



Photo-cross-linking and de-cross-linking of modified polystyrenes having degradable linkages

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ABSTRACT

Modified polystyrenes having both epoxy moieties and tertiary ester linkages, tertiary ether linkages, or carbonate linkages were synthesized. The polymer films containing a photoacid generator were photo-cross-linkable. The cross-linked polymer films became soluble in tetrahydrofuran after thermolysis. Photo-cross-linking and thermal decomposition behaviors of the polymers were investigated and discussed in terms of the chemical structures of degradable units. The thermal stability of the polymers was found to be in the order: tertiary ester > tertiary ether > tertiary carbonate.

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1. Introduction

Epoxy resins are widely used to increase the toughness of adhesives, inks, coatings, and matrix materials for fiber-reinforced composites because they form insoluble and infusible networks through cross-linking processes. The network structure generates the chemical toughness and mechanical strength of the cured resins. However, the stability can be significantly disadvantageous when the network is needed to be removed since mechanical scratching or strong acid treatment methods must be applied. Thus, removing the cross-linked resins is difficult or impossible without damaging underlying materials.

Recently, much attention has been paid to develop epoxy resins which are thermally or chemically degradable under a given condition [1]. These resins were multifunctional epoxides connected with degradable units in the molecule. As degradable units, disulfide [2,3], acetal [4], primary [5–8], secondary [5,9] or tertiary [5,9–13] ester of carboxylic acid, carbamate [14], carbonate [15,16], and sulfonate [17–19] were studied. In the previous paper, we have reported the polymers having both epoxy moieties and thermally cleavable tertiary ester moieties in the side chain [10]. On UV irradiation, the polymer films containing photoacid generators became insoluble in organic solvents, and the cross-linked films became soluble in methanol when baked at 160–180 °C. However, no systematic work has been done to clarify the

relationship between chemical structures of degradable units of the resins and decomposition or dissolution properties of the decomposed ones. For practical use, it is important to optimize the structures of de-cross-linking units.

In this paper, we report the synthesis of a series of modified polystyrene having epoxy units and various types of thermally degradable linkages. As thermally degradable units, tertiary ester, tertiary ether, and tertiary carbonate were chosen. We have reported the synthesis of *p*-styrenesulfonate-based monomers 7-oxabicyclo[4.1.0]hept-3-yl)methyl *p*-styrenesulfonate and 2-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)propyl *p*-styrenesulfonate [17]. Moreover, poly(*p*-*tert*-butoxystyrene) (PTBOS) [20] having tertiary ether units and poly(*p*-*tert*-butoxycarbonyloxystyrene) (PBOCS) [21] bearing tertiary carbonate units were reported to be precursors of poly(4-hydroxystyrene) by acidolysis. Thus, 1-ethenyl-4-[1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethoxy]benzene (MMOES) and 1-ethenyl-4-[1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethoxycarbonyloxy]benzene (MMOCS) were newly synthesized as monomers. MMOCS was synthesized using 4-ethenylphenyl 2-(3-methylcyclohex-3-enyl)-2-propyl carbonate [15] as a starting material. In addition, we newly synthesized 4-ethenylbenzoic acid 1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl ester (MMOVBA) via the reaction of 4-ethenylbenzoyl chloride and the alkoxide of α -terpineol. Regio-selective epoxidation of the alkene of the precursor monomers proceeded to give monomers MMOES, MMOCS, and MMOVBA.

The concept of the present system is shown in Fig. 1. On irradiation, network formation occurs by the photoinduced-acid

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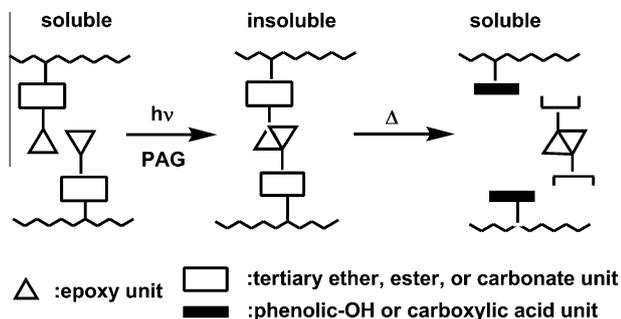


Fig. 1. Concept of photo-cross-linking and de-cross-linking of the polymers used in this work.

catalyzed reaction of the epoxy moieties of the polymer. Thermal treatment of the cross-linked polymers induces the cleavage of the thermally degradable linkages. The cross-linking and de-cross-linking properties were discussed in terms of the structure of the degradable units chosen. The reaction mechanism was studied by TGA analysis and FT-IR spectroscopy. This system is of importance as photo-cross-linkable materials which can be removed from substrates after use. Moreover, this system is essentially applicable to the fabrication of functional materials such as KrF photolithography for double exposure technologies [22,23], since poly(4-vinylphenol) (PVP), a useful polymer for KrF resist, is formed by thermal treatment.

