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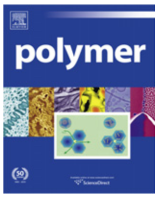

Novel photo-cross-linkable dendrimers having thermal de-cross-linking properties

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ABSTRACT

Novel poly(aryl ether) type dendrimers having photo-cross-linking and thermal de-cross-linking properties were synthesized by a convergent method. A protected A_2B monomer, 1-allyloxy-3,5-bis(bromomethyl)benzene, was newly prepared for the dendrimer synthesis. Palladium-catalyzed deprotection of an allyl group proceeded in high yields. The films of dendrimers containing a photoacid generator (PAG) became insoluble in solvents on irradiation. The irradiated films became soluble in solvents after baking at 120–200 °C. The insolubilization and redissolution profiles were strongly affected by irradiation and baking conditions and the generation of the dendrimers. A reaction pathway was studied by TGA and DTA analysis and FT-IR spectroscopy.

1. Introduction

Dendrimers have attracted much attention due to their perfect branches, spherical shapes, easy control of their molecular weights, and unique functionalities [1–15]. Recently, dendrimers have investigated as functional materials such as optical devices [4,5], biomedical applications [6], and photo-curable resins [7–10]. Especially, dendritic or hyperbranched resins with photo-curable properties were extensively studied by many researchers due to a lot of advantages such as easy formulation, low organic volatile compounds, high sensitivity and reactivity, and low viscosity [7–10,16–23]. Our interest is the development of the photo-curable resins with reworkable properties having dendritic structures. We have developed a series of the reworkable epoxy or (meth)acryalte resins having tertiary ester linkages [24–26] and sulfonate ester linkages [27] as thermally cleavable units. We have found that a series of multi-functional epoxides showed higher reactivity and sensitivity compared to mono- and di-functional epoxides [25,26]. We consider that multi-functional materials having dendritic structures improve their reactivity, sensitivity, thermal or chemical stability, and redissolution properties. Especially, our interest of the work was to investigate the structure–property relationships of cross-linking and de-cross-linking of the films. It is important to clarify the relationship to design high-performance materials.

In this paper, the synthesis, cross-linking, and de-cross-linking properties of a new series of dendritic and multi-functional epoxides with thermally degradable units were investigated. The concept of the present system is shown in Fig. 1. The dissolution properties were discussed in terms of the cross-linking and de-cross-linking reactions. The photo-cross-linking and thermal degradation mechanism were investigated by TGA, DTA, and in situ FT-IR analyses. This system is useful for the application of photo-cross-linkable materials removable from substrates after use.

2. Experimental section

2.1. Materials

All reagents used in this work were summarized in Fig. 2. Limonene dioxide (LDO) was purchased from Merck. Poly(vinylphenol) (PVP) ($M_w = 8000$) was obtained from Aldrich. G0-TriEpo [26] and FITS [28] were synthesized according to the literatures. Synthesis of the dendrimers G1-TriEpo, G2-TriEpo, and G3-TriEpo were described in Supplementary material.

2.2. 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 dendrimers and a photoacid generator (PAG). 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.

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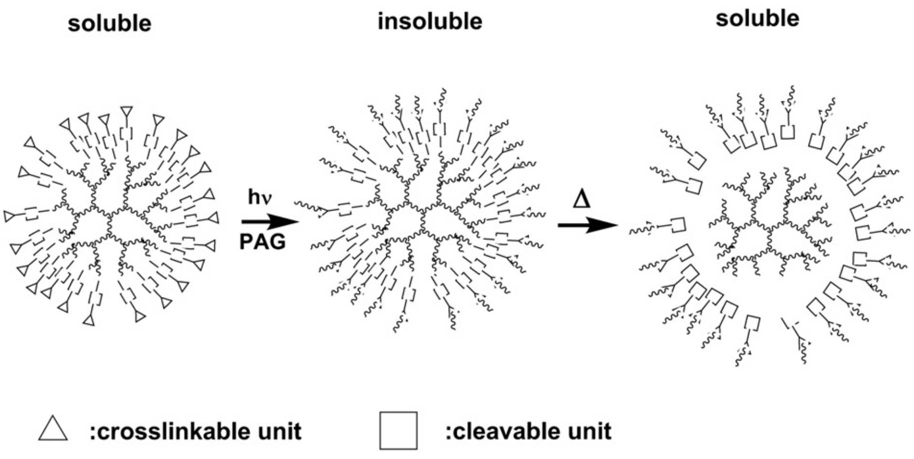


Fig. 1. Concept of photo-cross-linkable dendrimers with redissolution properties.

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, methanol, and 2.38 wt% tetramethylammonium hydroxide solution for 10 min. Thickness of films was measured by interferometry using a Nanometrics Nanospec M3000.

2.3. Measurements

^{1}H NMR spectra were observed at 400 MHz using a JEOL LA-400 spectrometer. Elemental analysis was carried out using a Yanaco CHN coder MT-3. UV–vis spectra were taken on a Shimadzu UV-2400 PC. In situ FT-IR measurements were carried out using a Lithotech Japan PAGA-50. Thermal decomposition and heat flow of films were investigated with a Shimadzu DTG 60 simultaneous TG/DTA instrument under a nitrogen flow. Onset glass transition

