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Unexpected Volume Expanding Behavior on Ring-Opening Metathesis Polymerization of Norbornene Bearing a Five- or Six-Membered-Ring Cyclic Carbonate Followed by a Cationic Ring-Opening Cross-Linking Reaction

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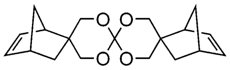
Introduction. Since all polymerizations and curing processes usually involve shrinkage in volume,[1] the volume shrinkage in the field of materials sciences has been a serious problem due to lowering of adhesion, void, microcrack, residual stress, and so on. For the past several decades, we have reported that several cyclic monomers, such as spiro-orthocarbonates, cyclic carbonates, and bicyclic bis(γ-lactone)s, undergo expansion or no shrinkage in volume on their polymerizations.[1,2] We have also reported that the volume shrinkage of common polymerizations can be controlled by copolymerization with various amounts of these expanding monomers to give the corresponding copolymers, depressing the volume shrinkage.[3] Furthermore, we have recently reported that networked copolymers[4] without volume shrinkage during the polymerizations can be synthesized by use of norbornene-containing six-membered ring spiro-orthocarbonate (**1**) and cyclic carbonate (**2**) as a comonomer:[5] Volume-controlled networked copolymers were synthesized by cationic ring-opening copolymerizations of cyclic ether compounds with these norbornene-containing monomers, in which a cross-linking-reaction was carried out on a reactive cyclic olefin moiety(s) along with the volume expanding ring-opening copolymerization. In addition, the corresponding volume-controlled networked copolymers indicated relatively higher thermal and chemical resistance than those of the corresponding homopolymers, poly(ether)s.

In the course of development of a new volume-controlled networked product, we paid attention to norbornene-containing cyclic carbonates again because norbornenes can give rise to ring-opening metathesis polymerization (ROMP)[6] to yield the polyalkenamers, which are widely used in various fields of materials sciences. Incidentally, ROMP generally causes volume shrinkage during polymerization, similar to other common polymerizations. Furthermore, cyclic carbonates have been attracted considerable attention. Ring-opening reactions of cyclic carbonates yield the corresponding products with unique properties derived from the fascinating carbonate structure.[7] Cationic and/or anionic ring-opening polymerization behaviors of various membered ring cyclic carbonates have been widely investigated.[8] In particular, six-membered-ring cyclic carbonates are known as an important class of monomers in polymer chemistry[9] since the monomers are smoothly transformed to the corresponding poly(carbonate)s with volume expansion or no volume shrinkage during the cationic ring-opening polymerizations. The volume expansion is caused by change in the intermolecular interaction which exists before vs after the polymerization. The intermolecular interaction between the monomers should be higher than that between the resulting polymers with the acyclic carbonate structure. In particular, the dipole−dipole interaction might be a major factor in the change in intermolecular interaction in this case. In addition, dipole moments of 2-oxo-1,3-dioxane (six-membered-ring cyclic carbonate) and acyclic methyl butyl carbonate are calculated to be 5.38 and 0.92 D, respectively.[9] Thus, these considerations prompted us to develop a new type of cross-linked polymer which would form without volume shrinkage via the following stepwise polymerization of **2**:[10,11] The ROMP on the cyclic olefin moiety followed by the cationic ring-opening reaction of the cyclic carbonate brings about simultaneous volume expansion and network formation. Additionally, we also describe herein a similar ROMP behavior of **3**[11] as the reference. Cationic ring-opening polymerizations of five-membered-ring cyclic carbonates are almost never observed.[12]



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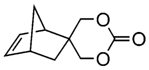

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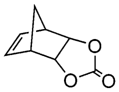

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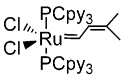

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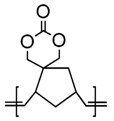

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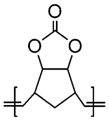

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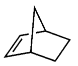

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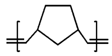