2. Experimental

2.1. Materials

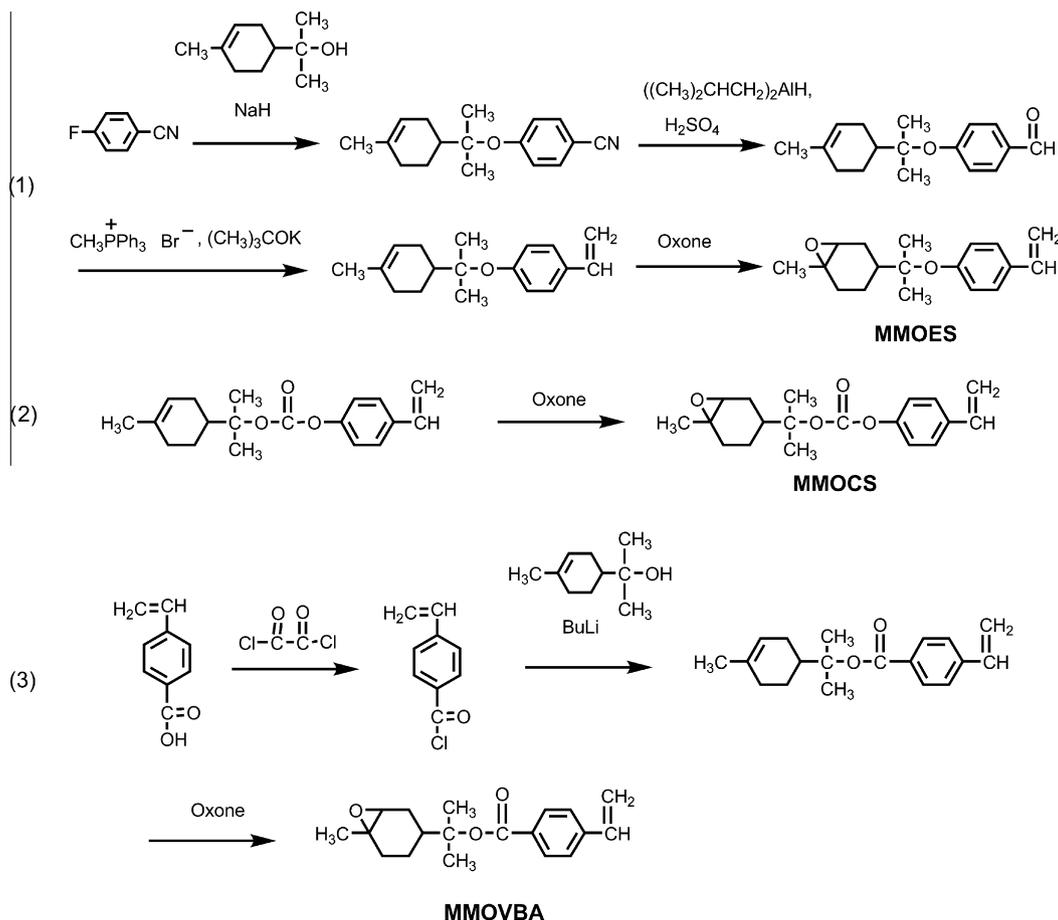
Tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and toluene were distilled over CaH_2 before use. 2,2'-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. 9-Fluorenylideneimino *p*-toluenesulfonate (FITS) [24] and 4-ethenylphenyl 2-(3-methylcyclohex-3-enyl)-2-propyl carbonate [15] were prepared according to the method described elsewhere. Poly(4-vinylphenol) (PVP) ($M_n = 8000$, $M_w/M_n = 1.1$), OXONE, monopersulfate compound ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), 4-vinylbenzoic acid, and *p*-*tert*-butoxycarbonyloxystyrene (BOCS) were purchased from Sigma–Aldrich and used without further purification. Other solvents and reagents including *p*-*tert*-butoxystyrene (TBOS) were purchased from Wako Chemicals and used as received.

2.2. Synthesis of monomers

Monomers were synthesized according to the route shown in Scheme 1.

2.2.1. 1-Cyano-4-[1-methyl-1-(4-methylcyclohex-3-enyl)ethoxy]benzene

Introduction of a tertiary ether group was carried out according to the method reported. [25]. Into a four-necked round-bottom flask fitted with an efficient magnetic stirrer, a Claisen adapter, and two addition funnels were placed sodium hydride (60%, dis-



Scheme 1. Synthesis of monomers.

persed in mineral oil) (7.14 g, 119 mmol), α -terpineol (15.3 g, 82.6 mmol), catalytic amount of 15-crown-5, and THF (200 mL) under nitrogen atmosphere. A THF solution (200 mL) of 4-fluorobenzonitrile (10.0 g, 82.6 mmol) was added to the solution and heated at 60 °C for 20 h. A 200 mL aliquot of toluene was added to the solution and then 100 mL of water was added to quench remaining sodium hydride. The organic phase was separated and washed with water five times. The organic layer was dried over anhydrous MgSO_4 . The product was purified by column chromatography (silica gel, chloroform); yellow liquid; yield 3.65 g (17%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.48 (d, 2H, phenyl), 6.94 (d, 2H, phenyl), 5.32 (s, 1H, C = CH-), 2.14–1.20 (m, 16H, CH, CH_2 , CH_3).

2.2.2. 1-Formyl-4-[1-methyl-1-(4-methylcyclohex-3-enyl)ethoxy]benzene

Into a four-necked round-bottom flask fitted with an efficient magnetic stirrer and two addition funnels were placed 1-cyano-4-[1-methyl-1-(4-methylcyclohex-3-enyl)ethoxy]benzene (7.87 g, 30.8 mmol) and toluene (32 mL) under nitrogen atmosphere and cooled to -15 °C. Diisobutylaluminum hydride solution (1.0 M in toluene, 31 mL, 31 mmol) was added dropwise and the solution was kept at 0 °C for 3.5 h. A 100 mL aliquot of 2N sulfuric acid was added to the solution and the organic phase was extracted with diethyl ether twice, and washed with sodium bicarbonate and then with water. The organic layer was dried over anhydrous MgSO_4 . The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 7:2, v/v); yellow liquid; yield 4.57 g (57%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 9.88 (s, 1H, HC = O), 7.77 (d, 2H, phenyl), 7.07 (d, 2H, phenyl), 5.40 (s, 1H, C = CH-), 2.14–1.20 (m, 16H, CH, CH_2 , CH_3).

2.2.3. 1-Ethenyl-4-[1-methyl-1-(4-methylcyclohex-3-enyl)ethoxy]benzene

Into a four-necked round-bottom flask fitted with an efficient magnetic stirrer and two addition funnels were placed methyltriphenylphosphonium bromide (6.20, 17.4 mmol), potassium *tert*-butoxide (1.95 g, 17.4 mmol), and THF (60 mL) under nitrogen atmosphere and kept at the room temperature for 1 h. A THF solution (10 mL) of 1-formyl-4-[1-methyl-1-(4-methylcyclohex-3-enyl)ethoxy]benzene (3.00 g, 11.6 mmol) was added dropwise to the solution and kept at the room temperature for 48 h. A 200 mL aliquot of water was added to the solution and the organic phase was extracted with ethyl acetate twice, and washed with sodium bicarbonate and then with water. The organic layer was dried over anhydrous MgSO_4 . The product was purified by column chromatography (silica gel, chloroform); yellow liquid; yield 0.650 g (22%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.24 (d, 2H, phenyl), 6.85 (d, 2H, phenyl), 6.59 (dd, 1H, $\text{CH}_2 = \text{CH}$ -), 5.55 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 5.32 (s, 1H, C = CH-), 5.05 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 2.11–1.21 (m, 16H, CH, CH_2 , CH_3).

