Cationic polymerization behavior of β-methylglycidyl ether derivatives and physical properties of their cationically cured materials

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ABSTRACT: β-Methylglycidyl ethers have been applied to Electrical and Electronic adhesives. However, there is no report about the detailed polymerization behavior and physical properties of their cured products. Hence, we investigated cationic polymerization behavior of bisphenol A di(β-methylglycidyl) ether (Me-BADGE) and physical properties of the cured products containing Me-BADGE. DSC analysis suggested that Me-BADGE could be cured completely at lower temperature than bisphenol A diglycidyl ether (BADGE). Physical properties were analyzed by dynamic viscoelastic analysis. Glass transition temperature (T_g) of BADGE homopolymer was 194°C. In contrast, the copolymer of BADGE (50 wt %) with Me-BADGE (50 wt %) showed T_g at 124°C. According to the data of E' and tan δ, crosslink density of the cured products decreased with increasing the Me-BADGE content. The analysis of cationic polymerization of monofunctional β-methylglycidyl ether suggested that the cationic polymerization proceeded not only through oxonium cation but also through carbocation formed by ring-opening reaction of oxonium cation. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42377.

INTRODUCTION

Epoxy resins are widely used as paints, adhesives, and molding materials due to their excellent chemical resistance, electrical and mechanical properties, heat resistance, and adhesion properties to various substrates.[1–5] Generally, normal epoxy resins, which are synthesized from epichlorohydrin and phenol derivatives have been used. On the other hand, β-methylglycidyl ether type epoxy resins derived from β-methylepichlorohydrin (MECH) have not been developed well so far, although they are quite attractive for utilization of C4 fraction which is one of the byproducts of petroleum cracking.[6] Several researches has been done on β-methylglycidyl ethers as rapidly curable epoxy resins in cationic polymerization conditions,[7] and there has been applied to Electrical and Electronic adhesives.[8–10] However, basic investigation reports about β-methylglycidyl ether are not so many. Maeda *et. al.* investigated the reactivity of phenyl β-methylglycidyl ether (Me-PGE) derived from MECH and phenol and phenyl glycidyl ether (PGE) with amine reagents, and reported that Me-PGE showed lower reactivity with amine reagents than PGE.[6] Iwasa *et al.* reported that ring-opening polymerization of methyl β-methylglycidyl ether using organo-tin catalyst did not take place.[11] To the best of our knowledge,

there is no report about the detailed cationic polymerization behavior of β-methylglycidyl ether and physical properties of their cured materials. In order to apply them to practical materials, we consider that it is important to know their fundamental characteristics.

In this article, we investigated cationic polymerization behaviors of bisphenol A di(β-methylglycidyl) ether (Me-BADGE) by differential scanning calorimetry (DSC) analysis, and the physical properties (thermal and mechanical properties) of the cured materials containing Me-BADGE by dynamic viscoelastic analysis, which were compared with the cured materials of bisphenol A diglycidyl ether (BADGE).

EXPERIMENTAL

Materials

Bisphenol A (BPA), MECH, phenyl glycidyl ether (PGE), and Sulfonium, (4-hydroxyphenyl)methyl[2-methylphenyl]methyl]-, (OC-6–11)-hexafuluoroantimonate (San-Aid SI-80L) were purchased from Mitsubishi Chemical Corporation (Tokyo, Japan), Chemexcel (Zhangjiakou) Fine Chemicals Co. Ltd. (Beijing, China), Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan), and Sanshin Chemical Industry (Yamaguchi, Japan), respectively.
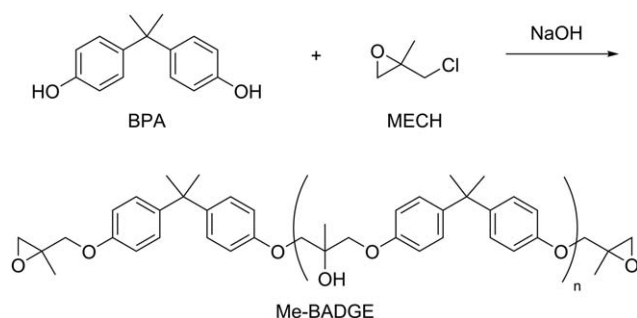
Figure 1. Synthesis of Me-BADGE.