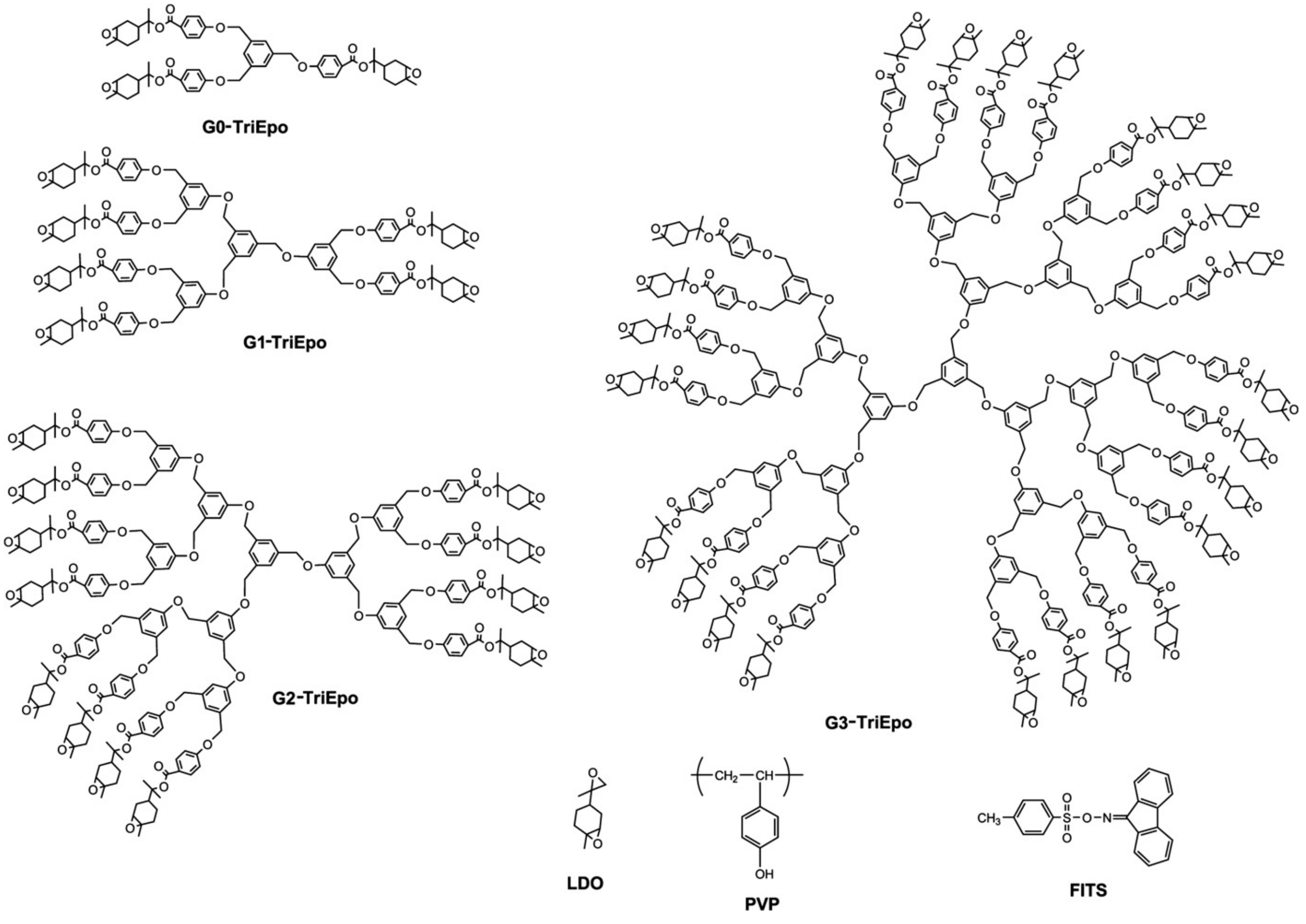
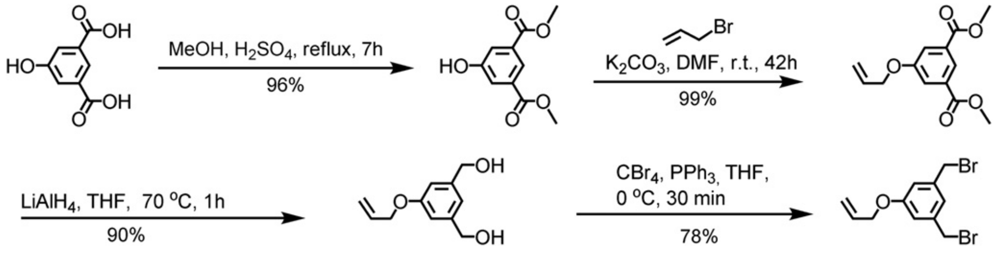


Fig. 2. Chemical structures of reagents used in this work.



Scheme 1.

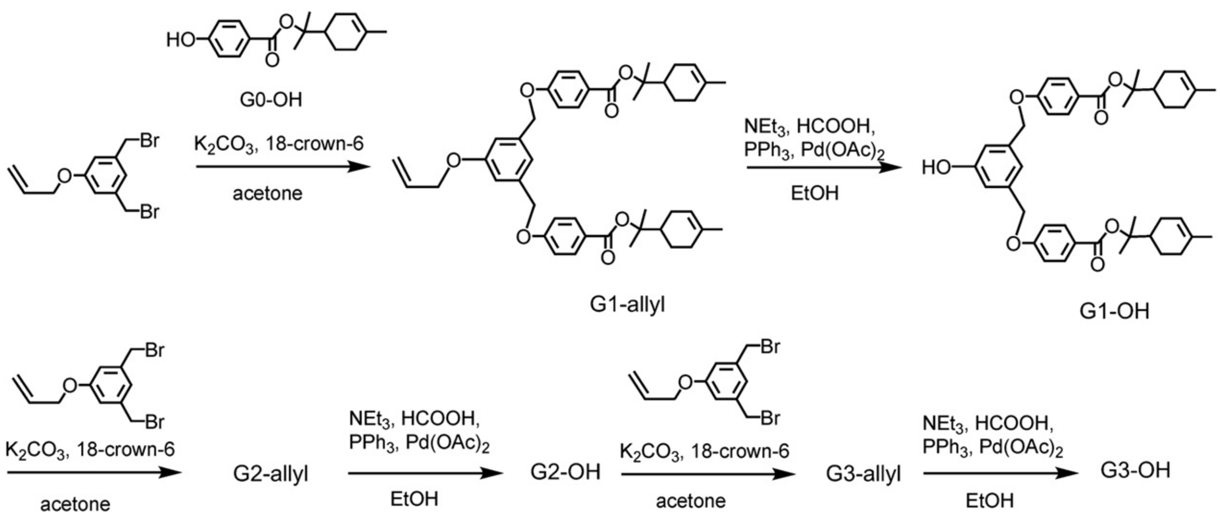
temperatures of the dendrimers were measured by a DSC 60 differential scanning calorimeter (DSC) under a nitrogen flow. Size exclusion chromatography (SEC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GMNHR-$_H$ + GMNHR-$_N$; 8.0 mm i.d. × 30 cm 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. The absolute molecular weight of G3-Tri was determined by another SEC system equipped with a multiangle laser light-scattering (MALLS) detector shown below. The SEC system contained a Shodex GPC-101 liquid chromatography (Tokyo, Japan) equipped with two Shodex KF-804L polystyrene mixed gel columns (300 × 8.0 mm; bead size = 7 mm; pore size = 20–200 Å). THF was used as eluent (40 °C). Flow rate was 0.8 mL/min. The column system was calibrated with standard polystyrenes. Sample detection was a MALLS detector, a Wyatt Technology DAWN EOS (CA, USA), equipped with a Ga–As laser ($\lambda = 690$ nm). The refractive index increment dn/dc was determined to be 0.157 mL g^{-1} by a Wyatt Technology OPTILAB DSP differential refractometer ($\lambda = 690$ nm).