2.2.4. 1-Ethenyl-4-[1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethoxy]benzene (MMOES)

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 1-ethenyl-4-[1-methyl-1-(4-methylcyclohex-3-enyl)ethoxy]benzene (2.34 g, 9.14 mmol), chloroform (23 mL), acetone (21 mL), phosphate buffer (pH = 7.4, 100 mL), and 18-crown-6 (0.11 g, 0.42 mmol). The flask was cooled to 0–5 °C using an ice-water bath. Oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) (6.43 g, 10.5 mmol) in 26 mL of water was added dropwise over the course of 30 min. 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 2.5 h. The resulting mixture was filtered and extracted with three 50 mL aliquots of

chloroform, 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 (silica gel, hexane:ethyl acetate:diethyl ether = 3:1:1 (v/v/v)); colorless liquid; yield 1.05 g (32%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.28 (d, 2H, phenyl), 6.98 (d, 2H, phenyl), 6.62 (dd, 1H, $\text{CH}_2 = \text{CH}$ -), 5.68 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 5.14 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 3.05 (m, 1H, epoxy HCOC), 2.36–1.11 (m, 16H, CH, CH_2 , CH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2$: C, 79.37; H, 8.88. Found: C, 79.66; H, 9.09.

2.2.5. 1-Ethenyl-4-[1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethoxycarbonyloxy]benzene (MMOCS)

MMOCS was synthesized by the epoxidation of 4-ethenylphenyl 2-(3-methylcyclohex-3-enyl)-2-propyl carbonate [15] (1.28 g, 4.26 mmol) using the same method employed for MMOES. After purification by flash chromatography (silica gel, chloroform), MMOCS was obtained as colorless liquid; yield 0.70 g (55%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.37 (d, 2H, phenyl), 7.08 (d, 2H, phenyl), 6.66 (dd, 1H, $\text{CH}_2 = \text{CH}$ -), 5.68 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 5.23 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 3.02 (m, 1H, epoxy HCOC), 2.30–1.02 (m, 16H, CH, CH_2 , CH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2$: C, 72.13; H, 7.65. Found: C, 72.01; H, 7.90.

2.2.6. 4-Ethenylbenzoic acid 1-methyl-1-(3-methylcyclohex-3-enyl)ethyl ester

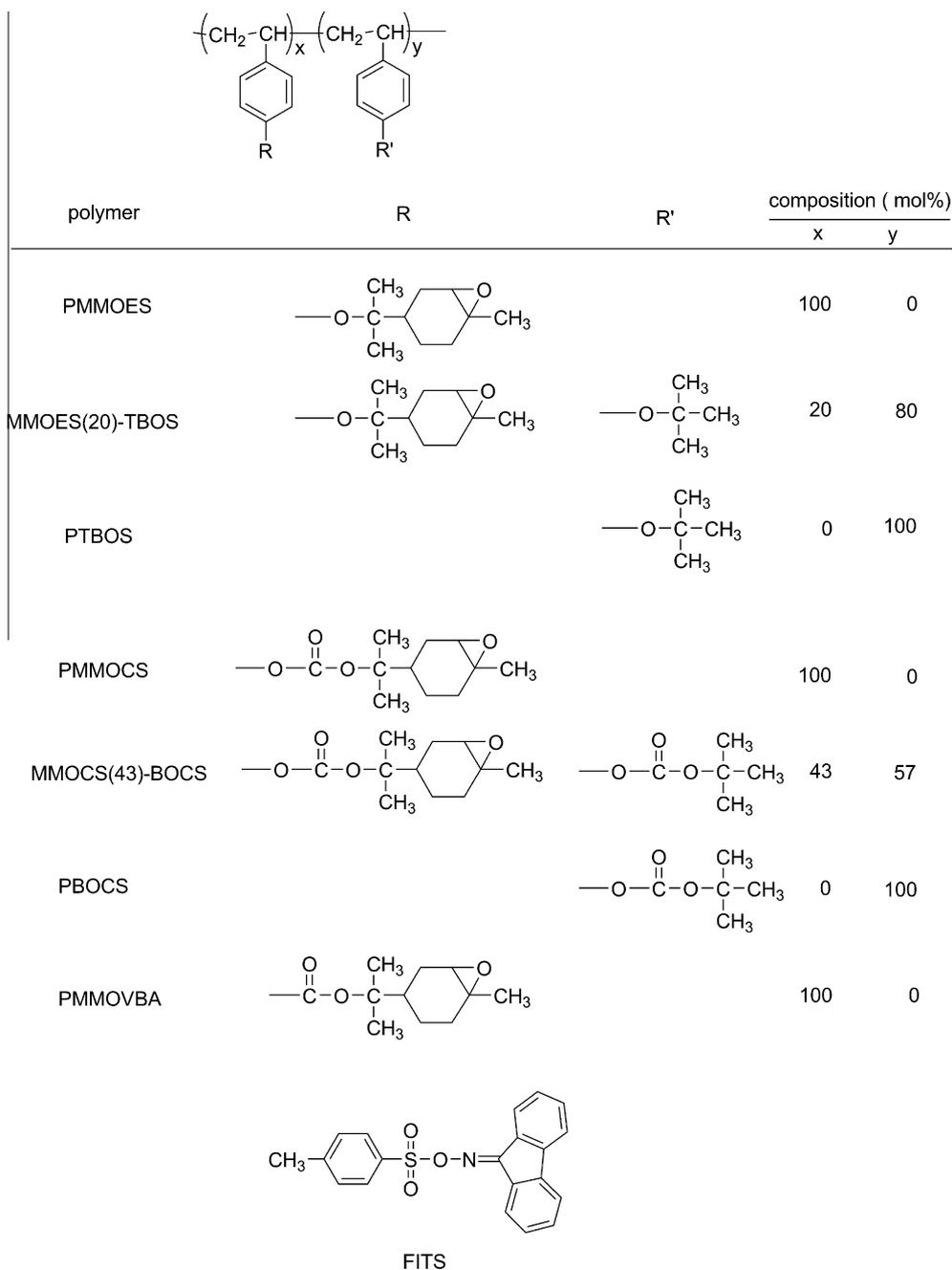
Into a three-necked round-bottom flask fitted with an efficient magnetic stirrer and two addition funnels were placed 4-vinylbenzoic acid (3.00 g, 20.2 mmol), oxalyl chloride (2.4 mL, 17.4 mmol), one drop of DMF, and benzene (30 mL) and stirred for 2 h. The solution was added dropwise into a chilled solution of the mixture of α -terpineol (3.73 g, 20.2 mmol) and butyllithium solution (1.6 N in hexanes, 12.6 mL, 20.2 mmol) in 30 mL of THF at 0 °C. The mixture was refluxed for 1 h. A 40 mL aliquot of water was added to the solution and the organic phase was extracted with diethyl ether twice, and washed with sodium bicarbonate and then with water. The organic layer was dried over anhydrous MgSO_4 . The product was purified by column chromatography (silica gel, hexane:ethyl acetate = 5:1 (v/v)); colorless liquid; yield 4.40 g (76%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.96 (d, 2H, phenyl), 7.43 (d, 2H, phenyl), 6.72 (dd, 1H, $\text{CH}_2 = \text{CH}$ -), 5.83 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 5.34 (s, 2H, C = CH- and $\text{CH}_2 = \text{CH}$ -), 2.21–0.85 (m, 16H, CH, CH_2 , CH_3).

