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Effect of Oligo(spiroorthocarbonate)s on the Volume Shrinkage of Epoxides during Crosslinking by Sulfonium Salt-Initiated Cationic Polymerization of Epoxides

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ABSTRACT

Oligo(spiroorthocarbonate)s **1**, which were synthesized by the polycondensation of pentaerythritol-derivatives with tetraethylorthocarbonate, were employed as comonomers in the cationic polymerization of epoxide initiated by sulfonium salt. In the copolymerization, the spiroorthocarbonate moiety of **1** underwent double ring-opening reaction, leading to the efficient **diminution** of the volume shrinkage upon the copolymerization. Thermal properties of the resulting networked polymers were evaluated by thermogravimetric analysis (TGA).

KEYWORDS: epoxide; oligo(spiroorthocarbonate); volume shrinkage; cationic polymerization; ring-opening polymerization

INTRODUCTION

Epoxide-based materials are important for adhesive, sealant, and coating applications.¹ One of the serious problems of the epoxides has been the volume shrinkage that accompanies the ring-opening polymerization. The volume shrinkage causes adhesion failure, formation of void and microcrack, and residual stress in the resulting polymers. **The epoxy-cation curing system has been used in electro-chip bonding and dental treatment, where highly precise control of shapes and sizes with minimizing volume shrinkage is necessary. These circumstances have prompted us to develop useful comonomers that undergo copolymerization with epoxide with showing volume expansion.**²

Spiroorthocarbonates (SOCs) have been known as a class of volume expanding monomers. Their cationic ring-opening polymerization accompanies volume expansion or no volume shrinkage as a result of the double ring-opening reaction involved in the polymerization mechanism.^{2,3} Based on this volume expanding nature, copolymerization of epoxides with SOC has been investigated with **the hypothesis** that the volume expansion arisen by the double ring-opening reaction of SOC would compensate the shrinkage caused by the polymerization of epoxides (Scheme 1).⁴⁻¹⁷ As expected, the addition of SOC resulted in remarkable suppression of the volume shrinkage; however, the use of SOC as comonomers often gives polymers with seriously deteriorated thermal stability because of the decrease in crosslinking degree as well as the incorporation of the

flexibility of the SOC-derived units in the main chains.⁵⁻¹³

Recently, we reported a facile synthesis of oligo(spiroorthocarbonate)s **1**, a new series of multifunctional SOC, by polycondensation of tetraethylorthocarbonate with pentaerythritol or its derivatives.¹⁸ As shown in Scheme 2, **1** bearing various substituents can be prepared. In contrast to unsubstituted **1a** insoluble in any organic solvents,¹⁹ the other ones **1b-1d** gained much higher solubility as a result of the introduction of substituents in the side chains. Due to the presence of SOC moieties in the main chain, **1a** underwent cationic crosslinking to give the networked poly(ether-carbonate) with exhibiting 29% volume expansion during the polymerization.²⁰ This volume expanding nature as well as ability to afford crosslinked structure make oligo(spiroorthocarbonate)s **1** highly attractive as potential additives for curing system of epoxy monomers.

Here, we report a sulfonium salt-initiated cationic copolymerization of bisphenol A-diglycidyl ether (BADGE) and **1** (Scheme 2). As the initiator, a benzylium salt BHPMS-HFA was employed.²¹ This sulfonium salt that can be obtained easily by S-methylation of inexpensive 4-(methylthio)phenol has been practically used as a thermally latent cationic initiators for polymerization of epoxides. The shrinkage suppression effects of **1** and the thermal properties of the resulting polymers are presented.

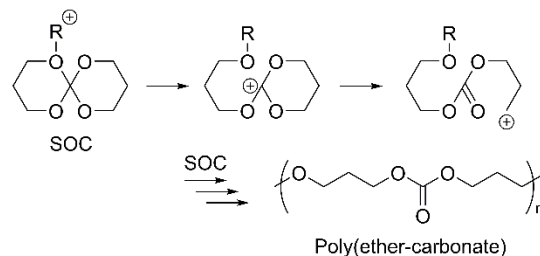
EXPERIMENTAL

Materials

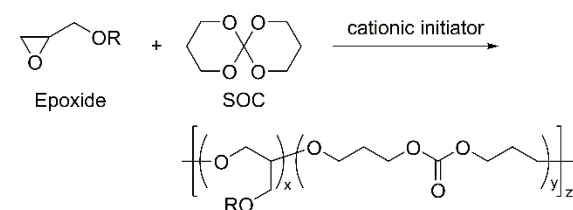
Benzyl(4-hydroxyphenyl)methylsulfonium hexafluoroantimonate (BHPMS-HFA) was provided by Sanshin Chemical Industry Co., Ltd. and was used without further purification. Bisphenol A-diglycidyl ether (BADGE) was purchased from Tokyo Chemical Industry Co., Ltd. and was used without further purification. Oligo(spiroorthocarbonate)s **1a**, **1b** ($M_n = 1000$,

$M_w/M_n = 1.61$), **1c** ($M_n = 1500$, $M_w/M_n = 1.81$), and **1d** ($M_n = 1300$, $M_w/M_n = 1.86$) were synthesized by the previously reported method.¹⁸ The number-average molecular weights (M_n) and weight-average molecular weights indices (M_w) were estimated by size exclusion chromatography (eluent = DMF with 10 mM LiBr, polystyrene standards). In the calibration, polystyrene standards were used for the determination of their elution times. The molecular weights of **1** were estimated based on the comparison of their elution times with those of the standards.

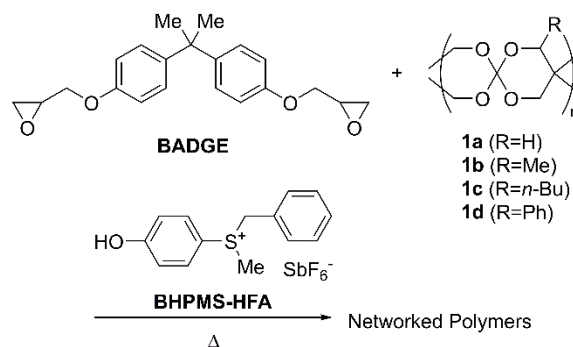
Double Ring-Opening Polymerization of SOC



Copolymerization of SOC with Epoxides



SCHEME 1. Double ring-opening polymerization of SOC and copolymerization of SOC with Epoxides.



