirmed that Cr-1 and Cr-2 photochemically generated sulfonic acid, while Cr-3 was photochemically stable. Cr-1 and Cr-2 initiated photo-crosslinking reaction with poly(vinylphenol) (PVP), a copolymer of methacrylic acid and ethyl methacrylate (P(MAA-EMA)), and poly(7-oxabicyclo[4.1.0]hept-3-yl)methyl *p*-styrenesulfonate) (POHMSS). After irradiation at 254 nm, the Cr-1 or Cr-2/polymer blended film became insoluble and the degree of insolubilisation increased with baking at 100–140 °C. Solubilisation due to decrosslinking was observed by baking at higher temperatures (150–200 °C). The crosslinker/POHMSS system showed high efficiency in photo-thermal crosslinking and thermal decrosslinking at high temperatures.

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**Keywords:** Photo-crosslinking; Thermal degradation; Sulfonate ester; Epoxide

## 1. Introduction

Photo-crosslinkable polymer systems are now used as photosensitive materials such as photo-resists, inks, and photo-curable adhesives. However, the complete removal of these networks from substrates is difficult or impossible without damaging underlying materials. Recently, we reported photo-crosslinkable polymer systems with thermally degradable tertiary ester or sulfonate ester linkages, and decrosslinking was successfully performed by thermal treatments at 90–180 °C [1–3]. In those systems, however, there are some limitations concerning synthesis. Thus, blended systems of a base polymer and a crosslinker having thermal degradation properties are expected to be better for the thermally degradable photo-crosslinking system. Thermally degradable thermosets using some crosslinkers having tertiary ester, carbamate,

acetal, bicyclo ortho ester, or carboxylate units have been reported [4–11].

In this study, three kinds of new crosslinkers (Cr-1, Cr-2, and Cr-3) having two epoxy groups and two thermally degradable sulfonate ester groups in a molecule were synthesized (Scheme 1). The photo-crosslinking and thermal decrosslinking reactions of the blend of these crosslinkers and base polymers such as poly(vinylphenol) (PVP), a copolymer of methacrylic acid and ethyl methacrylate (P(MAA-EMA)), and poly(7-oxabicyclo[4.1.0]hept-3-yl)methyl *p*-styrenesulfonate) (POHMSS) (Scheme 1) were investigated. This class of photopolymers is significant in the field of adhesives and coating materials which are needed to be removed after use.

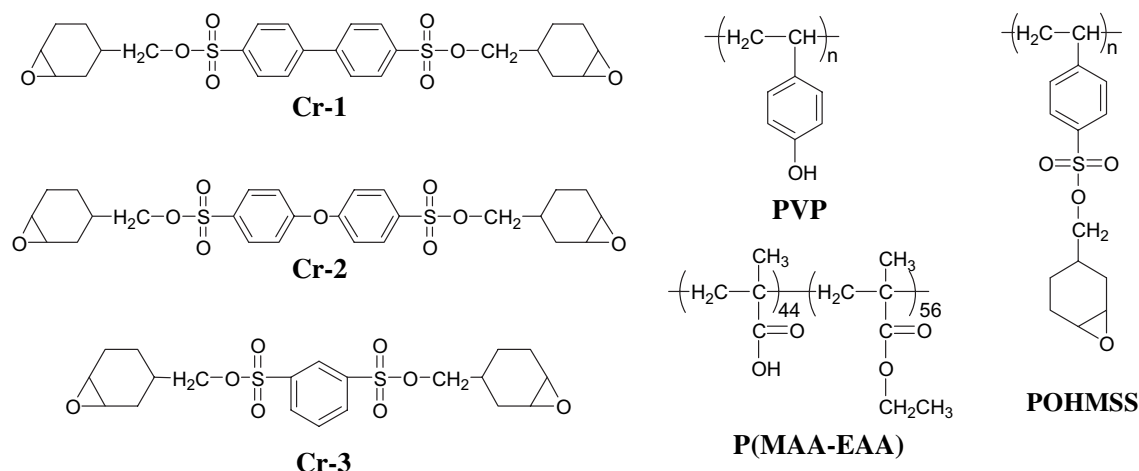
## 2. Experimental

### 2.1. Materials

*N,N*-dimethylformamide (DMF) and pyridine were distilled over CaH<sub>2</sub> before use. Tetrahydrofuran (THF)

