Macromol. Symp. ***132****, 371-376 (1998)*

Cationic Equilibrium Ring-Opening Polymerization of Bicyclic Monomers and Its Application to Chemical Recycling

Takeshi Endo, Fumio Sanda*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
Nagatsuta-cho, Midori-ku, Yokohama 226, Japan

SUMMARY:

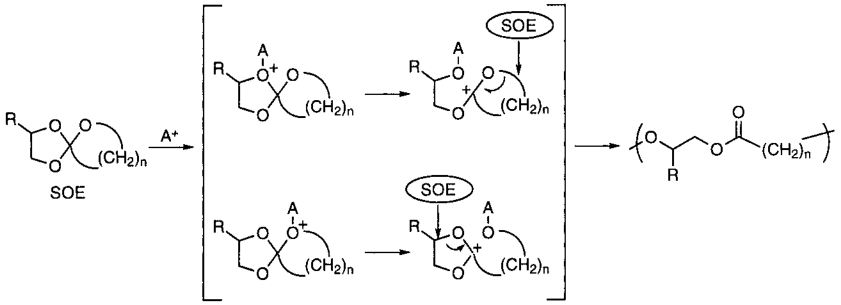
Spiro orthoesters give poly(cyclic orthoester)s by single ring-opening polymerization in the presence of acid catalysts, and this process undergoes the equilibrium polymerization. We have applied the function of equilibrium polymerization to chemical recycling of polymeric materials. Crosslinked poly(cyclic orthoester)s, prepared by radical additions of poly(cyclic orthoester)s possessing exomethylene groups and dithiols, efficiently decrosslinked to bifunctional spiro orthoesters in the presence of CF_3CO_2H in CH_2Cl_2. The dithiol-linked bifunctional spiro orthoester monomers, prepared by the radical additions of spiro orthoester possessing exomethylene group and dithiols, afforded the corresponding crosslinked polymers in the presence of CF_3CO_2H as a catalyst in bulk. The decrosslinking of the obtained crosslinked polymer proceeded quantitatively to obtain the corresponding bifunctional monomer at room temperature in CH_2Cl_2. Further, an acid-catalyzed reversible crosslinking-decrosslinking of a polymer having a spiro orthoester group in the side chain was carried out. The copolymer obtained by the radical copolymerization of 2-methylene-1,4,6-trioxaspiro[4.6]undecane with acrylonitrile was treated with CF_3CO_2H at -10 °C in CH_2Cl_2 to afford the crosslinked polymer quantitatively. The crosslinked polymer was then treated with CF_3CO_2H at room temperature at a low concentration in CH_2Cl_2 to recover the original polymer.

Introduction

Development of an excellent method for recycling of polymeric materials is an extremely important subject in recent polymer science and technology.[1)] Among the few technologies for recycling, chemical recycling may be the most important and essential. Spiro orthoesters (SOEs) polymerize with cationic catalysts to yield poly(ether-ester)s via double ring-opening polymerization (Scheme 1),[2)] and no shrinkage in volume is observed on this polymerization. This may be explained by the compensation effect by the double ring-opening in the decrease in free volume due to nearing molecules from van der Waals distance to covalent distance. Recently, we have found that SOE (**1**) polymerizes with $Al(acac)_3$ as a catalyst at room temperature to give poly(cyclic orthoester) (**2**) which can be regarded as being formed via a selective single ring-

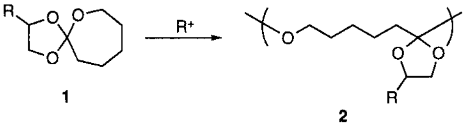
CCC 1022-1360/98/$ 17.50

Scheme 1:



opening of the seven-membered ether ring (Scheme 2).[3] In this article, we report [1] cationic polymerization of SOEs at low temperature to afford single ring-opened poly(cyclic orthoester)s, [2] the polymerization is one of the equilibrium polymerizations, [3] reversible crosslinking-decrosslinking system between bifunctional SOEs and network polymers utilizing the equilibrium polymerization of SOEs, and [4] reversible crosslinking-decrosslinking system between linear polymers with SOE moieties and network polymers.

