

Volume-Expandable Monomer 5,5-Dimethyl-1,3-dioxolan-2-one: Its Copolymerization Behavior with Epoxide and Its Applications to Shrinkage-Controlled Epoxy-Curing Systems

Hiroshi Morikawa,¹ Atsushi Sudo,¹ Haruo Nishida,¹ Takeshi Endo^{1,2}

¹Henkel Research Center of Advanced Technology, Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan

²Faculty of Engineering, Yamagata University, 4-3-6 Jyonan, Yonezawa, Yamagata 992-8510, Japan

Received 30 April 2004; accepted 11 October 2004

DOI 10.1002/app.21431

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The copolymerization of epoxides and a six-membered cyclic carbonate, 5,5-dimethyl-1,3-dioxan-2-one (DM6CC), was carried out with 1,8-diazabicyclo[5.4.0]undec-7-ene as an initiator. In the copolymerization of glycidyl phenyl ether (GPE) and DM6CC, DM6CC remarkably accelerated the polymerization rate of GPE and also effectively suppressed chain-transfer reactions, which occur in the homopolymerization of the epoxide. This suppression resulted in the formation of the corresponding copolymer with a higher molecular weight. Similar effects of DM6CC

were also observed in a curing system with a Novolac-type multifunctional epoxide (Novolac glycidyl ether). The curing reaction of the epoxide in the presence of DM6CC smoothly proceeded and yielded the corresponding networked polymer, showing a decrease in the volume shrinkage as the DM6CC content increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 372–378, 2005

Key words: anionic polymerization; polycarbonates; ring-opening polymerization; volume change; epoxide

INTRODUCTION

Six-membered cyclic carbonate (6CC) undergoes both cationic and anionic polymerizations^{1–7} and thus is expected to be adopted to various curing systems under a wide range of reaction conditions.^{8–10} A more attractive feature of 6CC is its intrinsic volume-expandable nature during polymerizations (degree of expansion = 3.3–7.7%).⁹

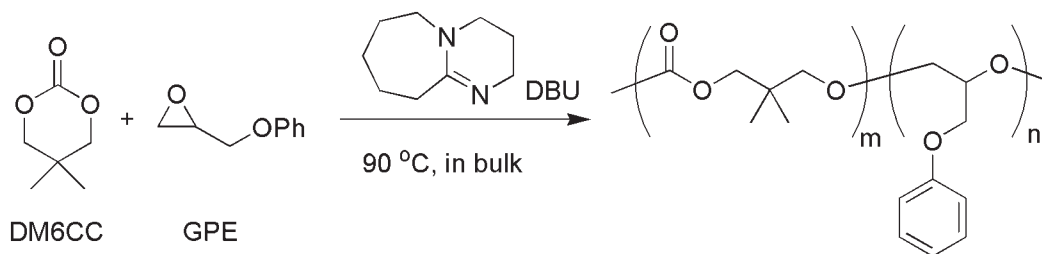
The polymerization of epoxy monomer always suffers from a significant degree of volume shrinkage (4–5%).^{11,12} In the field of adhesive and coating applications, this shrinkable nature of epoxy monomer leads to the formation of voids and microcracks in the formed material, which reduce its mechanical properties. The addition of an inorganic filler is the usual way of solving this shrinkage problem, but it is normally accompanied by several disadvantages, such as a serious increase in the viscosity of the formulation. On the other hand, the addition of a volume-expandable monomer to the polymerization of epoxides would be a more fundamental solution because the

shrinkable nature of epoxides can be compensated by the inherent nature of the expandable monomer. 6CC is a typical expandable monomer and is polymerizable under the same conditions required for epoxide polymerization. Despite the potential of 6CC to modify epoxy formulations into less shrinkable ones for precise adhesion and coatings, only a few reports have dealt with its copolymerization with epoxide monomers.^{13,14} In our previous study,¹³ the copolymerization of glycidyl naphthyl ether and 5,5-(bicyclo[2.2.1]hept-2-en-5,5-ylidene)-1,3-dioxan-2-one was used to achieve a shrinkage-free curing formulation. On the basis of this successful result for a specific combination of monomers, we next focused our attention on the development of more general methods to modify epoxy formulations by the addition of 6CC.