SCHEME 2. Cationic copolymerization of BADGE with **1**.

Instruments

Infrared spectra were recorded on a Thermo Fischer Scientific Nicolet iS10 spectrometer with attenuated total reflection (ATR) method. Thermogravimetric analysis (TGA) was carried out on a Seiko Instrument Inc. TG-DTA 6200 with an aluminum pan under 200 mL/min N₂ flow at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis was carried out on a Seiko Instrument Inc. DSC-6200R with an aluminum pan under 50 mL/min N₂ flow at a heating rate of 10 °C/min. The measurement of density was carried out with SHIMADZU AccuPyc 1330 gas pycnometer.

Sulfonium Salt-Initiated Cationic Copolymerization of BADGE with Oligo(spiroorthocarbonate)s **1**

Typical Procedure: BADGE (1.685 g, 4.95 mmol), **1b** (7.9 mg, amount of SOC unit in **1b** = 0.05 mmol), and BHPMS-HFA (46.7 mg, 0.01 mmol) were mixed to obtain the corresponding curable formulation. The formulation was divided into three portions: The first portion was for its TGA analysis, the second one was for its DSC analysis, and the third one was for density measurement by a gas-pycnometer. The third one was poured into a measurement cell for density measurement and de-aerated under vacuum for 1 h, and then its density was measured. The density measurement was performed five times and the average of the middle three data was calculated. This density was defined as D_{before} . Then, the formulation was transferred into a vial, and was de-aerated under vacuum for 1 h. Then, the formulation was heated at 180 °C for 1 h. The resulting solid was dried for 1 h and its density, D_{after} , was measured. The volume change degree was calculated according to the equation: volume change degree [%] = $[1 - (D_{\text{after}})/(D_{\text{before}})] \times 100$.

RESULTS AND DISCUSSION

Sulfonium Salt-Initiated Copolymerization of BADGE with Oligo(spiroorthocarbonate)s **1**

As shown in Scheme 2, **1** was added as a comonomer to a sulfonium salt-initiated polymerization of BADGE. First, **1b** bearing methyl group in the side chain was employed. The molar ratio [BADGE]₀:[SOC unit in **1b**]₀:[BHPMS-HFA]₀ was 95:5:2. The polymerization behavior was studied with differential scanning calorimetric (DSC) analysis. As shown in Figure 1(a), the resulting thermogram consisted of two exothermic peaks. Besides, the polymerization behavior in the absence of **1b** was studied similarly with DSC, with setting the initial molar ratio [BADGE]₀:[BHPMS-HFA]₀ to 100:2. The resulting thermogram, shown in Figure 1 (b), was quite similar to that for the polymerization in the presence of **1b**. Although the reason for the presence of the two exothermic peaks is not clear at present, we speculate that there would be two initiation mechanisms, and the two exotherms could be attributed to them. The exotherm in the lower temperature region could be due to the polymerization initiated by the phenol moiety in the initiator. The other exotherm in the high temperature region would be the polymerization initiated by the benzyl cation dissociated from the sulfonium salt.

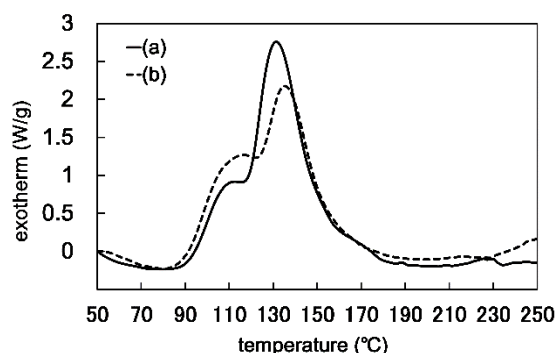


FIGURE 1. DSC profile for a mixture comprised of (a) BADGE, **1b**, and BHPMS-HFA ([BADGE]₀:[SOC unit in **1b**]₀:[BHPMS-HFA]₀ = 95:5:2), (b) BADGE and BHPMS-HFA ([BADGE]₀:[BHPMS-HFA]₀ = 100:2); heated in a rate of 10 °C/min, under N₂ flow.

Figure 2 shows IR spectrum of the formulation before the polymerization and that of the obtained networked polymer. Before the polymerization, there was an absorption at 917 cm^{-1} attributable to the epoxy moiety of BADGE.²¹ In the spectrum of the polymer, this absorption disappeared. In addition, a new absorption appeared at 1745 cm^{-1} , which was attributed to the carbonate moiety formed by the ring-opening polymerization of the spiroorthocarbonate moieties of **1b**.²⁰ Moreover, the increase of the absorption intensity around 1100 cm^{-1} was attributable to the C–O stretching formed by ring-opening polymerization of the epoxide and spiroorthocarbonate. These results confirmed the successful copolymerization of **1b** with BADGE.

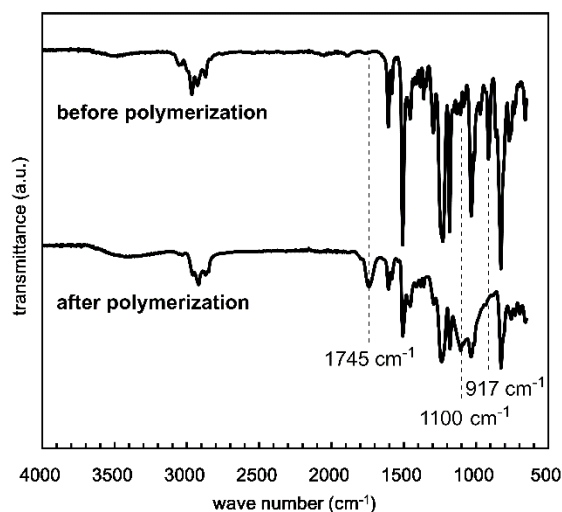


FIGURE 2. IR spectra of a formulation comprised of BADGE, **1b**, and BHPMS-HFA ($[\text{BADGE}]_0:[\text{SOC unit in } \mathbf{1b}]_0:[\text{BHPMS-HFA}]_0 = 95:5:2$) and the corresponding polymer obtained by heating the formulation at $180\text{ }^\circ\text{C}$ for 1 h.