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Results and Discussion. At first, ROMP of **2** was carried out under the following polymerization conditions: 1 mol % of ruthenium catalyst **4**; 1 M of the monomer concentration, as shown in Table 1 (run 1). The corresponding polymer (**5-1**) was efficiently formed, and it was readily soluble in dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and $MeNO_2$. The ^1H NMR spectrum of **5-1** indicated the corresponding peaks assigned to the expected polymer structure without peaks derived from the cyclic olefin group (see Figure A-(b) in the Supporting Information), and the IR spectrum showed a peak based on the ring-opened trans-olefin moiety around 975 cm^{-1} along with the peak arising from the cyclic carbonate (Figure 1b). The number-average molecular weight (M_n) of **5-1** was lower than that of poly(norbornene) (**8**) formed via the similar reaction of norbornene itself (**7**, run 2), but the thin polymer film can be prepared. The lower M_n of **5-1** than that of **8** might depend on the relatively high dipole moment of six-membered-ring cyclic carbonate unit, for example, ethylene carbonate: μ = 5.38 D.[9] Thus, the decrease of the catalytic activity might be depend on coordination between the catalyst and **2** bearing the

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Table 1. ROMPs of 2 and 3 Followed by the Cationic Ring-Opening Reactions

		ring-opening metathesis polymerization[a]						cationic ring-opening reaction[b]		
run	monomer	concn[c] (M)	initiator (mol %)	product[d]/ yield (%)	M_n[e] (M_w/M_n)	T_{d10}[f]/T_g[g] (°C)	volume[h,i] change (%)	product[j]/ yield (%)	T_{d10}[f]/T_g[g] (°C)	volume[h,k] change (%)
1	**2**	1	1	**5-1**/88	34000 (1.68)	320/193	+2.0	**5′-1**/42	337/ND	−0.3
2	**7**	1	1	**8**/98	130000 (−)	400/55	−1.6			
3	**2**	1	5	**5-2**/97	23800 (1.32)	322/188	+1.0	**5′-2**/20	268/ND	+3.3
4	**2**	0.5	1	**5-3**/78	87700 (1.83)	323/213	+2.1	**5′-3**/76	331/ND	+2.6
5	**3**	1	1	**6-1**/98	110800 (1.33)	345/ND	+6.3			
6	**3**	1	5	**6-2**/91	54800 (1.80)	332/ND	+5.6			
7	**3**	0.5	1	**6-3**/89	104000 (1.60)	346/ND	+2.3			

[a] Polymerization conditions: initiator **4**; 25 °C; 24 h; in CH_2Cl_2. [b] Reaction conditions: $Sc(OTf)_3$ (1 mol %); 60 °C; 24 h; in $MeNO_2$ (1 M). [c] Concentration of the monomer. [d] MeOH-insoluble part. [e] M_n was determined by GPC (DMF, polystyrene standard). [f] Determined by thermogravimetric analysis under a N_2 atmosphere. [g] Determined by differential scanning calorimetry; ND means the T_g peak is not clearly detected. [h] Determined by a solid density measurement at 25 °C (Shimadzu, Micromeritics gas pycnometer accupyc 1330); minus and plus signs mean volume shrinkage and expansion. [i] Volume change was calculated from density change vs density of the monomer. [j] DMSO-insoluble part. [k] Volume change was calculated from density change vs density of the product formed via the ROMP.

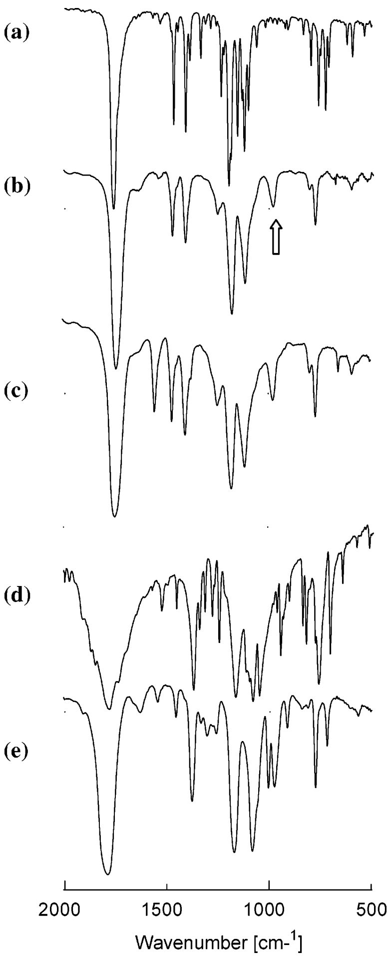

Figure 1. IR spectra of **2** (a), **5-1** (b), **5′-1** (c), **3** (d), and **6-1** (e).

cyclic carbonate unit. The 10% weight loss decomposition temperature (T_{d10}) of **5-1** was also lower than that of **8**, probably due to introduce the aliphatic carbonate structure. Meanwhile, the glass transition temperature (T_g) of **5-1** drastically increased compared with that of **8**. It should be caused by increase of the crystallinity of the resulting polymer based on the relatively higher dipole−dipole interaction between the cyclic carbonate units.