3. Results and discussion

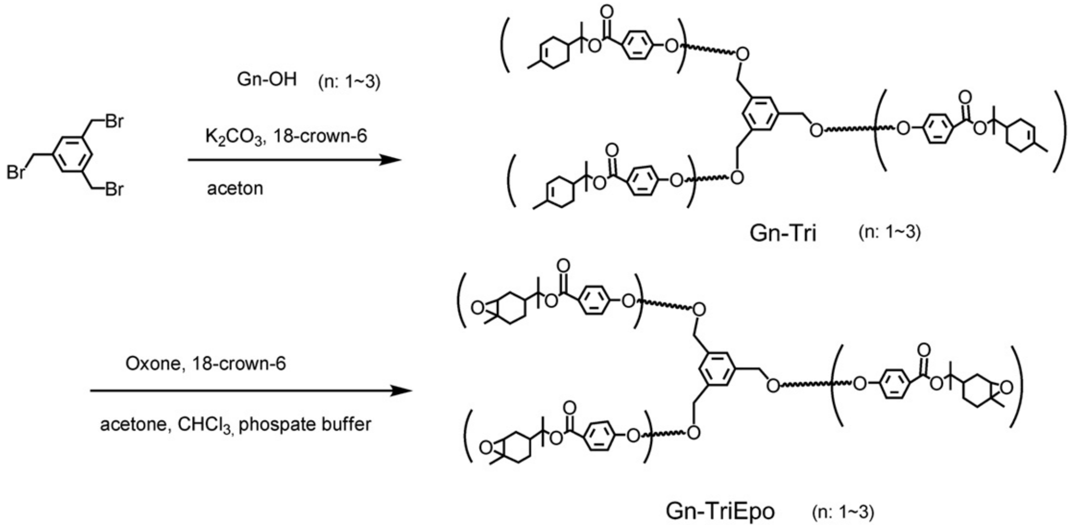
3.1. Synthesis and characterization of dendrimers

We have reported that multi-functional cross-linkers which have both epoxy moieties and tertiary ester linkages in a molecule acted as photo-cross-linkable resins which can be removed easily after use [26]. The convergent approach in the work was effective to increase functionality of epoxy and tertiary ester units. To apply the convergent synthetic pathway, we developed a new synthetic route to obtain dendrimers having desired structures. Our target dendrimers contained both tertiary ester groups and carbon–carbon double bonds which were sensitive to strong acid or base conditions and electrophilic addition reactions. Common Frechet-type dendrimers extended their generations by Williamson ether reactions with mild conditions [3]. Introduction of bromomethyl functionalities in the presence of the C=C bonds may cause undesired reactions. Thus, we have chosen 5-allyloxy-1,3-bis(bromomethyl)benzene [29] as a building unit. Synthesis of 5-allyloxy-1,3-bis(bromomethyl)benzene was shown in Scheme 1. Total yields of 5-allyloxy-1,3-bis(bromomethyl)benzene was 67% from 5-hydroxyisophthalic acid, which has a large potential for industrial applications. Synthesis of dendrons was shown in Scheme 2. Aromatic allyloxy groups were easily converted into aromatic OH groups in good yields by palladium-catalyzed reduction reactions (80–90%) [26]. The reaction of the phenol derivatives and 5-allyloxy-1,3-bis(bromomethyl)benzene proceeded in good yields (71–88%) under mild conditions, i.e., relatively low temperatures (<50 °C) and without strong acids or bases. Thus, the sequential operation of phenol derivatives by deprotection of allyloxy unit and Williamson ether reaction was of a great success to synthesize multi-functional dendritic epoxides. Synthesis of dendrimers was shown in Scheme 3. It was surprising that coupling reactions of the dendrons and 1,3,5-tris(bromomethyl)benzene with no spacers proceeded (yields: 33–65%, see Table 1) despite of increased steric hindrances with the generation of the dendrons.

The conversion of olefinic double bonds into epoxy moieties proceeded in fair yields (see Table 1). Characterization of the dendrons and dendrimers was carried out using ^{1}H NMR spectroscopy and SEC measurements. Especially, ^{1}H NMR analysis was a powerful tool to identify the purity of the monodendrons of G1 and G2



Scheme 2.



Scheme 3.

generations. As shown in Fig. 3, characteristic peaks ascribed to allyloxy functions of G*n*-allyl compounds clearly observed for all generations. Conversion of G*n*-allyl to G*n*-OH was estimated by the complete disappearance of the peaks ascribed to the allyloxy functions. The ^{1}H NMR spectrum of G3-allyl showed some broadening of the peaks due to low mobility of the compound. As expected from the ^{1}H NMR spectra of the precursors, SEC curves of G*n*-OH in Fig. 4 showed narrow polydispersity. In the ^{1}H NMR spectra of G2 or G3 dendrons, the amounts of the errors were within 5% for the intensities of the alkyl hydrogens consisting cycloaliphatic rings. We consider the peak of water (around 1.6 ppm) was overlapped within the region. The peaks at around 2.3 ppm in the G3-allyl and G3-OH spectra may be residual acetone. Unfortunately, our attempt to characterize the monodendrons and the dendrimers in this work by MALDI-TOF mass spectroscopy failed due to easily degradable properties of the compounds.