BADGE was supplied by ADEKA Corporation (Tokyo, Japan) (ADEKA Resin EP-4100E, epoxy equivalent weight EEW = 190 g/eq.). Sodium hydroxide (NaOH), methyl isobutyl ketone (MIBK), chloroform, and phenol were purchased from Wako Pure Chemical Industries (Osaka, Japan). All materials were used without further purification.

Synthesis of Bisphenol A Di(β-methylglycidyl) Ether (Me-BADGE)

BPA (288 g, 1 mol) and MECH (1065 g, 10 mol) were added to a round-bottom flask which equipped stirring blade, dropping funnel, reflux condenser and thermometer. The reaction mixture was heated until reflux temperature (121°C) and 48%NaOH (183 g, 2.2 mol) was added dropwise for 2 h. After the reaction mixture was stirred for 1 h, the excess amount of MECH was removed by evaporation. MIBK (300 mL) and distilled water (200 mL) were added to the residue. The mixture was transferred to a separating funnel and the products were extracted with MIBK. The organic layer was washed with distilled water (200 mL) until pH of water layer became less than 8. Solvent was removed by evaporation, and the residue was filtrated and dried in vacuo to give DMGEBA as a yellow liquid (300 g, 81.5%). Epoxy equivalent weight of the product was 216 g/eq.

Synthesis of Phenyl β-Methylglycidyl Ether (Me-PGE)[12]

Phenol (9.4 g, 100 mmol) and MECH (44.1 g, 500 mmol) were added to a round-bottom flask equipped with a magnetic stirrer, a dropping funnel, a reflux condenser and a thermometer. The reaction mixture was heated until reflux temperature (120°C), and a solution of 48% NaOH (8.8 g, 105 mmol) was added dropwise over a period of 45 min. After the reaction mixture was stirred for 1 h, the mixture was cooled to room temperature and chloroform (100 mL) was added. The mixture was transferred to a separating funnel and washed twice with distilled water (50 mL). The organic layer was dried by anhydrous magnesium sulfate, and the solvent was removed by evaporation to give crude PMGE as a yellow liquid (16 g). The crude PMGE was purified by distillation, to give pure PMGE as a colorless liquid (8.7 g, 53.2%, boiling point 75°C at 4 mm Hg).

^{1}H NMR (400 MHz, CDCl$_3$, δ): 1.48 (s, 3H, CH$_3$), 2.82 (d, J = 4.8 Hz, 1H, CH$_2$), 2.86 (d, J = 4.8 Hz, 1H, CH$_2$), 3.94 (d, J = 10.3 Hz, 1H, CH$_2$), 4.01 (d, J = 10.5 Hz, 1H, CH$_2$), 6.89-6.97 (m, 3H, ArH), 7.24–7.29 (m, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$, δ): 18.7, 52.2, 55.7, 71.6, 114.8, 121.3, 129.6, 158.7

Preparation of Cured Products

An epoxy resin (5 g, 98 wt %) and a cationic polymerization initiator SI-80L (0.1 g, 2 wt %) were mixed. After heating at 120°C for 2 h and then 180°C for 2 h on a copper foil, film-like cured products were obtained.

Cationic Polymerization of Monofunctional Epoxy Resins (PGE or Me-PGE)

PGE or Me-PGE (1.0 g, 98 wt %) and SI-80L (0.02 g, 2 wt %) were mixed in a test tube which equipped a magnetic stirrer and a reflux condenser. After heating the mixture at 120°C for 2 h with stirring, the mixture was analyzed by IR, NMR, and SEC.