This article describes one of our current studies on shrinkage-free epoxy resin systems containing volume-expandable monomers, focusing on a simple combination of glycidyl phenyl ether (GPE) and 5,5-dimethyl-1,3-dioxan-2-one (DM6CC). It consists of (1) detailed information on the anionic copolymerization of DM6CC and epoxide, providing us with some new aspects on the reaction mechanism, and (2) information on the addition effects of DM6CC for a curing reaction of a multifunctional epoxy monomer, which involves the precise evaluation of the degree of the corresponding volume change.

Correspondence to: T. Endo (tendo@mol-eng.fuk.kindai.ac.jp).

Contract grant sponsor: Henkel KGaA.



Scheme 1

EXPERIMENTAL

Materials

DM6CC was prepared from 2,2-dimethyl-1,3-propanediol and ethyl chloroformate according to the literature.⁵ GPE (99%) was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), and was purified by distillation over calcium hydride under reduced pressure (66–68°C at 100 Pa). A multifunctional epoxide, Novolac glycidyl ether (NGE), the epoxy equivalent of which was 175 g, was supplied by Nihon Kayaku Co., Ltd. (Tokyo, Japan), and was used as received. The initiator 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 97%), was purchased from Wako Chemicals Co., Ltd. (Osaka, Japan), and was purified by distillation.

Measurements

¹H-NMR spectra were recorded on a Varian Inova 400 VLX spectrometer (Varian; Palo, Alto, CA) with tetramethylsilane as an internal standard in chloroform-*d* (CDCl₃). Number-average (M_n) and weight-average (M_w) molecular weights were estimated by size exclusion chromatography (SEC) on a Tosoh HPLC-8220 system (Tosoh; Tokyo, Japan) with refractive-index and ultraviolet (wavelength = 254 nm) detectors under the following conditions: TSKgel Super HM-H linear column (linearity range = 1×10^3 to 8×10^6 ; molecular weight exclusion limit = 4×10^8), chloroform (high-performance-liquid-chromatography-grade) as an eluent at a flow rate of 0.6 mL min⁻¹, and

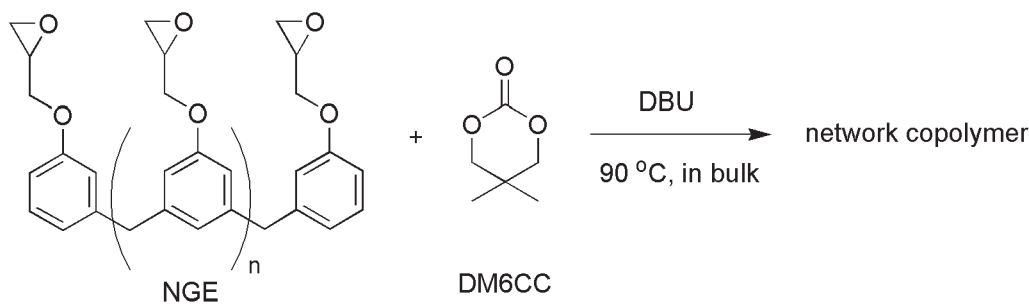
a column temperature of 40°C. The calibration curves for SEC analysis were obtained with polystyrene standards with a low polydispersity. Dynamic mechanical analysis (DMA) was performed with a non-resonance-forced vibration viscoelastometer (DVE-4, Rheology Co., Ltd., Kyoto, Japan) at a heating rate of 2°C min⁻¹. The frequency and amplitude of the vibration were adjusted to 10 Hz and 5 μm, respectively.

Copolymerization of GPE with DM6CC (scheme 1)

In a typical procedure, GPE (0.377 g, 2.51 mmol) and DM6CC (0.325 g, 2.50 mmol) were placed in a 3-mL silanized vial, and then DBU (30 μL, 0.2 mmol) was added. The vial was filled with argon gas, sealed, and heated at 90°C in an oil bath. After stirring for 4 h, the reaction mixture was cooled to the ambient temperature, and a solution of acetic acid (50 μL) in dichloromethane (1 mL) was added to quench the reaction. The ¹H-NMR spectrum of the reaction mixture was then measured, and the conversion values of the monomers were calculated from integral values of the corresponding signals of both the monomers and the copolymer in the ¹H-NMR spectrum. The average molecular weights of the copolymer were estimated by SEC analysis.