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Scheme 1.

was purchased from Wako Pure Chemical and distilled over sodium before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallisation from ethanol. 3-Cyclohexene-1-methanol, 1-dodecanethiol, and OXONE (potassium peroxy monosulfate, for epoxidation) were purchased from Aldrich. 4,4'-Biphenyl disulfonyl chloride and 1,3-benzenedisulfonyl chloride were purchased from Tokyo Kasei Kogyo. Diphenyl ether and chlorosulfonic acid were purchased from Wako Pure Chemical. 1,1-Oxybis(benzene)-4,4'-disulfonyl chloride was prepared by the reaction of chlorosulfonic acid with diphenyl ether as described elsewhere [12]. *p*-Styrenesulfonyl chloride was prepared by the reaction of thionyl chloride with sodium *p*-styrenesulfonate as described elsewhere [13]. PVP ( $M_n = 8000$ ) was purchased from Aldrich.

## 2.2. Synthesis of crosslinkers

Cr-1, Cr-2, and Cr-3 were prepared from the epoxidation of precursors which were synthesized from the reactions between 3-cyclohexene-1-methanol and disulfonyl chlorides such as 4,4'-biphenyldisulfonyl chloride, 1,1-oxybis(benzene)-4,4'-disulfonyl chloride, and 1,3-benzenedisulfonyl chloride, respectively.

Cr-1: m.p. 157–159 °C,  $T_d$  183 °C,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz),  $\delta$  0.93–1.00 (m, 2H, CH), 1.12–1.53 (m, 4H,  $\text{CH}_2$ ), 1.62–2.09 (m, 8H,  $\text{CH}_2$ ), 3.03–3.11 (m, 4H, CH–O–CH), 3.77–3.89 (octa, 4H,  $\text{CH}_2$ –O), 7.69–7.72 (d, 4H, Ar–H), 7.92–7.95 ppm (d, 4H, Ar–H); FT-IR (KBr) 786.0 (epoxy), 957.0 (S–O–C), 1176.7, 1185.0 ( $\text{SO}_2$ ,  $\nu_s$ ), 1356.0 ( $\text{SO}_2$ ,  $\nu_{as}$ ), 1596.0  $\text{cm}^{-1}$  (Ar). Anal. calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_8\text{S}_2$ : C 58.41, H 5.66, Found. C 58.19, H 5.75.

Cr-2: m.p. 46–47 °C,  $T_d$  162 °C,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz),  $\delta$  0.85–1.18 (m, 2H, CH), 1.30–1.50 (m, 4H,  $\text{CH}_2$ ), 1.63–2.13 (m, 8H,  $\text{CH}_2$ ), 3.07–3.15 (m, 4H, CH–O–CH), 3.77–3.87 (octa, 4H,  $\text{CH}_2$ –O), 7.16–7.19

(d, 4H, Ar–H), 7.91–7.94 ppm (d, 4H, Ar–H); FT-IR (KBr) 786.0 (epoxy), 957.0 (S–O–C), 1166.7, 1187.0 ( $\text{SO}_2$ ,  $\nu_s$ ), 1249.0 (Ar–O–Ar), 1361.0 ( $\text{SO}_2$ ,  $\nu_{as}$ ), 1486.0 (Ar–O–Ar), 1583.0  $\text{cm}^{-1}$  (Ar). Anal. calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_9\text{S}_2$ : C 56.71, H 5.49, Found. C 57.17, H 5.48.

Cr-3: colourless viscous liquid,  $T_d$  157 °C,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz),  $\delta$  0.89–1.09 (m, 2H, CH), 1.35–2.18 (m, 12H,  $\text{CH}_2$ ), 3.02–3.18 (m, 4H, epoxy), 3.81–3.97 (d, 4H,  $\text{CH}_2$ –O–S), 7.71–8.43 ppm (4H, Ar–H); FT-IR (KBr) 808.3 (epoxy), 954.4 (S–O–C), 1174.0, 1199.0 ( $\text{SO}_2$ ,  $\nu_s$ ), 1174.0 (CH–O–CH), 1373.0  $\text{cm}^{-1}$  ( $\text{SO}_2$ ,  $\nu_{as}$ ).