Shrinkage Suppression Ability of **1**

Next, we investigated the shrinkage suppression effect of **1** on the cationic polymerization of epoxide. BADGE, OSOC **1**, and BHPMS-HFA were

mixed in a molar ratio ($[\text{BADGE}]_0:[\text{SOC unit in } \mathbf{1}]_0:[\text{BHPMS-HFA}]_0$) of 99:1:2. OSOC **1**, insoluble in BADGE at room temperature, was successfully dispersed in the formulation without sedimentation. Then, the formulation was heated at $180\text{ }^\circ\text{C}$ for 1 h. The density before polymerization (D_{before}) and density after polymerization (D_{after}) were measured using a gas pycnometer, and according to the following equation, volume change degree [%] = $[1 - (D_{\text{after}})/(D_{\text{before}})] \times 100$, the volume change upon the polymerization was calculated. The minus and plus signs of the volume change degree represent volume shrinkage and expansion, respectively. The results are summarized in Table 1.

The polymerization without **1** accompanied volume change of -3.1% (3.1% shrinkage) (entry 1). On the other hand, in the presence of **1**, the volume change became smaller with ranging from -1.2 to -2.1% (entries 2–5), confirming the **diminution** of volume shrinkage by using **1** as a comonomer. Among **four** OSOC **1a–1d**, **1b** exhibited the highest shrinkage **diminution** effect.

The degrees of shrinkage **diminution** by **1** can be correlated with two factors, their densities and solubility in BADGE. As shown in Table 1, the densities of **1a–1d** depend on bulkiness of their substituents, implying that rigid rod-like chains of **1** with smaller substituents can be more densely packed. As was reported previously, **1a** can undergo cationic ring-opening polymerization **along with** a large volume expansion, which is attributable not only to the intrinsic ability of SOC to undergo double ring-opening reaction accompanying volume expansion but also the increase in free volume arisen by the collapse of the dense packing of the oligomer chains upon the polymerization.²⁰ From this point of view, the most densely packed **1a** would be most suitable for shrinkage **diminution** and **1b** would be second most suitable; however, actually, **1a** was inferior to **1b** in terms of shrinkage **diminution** ability, suggesting that the other factor, solubility of **1** in

BADGE, would dominate the shrinkage diminution ability. A part of **1a** was dissolved in

TABLE 1 Volume Changes upon Copolymerization of BADGE and **1**

entry	1	Density of 1 (g/cm ³) ^a	[BADGE] ₀ : [SOC unit in 1] ₀	<i>D</i> _{before} (g/cm ³) ^a	<i>D</i> _{after} (g/cm ³) ^a	volume change (%) ^b
1	-	-	100:0	1.1772	1.2131	-3.1
2	1a	1.6567	99:1	1.1797	1.2009	-1.8
3	1b	1.5972	99:1	1.1804	1.1946	-1.2
4	1c	1.3003	99:1	1.1803	1.2033	-2.0
5	1d	1.3814	99:1	1.1785	1.2027	-2.1
6 ^c	1b	1.5972	95:5	1.1883	1.2020	-1.2
7 ^c	1b	1.5972	90:10	1.1993	1.1978	+0.1

^a Measured by a fully automatic gas displacement pycnometer. ^b Volume change was calculated from density change vs density of monomer or monomer mixture; minus and plus signs mean volume shrinkage and expansion, respectively. ^c The formulation was heated at 80 °C for 0.5 h, then at 180 °C for 1 h.

BADGE at 180 °C and underwent the ring-opening polymerization leading to the suppression of volume shrinkage. However, the rest of **1a** remained intact in the polymer of BADGE without exhibiting its potential shrinkage diminution ability. In contrast, **1b**, which was more soluble than **1a** in various organic solvents,¹⁸ became soluble in BADGE upon heating, and thus efficiently underwent copolymerization with BADGE to exhibit its shrinkage diminution ability.

Upon confirming the highest shrinkage diminution ability of **1b** among the oligo(spiroorthocarbonate)s **1** examined herein, its amount was increased to 5 and 10 mol% with expecting the shrinkage can be further suppressed (entries 6 and 7). In these cases, the formulations were pre-heated at 80 °C for 0.5 h to ensure degassing from them before their polymerizations at 180 °C, because the formulations were more viscous than that with smaller amount of **1b**. As a result, by using 10 mol% of **1b**, the corresponding volume change became +0.1%, achieving complete suppression of the shrinkage.

Thermal Property of the Obtained Polymers

The thermal stability of the obtained polymers was evaluated by thermogravimetric analysis (TGA). The 5% weight loss temperature (*T*_{d5}) and 10% weight loss temperature (*T*_{d10}) are shown in Table 2. As typical examples, the thermogram of the homopolymer of BADGE and that of the copolymer of BADGE with **1b** ([BADGE]₀: [SOC unit in **1b**]₀ = 90:10) are shown in Figure 3. These data showed that the use of **1b** as a comonomer did not lead to deterioration of thermal stability, which was serious in some cases when monofunctional or bifunctional volume expanding monomers were used.⁵⁻¹³ Such a successful prevention of deterioration of thermal stability achieved by the utilization of **1b** as a comonomer would be due to the role of **1b** as a multifunctional monomer to avoid serious decrease in crosslinking density.

TABLE 2 Thermal Properties of Homopolymer of BADGE and Copolymers of BADGE with **1b**

entry	[BADGE] ₀ : [SOC unit in 1b] ₀	<i>T</i> _{d5} (°C) ^a	<i>T</i> _{d10} (°C) ^a
1	100:0	398	409
2	99:1	397	408

3	95:5	394	408
4	90:10	390	405

^a Determined by TGA.

