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A Novel Synthetic Approach to Networked Polymers without Volume Shrinkage on Cross-Linking Polymerization: Cationic Copolymerization of a Monofunctional Epoxide and a Spiro Orthocarbonate Bearing Norbornene Backbone

Tetsuo Hino and Takeshi Endo*

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

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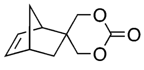
Introduction. All polymerizations and curing processes usually involve shrinkage in volume; for example, vinyl and cyclic monomers generally undergo polymerization with extensive volume shrinkage by ca. 10−20%.[1] In the field of materials sciences, the volume shrinkage has been a serious problem due to lowering of adhesion, void, microcrack, remaining stress, and so on. For the past several decades, we have reported that several cyclic monomers, such as spiro orthocarbonates (SOCs), cyclic carbonates (CCs), and bicyclic bis(γ-lactone)s, undergo expansion or no shrinkage in volume on their polymerizations.[1,2] Furthermore, we have reported that the volume shrinkage can be controlled by copolymerization with various amounts of these expanding monomers to give the corresponding copolymers, depressing the volume shrinkage. For instance, the volume shrinkage of phenyl glycidyl ether (PGE), which generally shows volume shrinkage in the homopolymerization by ca. 8−9%, was controlled by copolymerizations using a six-membered SOC[1,3] and bicyclic bis(γ-lactone)s[2d−f] under both cationic and anionic conditions, respectively. As far as we know, these controls by use of expanding monomers have been mainly carried out on linear copolymers.

There are not so many reports about *network polymers* showing no volume shrinkage during cross-linking,[4,5] although networked polymers generally have many significant practical advantages compared to linear polymers, such as rather high mechanical strength and chemical and/or thermally stability.[6] Therefore, development of methodology of the networked polymer without volume shrinkage on cross-linking has been widely expected from the viewpoint of development of super-performance materials. Particularly, a novel synthetic approach to the networked polymers without volume shrinkage from *monofunctional cyclic ethers*, such as monofunctional epoxides, will be of importance because of its notable utilities, simple synthetic procedure, and easy handling.[7]

These results and considerations prompted us to investigate the volume control of networked polymers. In this communication, we describe cationic ring-opening copolymerizations of PGE with expanding monomers, norbornene containing CC **1** and SOC **2**, which have one or two cyclic olefin moieties besides a volume expanding moiety on the ring-opening polymerization. Since the cyclic olefin groups could be utilized for a cross-link, we expect that the desired network polymers may be synthesized by copolymerization of PGE with such monomers **1** and **2**.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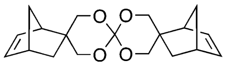
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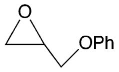

PGE

Results and Discussion. Table 1 shows the results of cationic ring-opening homo- and copolymerizations of the norbornene containing monomers (**1** and **2**) and/or PGE at 100 °C for 24 h.[8,9] At first, BF$_3$·OEt$_2$ was used as a cationic initiator for the copolymerization of CC **1** and/or PGE (runs 1−3). As a result, the BF$_3$·OEt$_2$ mediated copolymerization (**1**:PGE = 5:95) was found to give product **CP1** with rather high yield and M_n compared with those of the homopolymers (**HP1** and **HP2**) of PGE or CC **1**. The copolymer was, however, readily soluble in common organic solvents, such as CHCl$_3$, CH$_2$Cl$_2$, and THF. In addition, similar copolymerizations with various monomer ratios and with other cationic initiators, such as TfOMe and Sc(OTf)$_3$, yielded products which were soluble in common organic solvents. Next, copolymerizations with SOC **2** were carried out, in which the copolymers can be expected to have a relatively higher networked structure than those with CC **1**, because of SOC **2** bearing *two* olefin units necessarily in its unimolecule. However, the BF$_3$·OEt$_2$ mediated copolymerization of SOC **2** and PGE (monomer ratio: 5:95) gave product **CP2** with higher yield and M_n than those of homopolymer **HP3** of SOC **2** (runs 4 and 5), similar to the case of CC **1**. Then, similar copolymerizations of SOC **2** were also carried out with other cationic initiators. Although the TfOMe initiated copolymerization afforded similar results to the BF$_3$·OEt$_2$ mediated one, the Sc(OTf)$_3$ initiated one gave insoluble polymer **CP3** in THF, CHCl$_3$, and DMSO in a good yield (run 6). Further, in the same copolymerizations with various monomer ratios (**2**:PGE = 10:90 and 20:80), similar insoluble polymers, **CP4** and **CP5**, were obtained (runs 7 and 8).[10] This drastic result in the copolymerizations with Sc(OTf)$_3$ is not sufficiently clear at the present time, but it would depend on its high ability to maintain the catalytic activity and on its strong Lewis acidity due to its hard character and electron-withdrawing trifluoromethanesulfonyl groups.[11]