Dendrimers G*n*-Tri and G*n*-TriEpo were also characterized using ^{1}H NMR spectroscopy and SEC measurements. Fig. 5 shows ^{1}H NMR spectra of G0-Tri, G1-Tri, G2-Tri, G3-Tri, and G0-TriEpo. The sharpness of the peak at around 7.50 ppm ascribed to three protons of the core phenyl moieties in the compounds proved the uniformity of the compounds even in high generations such as G3-Tri. The methyleneoxy protons of the dendrimers became broader with higher generations, which showed lower mobility of the dendrimers with high generations. Complete conversion of the cyclic double bonds in G*n*-Tri into epoxy rings was confirmed by the disappearance of the peak at around 5.3 ppm and appearance of the new peak at around 3 ppm. SEC charts of the final compounds (G*n*-TriEpo) (Fig. 6) showed narrow polydispersity as same as those of the monodendrons. In Figs. 4 and 6, some small peaks or shoulders in the SEC traces may be due to impurities such as triphenylphosphine oxide or 18-crown-6. The absolute molecular weight of G3-Tri was determined to be 9100 by a MALLS measurement, which corresponded to the nominal molecular weight of G3-Tri (9179, see Table 1).

Thermal properties of the G*n*-TriEpo were investigated using DSC, TGA and DTA measurements. Glass transition temperatures of G1-TriEpo, G2-TriEpo, and G3-TriEpo were 73, 76, and 83 °C. Slight increase of the temperature was observed with the generations. Tertiary esters are known to decompose to carboxylic acid and alkene by thermal treatment at temperatures lower than those for primary and secondary esters. Furthermore, the temperature for the tertiary ester cleavage is lowered in the presence of strong acids [30]. Fig. 7 shows the TGA and DTA curves of G0-TriEpo, G1-TriEpo, G2-TriEpo, and G3-TriEpo. When the dendrimers were heated under nitrogen at the heating rate (10 °C/min), G0-TriEpo,

Table 1
Yields and SEC data of monodendrons and dendrimers.

Compound	FW	M_n (RI)	PDI (SEC)	Yield (%)
G1-allyl	707	–[a]	–[a]	88
G1-OH	667	620	1.06	90
G2-allyl	1492	–[a]	–[a]	75
G2-OH	1452	1480	1.08	86
G3-allyl	3062	–[a]	–[a]	71
G3-OH	3022	2460	1.08	80
G1-Tri	2115	2790	1.04	65
G2-Tri	4470	4520	1.06	61
G3-Tri[b]	9179	11,800	1.05	33
G1-TriEpo	2211	2630	1.04	48
G2-TriEpo	4662	5200	1.05	61
G3-TriEpo	9563	8250	1.04	69

[a] Not measured.
[b] MALLS molecular weight: 9100.

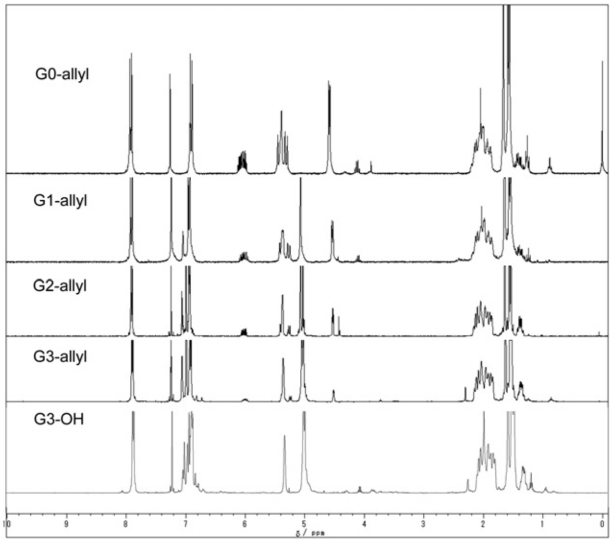


Fig. 3. ^{1}H NMR spectra of G*n*-allyl (*n*: 0–3) in $CHCl_3$ at 400 MHz.

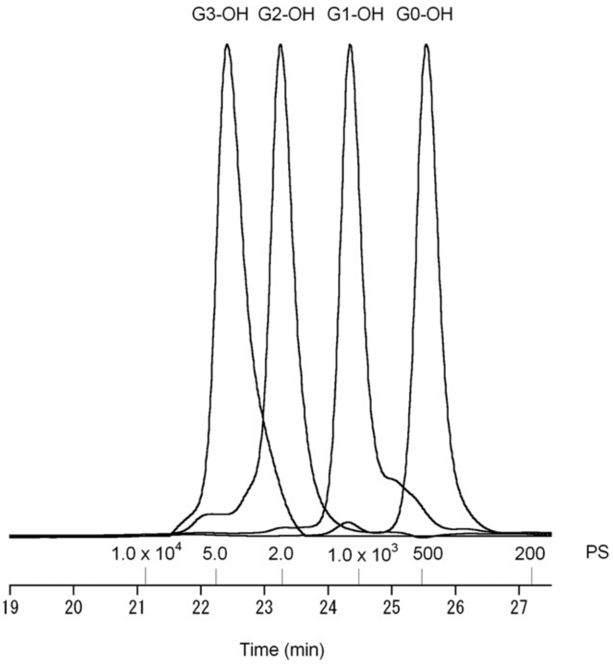


Fig. 4. SEC curves of G*n*-OH (*n*: 0–3).