Copolymerization of NGE with DM6CC (scheme 2)

In a typical procedure, a mixture of NGE (11.62 g, 66.4 mmol for the epoxy moiety) and DM6CC (2.16 g, 16.6 mmol) was degassed for 30 min under reduced pres-



Scheme 2

TABLE I
Anionic Ring-Opening Copolymerization of GPE with DM6CC^a

Sample	DBU (mol %) ^b	Feed ratio [GPE]:[DM6CC]	Time (h)	Conversion (%) ^c		M_n ^d	M_w ^d
				GPE	DM6CC		
G-1	4	100:0	12	30	—	640	770
G-2	4	100:0	90	39	—	650	860
G-3	20	100:0	12	> 90	—	640	830
G-4	4	80:20	12	95	97	1,060	1,570
G-5	4	67:33	12	96	94	1,080	1,670
G-6	4	50:50	1	43	97	1,030	2,120
G-7	4	50:50	4	91	99	1,020	1,820
G-8	1	50:50	1	< 5	97	2,540	7,950
G-9	1	50:50	4	25	98	2,220	5,160

^a Copolymerization at 90 °C in bulk.

^b Based on the total amount of monomers.

^c Determined by ¹H-NMR analysis.

^d Estimated by SEC with polystyrene standards.

sure. Then, DBU (490 μ L, 3.32 mmol) was added to the mixture and stirred for 10 min. For the measurement of the density value of the mixture before the curing reaction, the mixture was transferred to a 5.00-mL volumetric flask at 23°C, and the flask was weighed. Next, the mixture was transferred into a silicon rubber mold in an argon atmosphere and cured at 90°C for 12 h in a thermostated oven to obtain the cured product, the density of which was measured with an electronic densimeter (MD-200S, Alfa Mirage Co., Ltd., Osaka, Japan) at 23°C. The cured product was extracted with refluxing chloroform in a Soxhlet extraction apparatus and separated into insoluble and soluble parts. The soluble part was dried under reduced pressure and weighed to calculate the gel fraction ratio to avoid the measurement error caused by the weight of chloroform that could not be removed from the insoluble part.

RESULTS AND DISCUSSION

Copolymerization of GPE with DM6CC

The copolymerization of GPE with DM6CC was carried out at 90°C with DBU as an anionic initiator in bulk. The homopolymerization of GPE was performed under similar conditions. The results are listed in Table I.

The homopolymerization of GPE with 4 mol % DBU proceeded so slowly that the conversion reached only 39% even after 90 h. The homopolymerization quantitatively proceeded with 20 mol % DBU after 12 h. However, because of the significant chain-transfer reactions often occurring during the epoxide polymerization, no polymeric product with $M_n > 1000$ was detected.

This limit in M_n could be contrasted with the copolymerization of GPE with DM6CC, which smoothly proceeded to give the corresponding copolymers with

higher molecular weights. The copolymer structure was determined by ¹H-NMR spectrum analysis, and a typical ¹H-NMR spectrum of the reaction mixture is shown in Figure 1 (sample G-7 in Table I). The major signals at 1.00 and 3.96 ppm, which were assigned to methyl and methylene protons (*a* and *b*) adjacent to carbonate groups,⁵ show the predominance of the homosequence DM6CC–DM6CC. The signals at 6.8–7.4 ppm and 4.1 ppm, which were attributed to phenyl protons (*f–h*) and methylene protons (*e*), indicate the GPE unit in the copolymer. The presence of the heterosequence DM6CC–GPE was also confirmed by the signals at 0.85–0.95 and 5.0–5.2 ppm, which were attributed to methyl protons *a'* and methine proton *d'* in the heterosequence unit, respectively. Small signals at 4.03 and 4.45–4.65 ppm were assigned to the protons of the vinylidene group and α -methylene group between the vinylidene and phenoxy groups at the chain ends, these groups being formed by the chain-transfer reactions.^{15,16}

The conversion of DM6CC was calculated from the intensity ratio of the signals at 0.85–1.0 and 1.13 ppm, which were attributed to methyl protons of the copolymer and monomer, respectively. On the other hand, the conversion of GPE was calculated from the integrated intensity of the doublet at 2.73–2.88 ppm, which was attributed to methylene protons of GPE, in comparison with that attributable to the phenyl protons (*f–h*).