2.2.7. 4-Ethenylbenzoic acid 1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl ester (MMOVBA)

MMOVBA was synthesized by the epoxidation of 4-ethenylbenzoic acid 1-methyl-1-(3-methylcyclohex-3-enyl)ethyl ester (2.00 g, 7.00 mmol) using the same method employed for MMOES. After purification by flash chromatography (silica gel, chloroform), MMOVBA was obtained as colorless liquid; yield 1.36 g (64%). $^1\text{H NMR}$ (270 MHz, CDCl_3) δ 7.86 (d, 2H, phenyl), 7.36 (d, 2H, phenyl), 6.67 (dd, 1H, $\text{CH}_2 = \text{CH}$ -), 5.78 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 5.29 (s, 1H, $\text{CH}_2 = \text{CH}$ -), 2.93 (m, 1H, epoxy HCOC), 2.24–1.07 (m, 16H, CH, CH_2 , CH_3). Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}_2$: C, 75.97; H, 8.05. Found: C, 75.56; H, 8.27.

2.3. Synthesis of polymers

Poly(MMOES) (PMMOES), poly(MMOES-co-TBOS) (MMOES(20)-TBOS), poly(MMOCS) (PMMOCS), poly(MMOCS-co-BOCS) (MMOCS(43)-BOCS), and poly(MMOVBA) (PMMOVBA) were prepared by photo-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 cut-off filter (Toshiba UV-35). Poly(TBOS) (PTBOS) and poly(BOCS) (PBOCS) were prepared by thermal radical polymerization of the



Scheme 2. Structures of polymers and a photoacid generator.

corresponding monomers in degassed toluene solution at 60 °C using AIBN as an initiator. The resulting polymers were purified by reprecipitation from chloroform / hexane. The fraction of the MMOES or MMOCS incorporated into the polymer was determined from ¹H NMR spectra. The structures of the polymers and the photoacid generator FITS are shown in Scheme 2. Polymerization conditions and characteristics of the polymers are summarized in Table 1.

2.4. 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 (1.9 μm) for FT-IR 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. Baking 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 THF. Thickness of films was measured by interferometry using a Nanometrics Nanospec M3000.

2.5. Measurements

¹H NMR spectra were observed at 270 MHz using a JEOL GX-270 spectrometer. Elemental analysis was carried out using a Yanako CHN coder MT-3. UV–vis spectra were taken on a Shimadzu UV-2400 PC. FT-IR measurements were carried out using a JASCO IR-

Table 1
Polymerization conditions and characteristics.

Polymer	Monomer in feed (mmol)					Solvent (mL)	AIBN (mmol)	Polym time. (h)	Yield (%)	Composition ^e (mol%)	$M_n \times 10^{-3}$ ^f	M_w/M_n	T_d (°C) ^g
	MMOES	TBOS	MMOCS	BOCS	MMOVBA								
PMMOES ^a	3.7					1.0 ^c	0.061	48	52	100	6.0	1.84	250
MMOES(20)-TBOS ^a	0.38	0.59				0.20 ^c	0.014	49	59	20	11.0	2.07	252
PTBOS ^b		11.5				2.0 ^d	0.140	4	25	0	37.7	1.82	314
PMMOCS ^a			1.55			0.50 ^c	0.073	45.5	52	100	9.1	1.80	182
MMOCS(43)-BOCS ^a			1.7	2.48		1.2 ^c	0.037	29	59	43	21.0	1.70	173
PBOCS ^b				11.5		2.6 ^d	0.120	17.5	50	0	85.0	1.80	185
PMMOVBA ^a					2.00	0.60 ^c	0.11	7	42	100	24.7	2.00	223

^a Polymerization was carried out at 30 °C with UV irradiation.

^b Polymerization was carried out at 60 °C.

^c DMF.

^d Toluene.

^e Composition of MMOES, MMOCS, or MMOVBA.

^f Determined by SEC.

^g Determined by TGA.

410. In situ FT-IR measurements were carried out using a Lithotech Japan PAGA-50. Thermal decomposition behavior of films was investigated with a Shimadzu TGA 50 thermogravimetric analyzer (TGA) under a nitrogen flow. Size exclusion chromatography (SEC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GMNHR-H + GMNHR-N; 8.0 mm i.d. × 30 cm each) and a differential refractometer JASCO RI1530. Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were estimated on the basis of a polystyrene calibration.