Measurements

In order to investigate the curing behavior of epoxy resins, DSC was performed on SEIKO Instrument EXSTAR6000 at a heating rate of 10°C/min under N$_2$ atmosphere. For the investigation of physical properties, dynamic viscoelasticity data were obtained by tensile mode using A&D Rheovibron DDV-01FP at a heating rate of 2°C/min at frequency of 1 Hz. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS400 spectrometer in CDCl$_3$ using tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were measured by ATR method with the optical range of 2500–25,000 nm using Thermo Fisher Scientific Nicolet iS10 FT-IR. Size exclusion chromatography (SEC) was performed on TOSOH HLC-8220GPC analysis equipped with three consecutive polystyrene columns (TSKgel Super AW4000, AW3000, and AW2500) using THF as an eluent. NMR, IR, and SEC measurements were performed to analyze of reaction mixture before and after reaction. All measurements were performed only once, respectively.

RESULTS AND DISCUSSION

Synthesis and Characterization of Me-BADGE

Me-BADGE was synthesized from BPA and MECH (Figure 1). Figure 2 shows the ^{1}H-NMR spectra of Me-BADGE. The signals at 1.62 ppm and 6.78–7.13 ppm were assigned to the protons of BPA backbone. The signals, which are attributed to the protons of β-methylglycidyl group, were observed at 2.72 ppm, 2.85 ppm, and 3.95 ppm. The protons of glyceryl ether moiety produced by oligomerization were observed at 1.57 ppm and 3.95
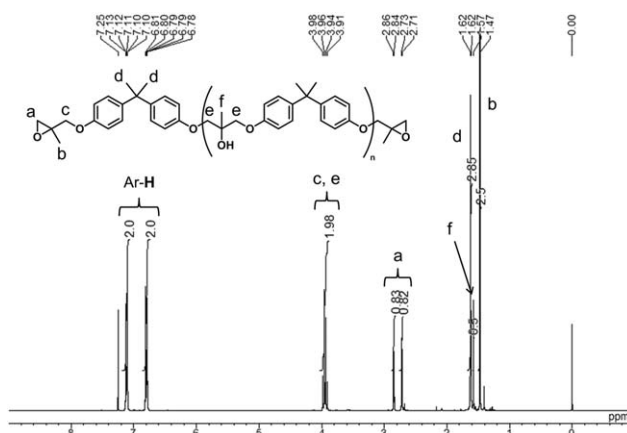

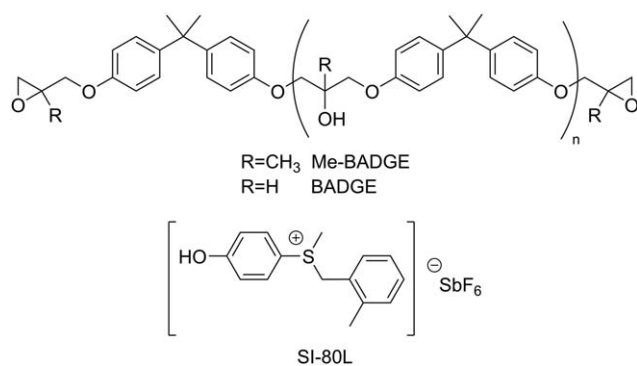**Figure 2.** ^{1}H-NMR spectrum of Me-BADGE.

Figure 3. Materials used for DSC measurement.

Figure 5. Dynamic viscoelasticities of cured products.

ppm. The number average degree of polymerization calculated from integrated value was 0.17.

Cationic Polymerization Behavior of β-Methylglycidyl Ether

To investigate the cationic polymerization behavior of β-methylglycidyl ether, cationic polymerization of Me-BADGE using SI-80L as an initiator (Figure 3) was analyzed by DSC. Figure 4(a) shows the DSC curve in which large and small peaks were observed at 120°C and 157°C. On the other hand, the DSC curve of BADGE in the presence of SI-80L exhibited three peaks at 118°C, 129°C, and 218°C respectively [Figure 4(b)]. Initiation temperatures of the exothermic reactions were determined to be 109°C and 104°C for Me-BADGE and BADGE, respectively. These results mean that cationic polymerization of Me-BADGE using SI-80L initiated at the almost same temperature as that of BADGE. However, completion temperature of the exothermic reactions for Me-BADGE was rather lower than that of BADGE. These results suggested that Me-BADGE can complete the curing reaction at lower temperature than BADGE.