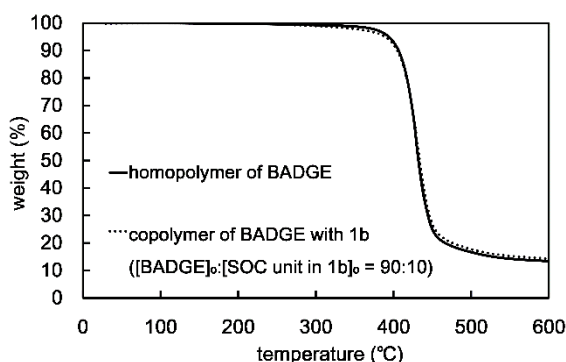


FIGURE 3. TG Thermograms of the homopolymer of BADGE and the copolymer of BADGE with **1b** ([BADGE]₀:[SOC unit in **1b**]₀ = 90:10)

CONCLUSIONS

Cationic copolymerization of bisphenol A-diglycidyl ether (BADGE) with oligo(spiroorthocarbonate)s **1** was performed and the resulting volume changes were evaluated. The heat evolution during the copolymerization was studied by DSC to determine the suitable temperature (= 180 °C) for the copolymerization. The successful ring-opening reaction of **1** was confirmed by the IR analysis of the resulting copolymer, where an absorption attributable to the carbonate linkage formed by the ring-opening of **1** was observed. Among four oligo(spiro*ortho*carbonate)s studied herein, **1b** bearing methyl group in the side chain exhibited the highest volume shrinkage **diminution** effect, allowing almost complete suppression of volume shrinkage upon the copolymerization. In addition to this remarkable shrinkage suppression effect, the use of **1b** as a comonomer brought about another advantage, minimized deterioration of the thermal stability

of the homopolymer of BADGE. These advantageous characteristics of the copolymerization of epoxide and **1b** would permit its application to adhesion and molding where precise control in size is required.

ACKNOWLEDGEMENTS

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REFERENCES

1. C. A. May, *Epoxy resins: chemistry and technology*; Marcel Dekker: New York, **1988**, 1.
2. T. Takata; T. Endo, *Expanding Monomers; Synthesis, Characterization, and Applications*; R. K. Sathir, R. M. Luck, Eds.; CRC Press: Boca Raton, FL, **1992**, 63.
3. W. J. Bailey; R. R. Sun; H. Katsuki; T. Endo; H. Iwama; K. Tsushima; K. Saigo; M. Bitritto, *Ring-Opening Polymerization with Expansion in Volume*; ACS Symposium Series 59; T. Saegusa, E. Goethals, Eds.; American Chemical Society: Washington, DC, **1977**, 38.
4. T. Takata, T. Endo, *Polym. Prepr. Jpn.* **1988**, 37, 241.
5. T. Hino, T. Endo, *Macromolecules* **2003**, 36, 5902.
6. T. Hino, N. Inoue T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, 42, 5113.
7. R. Cervellera, X. Ramins, J. M. Salla, A. Serra, A. Manteón, *Polymer* **2005**, 46, 6878.
8. M. Sangermano, R. A. Ortiz, B. A. P. Urbina, L. B. Duarte, A. E. G. Valdez, R. G. Santos, *Eur. Polym. J.* **2008**, 44, 1046.
9. M. Sangermano, M. L. L. B. Duarte, R. A. Ortiz, A. G. S. Gómez, A. E. G. Valdez, *React. Funct. Polym.* **2010**, 70, 98.

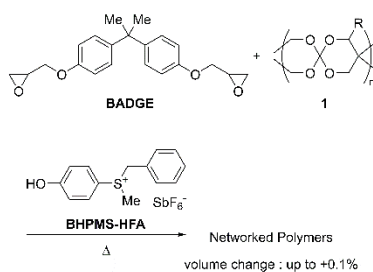
10. R. A. Ortiz, M. L. B. Duarte, A. G. S. Gómez, M. Sangermano, A. E. G. Valdez, *Polym. Int.* **2010**, *59*, 680.
11. R. A. Ortiz, M. L. B. Duarte, J. L. R. Olivares, M. Sangermano, *Des. Monomers Polym.* **2013**, *16*, 323.
12. R. A. Ortiz, M. L. B. Duarte, A. G. S. Gómez, M. Sangermano, A. E. G. Valdez, M. P. Ramírez, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2012**, *49*, 361.
13. R. A. Ortiz, A. G. S. Gómez, M. L. B. Duarte, M. Sangermano, *Polym. Int.* **2012**, *61*, 587.
14. X. Xu, L. Zhou, B. Liang, Y. Wu, C. Wang, *Polym.-Plast. Technol. Eng.* **2014**, *53*, 753.
15. R. A. Ortiz, A. G. S. Gómez, M. L. B. Duarte, A. E. G. Valdez, *Des. Monomers Polym.* **2015**, *18*, 73.
16. R. A. Ortiz, A. E. G. Valdez, R. A. Flores, R. I. L. Palacios, M. L. B. Duarte, A. E. G. Valdez, *J. Polym. Res.* **2015**, *22*, 163.
17. X. Xu, Y. Wu, C. Wang, *Des. Monomers Polym.* **2015**, *18*, 690.
18. Y. Mori, A. Sudo, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2019**, *57*, 792.
19. D. T. Vodak, M. Braun, L. Iordanidis, J. Plévert, M. Stevens, L. Beck, L.; J. C. H. Spence, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 4942.
20. T. Hino, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 5323.
21. Y. Kawaoka, K. Koge, A. Sudo, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 2096.