3. Results and discussion

3.1. Synthesis of polymers

A series of modified polystyrene having epoxy units and various types of thermally degradable linkages was prepared. In this work, polystyrene was chosen as a backbone due to easy incorporation of various functional groups. 1-Ethenyl-4-[1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethoxy]benzene (MMOES) and 1-ethenyl-4-[1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethoxycarbonyloxy]benzene (MMOCS) were chosen as monomers. There are few reports on the incorporation of a tertiary ether linkage in a phenyl moiety. The aromatic nucleophilic substitution reaction of *p*-cyanofluorobenzene using a bulky alkoxide was employed according to the method of DeCosta et al. [25]. The cyano group of the resulting compound was transformed into the vinyl group via reduction into the formyl group and followed by Wittig reaction without the loss of the tertiary ether linkage as shown in Scheme 1. MMOCS was synthesized using 4-ethenylphenyl 2-(3-methylcyclohex-3-enyl)-2-propyl carbonate [15] as a starting material. We have attempted the synthesis of 4-ethenylbenzoic acid 1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl ester (MMOVBA) via the reaction of 4-ethenylbenzoyl chloride and α -terpineol. The precursor 4-ethenylbenzoic acid 1-methyl-1-(3-methylcyclohex-3-enyl)ethyl ester was not obtained. The use of the alkoxide of α -terpineol gave a good result. Regio-selective epoxidation of the alkene of the precursor monomers proceeded to give the monomers MMOES, MMOCS, and MMOVBA.

MMOES, an analogue of TBOS having an epoxy moiety was homopolymerized and copolymerized with TBOS by the photopolymerization using AIBN at 30 °C with UV irradiation to prevent gel formation. The ¹H NMR spectra of MMOES, poly(MMOES) (PMMOES), and poly(MMOES-co-TBOS) (MMOES(20)-TBOS) are

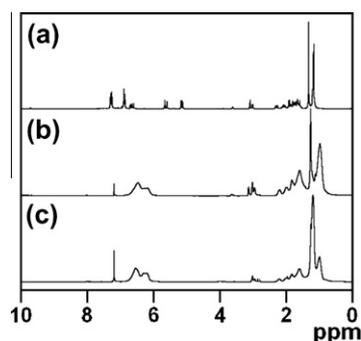


Fig. 2. ¹H NMR spectra of (a) MMOES, (b) PMMOES, and (c) MMOES(20)-TBOS in CDCl₃ at 270 MHz.

shown in Fig. 2. Although the peaks ascribed to vinyl groups (5.39–6.70 ppm) of the monomers disappeared, the peak due to aliphatic epoxides (ca. 3 ppm) remained. A characteristic peak around 1.3 ppm ascribed to *tert*-butoxy groups of TBOS units was observed in the spectrum of MMOES(20)-TBOS (Fig. 2c). Monomer composition of MMOES(20)-TBOS was calculated using the aromatic peaks (6–7 ppm) and the epoxy peaks (ca. 3 ppm). Poly(MMOCS) (PMMOCS) and poly(MMOCS-co-BOCS) (MMOCS(43)-BOCS) were also prepared to investigate the effect of epoxy contents of the polymers. Abbreviations of the polymers and polymerization conditions and characteristics of the polymers are summarized in Table 1. The molecular weights of PMMOES and PMMOCS were smaller than that of PMMOVBS. The bulkiness of the terpene moiety may affect the polymerization rates and chain length of the polymers. Insolubilization properties of the cross-linked polymers strongly were affected by the molecular weights as mentioned below.

Thermal properties of the polymers were investigated by TGA measurements. Fig. 3 shows the TGA curves of PMMOES, PMMOCS, and PMMOVBS together with those of PTBOS and PBOCS. The TGA curve of PMMOES was quite different from that of PTBOS. PMMOES started the first weight loss from ca. 250 °C. The observed weight loss (50 %) was correspondent to the complete elimination of the terpene units in PMMOES to form poly(4-vinylphenol) (PVP) (calculated weight loss: 56%) by the cleavage of the tertiary ether linkages. PTBOS started to decompose at ca. 300 °C. No characteristic information indicating the structural changes of PTBOS such as the fragmentation of isobutene was obtained from the TGA curves.

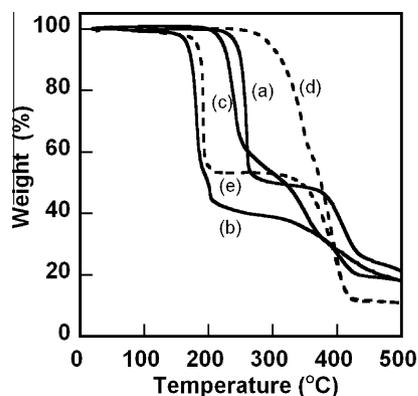


Fig. 3. TGA curves of (a) PMMOES, (b) PMMOCS, (c) PMMOVBA, (d) PTBOS, and (e) PBOCS in N_2 . Heating rate: $10\text{ }^\circ\text{C}/\text{min}$.

On the other hand, TGA curves of PMMOCS and PBOCS resembled with each other. The first weight loss of PMMOCS and PBOCS started at 182 and $185\text{ }^\circ\text{C}$, respectively. The results strongly indicated that decomposition of the polymers started from the scission of tertiary carbonate linkages. The first weight loss was 60% for PMMOCS and 48% for PBOCS, and those values strongly suggested the formation of PVP (calculated weight loss: 65% and 52% , respectively). The first weight loss of PMMOVBA started at $223\text{ }^\circ\text{C}$, which was similar to that observed for poly(1-methyl-1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-yl)ethyl methacrylate)) ($216\text{ }^\circ\text{C}$) [10]. The weight loss at $250\text{ }^\circ\text{C}$ was 42% , which was ca 10% lower than that of the complete elimination of the terpene units in PMMOVBA to form poly(4-vinylbenzoic acid) (weight loss: 51%).

3.2. Photo-cross-linking, thermal cross-linking, and thermal de-cross-linking

Polymer films containing a PAG were irradiated at 254 nm and insoluble fraction was studied. FITS (see Scheme 2) as a PAG was photolyzed to generate *p*-toluenesulfonic acid [22]. The photoinduced acid initiated cationic polymerization of epoxy units in the side chain to generate networks. Fig. 4 shows the insolubilization properties of PMMOES, MMOES(20)-TBOS, and PTBOS. The insoluble fraction was determined by comparing the thickness of the films before and after dipping into THF. When the films were irradiated with $60\text{ mJ}/\text{cm}^2$ and baked below $60\text{ }^\circ\text{C}$ for 10 min , insolubilization was not observed for all films. The insolubilization

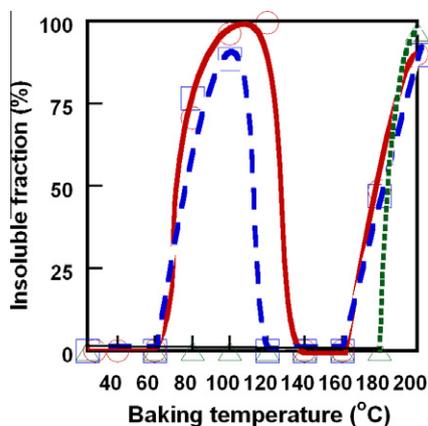


Fig. 4. Photoinduced insolubilization of (○) PMMOES, (□) MMOES(20)-TBOS, and (△) PTBOS films containing $5\text{ wt.}\%$ FITS. Exposed at 254 nm with $60\text{ mJ}/\text{cm}^2$. Dissolution: THF for 10 min .