The structure of the resulting insoluble polymers was confirmed by IR and NMR spectroscopy. Absorption bands of the aromatic group were observed around 1600 and 1500 cm^{-1} (cyclic stretching) and around 750 and 700 cm^{-1} (cyclic out-of-plane bending), which should be derived from PGE structure. Further, the spectrum of polymer **CP3** showed the characteristic absorption of the carbonate group around 1770 cm^{-1} (C=O stretching), which should be derived from the ortho ester structure of SOC **2**. These results strongly suggest that the insoluble polymer has the copolymerized structure of SOC **2** and PGE. Figure 1 shows ^{1}H NMR spectra of monomer **2** (top) and a copolymer collected before the Sc(OTf)$_3$ initiated polymerization, yielding the insoluble polymer **CP3** which went essentially to completion (bottom). In the spectrum of the copolymer, the complete

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* To whom correspondence should be addressed: phone and Fax +81-238-26-3090; e-mail tendo@yz.yamagata-u.ac.jp.

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Table 1. Cationic Polymerization of the Norbornene Containing Monomers (1 and 2) and/or PGE[a]

run	feed ratio **1** or **2**:PGE (ratio)	cationic initiator	yield/%[b] (polymer)	M_n[c] ($\times 10^3$)	T_{d10}[d] (°C)	T_{d5}[e] (°C)	T_g[e] (°C)	vol[f] change (%)
1	−:PGE (0:100)	$BF_3{\cdot}OEt_2$	58 (**HP1**)	3.87	299	189		−8.8
2[g]	**1**:− (100:0)	$BF_3{\cdot}OEt_2$	25 (**HP2**)	1.50				+7.7[h]
3	**1**:PGE (5:95)	$BF_3{\cdot}OEt_2$	72 (**CP1**)	7.97				
4[g]	**2**:− (100:0)	$BF_3{\cdot}OEt_2$	50 (**HP3**)	3.10				+7[h]
5	**2**:PGE (5:95)	$BF_3{\cdot}OEt_2$	64 (**CP2**)	9.15				
6	**2**:PGE (5:95)	$Sc(OTf)_3$	86[i] (**CP3**)	insoluble	283	253	93	−6.2
7	**2**:PGE (10:90)	$Sc(OTf)_3$	79[i] (**CP4**)	insoluble	285	248	99	−3.9
8	**2**:PGE (20:80)	$Sc(OTf)_3$	80[i] (**CP5**)	insoluble	292	260	108	−1.4

[a] Polymerization conditions: initiators (5 mol %); 100 °C; 24 h; bulk. [b] Ether/hexane-insoluble part (ether/hexane = 1/10). [c] M_n was determined by GPC (THF, polystyrene standard). [d] Determined by thermogravimetric analysis under a N_2 atmosphere. [e] Determined by differential scanning calorimetry. [f] Determined by a density gradient tube at 25 °C (standard error of the measurement = ±0.15%); volume change was calculated from density change vs density of monomer or monomer mixture; minus and plus signs mean volume shrinkage and expansion, respectively. [g] Polymerization conditions: $BF_3{\cdot}OEt_2$ (5 mol %); 100 °C; 24 h; PhCl (100 wt %), ref 13. [h] Reference 1. [i] MeOH-insoluble part.

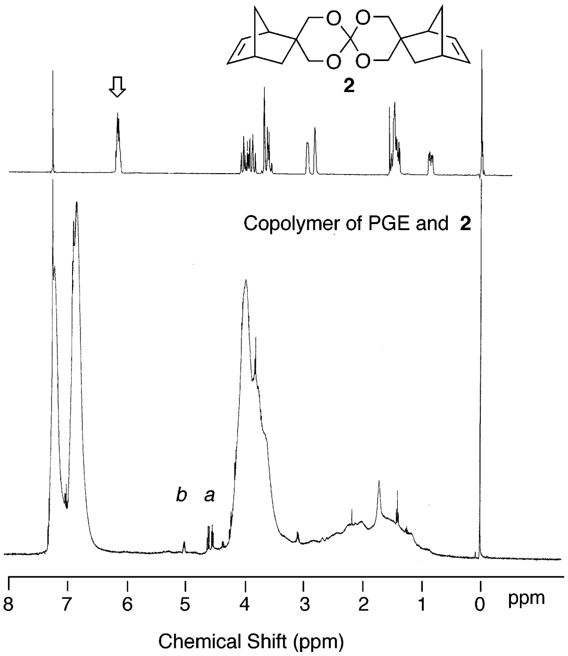
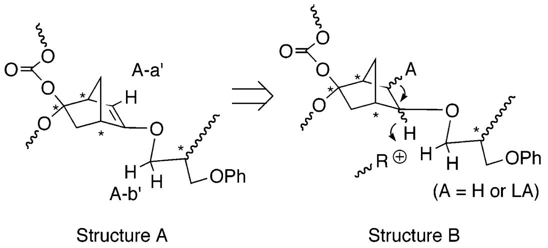