Preparation of Cured Products and their Physical Properties

Cured epoxy resin samples were prepared by heating the epoxy resin/SI-80L mixtures at 120°C for 2 h and then 180°C for 2 h. However, the heating of Me-BADGE/SI-80L generated a black liquid instead of cured product. In contrast, a brown cured product was obtained from BADGE/SI-80L. In order to prepare cured products containing Me-BADGE, copolymerization of Me-BADGE and BADGE was carried out. No cured products
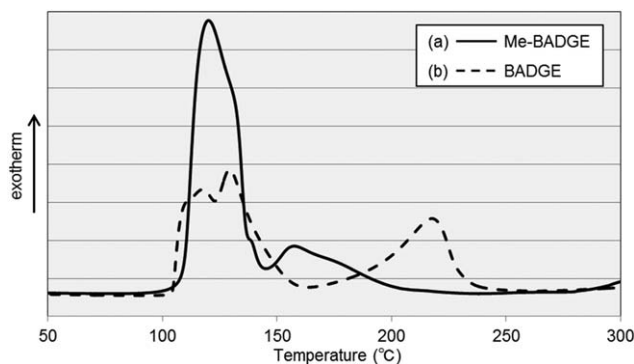

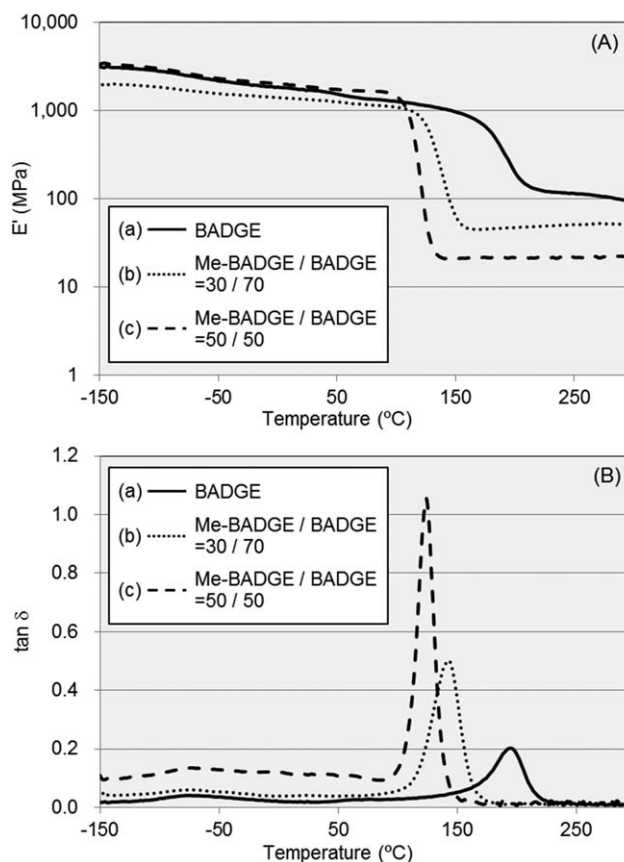Figure 4. DSC curves of Me-BADGE (a) and BADGE (b) in the presence of SI-80L.

were obtained when the BADGE content was less than 30%. On the other hand, dark brown cured products were obtained when the BADGE contents were higher than 50% (Me-BADGE/BADGE=50/50 and 30/70).

The physical properties of these cured products were analyzed by dynamic viscoelasticity (Figure 5). The storage modulus (E') of the cured products of BADGE, Me-BADGE/BADGE = 50/50, and Me-BADGE/BADGE = 30/70 at approximately 25°C were 1.7 GPa, 1.3 GPa, and 1.9 GPa, respectively [Figure 5(A)]. These results suggested that the cured products containing Me-BADGE is hard as much as the homopolymer of BADGE at room temperature. The E' values of all cured products remained almost constant until 100°C. However these values were drastically decreased at slightly lower temperature than the T_g of each cured products. T_g of the cured product of BADGE was observed at 194°C and the peak top value of tan δ was 0.20 [(a) in Figure 5(B)]. On the other hand, T_g of the cured products decreased and the tan δ peak top value increased with the increase of the Me-BADGE content. In addition, the E' of the cured products decreased with the increase of the Me-BADGE content in the temperature higher than T_g. The results suggested that the cured materials containing Me-BADGE were lower crosslink density.

