Novel ring-opening polymerization and its function

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SUMMARY: This article deals with cationic ring-opening polymerization of spiro orthoesters, depolymerization of the obtained polymers, and its application to chemical recycling systems. Further, we describe novel living cationic ring-opening polymerization of a cyclic dithiocarbonate based on neighboring group participation.

Cationic polymerization of spirocyclic monomers and depolymerization of the obtained polymers

Degradable polymers have been widely developed from environmental points of view.[1] Development of a method of recycling of polymeric materials is also an issue of great interest for utilization of the limited petroleum resources. Among a few methods of recycling of polymeric materials such as thermal and material recycling, chemical recycling is the most important and essential, because it can recover original monomers by depolymerization. Several works on depolymerization have been reported concerning poly(methyl methacrylate),[2] poly(saccaride),[3] poly(chloroacetaldehyde),[4] poly(2,2-dialkyl-3-hydroxypropionic acid),[5] and poly(e-caprolactone).[6] Spiro orthoesters (SOEs) undergo cationic polymerization at high temperature (> 100 °C) *via* a double ring-opening process to give poly(ether-ester)s.[7] Recently, we have found that the cationic polymerization of SOEs consisting of a seven-membered ether ring and a five-membered acetal ring afford poly(cyclic orthoester)s at low temperature (<10 °C) *via* a single ring-opening of the seven-membered cyclic ether ring.[8] This polymerization is an equilibrium one, and the obtained polymers can be readily converted into the original monomers by the treatment with acid catalysts at room temperature. We have developed a reversible crosslinking - decrosslinking system between a bifunctional monomer linked by a dithiol and a network polymer with utilizing the equilibrium polymerization of SOEs.[9] The reversible crosslinking - decrosslinking can be controlled by changing the concentration of the reagents and temperature. This system may demonstrate one of the basic concepts to develop recyclable thermosetting resins as well as thermoplastic resins. We report synthesis and cationic single ring-opening polymerization of a novel monofunctional spiro orthoester (**1**) having an ester group, and depolymerization of the obtained polymer. The ester group can be hydrolyzed into a hydroxyl group, which can be converted into other functional groups. This enlarges the possibility of SOEs for the application to functional recyclable materials. Further, we describe the

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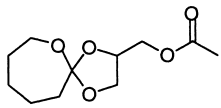
development for synthesis and cationic crosslinking - decrosslinking of bifunctional spiro orthoesters (**3a**, **3b**, **3c**) derived from dicarboxylic acids.



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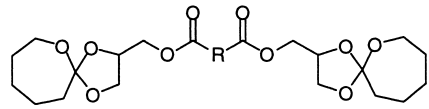
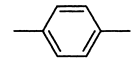
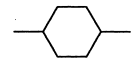


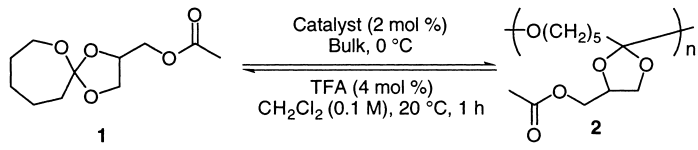
3a: R = 

3b: R = $-(CH_2)_2-$

3c: R = 

Cationic polymerization of monofunctional SOE (**1**)[10] was carried out with several cationic catalysts (TfOH, TFA, $SnCl_4$, BF_3•OEt_2, TfOMe; 2 mol % *vs.* **1**) in bulk at 0 °C under a nitrogen atmosphere (Scheme 1). In every case, stirring stopped within a few minutes during the polymerization due to the increase of the viscosity. Polymers with M_ns 3,600 ~ 15,000 were obtained in 20 ~ 75% yields. $SnCl_4$ afforded the polymer with the highest M_n in the highest yield. The structure of the obtained polymer was analyzed by IR and NMR spectroscopy. The polymer and **1** showed similar intensity ratios of the carbonyl absorption peak compared with the other peaks in the IR spectra, which suggested the selective occurrence of a single ring-opening polymerization of the seven-membered ring, without accompanying a double ring-opening polymerization. The ^1H NMR spectrum supported strongly the single ring-opened structure (**2**), which had been reported in the polymerization of several SOEs.[11] The ester group of **1** did not affect the polymerization behavior so much. Participation of the ester group into the propagating structure might be negligible.[12]