As shown in Table I, the addition of DM6CC to GPE caused the quantitative consumption of GPE within 12 h (G-4 and G-5). The addition of 50 mol % to the feed induced a much higher reaction rate of GPE and resulted in a GPE conversion of 91% after 4 h. Interestingly, despite the conversion of DM6CC reaching 97% after 1 h (sample G-6), GPE was smoothly converted from 43% after 1 h to 91% after 4 h (sample G-7). The same result was obtained with 1 mol % DBU

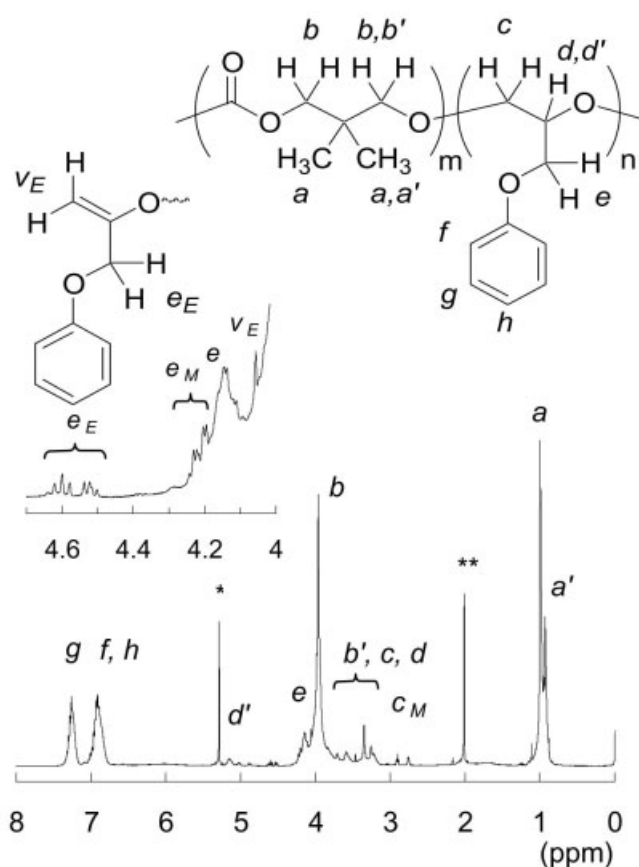


Figure 1 $^1\text{H-NMR}$ spectrum obtained from the copolymerization of GPE with DM6CC (sample G-7 in Table I). c_M and e_M represent the methylene and methine protons, respectively, in the GPE monomer; the double asterisk and the single asterisk represent CH_3COOH as a quencher and CH_2Cl_2 as a solvent, respectively.

(samples G-8 and G-9). These results suggest that the reaction of GPE was accelerated by the carbonate groups not only in DM6CC but also in the copolymers.

In Figure 2, methyl proton signals a and a' in homosequence and heterosequence units are shown with the integrated value ratio, $a:a'$. Obviously, signal a changed to signal a' as both the reaction time and the feed ratio of GPE were increased. This shows the change from the homosequence to the heterosequence in the copolymer. Furthermore, the average molecular weights of the copolymer decreased with the reaction time (G-6 vs G-7 and G-8 vs G-9 in Table I). This reduction may have been caused by a chain-transfer reaction of DM6CC in the copolymer. Taking all of these results into consideration, we can summarize the copolymerization behavior as follows:

1. The polymerization rate of DM6CC in the anionic process was much higher than that of GPE because the carbonyl carbon in the DM6CC unit was more electron-negative on account of the three adjacent oxygen atoms.