## 2.3. Synthesis of (7-oxabicyclo[4.1.0]hept-3-yl) methyl *p*-styrenesulfonate (OHMSS)

OHMSS was prepared from the epoxidation of the precursor which was synthesized from the reactions between 3-cyclohexene-1-methanol and *p*-styrenesulfonyl chloride in pyridine. (49% yield).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  7.75 (d, 2H, phenyl), 7.46 (d, 2H, phenyl), 6.75 (dd, 1H,  $\text{CH}_2=\text{CH}-$ ), 5.81 (s, 1H,  $\text{CH}_2=\text{CH}-$ ), 5.35 (s, 1H,  $\text{CH}_2=\text{CH}-$ ), 3.67 (m, 2H, –O– $\text{CH}_2$ –), 3.02 (m, 2H, epoxy HCOC), 0.80–2.22 ppm (m, 7H, CH,  $\text{CH}_2$ ). Anal. calcd for  $\text{C}_{15}\text{H}_{18}\text{O}_4\text{S}$ : C 61.20, H 6.16, Found. C 60.99, H 6.19.

## 2.4. Polymerisation

Poly(methyl methacrylate) (PMMA) ( $M_n = 80000$ ) and P(MAA-EMA) ( $M_n = 43000$ ,  $M_w/M_n = 1.55$ ) were synthesized by the radical polymerisation of corresponding monomers using AIBN in DMF at 55 °C. POHMSS ( $M_n = 2700$ ,  $M_w/M_n = 1.77$ ) was prepared by conventional radical polymerisation in degassed THF or chloroform solution at 50 °C using AIBN as an initiator and 1-dodecanethiol as a chain transfer reagent. The resulting polymers were purified by reprecipitation from chloroform/hexane.

## 2.5. Measurements

$^1\text{H}$  NMR spectra were observed at 270 MHz with a JEOL GX-270 spectrometer. FT-IR measurements were carried out with a JASCO IR-410. The thermal decomposition behaviour was investigated with a Shimadzu TGA-50 thermogravimetric analyser under a flow of  $\text{N}_2$ . The thickness of films was measured by interferometry (Nanometrics Nanospec M3000). Elemental analysis was carried out using a Yanako CHN coder MT-3. Size exclusion chromatography (SEC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex  $\text{GMN}_{\text{HR-H}} + \text{GMN}_{\text{HR-N}}$ ; 8.0 mm id.  $\times$  30 cm each) and a differential refractometer JASCO RI1530. Number-average molecular weight ( $M_n$ ) and molecular weight distribution (MWD) were estimated on the basis of a polystyrene calibration.

All sample films were prepared on silicon wafers by spin casting from solution of cyclohexanone containing polymer and crosslinker. 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. The insoluble fraction was determined by a comparison of the film thickness before and after dipping sample films in methanol or THF.

## 3. Results and discussion

### 3.1. Photolysis and thermolysis of crosslinkers

The photolysis behaviours of Cr-1 and Cr-2 in PVP film were studied by FT-IR measurements as shown in Fig. 1. On irradiation at 254 nm, two peaks around  $1000\text{ cm}^{-1}$  corresponding to sulfonic acid appeared, while the peaks around 786 and  $957\text{ cm}^{-1}$  corresponding

to epoxy group and the sulfonate ester linkages, respectively, decreased. The change of a broad peak at  $3400\text{ cm}^{-1}$  was also observed. In the case of Cr-3 in PVP film, no change was observed in the FT-IR spectra. Thus, this result indicates that Cr-1 and Cr-2 generate sulfonic acid by photolysis, while Cr-3 is photochemically stable. The change of the UV spectrum of Cr-1 and Cr-2 in PMMA films was observed on UV irradiation at 254 nm. The absorption intensity at the maximum wavelength, 266 (Cr-1) and 250 (Cr-2) nm, gradually decreased with increasing exposure dose. The quantum yields for the photolysis of the Cr-1 and Cr-2 in PMMA films were 0.003 and 0.012, respectively.