The cationic ring-opening reaction of **5-1** was also carried out in the presence of $Sc(OTf)_3$ at 60 °C for 24 h (runs 1). As a result, product **5′-1**, which was insoluble in common organic solvents including DMSO and DMF, was formed in a moderate yield, and the T_{d10} was increased over 15 °C compared to that of the precursor, **5-1**. The increases of the chemical resistance and thermally stability strongly suggested that the expected cross-linking reaction efficiently proceeded via the ring-opening reaction of the cyclic carbonate unit to form expected networked structure, at least partially.[13] In addition, **5′-1** showed no distinct T_g peak. The IR spectrum of **5′-1** did not indicate drastic change to that of the precursor, **5-1**, as described above. However, the facts that the decrease of solubility and the disappearance of T_g peak strongly suggested that the value of the acyclic carbonate peak should accidentally coincide with that of the cyclic carbonate.

The volume changes before vs after the treatment were also summarized in Table 1. As a result, the cationic ring-opening reaction of **5-1** was expectedly found to undergo with the nearly zero volume shrinkage (run 1), although networked formation is generally known to cause volume shrinkage. In addition, the present volume changing behavior should be interesting from the viewpoint of conversion from a material (linear polymers) to some other material (networked polymers) without volume shrinkage. This is because the volume change by using volume expanding monomers including cyclic carbonates has been almost only applied to the system from monomer to polymer, inevitably.

On the other hand, unexpected volume changing behavior was observed in the ROMP of **2**, in which volume expansion was, to our surprise, carried out (run 1). Since the similar ROMP of **7** caused volume shrinkage (run 2), the unexpected result should be attributed to the carbonate structure. Although the ring-opening polymerization of six-membered-ring cyclic carbonate is known to generally proceed with volume expansion, to our best knowledge, it has been never reported such volume expanding behavior before vs after a treatment except for the ring-opening polymerizations of cyclic carbonates. Incidentally, the expanding behavior in the ring-opening polymerization of six-membered-ring cyclic carbonate is explained as follows.[9] Volume expansion during polymerization requires much increase in intermolecular distance after polymerization in order to overcome the shrinkage derived from the proximity of monomer molecules caused by the polymerization. On the other hand, the ring-opening polymerization of six-membered-ring cyclic carbonate meets the requirement, probably due to changing of intermolecular interaction before vs after polymerization besides generation of intermolecular repulsion after polymerization. Taking into account that **2** should also have relatively large dipole moment based on the six-membered-ring cyclic carbonate unit, the present unexpected behavior could be also explained as follows. Before the ROMP, the monomers should rather closely exist due to the relatively large dipole−dipole interaction based on the cyclic carbonate structure. However, the closely existed state should be disturbed along with the propagation of ROMP on the norbornene unit, mainly owing to steric factors including steric hindrance in the molecular/polymer structures. Thus, the ROMP of norbornene-containing six-membered-ring cyclic carbonate, **2**, should unexpectedly cause to overcome the volume shrinkage derived from the linkage between monomers.

To further investigate the present unexpected results, the similar ROMPs followed by cationic ring-opening reactions of **2** were also carried out under other reaction conditions. As a consequence, the ROMP with 5 mol % of the initiator yielded the corresponding polymer, **5-2**, with lower M_n than that of the case with 1 mol % of the initiator (run 3 vs run 1), while that with 0.5 M of monomer concentration gave **5-3** with higher M_n (run 4). In addition, similar tendencies to **5-1** were also observed in the T_{d10} and T_g measurements of **5-2** and **5-3**, and these resulting products were also readily soluble in DMSO, DMF, and $MeNO_2$. Furthermore, the all cationic ring-opening reactions of **5-2** and **5-3** also gave the corresponding networked products (**5′-2** and **5′-3**), and these resulting compounds were also insoluble in the common organic solvents including DMSO and DMF. Incidentally, these NMR and IR spectra were similar to those of **5-1** and **5′-1**.