G1-TriEpo, G2-TriEpo, and G3-TriEpo started to lose their weights at 218, 227, 224, and 224 °C, respectively. Generation of the dendrimers little affected their thermal stabilities. The weight loss of G0-TriEpo, G1-TriEpo, G2-TriEpo, and G3-TriEpo was 46, 38, 40, and 37% at 260 °C, respectively. The values agreed with the calculated values for formation of corresponding carboxylic acid (46, 41, 39, and 38%, respectively), suggesting the complete cleavage of tertiary ester linkages in G0-TriEpo, G1-TriEpo, G2-TriEpo, and G3-TriEpo. DTA curves also supported the decomposition mechanism. DTA curves of the dendrimers showed small exothermic peaks around 220 °C and large endothermic peaks around 240 °C. The former peaks were ascribed to thermal decomposition of the tertiary ester units in the dendrimers and the latter peaks were due to the volatilization of the decomposed fragments. The exothermal peak at around 380 °C was observed only for G2-TriEpo. Decomposition of the dendrimer structure may occur at that temperature.

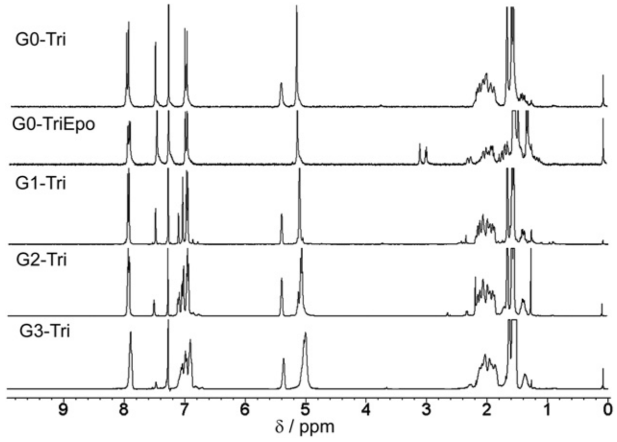


Fig. 5. ^{1}H NMR spectra of G*n*-Tri (*n*: 0–3) and G0-TriEpo in $CHCl_3$ at 400 MHz.

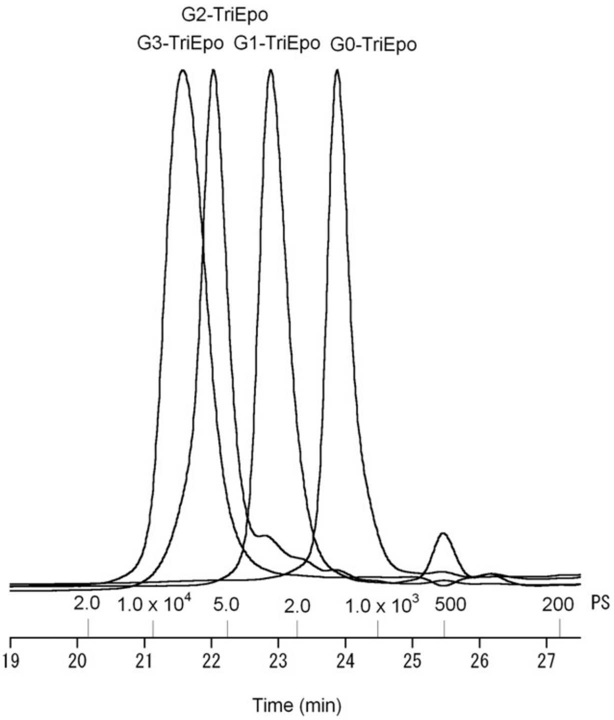


Fig. 6. SEC curves of G*n*-TriEpo (*n*: 0–3).

3.2. Photo-cross-linking and de-cross-linking properties

Fig. 8 shows the insolubilization profiles of the dendrimer films containing 5 wt% of FITS on irradiation with a dose of 60 mJ/cm^2 and followed by baking at above 60 °C for 10 min. FITS was used as a PAG which can generate *p*-toluenesulfonic acid on irradiation with UV light [28]. Insoluble fraction was determined by comparing the film thickness before and after dipping the films in THF for 10 min. THF was a good solvent for FITS, dendrimers, and the compounds generated by thermolysis of the dendrimers. Error values of the insoluble fractions were within 5% in each case. The curves in Fig. 8 were only eye guides, not the theoretical values predicted.

When the films were irradiated with 60 mJ/cm^2 and baked below 80 °C for 10 min, insolubilization was not observed for all films. The insolubilization degree of the G2-TriEpo and G3-TriEpo 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 °C.

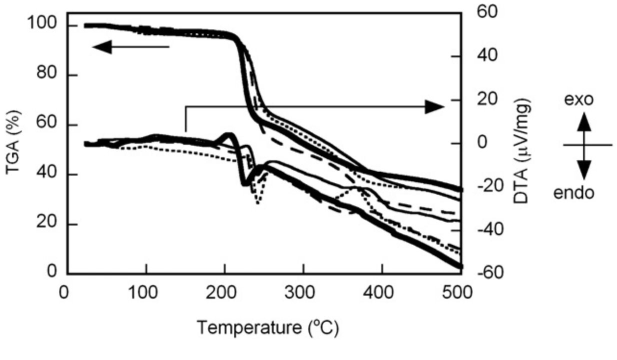


Fig. 7. TGA and DTA curves of G0-TriEpo (bold lines), G1-TriEpo (dotted lines), G2-TriEpo (broken lines), and G3-TriEpo (solid lines). Heating rate: 10 °C/min.

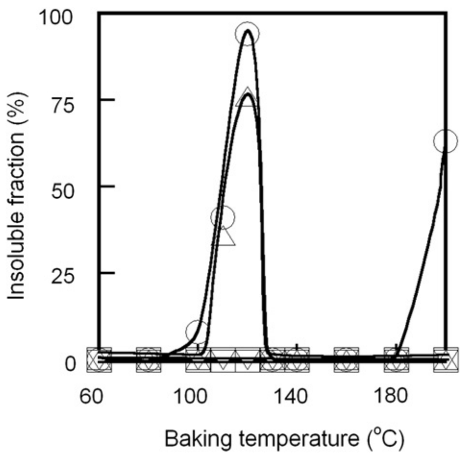


Fig. 8. Effect of baking temperature on insoluble fraction of the irradiated G0-TriEpo (▽), G1-TriEpo (□), G2-TriEpo (△), and G3-TriEpo (○) films. Additive: 5 wt% FITS. Irradiation dose: 60 mJ/cm^2. Heating time: 10 min. Dissolution: THF for 10 min.