Figure 1. ^{1}H NMR spectra of SOC **2** (top) and a copolymer collected before the $Sc(OTf)_3$ initiated polymerization, yielding the insoluble polymer **CP3** which went essentially to completion (bottom), recorded in $CDCl_3$. An arrow indicates the position of the olefin signals of SOC **2**.

disappearance of the norbornene olefin peaks around 6.1 ppm suggests that the olefin units should act as a reaction group, as we expected. Thus, the insoluble polymer might have structure A cross-linked with PGE at the olefin units of SOC **2**, as shown below.[12,13] In addition, peaks *a* and *b* around 4.5 and 5.0 ppm (integration ratio 2:1) can be assigned to the methine proton A-a′ of the norbornene olefin site connected to the ether oxygen and to the proton A-b′ of the methylene group derived from addition of PGE to the olefin moiety(s), respectively. Compared with the signals of the norbornene olefin of SOC **2**, the signals of methine proton *a* in the olefin unit of expected structure A are shifted upfield because of the corresponding *β*-proton of the vinyl ether structure to increase the electron density around the proton (RCH=CR−O−R ↔ RC^-H−CR=O^+−R). The multiple resonances for protons *a* and *b* should be attributed to the constitutional disorder introduced by the asymmetrical moieties of the norbornene and poly-PGE. In addition, similar results were also observed in insoluble polymers **CP4** and **CP5**. According to these results, in the $Sc(OTf)_3$ initiated polymerizations, the expected cross-linkage should be suggested to proceed at the norbornene olefin part(s) to yield the corresponding network copolymers bearing the structure A, which might be formed via 1,2- elimination from the precursor B on the basis of the Bredt rule.



The thermal stability and volume change are also summarized Table 1. The 10% weight loss decomposition temperatures of compounds **CP3**−**5** were almost same as that of homopolymer **HP1**, while the 5% weight loss decomposition temperatures increased by ca. 60−70 °C. In particular, the thermal stability was drastically improved by copolymerization with only addition of ca. 5% of SOC **2** to PGE. Further, the glass transition temperatures (T_g) ranged from 93 to 108 °C, and the T_g increased with increase of feed ratio of SOC **2**. The volume changes were investigated on the basis of the density of the monomer mixture, and as a result, the volume shrinkage was controlled by a proportion of PGE and SOC to achieve the nearly zero volume shrinkage in the resulting networked polymers. As mentioned above, the cationic homopolymerization of PGE is known to accompany by 8−9% volume shrinkage, and the present $BF_3{\cdot}OEt_2$ initiated polymerization actually indicated 8.8% volume shrinkage (run 1), whereas the volume shrinkage of copolymers **CP3**−**5** was reduced up to 1.4% with increase of monomer ratio of SOC **2** (runs 6−8).

In summary, $Sc(OTf)_3$ initiated copolymerization of PGE and monomer **2** was demonstrated to be potentially useful for synthesis of networked polymers with nearly zero volume shrinkage from a monocyclic ether, PGE. Thus, SOC **2** was revealed to serve as *a volume controllable cross-linking agent*.[14,15] Particularly, the resulting copolymers were found to have relatively higher thermal and chemical stability than those of the corresponding homopolymers. A similar tendency was also observed in the copolymerization of SOC **2** and a monofunctional cyclic ether, 3-ethyl-3-phenoxymethyloxetane, and the results will be published soon.

References and Notes

(1) Luck, R. M.; Sadhir, R. S. In *Expanding Monomers: Synthesis, Characterization, and Applications*; Sadhir, R. K., Luck, R. M., Eds.; CRC: Boca Raton, FL, 1992.

(2) For example: (a) Endo, T.; Sanda, F. Cationic Ring-Opening Polymerization, (with Expansion in Volume). In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; p 7554. (b) Takata, T.; Endo, T. *Prog. Polym. Sci.* **1994**, *18*, 839. (c) Chikaoka, S.; Takata, T.; Endo, T. *Macromolecules* **1992**, *25*, 625. (d) Takata, T.; Chung, K.; Tadokoro, A.; Endo, T. *Macromolecules* **1993**, *26*, 6686. (e) Chung, K.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 3048. (f) Fukuchi, I.; Sanda, F.; Endo, T. *Macromolecules* **2001**, *34*, 4296. (h) Kameshima, H.; Nemoto, N.; Sanda, F.; Endo, T. *Macromolecules* **2002**, *35*, 5769.