Generally, the sulfonate ester linkage was thermally dissociable. Lee and co-workers reported that cyclohexyl *p*-toluenesulfonate was thermally degraded and produced sulfonic acid in the solid state [14]. The sulfonic acid produced could be used as a thermal initiator for cationic polymerisation. We also reported thermal degradation of a variety of crosslinked polymers containing sulfonate ester linkages in the side chains [1,3,13]. In this system, the crosslinked polymers became soluble in alkaline solution due to thermal dissociation of sulfonate ester linkages if baked at 120–200 °C. From the TGA measurements of the crosslinkers, the degradation temperatures ( $T_d$ ) of Cr-1 and Cr-2 were found to be 183 and 162 °C, respectively. Thus, the present crosslinkers can be used as a new photo-crosslinking and thermal decrosslinking system as shown in Scheme 2.

### 3.2. Crosslinker/PVP system

It was reported that a blended system of diepoxy compounds, PVP, and photoacid generator was photo-crosslinkable [6]. The photo-crosslinking experiments of blended system based on the present crosslinkers and

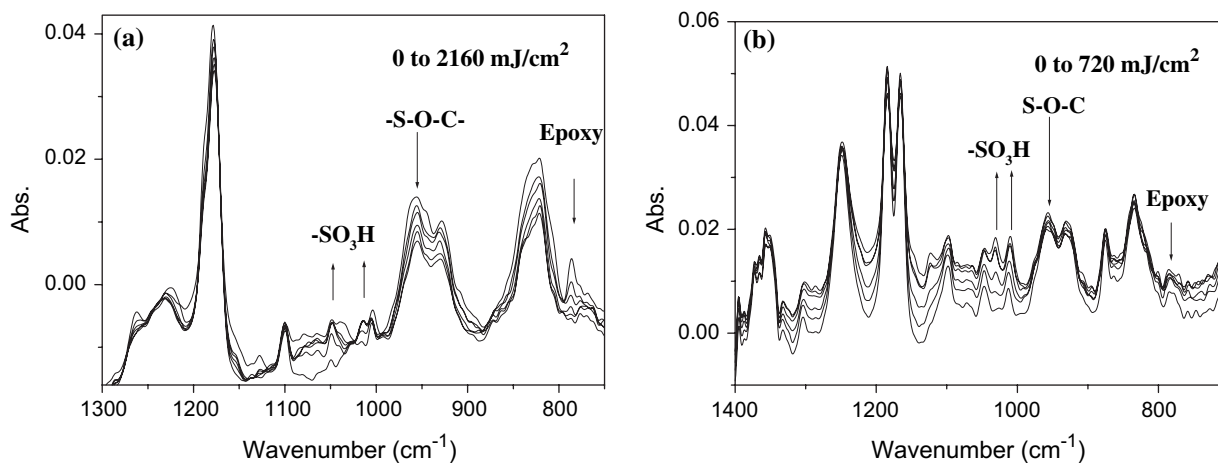
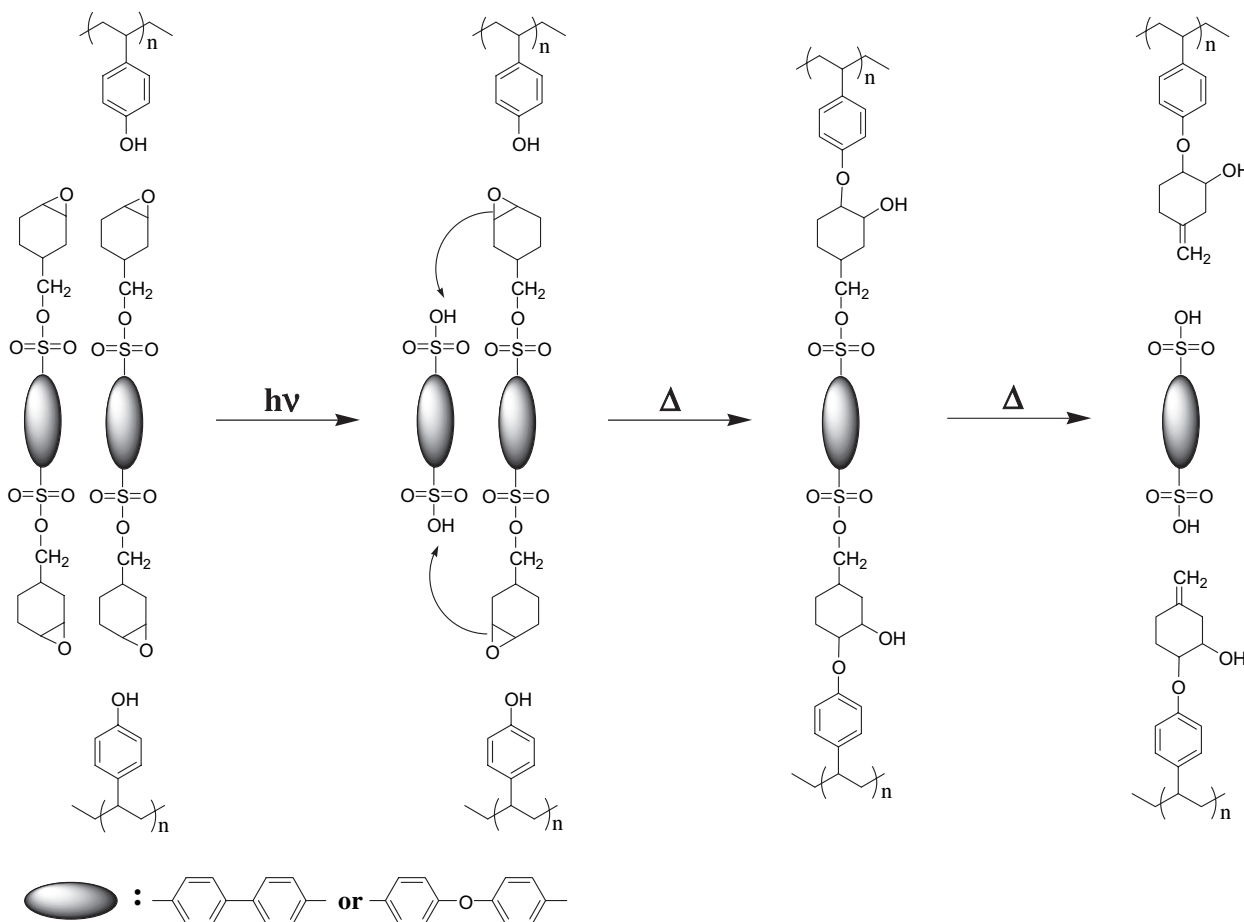