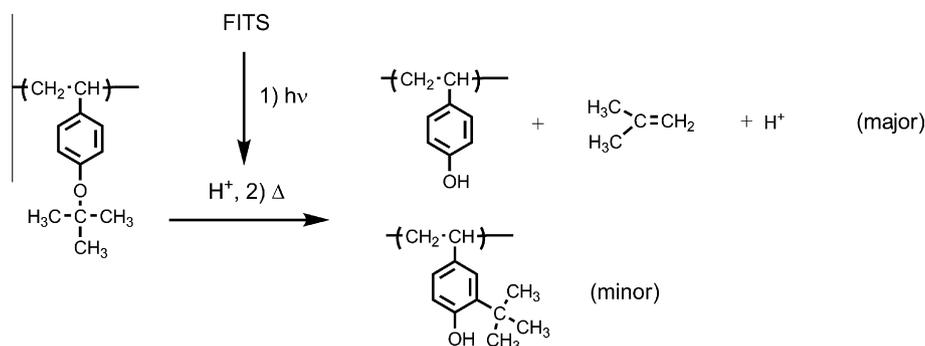
degree of the PMMOES and MMOES(20)-TBOS films increased, reached to a maximum value, decreased and increased again with a rise of baking temperature. The maximum insoluble fraction was observed for the films when baked at $120\text{ }^\circ\text{C}$ for PMMOES and at $100\text{ }^\circ\text{C}$ for MMOES(20)-TBOS. Insolubilization efficiency of the films increased with the fraction of a MMOES moiety when baked at between 80 and $140\text{ }^\circ\text{C}$ for 10 min after irradiation. The insolubilization was due to the photoinduced-acid catalyzed polymerization of epoxy moieties of the polymers. As mentioned above, insolubilization of the polymers was strongly affected by the molecular weights. Polymers having large molecular weights easily became insoluble in solvents by cross-linking reactions. The lower insoluble fraction of MMOES(20)-TBOS than PMMOES was mainly due to the lower molar fraction of the epoxide.

When the irradiated PMMOES and MMOES(20)-TBOS films were baked at 140 or $160\text{ }^\circ\text{C}$ for 10 min , insolubilization was not observed. Cleavage of tertiary ether linkages in the polymers was observed by in situ FT-IR measurements as discussed below. The re-insolubilization for PMMOES and MMOES(20)-TBOS films on baking at above $180\text{ }^\circ\text{C}$ for 10 min was due to undesired cross-linking of PVP derivatives which were formed by the thermolysis of PMMOES and MMOES(20)-TBOS polymers. The reaction mechanism was supported from the insolubilization of the irradiated PTBOS films on baking at $200\text{ }^\circ\text{C}$. Crivello reported the deblocking studies of polymers bearing *tert*-butoxy groups [20]. The model study of acidolysis of *tert*-butoxytoluene revealed that PTBOS decomposed to form PVP as a major product with compounds substituted by a *tert*-butyl group as minor products as shown in Scheme 3. Thus, the re-insolubilization may be due to electrophilic aromatic substitution reaction of phenyl moieties in PVP may occur to form phenyl ether linkages.

Fig. 5 shows the insolubilization profiles of PMMOCS, MMOCS(43)-BOCS, and PBOCS. The insolubilization profiles of the polymers were similar to those for PMMOES shown in Fig. 4. The insolubilization degree of the PMMOCS and MMOCS(43)-BOCS films increased, reached to a maximum value, decreased and increased again with a rise of baking temperature. The decrease of the insolubilization degree was due to the cleavage of the carbonate linkages in MMOCS units. The reaction was the analogue of that for PBOCS as shown in Scheme 4. Complete re-dissolution for PMMOCS was observed on baking at $130\text{ }^\circ\text{C}$, whereas the incomplete re-dissolution for MMOCS(43)-BOCS films was observed. We consider the reactions of de-cross-linking by the cleavage of the carbonate linkages in MMOCS units and re-cross-linking reactions of PVP derivatives which were formed by the thermolysis of MMOCS(43)-BOCS occurred simultaneously. The re-insolubilization of irradiated PMMOCS, MMOCS(43)-BOCS, and PBOCS films was observed at lower temperatures than those of PMMOES, MMOES(20)-TBOS, and PTBOS films. Investigation of the mechanism of the re-insolubilization is now in progress. A plausible reaction mechanism is discussed below.

The effect of the ether, ester, and carbonate linkages on the insolubilization profiles of the polymers was investigated. Fig. 6 shows the insolubilization profiles of PMMOES, PMMOCS, PMMOVBA, and PVP. For irradiated samples (open symbols), insolubilization efficiency on baking at lower temperatures ($<150\text{ }^\circ\text{C}$) decreased in the order PMMOCS > PMMOES > PMMOVBA. Generally, insolubilization efficiency of polymers increases with their molecular weights. The low efficiency for PMMOVBA contradicts the effect of the molecular weights of the polymers which decreased in the order PMMOVBA > PMMOCS > PMMOES.

The decreased insoluble fraction of the films on baking at 120 – $150\text{ }^\circ\text{C}$ was due to the cleavage of the ether, ester, and carbonate linkages in the polymers. The stability of the linkages in the presence of *p*-toluenesulfonic acid was estimated to be in the order: tertiary carbonate (PMMOCS) > tertiary ether (PMMOES) > ter-



Scheme 3. Reaction mechanism of photoinduced acid-catalyzed decomposition of PTBOS.