2. The addition of DM6CC effectively accelerated the polymerization of GPE.
3. It was suggested that the DM6CC unit in the copolymer had a similar acceleration effect.
4. An increase in the amount of DM6CC in the feed led to the formation of copolymers with higher molecular weights in the early stage of the copolymerization. However, the molecular weight gradually decreased with the reaction time.

Mechanism of copolymerization

Scheme 3 shows possible reactions involved in the copolymerization, some of which are chain-transfer reactions. One of the chain-transfer reactions is proton abstraction (path A).^{15,16} This reaction occurs when alkoxide anions at the propagating ends abstract protons from the tertiary carbons in the GPE monomer and in the GPE unit on the copolymer chain; this results in less reactive species such as enolate and phenolate anions. This kind of degradative chain-transfer reaction leads to a lower conversion and molecular weight. Such degradative chain reactions are prevented from occurring in the presence of DM6CC. Here, the copolymerization smoothly proceeded, with the addition reaction of DM6CC being in equilibrium with the back-biting depolymerization (path B).^{1,5} This

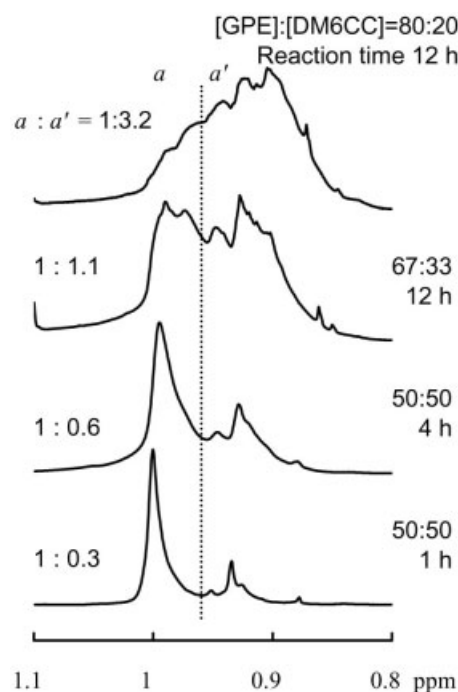
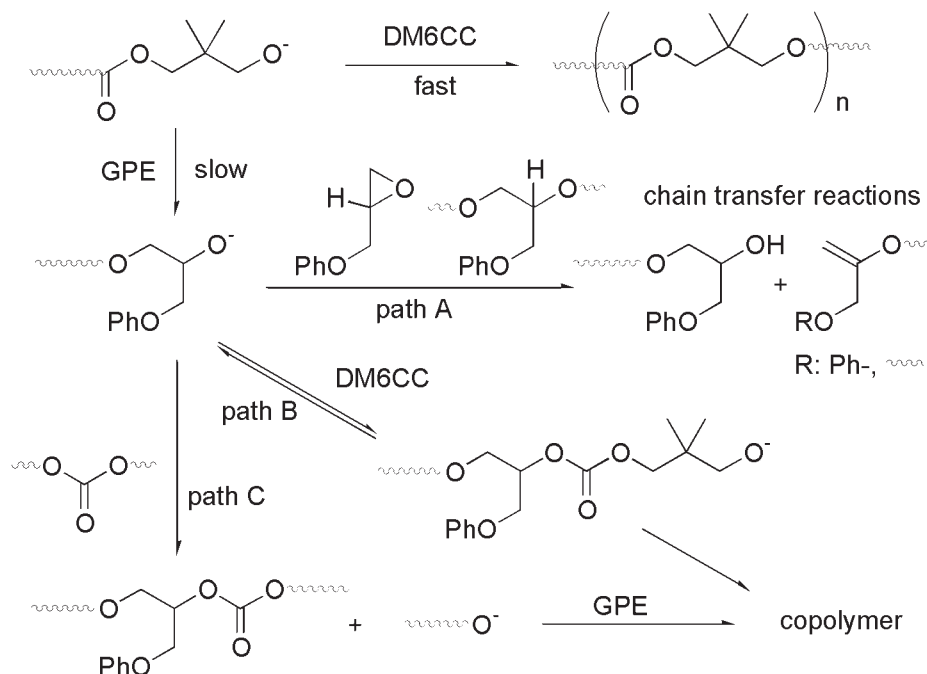


Figure 2 $^1\text{H-NMR}$ spectra obtained from the copolymerization of GPE with DM6CC with 4 mol % DBU. [GPE]:[DM6CC] was 80:20 for sample G-4, 67:33 for sample G-5, 50:50 for sample G-7 (reaction time = 4 h), and 50:50 for sample G-6 (reaction time = 1 h). $a:a'$ is the integrated value ratio.