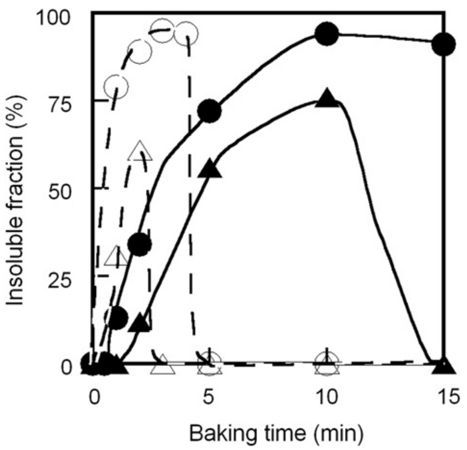


Fig. 9. Effect of baking time on insoluble fraction of the irradiated G2-TriEpo (▲,△) and G3-TriEpo (●,○) films. Baking temperature: 120 °C (▲,●), 140 °C (△,○). Additive: 5 wt% FITS. Irradiation dose: 60 mJ/cm^2. Dissolution: THF for 10 min.

Insolubilization efficiency of the films increased with the generation of the dendrimers when baked at between 90 and 130 °C for 10 min after irradiation. The insolubilization was due to the photoinduced-acid catalyzed polymerization of epoxy moieties of the dendrimers. We consider that one of the reason for the incomplete insolubilization of the films baked at 120 °C was short chain length of the polymerization of epoxy moieties initiated by *p*-toluenesulfonic acid. Hexafloroantimonic acid or hexafluorophosphic acid, stronger acid than *p*-toluenesulfonic acid, was commonly used as photoinduced cationic polymerizations of epoxide. In situ FT-IR measurements revealed that decomposition of tertiary ester linkages of the dendrimers did not occur by baking treatment at 100 and 110 °C for 10 min. The unirradiated films were soluble in THF when the film was baked below 180 °C.

When the blended films were baked at 140 °C for 10 min after irradiation, the films completely dissolved in THF. The films also dissolved in methanol and 2.38 wt% tetramethylammonium hydroxide solution. Cleavage of tertiary ester linkages in the dendrimers was observed by in situ FT-IR measurements as discussed below.

The re-insolubilization for G3-TriEpo films on baking at above 200 °C for 10 min was due to the formation of carboxylic anhydride by the dehydration of carboxylic acid units generated from the thermolysis of G3-TriEpo, which was confirmed by FT-IR measurements shown in Fig. 11.

The dependence of the insoluble fraction of the irradiated dendrimer films containing 5 wt% of FITS on baking time was investigated at two different temperatures (Fig. 9). When the G2-TriEpo film was baked at 120 °C for 10 min, the insoluble fraction of the films reached a maximum value (72%), and decreased to zero after bake treatment for 15 min. In the case of G3-TriEpo film, the insoluble fraction became 95% on baking at 120 °C for 10 min, and slightly decreased by prolonged baking. These results strongly suggest that cross-linking and de-cross-linking reactions at 120 °C and 140 °C occurred simultaneously. When baked at 140 °C, the insolubilizaion curves of G2-TriEpo and G3-TriEpo films shifted to shorter bake times than that at 120 °C. The dendrimers with higher functionality have an advantage for the network formation. The highest insoluble fraction (95%) was observed for G3-TriEpo film. However, higher functionality is unfavorable for the dissolution of cross-linked films because higher conversion for the decomposition of network is necessary.

The dependence of the insoluble fraction of the blended films on irradiation dose was investigated (Fig. 10). The sensitivities determined as 50% insolublization of G2-TriEpo and G3-TriEpo films was 7 and 3 mJ/cm^2, respectively, when the blended films were baked at 120 °C for 10 min after irradiation. The highly functionalized dendrimers showed the high sensitivity. Insolubilization G1-TriEpo and G0-TriEpo was not observed. Thus, sensitivity of G1-TriEpo and G0-TriEpo was not evaluated.

To investigate the reaction mechanism, in situ FT-IR measurements of the G3-TriEpo film were carried out (Fig. 11). The peaks due to ester carbonyl (1710 cm^{-1}) and ester C–O groups (1260 cm^{-1}) decreased with the increase of baking time. On the other hand, the peak due to ester carbonyl (1710 cm^{-1}) showed slight shift to 1700 cm^{-1}, which may be due to the formation of carboxylic acid groups. When the film was baked at 200 °C for 30 min, the peak at 1700 cm^{-1} due to carboxylic acid groups decreased and the new peaks at 1730 and 1775 cm^{-1} due to acid anhydride groups appeared. The observation supported the insolubilization mechanism of the film baked at 200 °C. Fig. 12 shows the decomposition rate of ester units of the cross-linked G3-TriEpo films on baking at 140 °C. In spite of incomplete separation of the two peaks (1710, 1700 cm^{-1}), the rate of the formation of carboxylic acid may contain errors, especially at early stages of the decomposition reaction. Thermal decomposition behavior of the tertiary

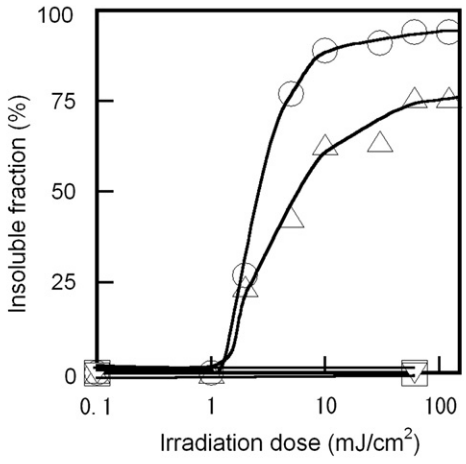


Fig. 10. Effect of irradiation dose on insoluble fraction of the irradiated G0-TriEpo (▽), G1-TriEpo (□), G2-TriEpo (△), and G3-TriEpo (○) films. Additive: 5 wt% FITS. Baking condition: 120 °C for 10 min. Dissolution: THF for 10 min.