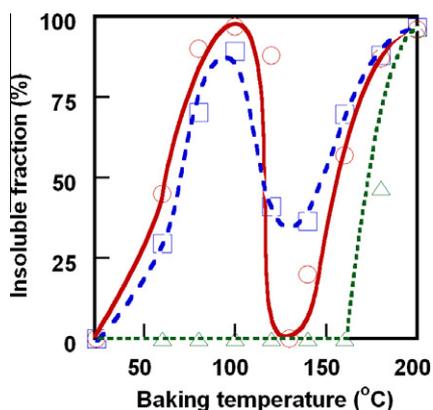


Fig. 5. Photoinduced insolubilization of (○) PMMOCS, (□) MMCOCS(43)-BOCS, and (△) PBOCS films containing 5 wt.% FITS. Exposed at 254 nm with 60 mJ/cm². Dissolution: THF for 10 min.

tiary ester (PMMOVBA). It is noteworthy that the thermal stability determined by TGA measurements increased in the order PMMOCS < PMMOVBA < PMMOES. The photogenerated-acid promoted the efficient cleavage of the tertiary ether linkages of PMMOES.

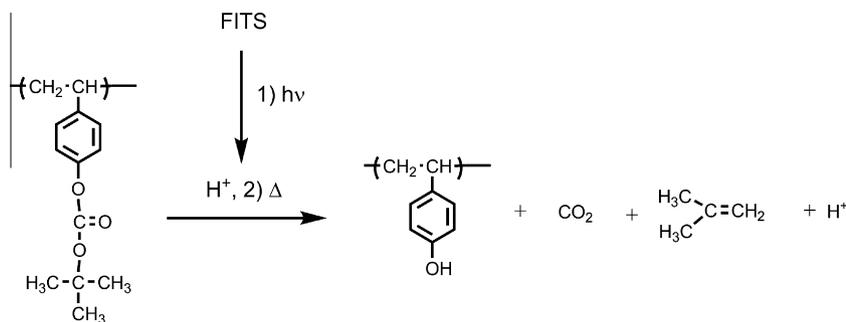
The photoinduced acid-catalyzed decomposition of PTBOS, PBOCS, and poly(*tert*-butyl methacrylate) (TBMA) was discussed using *E_a* values which were reported to correspond to the reaction controlled by activation energy [26]. The *E_a* values of PTBOS, PBOCS, and TBMA were reported to be 142, 136, and 130 kJ/mol, respectively [26]. Though the *E_a* values were strongly affected by the structure and concentration of acid, we expected that the higher stability of PMMOES compared to PMMOCS was due to the high activation energy of PMMOES.

The re-increase of the insoluble fraction of the films on baking at above 160 °C may be due to the network formation of the

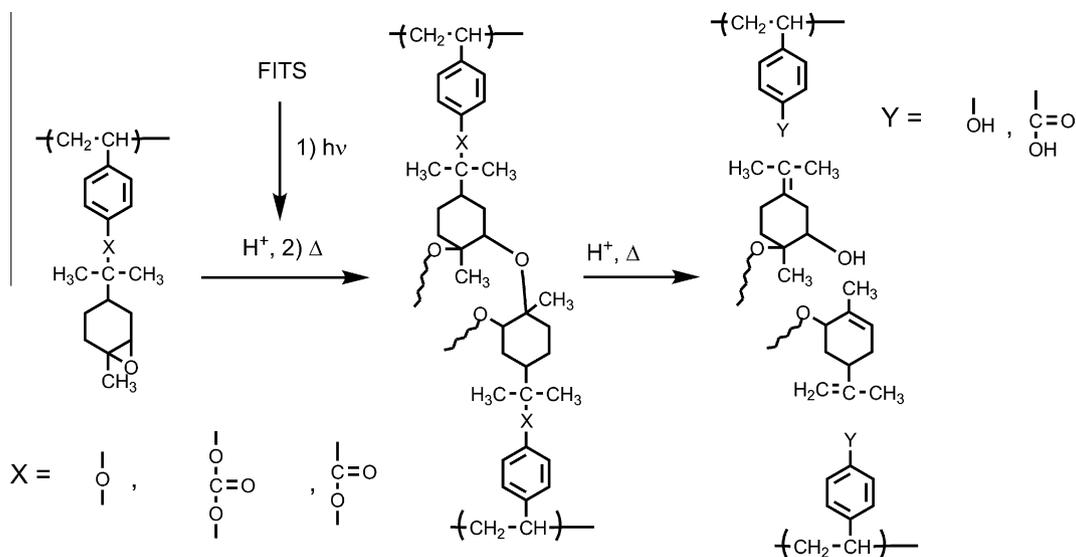
decomposed films. The irradiated films of PVP became insoluble on baking at above 220 °C. The insolubilization may be due to dehydration of phenolic OH groups in PVP. The re-insolubilization of irradiated PMMOES and PMMOCS occurred by baking at above 180 °C which was 40 °C lower than that of PVP. PTBOS formed compounds substituted by a *tert*-butyl group as shown in Scheme 3. The reaction concerned with the decomposed fragments such as limonene, a difunctional alkene, generated from the dehydration of α -terpineol, may occur. Moreover, the re-insolubilization profiles of the irradiated PMMOES and PMMOCS coincided with the insolubilization curves of unirradiated (solid symbols) PMMOES and PMMOCS. The insolubilization of PMMOES and PMMOCS may be due to the complicated reactions of cross-linking of epoxides, decomposition of tertiary ether or carbonate linkages, and the re-cross-linking of PVP generated by the decomposition of PMMOES and PMMOCS, simultaneously. The re-increase of the insoluble fraction of the irradiated PMMOVBA films occurred when baked at above 200 °C due to the formation of carboxylic anhydride linkages. The plausible reaction mechanism of the cross-linking and de-cross-linking of PMMOES, PMMOCS, and PMMOVBA is shown in Scheme 5.