GRAPHICAL ABSTRACT

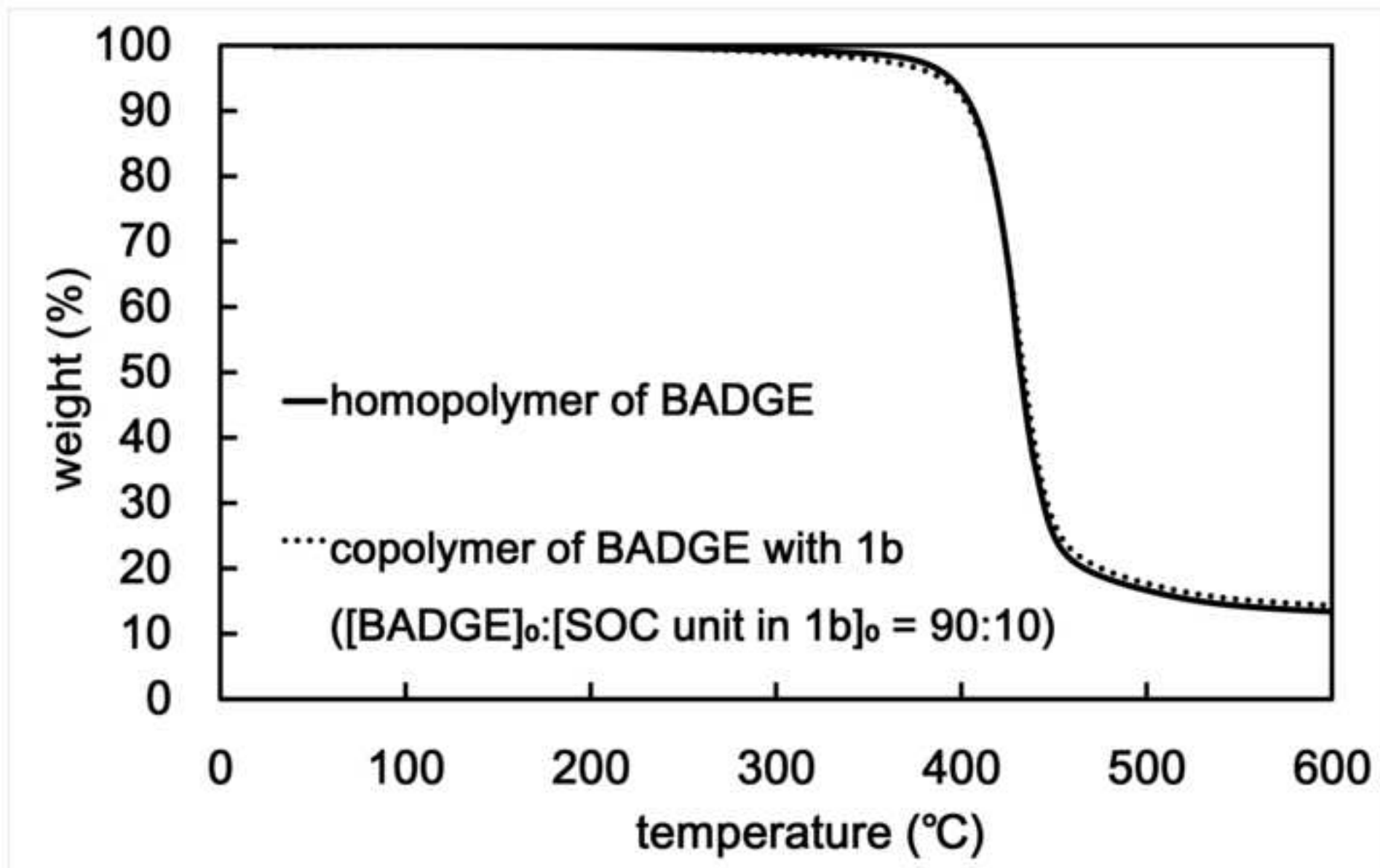
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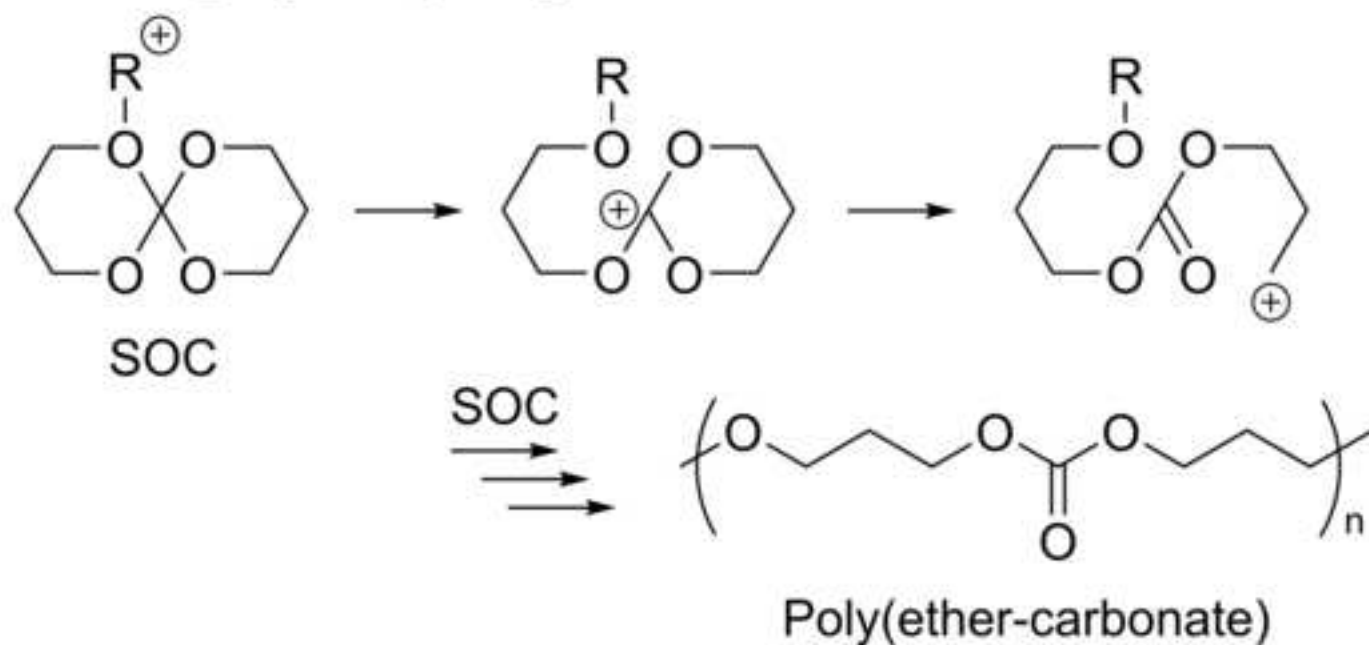
Sulfonium salt-initiated cationic copolymerization of bisphenol A-diglycidyl ether (BADGE) with oligo(spiroorthocarbonate)s **1** was demonstrated and the resulting volume changes were evaluated. In the copolymerization, the spiroorthocarbonate moiety of **1** underwent double ring-opening reaction, leading to the efficient **diminution** of the volume shrinkage upon the polymerization. Thermal properties of the resulting networked polymers were evaluated by thermogravimetric analysis (TGA).