Scheme 3

equilibrium most likely prevents the active chain ends from causing the degradative chain-transfer reactions.

Scheme 3 also depicts the acceleration process by the DM6CC unit in the copolymer (path C). Once the DM6CC has been completely converted, other types of chain-transfer reactions by terminal alkoxides may then occur on a DM6CC unit in the copolymer.¹⁷ The chain-transfer reaction to the polymer chain produces an active primary alkoxide terminal, thereby effectively consuming GPE. At the same time, this chain-transfer reaction causes a decrease in M_w of the copolymer. The predicted reduction is in good agreement with the results in Table I.

In summary, the addition of DM6CC suppressed the degradative chain-transfer reactions in the homopolymerization of GPE, and this accelerated the copolymerization and yielded higher molecular weight copolymers. The DM6CC units in the copolymer chains may induce other types of chain-transfer reactions by active chain ends, leading to an increase in the GPE conversion and a decrease in the molecular weight of the copolymer.

Copolymerization of NGE with DM6CC

Because DM6CC is an effective volume-expandable monomer,⁹ its addition to a bulk curing system with a multifunctional epoxide would be a promising way to develop a shrinkage-controlled curing system. To demonstrate this valuable effect, we used NGE, a commonly used multifunctional epoxide, for the copolymerization system with DM6CC (Scheme 2). The cur-

ing reaction was carried out with various feed ratios [Epoxide] : [DM6CC] at 90°C for 12 h in bulk with 4 mol % DBU based on the total amounts of the DM6CC and epoxide moiety. The homopolymerization of NGE was carried out with 20 mol % DBU to obtain a cured product. The volume change during the curing reaction was calculated from the density of a mixture of the monomers in comparison with that of the resulting cured product. The results are listed in Table II.

The homopolymerization of NGE resulted in a cured product with a volume shrinkage of 3.9% (sample R-0). Compared with the homopolymerization, the copolymerization of NGE with DM6CC successfully produced cured resins with a higher stiffness. This improved stiffness of the cured products must have been due to the high conversion of the epoxide moiety caused by the addition of DM6CC. The gel fraction ratio, which was estimated in terms of the ratio of the weight of the chloroform-insoluble fraction to that of the total cured product, was 99 wt % for samples R-1 and R-2, and this indicated high conversions of both monomers in the curing reaction. However, the gel fraction ratio of sample R-3 was 90 wt %, and the soluble part mainly consisted of polymeric components with high DM6CC unit contents. These results indicated that there was an optimum feed ratio to accomplish complete curing.

The volume shrinkage of this system was lessened as the amount of DM6CC increased; we obtained shrinkage values of 3.7, 2.9, and 1.7% for samples R-1, R-2, and R-3, respectively. In Figure 3, the relationship between the DM6CC feed ratio and the volume

TABLE II
Curing Reaction of NGE and DM6CC^a

Sample	DBU (mol%) ^b	Feed ratio [Epoxide]:[DM6CC]	Density (g/cm)		Volume change (%)	Soluble part (wt %) ^c
			Mixture of monomers	Cured product		
R-0	20	100:0	1.166	1.213	-3.9	nd ^d
R-1	4	80:20	1.175	1.221	-3.7	< 1
R-2	4	67:33	1.180	1.216	-2.9	< 1
R-3	4	50:50	1.185	1.206	-1.7	10
Literature data ^a		0:100	1.238	1.197	3.3	

nd = not determined.

^a Curing reaction at 90°C for 12 h in bulk.