Table 1 also exhibits the volume changing behaviors in ROMPs, yielding **5-2** and **5-3** followed by the cationic ring-opening reactions (runs 3 and 4), and similar tendencies to the cases of the transformation from **5-1** to **5′-1** were observed. The cationic ring-opening reactions of **5-2** and **5-3** proceeded without volume shrinkage, in which volume expansions were observed. Furthermore, all ROMPs giving **5-2** and **5-3** also efficiently proceeded with volume expansion. At the present stage, it is not clear that the difference of degree of volume changing derived from ROMP conditions, and the volume expanding ratio should be caused by complicated factors including the differences of M_n and M_w/M_n of the resulting polymers. In particular, the present specific volume changing behavior in the ROMP process should be of interest from the standpoint of development of a novel synthetic methodology of polyalkenamer derivatives along with volume changing before vs after the treatments. This is because the present results imply that introduction of cyclic carbonate unit to a monomer having reactivity for ROMP might be useful for preparation of the polyalkenamers without volume shrinkage before vs after the treatment. In addition, the degree of volume expansion could be controlled by the reaction conditions.

The present specific volume changing behavior also prompted to examine the similar ROMPs by using **3** as one of other norbornene-containing cyclic carbonates, and the results are also summarized in Table 1. The ROMPs also smoothly propagated under several reaction conditions to give the polymers (**6-1**, **6-2**, and **6-3**, runs 5−7) with the expected structure. The M_ns of the resulting polymers were higher than those of **2** under similar conditions, presumably due to rather weak coordination between the catalyst and **3** compared to the case of **2**. For example, the dipole moment of a typical five-membered-ring cyclic carbonate, propylene carbonate is 4.62 D.[9] As the similar case to **5**, the T_{d10}s of **6-1**, **6-2**, and **6-3** were rather lower than that of **8**, and these resulting products were also readily soluble in DMSO, DMF, and $MeNO_2$. The T_g measurements of **6-1**, **6-2**, and **6-3** showed no distinct peak in the measurement range from room temperature to 230 °C. Incidentally, these structures were also confirmed by IR and NMR measurements, and the typical spectra of **6-1** are indicated in Figure 1e and Figure A-(d) in the Supporting Information. In addition, the cationic ring-opening reaction was not examined because the ring-opening reactions of five-membered-ring cyclic carbonates (units) are known to hardly proceed by cationic initiators, as described above.[12]

The volume changing measurement exhibited that all ROMPs giving **6-1**, **6-2**, and **6-3** were also carried out with volume expansion (runs 5−7). Thus, the specific ROMP was found to proceed with volume expansion even in the case of monomer containing five-membered-ring cyclic carbonate which generally has a rather low dipole moment compared with that of six-membered-ring one. Additionally, the volume expanding ratio before vs after the treatment was rather higher than the cases of the ROMPs of **2**. The different volume changing behavior between the treatments of **2** and **3** should be also caused by a combination of various factors. In addition, the distinction of the conformation derived from these monomer structures, i.e., spiro-structure **2** or not **3**, and of the dipole moments[14] should be one of the factors besides the differences of M_n and M_w/M_n of the resulting polymers.

In summary, the ROMP followed by cationic ring-opening polymerization behavior of **2** or **3** was investigated in the presence of catalyst **4** to find that **2** or **3** unexpectedly indicated volume expansion during the only ROMPs without the ring-opening reaction of each carbonate units. In addition, it was also found that the degree of volume change can be controlled by the ring size of cyclic carbonate unit and the polymerization conditions. Furthermore, the $Sc(OTf)_3$-mediated cationic ring-opening reactions of **5**s smoothly proceeded to give the corresponding networked-polymers **5′**s with the volume expansion or nearly zero volume shrinkage. Although the different volume changing behavior in these systems is not clearly elucidated at this stage, the present unexpected results in the treatments of **2** or **3** should strongly suggest an important insight into the development of volume-controllable high performance (networked) materials. Further detailed investigations are now in progress, and the results will be reported elsewhere.

Supporting Information Available: Typical experimental procedures and the synthetic methods of **2** and **3** and typical ^1H NMR spectra of **5-1** and **6-1** besides these monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For example, vinyl and cyclic monomers generally undergo polymerization with extensive volume shrinkage by ca. 10−20%: 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) (a) Endo, T.; Sanda, F. Cationic R−O 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. (g) Kameshima, H.; Nemoto, N.; Sanda, F.; Endo, T. *Macromolecules* **2002**, *35*, 5769.

(3) References 1 and 2d−f. For instance, 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-ring spiro-orthocarbonate and bicyclic bis(γ-lactone)s under both cationic and anionic conditions.

(4) There are not so many reports about networked polymers showing no volume shrinkage during cross-linking, 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: Griskey, R. G. *Polymer Process Engineering*; Chapman & Hall: New York, 1995.