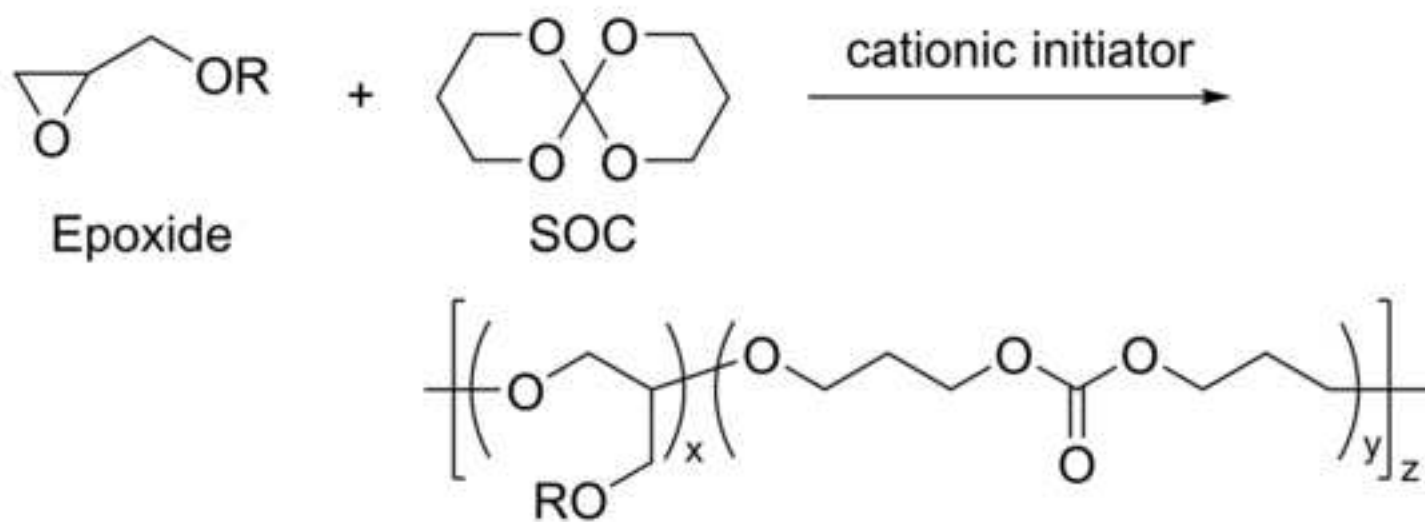
Volume shrinkage suppression ability depended on R group in oligo(spiroorthocarbonate) **1**

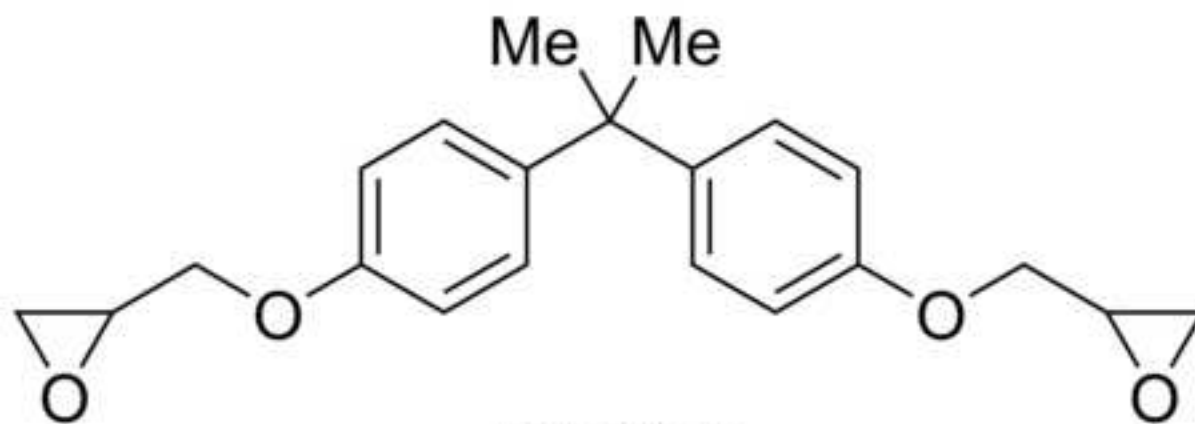
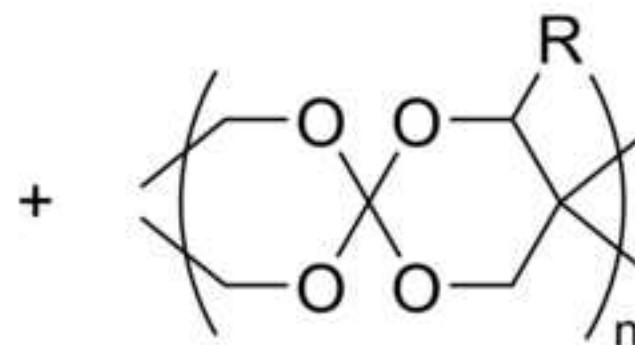
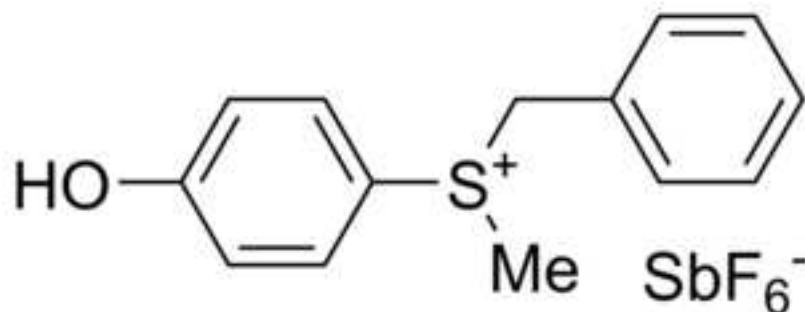
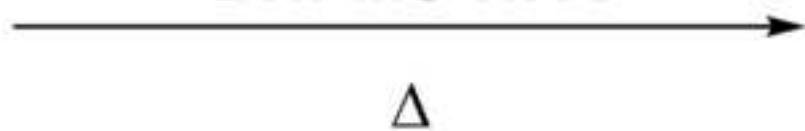