Fig. 1. FT-IR spectral changes of (a) Cr-1/PVP and (b) Cr-2/PVP films on irradiation at 254 nm. Film thickness: 370 nm. Crosslinker/PVP ratio was 1:1 (mol/mol).



Scheme 2.

PVP were performed at room temperature. In this system, no photoacid generators are necessary because the crosslinker itself is a photoacid generator. On irradiation at 254 nm, Cr-1/PVP and Cr-2/PVP systems showed photo-crosslinking behaviour, while Cr-3/PVP system did not. The Cr-2/PVP system was more efficient than Cr-1/PVP system. Although the quantum yields for the photolysis of Cr-1 and Cr-2 were pretty low, effective photo-crosslinking was observed for the Cr-1/PVP and Cr-2/PVP systems. This is because the photo-induced acid worked as a catalyst for the crosslinking reaction of epoxy units in the crosslinker and OH units in PVP.

Fig. 2 shows the effect of baking temperature on the insolubilisation properties of the irradiated PVP films containing Cr-1 or Cr-2. For the films with Cr-1 or Cr-2, the insoluble fraction, which ranged from 20 to 40% at room temperature on irradiation, began to increase over 100 °C, and reached at maximum values around 140 °C. Above 140 °C, the insoluble fraction decreased because the soluble parts of the polymer films increased with temperature at 180–200 °C. However, complete dissolution behaviour was not observed at higher temperatures (200–250 °C). This was due to the formation of new linkage from the reaction between

OH groups remaining in PVP and sulfonic acids generated by the thermolysis of the crosslinkers. The new crosslinking reaction at high temperature range was also affected by the content of Cr-1 or Cr-2.

### 3.3. Crosslinker/P(MAA-EAA) system

A blended system of diepoxy compounds and a polymer bearing COOH groups in the side chain is known as a crosslinking system, if used in the presence of an acid [15,16]. On irradiation at 254 nm, photo-crosslinking was not observed at room temperature in the crosslinker/P(MAA-EMA) system. The Cr-1/P(MAA-EMA) and Cr-2/P(MAA-EMA) blended films began to crosslink at 120 and 100 °C, respectively. The insoluble fraction of both films reached a maximum at around 140 °C, and decreased above 140 °C.