Scheme 2:



1 **2**

Results and discussion

Cationic Polymerization of SOEs at Low Temperature

Cationic polymerizations of SOEs (**1a**; R=CH_3, **1b**; R=Ph, **1c**; R=H, **1d**; R=$BrCH_2$) were carried out at 0 °C in bulk in the presence of $SnCl_4$ (2 mol %) as a catalyst.[4] Polymers with Mns 4,100-14,400 were obtained as *n*-hexane- insoluble parts in 40-84% yields. The yield and molecular weight of the polymer decreased by the substitution. The IR and NMR spectra of the polymers supported cleanly that the polymer consisted of a poly(cyclic orthoester) structure (**2**), which should be formed by a single ring-opening of the seven-membered cyclic ether moiety without production of a double ring-opened unit. Meanwhile, SOEs with five- and six-membered ether rings did not afford any polymer but were recovered completely. Their different polymerizabilities of the SOEs may be depended on their ring-strains.[3]

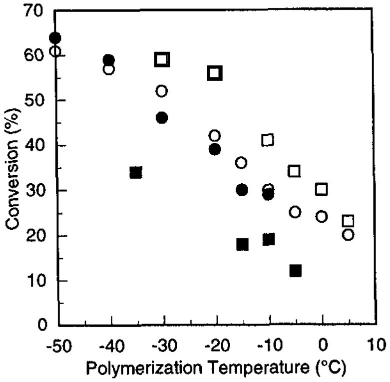


Fig. 1. The relationships between the polymerization temperatures and conversions of **1a** ~ **d** in the polymerizations with $SnCl_4$ (2 mol %) in CH_2Cl_2 (2 M) for 1 h, ○ R=Me (**1a**), ● R=Ph (**1b**), □ R=H (**1c**), ■ R=CH_2Br (**1d**)

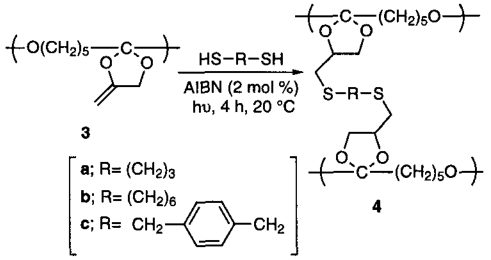
Equilibrium Polymerization of SOE

Dependence of the conversion of the SOEs was examined on the polymerization temperature. Generally, monomer conversion decreases at higher polymerization temperature in the equilibrium polymerization. Solution polymerizations of **1a** ~ **d** were performed with $SnCl_4$ (2 mol %) in CH_2Cl_2 (2 M) for 1 h. The relationships between the polymerization temperatures and the conversions of the monomers are illustrated in Fig. 1, which show similar tendency with common equilibrium polymerization. Further, since the plots of ln[M] vs 1/T have shown strait lines, this polymerization can be concluded as an equilibrium polymerization.

Reversible Crosslinking-Decrosslinking System between Bifunctional SOEs and Network Polymers

Poly(cyclic orthoester) (**3**) (Mn 4,900, Mw/Mn 2.13) possessing an exomethylene group was prepared by the dehydrochlorination of poly(chloromethyl cyclic orthoester) with *t*-BuOK (3.0 eq.) in THF.[4] Radical additions of **3** with dithiols (1.0 eq.) such as 1,3-propanedithiol (**a**), 1,6-hexanedithiol (**b**), and *p*-xylene-α,α'-dithiol (**c**) were carried out at 20 °C in the presence of AIBN (2 mol %) under UV irradiation in benzene for 4 h (Scheme 3).[5]

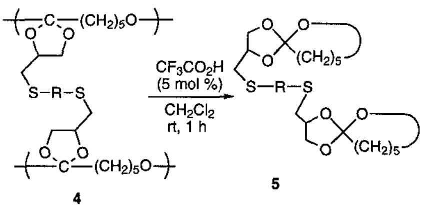
Scheme 3:



The radical additions efficiently proceeded to give the corresponding crosslinked poly(cyclic orthoester)s (yield; **4a**, 67%; **4b**, 70%; **4c**, 83%). The polymers **4a** ~ **c** were purified by washing the reaction mixtures with CH_2Cl_2 using a Soxhlet's extractor. **4a** ~ **c** were insoluble in various organic solvents (CH_2Cl_2, $CHCl_3$, C_6H_6, DMSO, DMF), and the IR absorptions of exomethylene group (1690 cm^{-1}) and thiol group (2550 ~ 2600 cm^{-1}) were not observed in the polymers at all, suggesting that the reaction proceeded quantitatively. The quantitative introduction of dithiols to **3** was also confirmed by elemental analyses.

A suspension of **4a** in CH_2Cl_2 (0.02 M) was treated with CF_3CO_2H (5 mol %) at room temperature for 1 h to change to a homogeneous solution, from which dithiol-linked bifunctional SOE (**5a**) was obtained in 66% yield. The crosslinked polymers **4b** and **4c** decrosslinked to the bifunctional monomers **5b** and **5c** in 69 and 82% yields under the similar conditions, respectively (Scheme 4).