Double Ring-Opening Polymerization of SOC

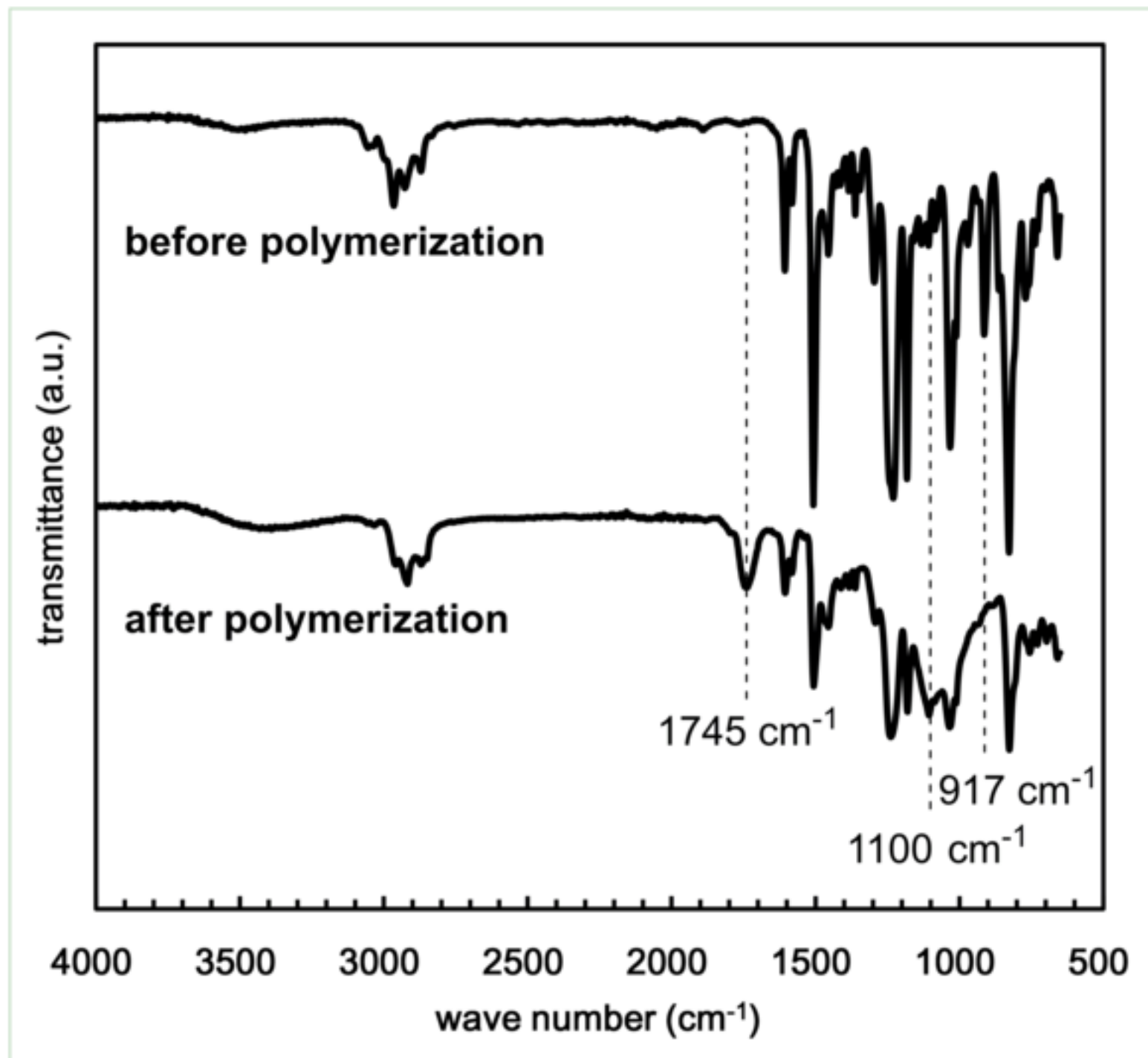


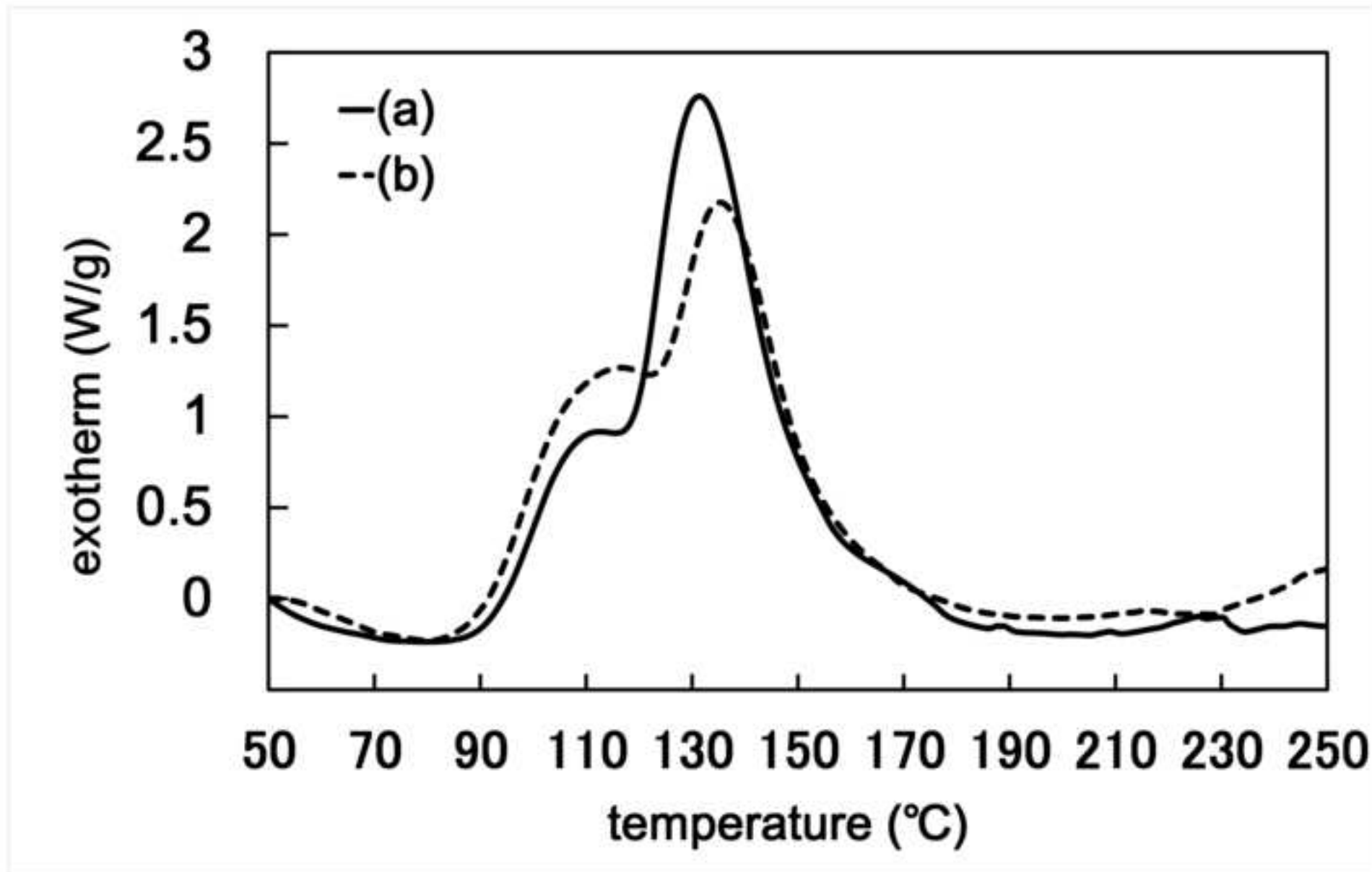
Copolymerization of SOC with Epoxides

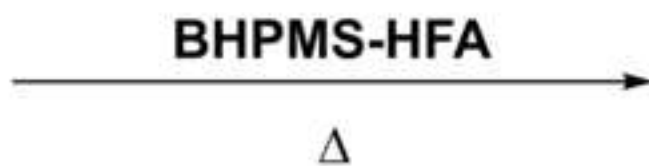
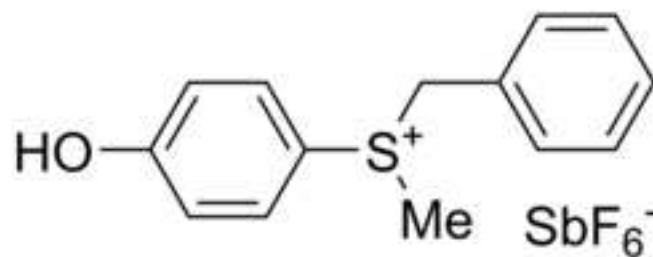