### 3.4. Crosslinker/POHMSS system

Unlike PVP or P(MAA-EAA), POHMSS which contains sulfonate ester linkages connected with epoxy groups in the side chain can generate sulfonic acid by thermal degradation. Fig. 3 shows the photo-thermal

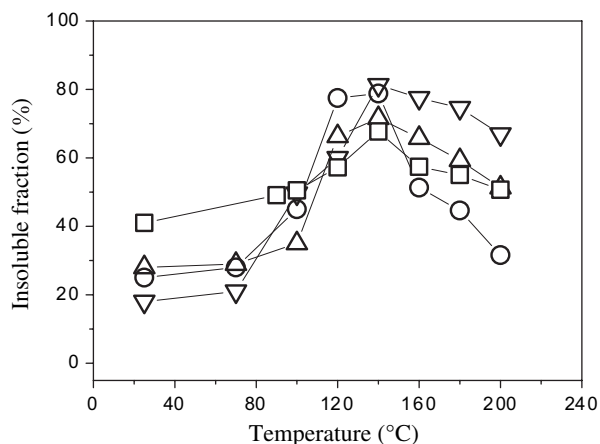


Fig. 2. Insolubilisation and redissolution behaviour of crosslinker/PVP systems. Cr-1 contents (mol%),  $\Delta$ : 10,  $\nabla$ : 25,  $\circ$ : 50; Cr-2 content (mol%),  $\square$ : 50. Irradiation dose:  $180 \text{ mJ/cm}^2$ . Baking time: 5 min. Film thickness was 200–500 nm. Development was performed in methanol for 10 min.

crosslinking and thermal decrosslinking behaviour of the crosslinker/POHMSS film. In the cases of irradiated films containing Cr-2, the crosslinking reaction occurred at room temperature and was enhanced by heating, reaching at maximum around 130–140 °C. In this system the crosslinking occurs by the acid-catalysed polymerisation of epoxy units in POHMSS and crosslinker. The acid was generated by the photolysis of Cr-2 or Cr-1. No photolysis was observed for the sulfonate ester units in POHMSS. The degradation of sulfonate ester linkage occurred at 140 °C and complete dissolution was observed above 160 °C. The Cr-1/POHMSS system showed a similar behaviour to that of Cr-2/POHMSS system.

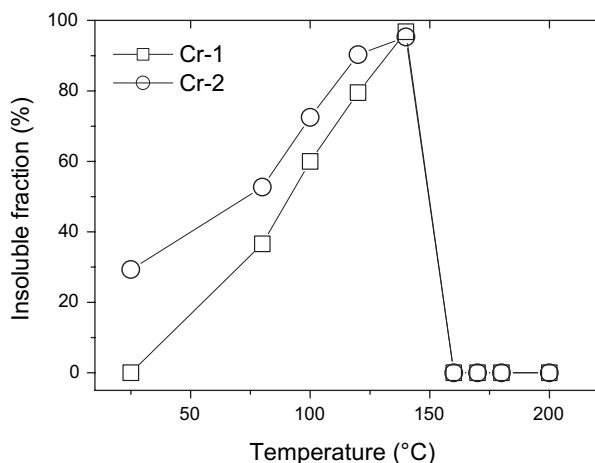


Fig. 3. Photo-induced crosslinking and thermal decrosslinking behaviour of Cr-1/POHMSS and Cr-2/POHMSS films. Crosslinker/POHMSS ratio was 1:1 (mol/mol). Film thickness: 100 nm. Irradiation dose:  $180 \text{ mJ/cm}^2$ . Baking time: 5 min. Development of films was performed in THF and followed in methanol for 10 min.

#### 4. Conclusions

We found that Cr-1 and Cr-2 photochemically generated sulfonic acids. They could be used in photocrosslinking systems without photoacid generator, and the crosslinked system was thermally degradable. Thus, the present system could be used as photoinduced crosslinkable and thermally decrosslinkable system. The crosslinker/POHMSS blended system showed high photo-thermal crosslinking and thermal decrosslinking properties.

#### Acknowledgements

This work was supported by the 21st Century COE Program 24403 E-1 from the Ministry of Education, Culture, Sports, Science and Technology. A part of this work was supported by a Grant-in-Aid for Scientific Research (B),(2) No.13450382 from the Japan Society for the Promotion of Science.

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