Scheme 1

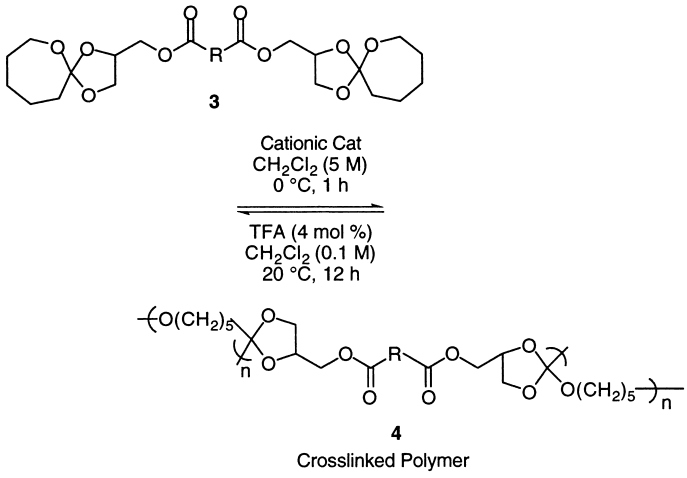


1 **2**

Next, the depolymerization of the obtained polymer (**2**) was carried out at 20 °C for 1 h in the presence of TFA (4 mol %) in CH_2Cl_2 (0.1 M) to regenerate the monomer in high yields, independent of the polymers obtained with different initiators. In the GPC before and after the depolymerization, the original polymer peak completely disappeared and that of the monomer appeared after the depolymerization, which confirmed the quantitative regeneration of the original monomer from the polymer.

Chemical recycling of thermosetting resins (network polymers) is much difficult compared with that of thermoplastics, because of infusibility and insolubility in solvents based on the network structure. If we can develop a decrosslinking system of network polymers, it may become one basis exploring the new fields of polymer recycling. Cationic crosslinking of **3a** was carried out at 0 °C for 1 h in the presence of several cationic catalysts (TfOH, TFA, $SnCl_4$, and BF_3•OEt_2, 5 mol % *vs.* **3a**) in CH_2Cl_2 (5 M) under a nitrogen atmosphere (Scheme 2) to obtain CH_2Cl_2-insoluble polymers in 30 ~ 60%. The rapid increase of the viscosity during the polymerization may be also the reason to prevent the increase of the crosslinking degree (molecular weight), which results in the formation of the solvent-soluble oligomers. The T_g and T_{d10} of **4a** under nitrogen were 15~36 and 241~299 °C, respectively.

Scheme 2



Decrosslinking of **4a** was carried out at 20 °C for 12 h in the presence of TFA (4 mol %) in CH_2Cl_2 (0.1 M) to regenerate the monomer and the CH_2Cl_2-soluble oligomer. The suspended solution of **4a** gradually changed to a homogeneous solution. No bifunctional monomer could be recovered from the crosslinked polymer obtained with TFA.

Further, cationic crosslinking of bifunctional SOEs (**3b**, **3c**) linked by aliphatic diesters was carried out at 0 °C for 1 h with $SnCl_4$ (5 mol %) in CH_2Cl_2 under a nitrogen atmosphere to obtain scarcely CH_2Cl_2-insoluble crosslinked polymers but CH_2Cl_2-soluble oligomers. Considerable amounts of unreacted monomers were recovered in all cases. No formation of solvent-insoluble crosslinked polymers from SOEs **3b** and **3c** might be due to their flexible aliphatic chain between the two SOE groups, which might be unfavorable for efficient crosslinking. In fact, SOE **3b**, having a more flexible methylene chain than the cyclohexyl

group of **3c**, afforded the oligomer in lower yields than **3c**. The rigid structure based on the terephthalate moiety of **3a** might be also effective to decrease the solubility of the polymer formed, resulting in the solvent-insoluble polymer.