Consideration of Possible Curing Mechanism

To consider the higher reactivity of Me-BADGE, a structure of β-methylglycidyl ether was investigated in detail. Sasaki
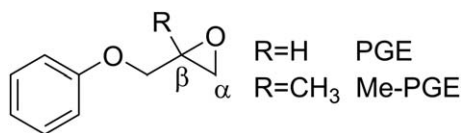
Figure 6. Structure of PGE and Me-PGE.[13]

Table I. Bond Length of Epoxy Group in PGE and Me-PGE[13]

	C_α-O (Å)	C_β-O (Å)	C_α-C_β (Å)
PGE	1.405	1.404	1.453
Me-PGE	1.405	1.410	1.456

calculated the structures of PGE and Me-PGE by molecular orbital method and reported C_β-O bond of Me-PGE was longer than that of PGE (Figure 6 and Table I).[13] IR spectra of PGE and Me-PGE were measured to obtain the further insights of the bond strength of epoxy groups (Figure 7). The peak at 916 cm^{-1} was assigned to C—O bond stretching of epoxy group in PGE [Figure 7(a)]. On the other hand, the peak due to C—O bond stretching of epoxy group in Me-PGE was observed at 900 cm^{-1}, which was lower wavenumber than that of PGE [Figure 7(b)]. These suggested that C—O bond of epoxy group in Me-PGE was weaker than that of PGE. Therefore, it was considered that the high reactivity of Me-BADGE was caused by the weaker C—O bond of epoxy group in Me-BADGE.

Next, to investigate the curing mechanism of β-methylglycidyl ether, monofunctional epoxy compounds (PGE or Me-PGE) were heated in the presence of SI-80L, and the products were analyzed by IR spectroscopy. Figure 8 shows IR spectra of the epoxides before and after heating. In the spectrum after heating of PGE in the presence of SI-80L, the peak at 916 cm^{-1} due to C—O bond stretching of the epoxy group decreased and a new peak appeared at 1131 cm^{-1}, which was assigned to C—O bond stretching of an acyclic ether [Figure 8(A)]. It is suggested that glyceryl ether was provided from epoxy group by the cationic polymerization of PGE. On the other hand, in the spectrum after heating of Me-PGE in the presence of SI-80L, the peak at 900 cm^{-1} which was assigned to C—O bond stretching of the epoxy group disappeared, and new peaks were observed at 1716 cm^{-1} and 3372 cm^{-1} [Figure 8(B)]. The peaks at 1716 cm^{-1} and
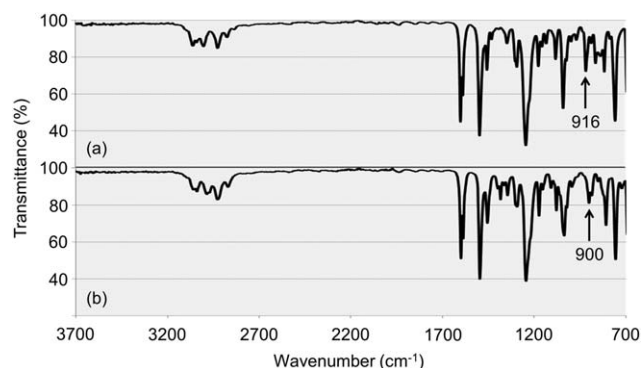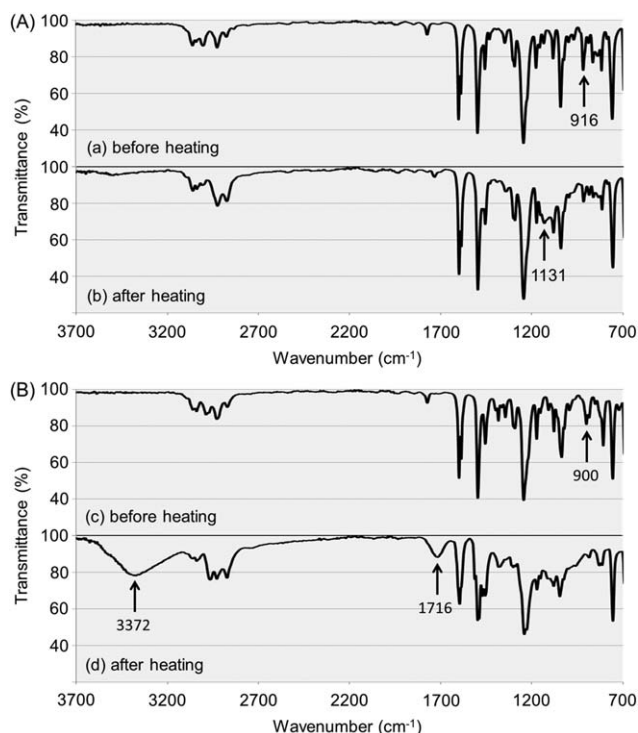