(3) Takata, T.; Endo, T. *Polym. Prepr. Jpn.* **1988**, *37*, 241.

(4) We have reported the following two types of synthetic approaches for the volume control of network polymers: (1) copolymerizations of *bifunctional epoxides* by using a six-membered SOC (see refs 1 and 3) or bicyclic bis(γ-lactone)s (see refs 2d−e) and (2) two steps copolymerization of isoprenes by using *SOCs having radically polymerizable groups* such as a vinyl moiety (see ref 5). These polymerizations, however, are distinct from the present approach; that is, the former required bifunctional epoxides, which inevitably gave the corresponding network structures, and the latter needed two different polymerizations manners, radical followed by cationic ones.

(5) (a) Igarashi, M.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 2628. (b) Tagoshi, H.; Endo, T. *J. Appl. Polym. Sci.* **1991**, *43*, 1933.

(6) (a) Seymour, R. B.; Carraher, C. E., Jr. *Polymer Chemistry*, 3rd ed.; Marcel Dekker: New York, 1992. (b) Griskey, R. G. *Polymer Process Engineering*; Chapman & Hall: New York, 1995.

(7) For example, some bifunctional epoxides such as bisphenol A diglycidyl ether and its derivatives are highly viscous oils that are extremely intractable.

(8) Monomers **1** and **2** were prepared by literature procedures. **1**: Chen, X.; McCarthy, S. P.; Gross, R. A. *Macromolecules* **1997**, *30*, 3470. **2**: Bailey, W. J.; Sun, R. L.-J.; Katsuki, T.; Endo, H.; Iwama, H.; Tsushima, R.; Saigo, K.; Bitritto, M. M. Ring-opening Polymerization with Expansion in Volume. In *Ring-Opening Polymerization*; Saegusa, T., Goethals, E., Eds.; ACS Symposium Series No. 59; America Chemical Society: Washington, DC, 1977; p 53.

(9) A typical polymerization procedure: A mixture of SOC **2** (79.1 mg, 0.25 mmol), PGE (713.3 mg, 4.75 mmol), and Sc(OTf)$_3$ (123 mg, 5 mol %) was heated at 100 °C for 24 h under an atmosphere of argon. The polymerization mixture was treated with CHCl$_3$−triethylamine and washed with methanol with a Soxhlet extractor. Methanol-insoluble polymer was collected and dried in vacuo at 60 °C for 48 h to yield 682 mg of a yellowish-brown solid (86%).

(10) When in the monomer feed ratio of SOC **2**:PGE, the proportion of SOC **2** was more than 20%, the bulk copolymerization cannot be carried out, since the polymerization system was extremely heterogeneous even at higher temperature.

(11) (a) Kabayashi, S. *Synlett* **1994**, 689. (b) Fukuzawa, S. Scandium (III) and yttrium (III). In *Lewis Acid Reagents A Practical Approach*; Yamamoto, H., Ed.; Oxford University Press: New York, 1998; p 185.

(12) We have already reported that *cationic homopolymerization of SOC **2** in PhCl* proceeded along a different mechanism from that of a common SOC (see ref 13); i.e., the homopolymerization underwent via the initial rapid decomposition of SOC **2** followed by successive (co)polymerization of the CC **1** and the corresponding oxetane derivative, in which almost complete disappearance of norbornene olefin signals in NMR presumably due to the polymerization with a skeleton rearrangement of the norbornene moiety(s) through a nonclassical carbenium ion intermediate before propagation. Meanwhile, the present copolymerizations were carried out under *bulk conditions with a large amount of PGE*. Thus, in the present polymerization, the cross-linkage by addition of PGE might proceed in preference to the skeleton rearrangement.

(13) Takata, T.; Amachi, K.; Kitazawa, K.; Endo, T. *Macromolecules* **1989**, *22*, 3188.

(14) Several papers have reported that the SOC bearing norbornene structure (**2**) was useful for carbon fiber composites and epoxy coatings, showing improved toughness and stability by reducing shrinkage stress of epoxy resin matrix (see ref 15). However, these reports investigated (co)-polymerizations with *bifunctional epoxide* and examined mainly mechanical properties, not thermal properties. In particular, these papers never refer to the structural analysis in detail. In addition, we consider that the improvement of such mechanical properties should depend on the cross-linkage structure at the olefin site(s), which was revealed in the present investigation.

(15) (a) *Chem. Eng. News* **1986**, May 12, 21. (b) Piggott, M. R.; Phshnov, T. *Polymer. Mater. Sci. Eng.* **1986**, *54*, 18. (c) Lam, S. M. Y.; Piggott, M. R. *33rd Int. SAMPE Symp.* **1988**, 736. (d) Bluestein, C.; Cohen, M. S.; Mehta, R. *Int. Radtech'88* **1988**, April, 389.

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