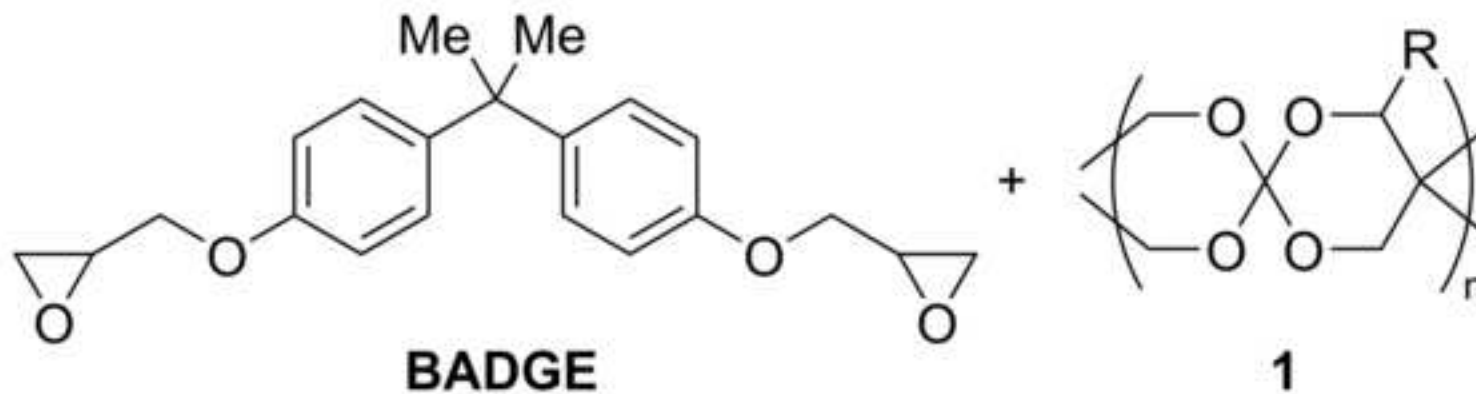


**BADGE****1a** (R=H)**1b** (R=Me)**1c** (R=*n*-Bu)**1d** (R=Ph)**BHPMS-HFA**

Networked Polymers







Networked Polymers

volume change : up to +0.1%

Volume shrinkage suppression ability depended on R group in oligo(spiroorthocarbonate) 1