Figure 8. IR spectra before and after heating of PGE (a) and Me-PGE (b) in the presence of SI-80L.

3372 cm^{-1} were assigned to a formyl group and a hydroxyl group, respectively. In the ^{1}H-NMR spectrum after heating of Me-PGE in the presence of SI-80L, a peak due to the formyl group was observed (Figure 9). These results suggested that the epoxy group of Me-PGE converted to formyl group and hydroxyl group under the cationic polymerization conditions.

Based on the results of the IR and NMR analysis, the possible cationic polymerization mechanism of PGE and Me-PGE were shown in Figure 10. In the cationic polymerization of PGE, epoxy group was activated by benzyl cation (Bn$^+$) derived from SI-80L,[14] and a nucleophilic attack of an epoxy oxygen to the activated epoxy carbon gave the oxonium dimer. Polymers were

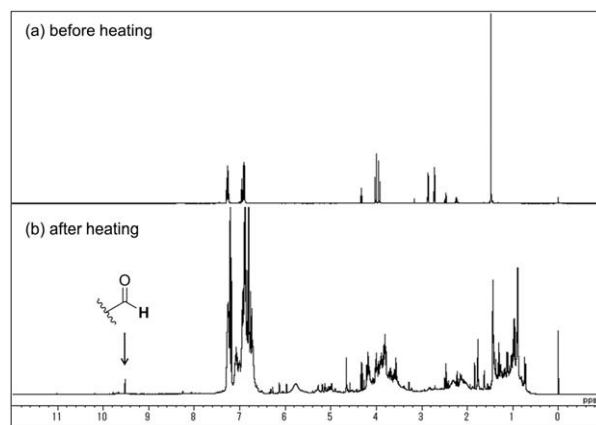Figure 7. IR spectra of PGE (a) and Me-PGE (b).

Figure 9. ^{1}H-NMR spectrum before heating (a) and after heating (b) of Me-PGE in the presence of SI-80L.
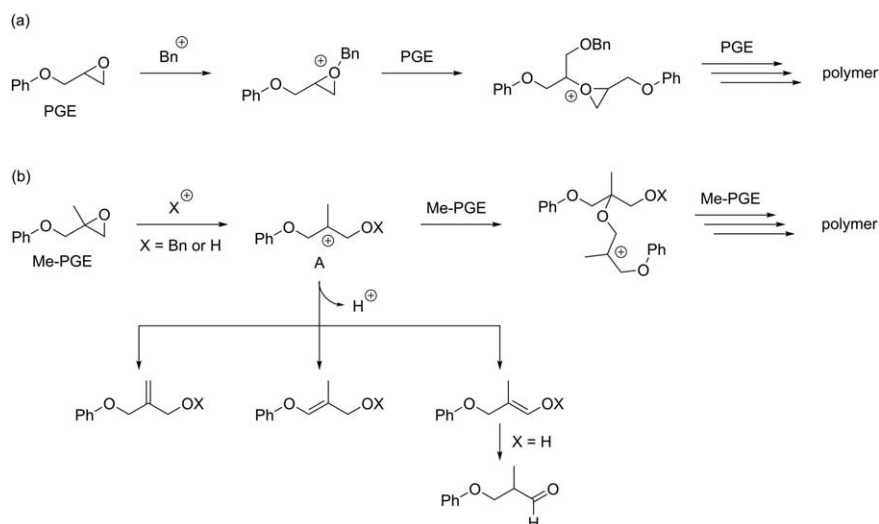
Figure 10. Possible cationic polymerization mechanisms of PGE (a) and Me-PGE (b).