(5) (a) We have reported that **1** acts as volume controllable cross-linking agent for mono-functionalized epoxide, PGE: Hino, T.; Endo, T. *Macromolecules* **2003**, *36*, 5902. (b) We also reported that **2** serve as a widely applicable volume controllable comonomer for various cyclic ether compounds compared to **1**: Hino, T.; Inoue, N.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5113.

(6) (a) Ivin, K. J.; Mol, J. C. In *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, CA, 1997. (b) Frenzel, U.; Nuyken, O. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2895. (c) Piotti, M. E. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4* 539.

(7) For instance, aliphatic polycarbonates are of interest for use as bioresorabable biomedical materials, and they are useful as oligomeric and polymeric additives with plasticizing or thickening properties. See ref 8a and references therein.

(8) For example: (a) Kricheldorf, H. R.; Weegen-Schulz, B. *Macromolecules* **1993**, *26*, 5991. (b) Chen, X.; McCarthy, S. P.; Gross, R. A. *Macromolecules* **1997**, *30*, 3470. (c) Ariga, T.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 581. (d) Kricheldorf, H. R.; Weegen-Schulz, B. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 2193. (e) Clements, J. H. *Ind. Eng. Chem. Res.* **2003**, *42*, 664. (f) Takata, T.; Endo, T. *Prog. Polym. Sci.* **1993**, *18*, 839. (g) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1994**, *27*, 3986. (h) Matsuo, J.; Sanda, F.; Endo, T. *Macromol. Chem. Phys.* **1998**, *199*, 2489. (i) Endo, T.; Sanda, F. *Macromol. Symp.* **2000**, *159*, 1. (j) Sudo, A.; Morioka, Y.; Sanda, F.; Endo, T. *Tetrahedron Lett.* **2004**, *45*, 1363. (k) Kihara, N.; Endo, T. *Macromol. Chem.* **1992**, *193*, 1481. (l) Takata, T.; Ariga, T.; Endo, T. *Macromolecules* **1992**, *25*, 3829. (m) Vogdanis, L.; Martens, B.; Uchtmann, H.; Hensel, F.; Heitz, W. *Makromol. Chem.* **1990**, *191*, 465. (n) Vogdanis, L.; Heitz, W. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 543. (o) Storey, R. F.; Hoffman, D. C. *Macromolecules* **1992**, *25*, 5369.

(9) Review: Takata, T.; Sanda, F.; Ariga, T.; Nemoto, H.; Endo, T. *Macromol. Rapid Commun.* **1997**, *18*, 461.

(10) Monomer **2** occurs volume expansion by 7.7% during the cationic ring-opening polymerization: Takata, T.; Amachi, K.; Kitazawa, K.; Endo, T. *Macromolecules* **1989**, *22*, 3188 and ref 9.

(11) Monomers **2** and **3** were prepared by literature procedures. Monomer **2**: ref 8b. Monomer **3**: Newman, M. S.; Addor, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 3789. See the Supporting Information.

(12) It is known that ring-opening polymerizations and reactions of five-membered-ring cyclic carbonates proceed by coordinated anionic initiators and anionic compounds, although cationic ring-opening ones of these carbonates hardly proceed, in general. Additionally, the polymerizations of five-membered-ring cyclic carbonates propagated along with decarboxylation, resulting in the formation of a copolymer comprised of ethylene oxide and ethylene carbonate repeat units, poly(ethylene−ether−carbonate): refs 8m−o and 9.

(13) It is considered that the cross-linking formation on trans-olefin site of the polymers formed by ROMP might hardly proceed. This is because the model reaction of propylene carbonate (six-membered-ring cyclic carbonate) and **8** under similar reaction conditions did not yield any networked polymers, in which the corresponding cationic ring-opening polymer was obtained with unreacted **8.** In addition, the IR spectrum of **5′** indicated the similar trans-olefin peak to that of **5** as shown in Figure 1.

(14) In general, the dipole moment of six-membered-ring cyclic carbonate is rather higher than that of five-membered-ring one, but the dipole moments of the corresponding acyclic ones of five- and six-membered ring cyclic carbonates are similar, e.g., the acyclic compounds of these carbonate indicate 0.97 and 0.92 D, respectively. See ref 9. Therefore, the phenomena might not be explained by only the difference of the dipole moment between five- and six-membered-ring cyclic carbonate units.

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