^b Based on the total amount of monomers.

^c Extracted with refluxing CHCl₃.

^d [DBU] = 20 mol %.

change value is plotted, and it suggests that no shrinkage in the copolymerization occurred with 62 mol % DM6CC in the feed. In this plot, the deviation of the NGE homocured product (sample R-0) must be due to contributions of the additional 20 mol % DBU and unreacted epoxide moieties.

Thermomechanical properties of the cured samples

The thermomechanical properties of the cured products were measured with DMA as shown in Figure 4. The DMA profiles exhibit typical tensile relaxation modulus curves for thermosetting resins.^{18,19} After the storage modulus (E') decreased in the first transition temperature range, it was then kept in the range of 10^7 – 10^8 Pa without melting. The $\log E'$ curve of sample R-1 showed a glass-transition profile in a relatively broad temperature range (40–120°C) and over 120°C gradually increased with an increase in the temperature. The increase in E' was due to a postcuring of

unreacted epoxy moieties remaining at a high level in the sample. Sample R-2 showed a relatively sharp transition profile and the highest glass-transition temperature (T_g) in the $\tan \delta$ curve, and this suggested a homogeneous network structure. The broadest $\tan \delta$ profile at the lowest temperature range (20–110°C) was observed for sample R-3, which had a high concentration of the DM6CC unit. The broadness of this $\tan \delta$ curve must be attributed to the presence of plural components such as DM6CC-unit-rich and NGE-unit-rich segments because the T_g values of the homopolymers were reported to be 27 and greater than 100°C for poly(5,5-dimethyl-1,3-dioxan-2-one) and poly(Novolac glycidyl ether), respectively.^{18–20} This result reflects the difference in the reactivities between the epoxide and DM6CC, which must have led to the formation of the DM6CC-unit-rich segment with its low crosslinking degree. Indeed, this DM6CC-rich segment was separated as a chloroform-soluble part

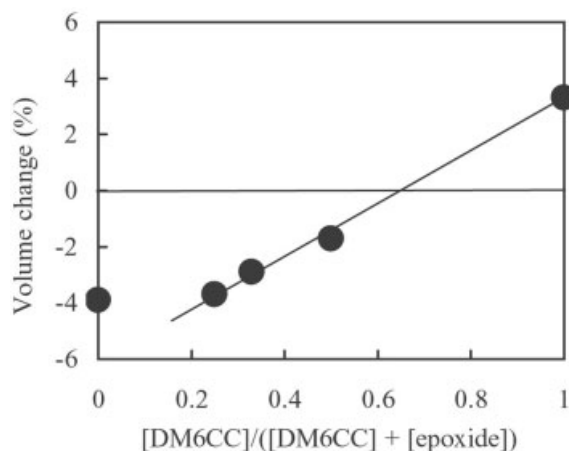


Figure 3 Volume change in the curing reaction of NGE and DM6CC with 4 mol % DBU at 90°C for 12 h in bulk. In the case of $[\text{DM6CC}]/([\text{DM6CC}] + [\text{epoxide}]) = 0$; 20 mol % DBU was used.

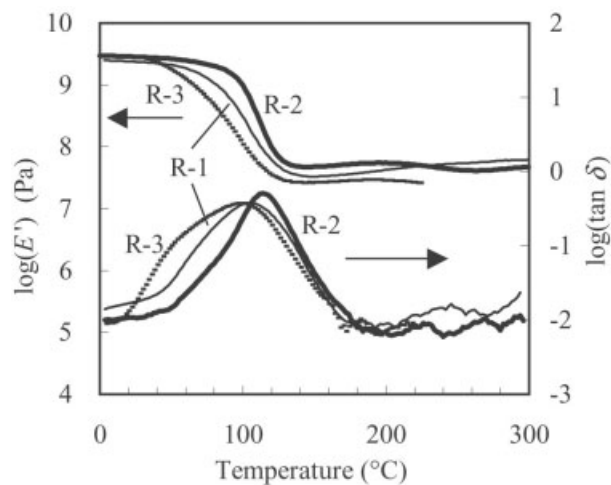


Figure 4 Dynamic mechanical properties of cured products of NGE and DM6CC with 4 mol % DBU at 90°C for 12 h in bulk. The feed ratio of epoxide to DM6CC was 80:20 for sample R-1, 67:33 for sample R-2, and 50:50 for sample R-3.

with the Soxhlet extraction method. Therefore, to obtain a homogeneous cured product with good properties, a proper feed ratio should be selected according to each combination used.