3.3. In situ observation of degradation of tertiary ether and tertiary carbonate

In situ FT-IR measurements revealed the precise decomposition behaviors of tertiary ether linkages of PMMOES and tertiary carbonate linkages and PMMOCS. Fig. 7 shows the FT-IR spectral changes of the irradiated (a) PMMOES and (b) PMMOCS film containing 5 wt.% FITS on baking at 130 °C. The peak at 1130 cm⁻¹ due to C–O–C stretching of tertiary ether linkages in PMMOES and the peak at 1760 cm⁻¹ due to carbonate carbonyl of PMMOCS decreased with baking time. Fig. 8 shows the disappearance of tertiary ether units of cross-linked PMMOES and carbonate units of cross-linked PMMOCS, and appearance of hydroxy units in the cross-linked PMMOES. Remaining ether group of PMMOES was



Scheme 4. Reaction mechanism of photoinduced acid-catalyzed decomposition of PBOCS.



Scheme 5. Plausible reaction mechanism of photo-cross-linking and thermal de-cross-linking.

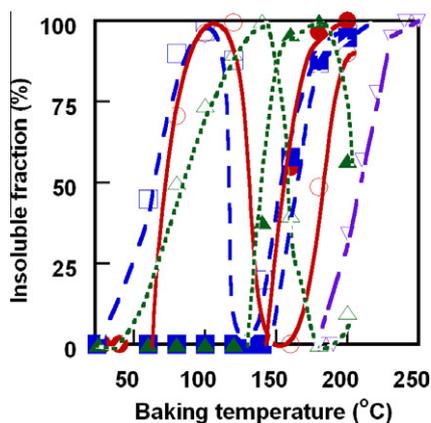


Fig. 6. Effect of baking temperature on insoluble fraction of PMMOES (○, ●), PMMOCS (□, ■), PMMOVBA (△, ▲), and PVP (▽) films. Additive: 5 wt.% FITS. Open symbol: irradiated with a dose of 60 mJ/cm². Solid symbol: no irradiation. Baking time: 10 min. Dissolution: THF for 10 min.

monitored using the peak at 1130 cm⁻¹. Remaining carbonate group of PMMOCS was monitored using the peak at 1760 cm⁻¹. Increased hydroxyl group of decomposed PMMOES was monitored using the peak at 3480 cm⁻¹. Tertiary ether units gradually decomposed to generate aromatic OH groups on heating at 130 °C. The decomposition of carbonate units suddenly occurred after heating at 130 °C for 6 min. The thermal decomposition was catalyzed by phenolic OH groups generated, which caused the self-acceleration properties. Thus, it was concluded that the decomposition of tertiary carbonate linkages was faster than that of tertiary ether linkages. The conclusion was supported by the discussion of *E_a* as mentioned above.

4. Conclusion

We have designed and synthesized novel photo-cross-linkable polymers having thermally degradable linkages. Homopolymers and copolymers which have an epoxy moiety and tertiary ether (MMOES), tertiary ester (MMOVBA), or tertiary carbonate (MMOCS) linkages in a molecule, were photo-cross-linkable on irradiation in the presence of a photoacid generator. The photochemically cross-linked polymers became soluble in solvents

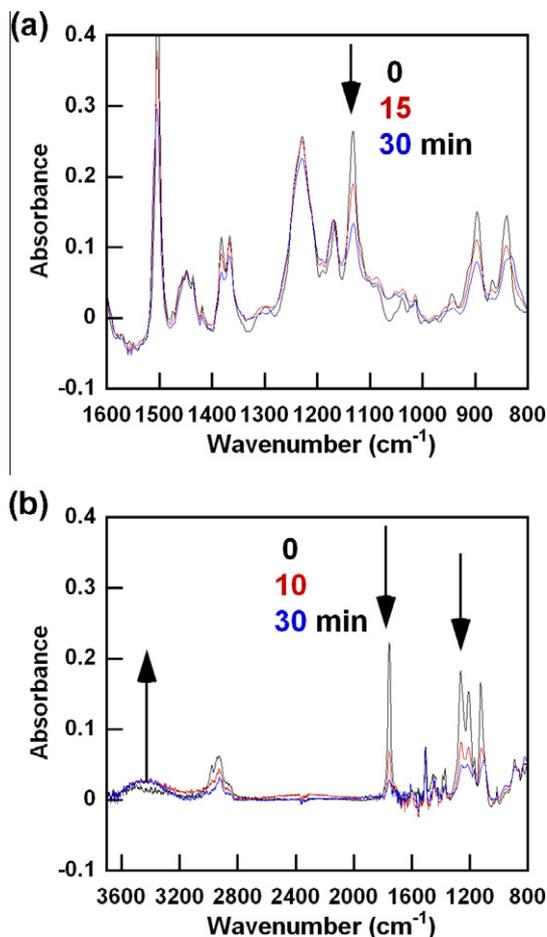


Fig. 7. FT-IR spectral changes of the photo-cross-linked (a) PMMOES and (b) PMMOCS films containing 5 wt.% FITS on baking at 130 °C. Film thickness: 1.0 μm. Irradiation dose to cross-link the polymer: 60 mJ/cm².

if baked at a given temperature. Thermal decomposition of the degradable linkage of the network generated linear polymers. The stability of the linkages of the polymers was found to be in the order: tertiary ester > tertiary ether > tertiary carbonate. As for tertiary ester and tertiary ether, the order was accountable to

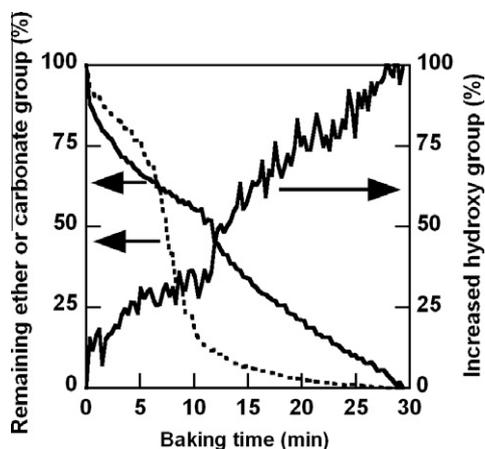


Fig. 8. Thermolysis of the photo-cross-linked PMMOES (solid lines) and PMMOCS (dotted line) films containing 5 wt.% FITS measured by in situ FT-IR spectroscopy. Irradiation dose: 60 mJ/cm². Heating temperature: 130 °C. Film thickness: 1.0 μm.

the order of the E_a values reported. Those polymers are environmentally friendly photo-cross-linkable materials because they can be used as degradable materials by thermal treatment.

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