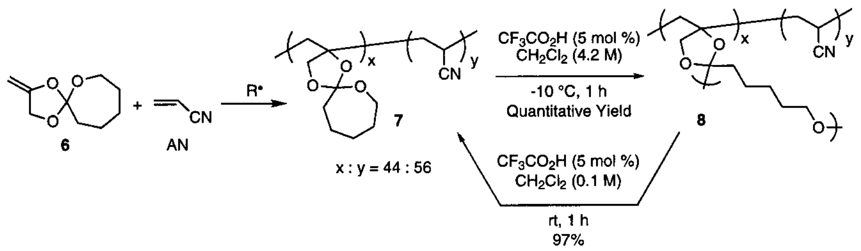
Scheme 4:



Several small peaks derived from oligomers were determined in the GPC trace of the crude reaction mixture from **4** to **5** in addition to the peak of **5**. The structures of **5a** ~ **c** were determined by their ^1H, ^{13}C NMR, and IR spectra in comparison with the authentic samples prepared by the radical additions of 2-methylene-1,4,6-trioxaspiro[4.6]undecane (**6**) and the corresponding dithiols. This decrosslinking proceeded smoothly by Lewis acids ($SnCl_4$, $BF_3{\bullet}OEt_2$, $TiCl_4$], and protic acids (CCl_3CO_2H, CH_3SO_3H), but weak acids like CH_3CO_2H did not promote the depolymerization.[6)]

The dithiol-linked bifunctional SOE (**5a**), which was prepared from **6** by the radical addition of 1,3-propanedithiol, could undergo the polymerization with CF_3CO_2H (2 mol %) as a catalyst in bulk to give the crosslinked polymer (**4a**). The yield of **4a** depended upon the reaction temperature. At 0 °C, **4a** was isolated in 52% yield. At 15 and 30 °C, the equilibrium on the polymerization of **5a** was shifted to the side of **5a** rather than the case of 0 °C. Consequently, **4a** was obtained in lower yields (43 and 19%, respectively). Depolymerization of **4a**, which was prepared from **5a**, efficiently proceeded with CF_3CO_2H in CH_2Cl_2 to obtain **5a** at room temperature in 82% yield without remaining the crosslinked polymer.

Scheme 5:



Reversible Crosslinking-Decrosslinking System between Linear Polymer and Network Polymer

Radical copolymerization of **6** with equivalent acrylonitrile (AN) efficiently proceeded in the presence of AIBN (2 mol %) at 60 °C in bulk for 24 h to afford the corresponding copolymer (**7**) in 85% yield. **7** was soluble in CH_2Cl_2, THF, and DMF. The Mn and Mw/Mn of **7** were 46,000 and 2.27, respectively. The copolymerization content in **7** was **6** : AN = 44 : 56, which was estimated by ^1H NMR besides elemental analysis.

The reaction of **7** was carried out with CF_3CO_2H (5 mol %) at -10 °C in CH_2Cl_2 (4.2 M) for 1 h to afford the crosslinked polymer (**8**) quantitatively. **8** was then treated with CF_3CO_2H at room temperature at a low concentration (0.1 M) in CH_2Cl_2 for 1 h to afford **7** in 97% yield (Scheme 5). The similar GPC profiles before crosslinking and after decrosslinking confirmed the acid-catalyzed reversible crosslinking-decrosslinking of the polymer possessing SOE group in the side chain.$^{7)}$

Conclusion

Cationic equilibrium polymerization of SOEs, and depolymerizations of crosslinked poly(cyclic orthoester)s linked by covalent bond with dithiols to bifunctional SOEs were accomplished, and the reversible crosslinking-decrosslinking system was controlled by changing temperature. Further, crosslinking system consisting of a reversible crosslinking-decrosslinking of a polymer having a SOE moiety in the side chain was explored. Our approach has demonstrated that even crosslinked polymers can be decrosslinked to bifunctional monomers and linear polymers under equilibrium polymerization conditions.

References

1) S. J. Huang, Ed., *Environmentally Degradable Polymers* (Elsevier, Oxford, 1994)

2) T. Takata, T. Endo, in *Expanding Monomers: Synthesis, Characterization and Applications* R. K. Sadhir, R. M. Luck, Eds. (CRC Press, Boca Raton, 1992) p. 63

3) S. Chikaoka, T. Takata, T. Endo, *J. Polym. Sci., Part A: Polym. Chem.* **28**, 3101 (1990)

4) S. Chikaoka, T. Takata, T. Endo, *Macromolecules* **24**, 6557 (1991)

5) S. Chikaoka, T. Takata, T. Endo, *Macromolecules* **27**, 2380 (1994)

6) T. Endo, T. Suzuki, F. Sanda, T. Takata, *Macromolecules* **29**, 3315 (1996)

7) (a) T. Endo, T. Suzuki, F. Sanda, T. Takata, *Macromolecules* **29**, 4819 (1996) (b) T. Endo, T. Suzuki, F. Sanda, T. Takata, *Bull. Chem. Soc. Jpn.* **70**, 1205 (1997)