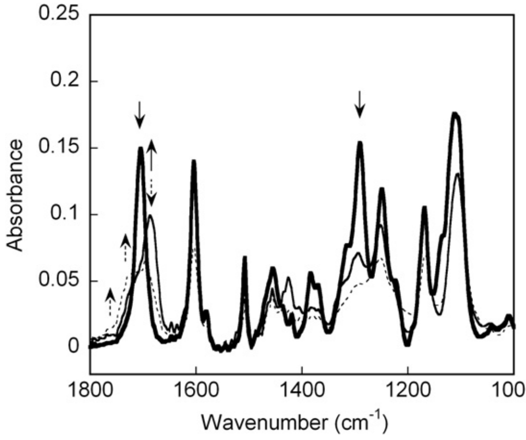


Fig. 11. FT-IR spectra of G3-TriEpo films containing 5 wt% FITS before (bold line) and after (solid line) irradiation with a dose of 60 mJ/cm^2 and followed by baking at 140 °C for 15 min and after prolonged baking at 200 °C for 30 min (broken line).

ester linkages in the dendrimer was clearly observed by using the peak at 1260 cm^{-1}. The baking time for 50% decomposition of ester groups was ca. 6 min. For the complete dissolution of the decomposed film in THF, 5 min baking at 140 °C was needed. Thus, complete decomposition of the ester units was not necessary for the dissolution of the cross-linked films in the system. This finding also suggests the low cross-linking density of the irradiated film. It was difficult to study the cross-linking process of epoxy units using FT-IR measurements.

A reaction mechanism of the dendrimers is as follows. On irradiation, FITS was photolyzed to generate *p*-toluenesulfonic acid. The acid catalyzed the polymerization of the epoxy moieties in the dendrimer. Baking treatment of the irradiated films at relatively lower temperatures enhanced the polymerization. Acid-catalyzed cleavage of tertiary ester linkages in the dendrimer occurred by baking treatment for a long time. Complete degradation of ester linkages in the dendrimer films occurred by proper baking conditions. However, if baked at above 200 °C, the insolubilization was observed again. The re-insolubilization was caused by the formation of the acid anhydrides from −COOH units generated by the thermolysis of the dendrimers.

The dendrimer G3-TriEpo showed photo-cross-linking and thermal de-cross-linking properties. However, the photo-cross-linking efficiency was not so high. To achieve high insoluble fraction, baking of the sample at 120 °C was needed, which caused the start of the degradation in parallel to the photo-curing. To enhance the photo-cross-linking efficiency, reactive diluent was added to the system. Photo-cross-linking and de-cross-linking properties of limonene dioxide (LDO)/G*n*-TriEpo (1/1, wt/wt) film containing 5 wt% FITS were investigated. The insolubilization of the G3-TriEpo/LDO films was observed when the film was baked at 120 °C for 10 min after irradiation. The insoluble fraction was 95%. When the films were baked at 80, 100, 140, 160, and 180 °C, insolubilization was not observed. When G1-TriEpo/LDO and G2-TriEpo/LDO films were baked below 200 °C after irradiation, insolubilization was not observed. The results were essentially the same as those without LDO. The results showed that the low activity for the cross-linking was due to low chain length of epoxide caused by toluenesulfonic acid, one of relatively weak acids. Glass transition temperatures of the dendrimers (73 to 83 °C) showed low mobility of the dendrimers at room temperature. However, low mobility of the dendrimers was not the main reason for the low efficiency of insolubilization. Unfortunately, the effect of reactive diluent was not observed.

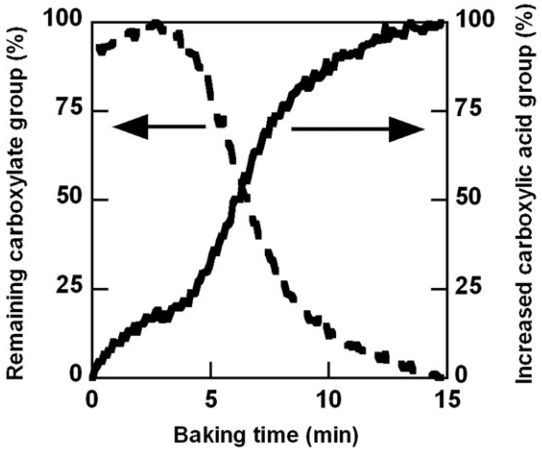


Fig. 12. Thermolysis of the photo-cross-linked G3-TriEpo film containing 5 wt% FITS measured by in situ FT-IR spectroscopy. Irradiation dose: 60 mJ/cm^2. Heating temperature: 140 °C. Film thickness: 1.0 μm. Dotted line: carboxylate group (1250 cm^{-1}). Broken line: carboxylic acid group (1700 cm^{-1}).

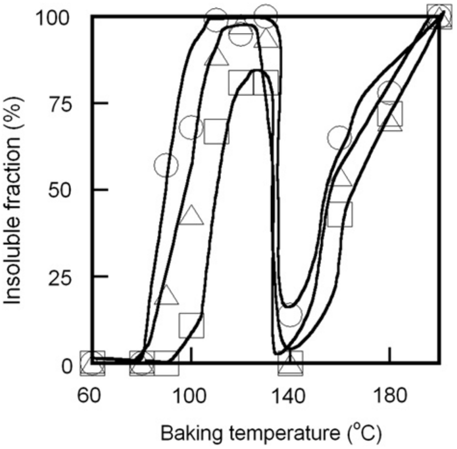


Fig. 13. Effect of baking temperature on insoluble fraction of the irradiated PVP/G1-TriEpo (□), PVP/G2-TriEpo (△), and PVP/G3-TriEpo (○) blended films. Molar ratio of epoxy in the dendrimers was adjusted to 20 mol% of hydroxyl groups in PVP. Additive: 5 wt% FITS. Irradiation dose: 60 mJ/cm^2. Heating time: 10 min. Dissolution: THF for 10 min.