Thus, we have examined the cationic single ring-opening polymerization of mono and bifunctional spiro orthoesters containing ester groups, and depolymerization of the obtained polymers. We have demonstrated the basic concept of chemical recycling for thermosetting resins as well as thermoplastics. The network polymer based on terephthalic acid successfully decrosslinked into the original bifunctional monomer. In the future, chemical recycling of polyesters may become possible by introducing SOE groups into the polymers.

Living polymerization based on neighboring group participation

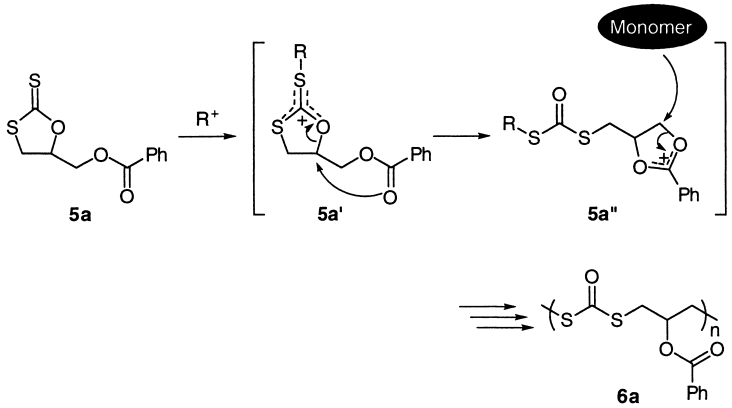
Living cationic polymerization is based on the stabilization of a growing carbocation by an added base or a counter anion. Recently, we have reported the first example of selective cationic ring-opening polymerization and isomerization of five-membered cyclic dithiocarbonates (**5**).[13] The monomer **5** selectively polymerizes with TfOMe as the initiator to afford the corresponding polydithiocarbonate, whereas **5** selectively isomerizes to the isomer in the presence of Lewis acids such as $ZnCl_2$ and $SnCl_4$, and protonic acids such as TfOH and CH_3SO_3H as the catalysts.[14]

Neighboring group participation plays an important role in selective chemical synthesis. If this neighboring group participation is employed to stabilize a propagating polymer end, a new class of living polymerization will be constructed. In this article, we wish to report the first example of a controlled living cationic ring-opening polymerization of a five-membered cyclic dithiocarbonate (**5a**) having a benzoxymethyl group based on the stabilization of the growing carbocation by neighboring group participation.

The cationic polymerization of **5a** was carried out with TfOMe as the initiator to give the polymer (**6a**) selectively. The molecular weight distributions (M_w/M_n) of the polymers obtained were very narrow even at 60 °C (M_w/M_n 1.14). The M_n values of the polymers estimated by GPC based on polystyrene calibration were in good agreement with the molecular weights determined from the ^{1}H-NMR peak integration ratio of the S-Me group at the initiating end. The M_n of the polymer increased in direct proportion to the monomer conversion and showed a good agreement with the molecular weight calculated by NMR. Further, the polymerization was quenched with myristyl trimethylammonium bromide to find the functionality of the terminating end group was 92%, supporting the living nature of the polymerization.

Scheme 3 illustrates a plausible mechanism of the polymerization of **5a**. The monomer **5a** forms a carbenium cation (**5a'**) by methylation, followed by isomerization to yield a more stable carbenium cation (**5a''**) stabilized by two oxygen atoms and phenyl group. The formation of the carbenium cation **5a''** was confirmed in the mixture of **5a** with TfOMe (1.2 eq) in $CDCl_3$ by NMR spectroscopy.

Scheme 3



In conclusion, we have demonstrated the first example of a controlled living cationic ring-opening polymerization of the five-membered cyclic dithiocarbonate based on the neighboring group participation. This new concept of living polymerization may be applied to the design of well-defined novel functional polymers.

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