obtained by repeating the activation of epoxy group and nucleophilic attack of PGE [Figure 10(a)].[15] On the other hand, in the cationic polymerization of Me-PGE, intermediate A was generated by ring-opening of the epoxy group after the epoxy group was activated by benzyl cation (Bn^+). This is because Me-PGE has more labile C_β-O bond to provide more stable tertiary carbocation intermediate A. The reaction of the intermediate A and Me-PGE produced the dimer, and polymers were obtained by further reaction. However, the intermediate A could easily undergo elimination of β-proton, and the elimination gave a proton and allyl alcohol derivatives or aldehydes. The eliminated proton (H^+) can reinitiate another cationic polymerization that is a chain transfer reaction. Therefore, polymerization of Me-PGE gave lower molecular weight polymers compared to polymerization of PGE. This phenomenon was confirmed by the SEC measurement of the polymers produced by the cationic polymerization of PGE and Me-PGE (Figure 11).

These results are consistent with the physical properties observed in Figure 5. The cured products containing Me-BADGE were lower crosslink density, which may be due to the frequent chain transfer reactions occurred in the cationic polymerization.
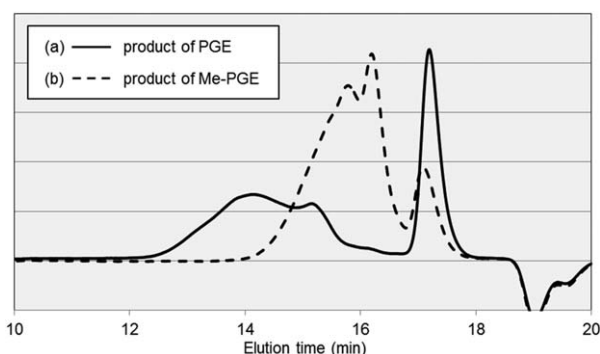
CONCLUSIONS

In this article, we investigated the behavior of cationic polymerization of β-methylglcidyl ether (Me-BADGE), and examined the cationic homo/co-polymerization of Me-BADGE with glycigyl ether (BADGE). In DSC analysis, completion temperature of the curing reaction of Me-BADGE was obviously lower than that of BADGE. It is suggested that Me-BADGE can complete the curing reaction at lower temperature than BADGE. Cationic homopolymerization of Me-BADGE did not give cured materials. On the other hand, copolymerization in which BADGE content was higher than 50% gave cured materials. Glass transition temperatures of the cured materials decreased with increasing the Me-BADGE content of the copolymers. By analyzing the cationic polymerization of monofunctional compound, Me-PGE, it was found that the C—O bond on the tertiary carbon atom of epoxy group in Me-PGE was more preferably cleaved. This is presumably due to the formation of stable tertiary carbocation intermediate. The polymerization with frequent chain transfer reactions may be the cause for the lower T_gs of the cured materials containing Me-BADGE.

These data suggested that the β-methylglycidyl ether is useful epoxy resins especially as adhesives, which are required to be cured rapidly at lower temperature. We expect that the obtained insights will be useful to develop novel epoxy-based functional materials.

Figure 11. SEC curves of cationic polymerization products of PGE (a) and Me-PGE (b).

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