Utilization of dendrimers as cross-linkers was examined to obtain the high efficiency of insolubilization. The work is a simple extension of PVP/6-functionalized crosslinker [26] blended system. Fig. 13 shows the insolubilization profiles of PVP/G*n*-TriEpo blended films containing 5 wt% of FITS on irradiation with a dose of 60 mJ/cm^2 and followed by baking at above 80 °C for 10 min. The amount of epoxy unit in all blended films was adjusted to 20 mol% for phenolic −OH units in PVP. THF was a good solvent for not only PVP but also FITS, dendrimers, and the compounds generated by thermolysis of the dendrimers.

When the blended films were irradiated with 60 mJ/cm^2 and baked below 80 °C for 10 min, insolubilization was not observed for all the films. The insolubilization degree of the blended films increased, reached to a maximum value, decreased and increased again with a rise of baking temperature. The maximum insoluble fraction was observed for all films when baked at 120 °C, suggesting that the reaction mechanism and reaction kinetics for the insolubilization and dissolution of the PVP/G*n*-TriEpo systems resemble each other. Insolubilization degree of PVP/G*n*-TriEpo blended films increased with the generation of the dendrimers when baked at between 90 and 130 °C for 10 min after irradiation. The insolubilization was due to the photoinduced-acid catalyzed cross-linking reaction of epoxy moiety of G*n*-TriEpo and phenolic –OH units in PVP. It is noteworthy that complete insolubilization was observed for the PVP/G3-TriEpo blended films. The high efficiency for the cross-linking was due to high functionality of the dendrimer.

When the blended films were baked at 140 °C for 10 min after irradiation, complete dissolution of the film was observed.

The re-insolubilization for the blended films on baking at above 160 °C for 10 min was due to the reaction of the –OH groups in PVP and corresponding carboxylic acid generated from the thermolysis of the dendrimers. The results were essentially the same as those for PVP/crosslinker system [26] except for the high efficiency of cross-linking.

4. Conclusion

Highly functionalized dendrimers having both tertiary ester unit and epoxy unit were synthesized by the convergent method. Conversion of allyloxy units to hydroxyl units by palladium-catalyzed reduction found to be a promising way to synthesize functional dendrimers. The epoxy-functional dendrimer films containing a photoacid generator became insoluble in solvents on UV irradiation and baking at relatively low temperatures (~120 °C). With a rise in baking temperature, the insoluble fraction of the irradiated films increased, passed through a maximum value, decreased, and increased again at elevated temperatures. The initial insolubilization was due to the photoinduced acid-catalyzed polymerization of the epoxy units. The dendrimer G3-TriEpo having 24 functionalities was the highest performance. Dissolution of the cross-linked film on baking was due to the thermal cleavage of tertiary ester units in the dendrimers. PVP/dendrimer blended system showed high efficiency of cross-linking and thermally degradable properties.

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.09.010.

References

[1] Tomalia DA, Frechet JMJ. J Polym Sci Part A Polym Chem 2002;40:2719–28.
[2] Bosman AW, Janssen HM, Meijer EW. Chem Rev 1999;99:1665–88.
[3] Grayson SM, Frechet JMJ. Chem Rev 2001;101:3819–67.
[4] Lo S-C, Burn PL. Chem Rev 2007;107:1097–116.
[5] Li W-S, Aida T. Chem Rev 2009;109:6047–76.
[6] Mintzer MA, Simanek EE. Chem Rev 2009;109:259–302.
[7] Hoyle CE, Lee TY, Roper T. J Polym Sci Part A Polym Chem 2004;42:5301–38.
[8] Hoyle CE, Bowman CN. Angew Chem Int Ed 2010;49:1540–73.
[9] Wang S-J, Fan X-D, Liu X, Kong J, Liu Y-Y, Wang X. Polym Int 2007;56:764–72.
[10] Aoki K, Ichimura K. J Photopolym Sci Technol 2008;21:75–6.
[11] Tyler TL, Hanson JE. Chem Mater 1999;11:3452–9.
[12] Shi Z-F, Zhou Z-L, Cao X-P. Chin J Chem 2006;24:103–8.
[13] Hawker CJ, Wooly KL, Frechet JMJ. J Chem Soc Perkin Trans 1; 1993:1287–97.
[14] Dvornic PR, Li J, de Leuze-Jallouli AM, Reeves SD, Owen MJ. Macromolecules 2002;35:9323–33.
[15] Killops KL, Campos LM, Hawker CJ. J Am Chem Soc 2008;130:5062–4.
[16] Trey SM, Nilsson C, Malmström E, Johansson M. Prog Org Coat 2010;68:151–8.
[17] Asif A, Shia W, Shenb X, Nie K. Polymer 2005;46:11066–78.
[18] Kudo H, Nishikubo T. J Polym Sci Part A Polym Chem 2007;45:709–26.
[19] Chen Y, Loccufier J, Vanmaelec L, Frey H. J Mater Chem 2007;17:3389–92.
[20] Chen Y, Loccufier J, Vanmaelec L, Barriau E, Frey H. Macromol Chem Phys 2007;208:1694–706.
[21] Wang H, Xu S, Shi W. Prog Org Coat 2009;65:417–24.
[22] Wang S-J, Fan X-D, Kong J, Lu J-R. Polymer 2009;50:3587–94.
[23] Maruyama K, Kudo H, Ikehara T, Nishikubo T, Nishimura I, Shisido A, et al. Macromolecules 2007;40:4895–900.
[24] Shirai M, Morishita S, Okamura H, Tsunooka M. Chem Mater 2002;14:334–40.
[25] Okamura H, Toda S, Tsunooka M, Shirai M. J Polym Sci Part A Polym Chem. 2002;40:3055–62.
[26] Okamura H, Shin K, Shirai M. Polym J 2006;38:1237–44.
[27] Shirai M, Kawaue A, Okamura H, Tsunooka M. Chem Mater 2003;55:4075–81.
[28] Shirai M, Kinoshita H, Tsunooka M. Eur Polym J 1992;28:379–85.
[29] Hosokawa Y, Maki S, Nagata T. Bull Chem Soc Jpn 2005;78:1773–82.
[30] Ito H, Ueda M. Macromolecules 1988;21:1475–82.