CONCLUSIONS

The copolymerization of epoxides with DM6CC was investigated with the anionic initiator DBU. In the copolymerization of the monofunctional epoxide GPE and DM6CC, carbonate groups accelerated the reaction, and this resulted in the almost complete consumption of GPE. Such an acceleration effect was also observed in the carbonate groups that were incorporated into polymer chains. In the curing system of the multifunctional epoxide NGE and DM6CC, the homogeneous cured product with the highest T_g value was obtained at a proper epoxide/DM6CC feed ratio of 0.67:0.33. With an increase in the feed of DM6CC, the volume shrinkage of the cured product was reduced to a minimum of 1.7% at the feed ratio of 50:50, as opposed to 3.9% for the homopolymer of NGE. Knowing the effects of the acceleration and reduction in the volume shrinkage of DM6CC will be very valuable for developing new curable formations for precise adhesion.

The authors greatly thank M. Ochi of the Faculty of Engineering at Kansai University for the dynamic mechanical analysis measurements.

References

1. Keul, H.; Bächer, R.; Höcker, H. *Makromol Chem* 1986, 187, 2579.
2. Zhu, K.-J.; Hendren, R. W.; Jensen, K.; Pitt, C.-G. *Macromolecules* 1991, 24, 1736.
3. Kricheldorf, H.-R.; Weegen-Schulz, B. *Macromolecules* 1993, 26, 5991.
4. Ariga, T.; Takata, T.; Endo, T. *Macromolecules* 1997, 30, 737.
5. Matsuo, J.; Aoki, K.; Sanda, F.; Endo, T. *Macromolecules* 1998, 31, 4432.
6. Sanda, F.; Fueki, T.; Endo, T. *Macromolecules* 1999, 32, 4220.
7. Ling, J.; Shen, Z.; Huang, Q. *Macromolecules* 2001, 34, 7613.
8. Takata, T.; Sanda, F.; Nemoto, T.; Endo, T. *Prog Polym Sci* 1993, 18, 839.
9. Takata, T.; Sanda, F.; Ariga, T.; Nemoto, H.; Endo, T. *Macromol Rapid Commun* 1997, 18, 461.
10. Matsuo, J.; Sanda, F.; Endo, T. *Macromol Chem Phys* 1998, 199, 2489.
11. Endo, T.; Ogasawara, M. *J Thermosetting Plast Jpn* 1984, 5, 98.
12. Takata, T.; Endo, T. In *Expanding Monomer: Synthesis, Characterization, Application*; Sadher, R. K.; Luck, R. M., Eds.; CRC: Boca Raton, FL, 1992; p 63.
13. Murayama, M.; Sanda, F.; Endo, T. *Macromolecules* 1998, 31, 919.
14. Hino, T.; Endo, T. *Macromolecules* 2003, 36, 5902.
15. Vazquez, A.; Bentaleb, D.; Williams, R. J. J. *J Appl Polym Sci* 1991, 43, 967.
16. Vázquez, A.; Deza, R.; Williams, R. J. J. *Polym Bull* 1992, 28, 459.
17. Li, M.-S.; Ma, C.-C. M.; Chen, J.-L.; Lin, M.-L.; Chang, F.-C. *Macromolecules* 1996, 29, 499.
18. Ochi, M.; Shimizu, Y.; Nakanishi, Y.; Murata, Y. *J Polym Sci Part B: Polym Phys* 1997, 35, 397.
19. Ochi, M.; Takahashi, R. *J Polym Sci Part B: Polym Phys* 2001, 39, 1071.
20. Kühling, S.; Keul, H.; Höcker, H.; Buysch, H.-J.; Schön, N. *Macromolecules* 1991, 24, 4229.