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A Novel Construction of Ring-Opening Polymerization and Chemical Recycling System

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Summary: This article summarizes our recent efforts to chemical recycling of polymeric materials based on the equilibrium polymerization character of cyclic monomers. Spiro orthoesters (**SOE**s), bicyclo orthoester, cyclic carbonates, and dithiocarbonates undergo ring-opening polymerization to afford the corresponding polymers, and the resulting polymers depolymerize to give the starting monomers under cationic or anionic conditions. Further, crosslinking and decrosslinking systems of bifunctional **SOE**s and a polymer having **SOE** moiety in the side chain are described.

Keywords: crosslinking; decrosslinking; depolymerization; equilibrium polymerization; recycling; ring-opening polymerization

Introduction

Development of useful recycling method for polymeric materials is an extremely important subject in recent polymer science and technology.[1) Polymer recycling can be classified into the following three methods: (1) material recycling (reuse of the materials after grinding and so on); (2) thermal recycling (use as thermal energy); (3) chemical recycling (transformation of polymers into the corresponding monomers). Among these few technologies for recycling of polymeric materials, chemical recycling may be the most important and essential, because only this method can regenerate the original materials from the used ones. Recycling of thermosetting resins is regarded as one of the urgent problems because of its technological difficulty. To get over this problem, we have proposed a possible approach, which apply the equilibrium polymerization system for chemical recycling of thermosetting resins. In this system, polymerization and depolymerization can be controlled by simply changing the conditions of the system. Several depolymerization systems such as polymethyl methacrylate,[2) polylactones,[3) polylactides,[4) polychloroacetaldehyde,[5) and polysaccharide xantan[6) have been reported;

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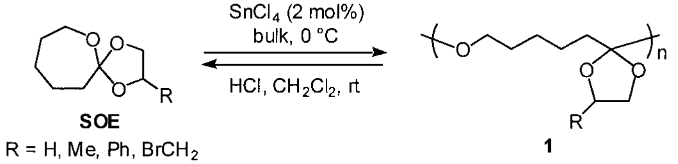
however, no reversible system between monomer and polymer has been reported yet. This article describes an idea of chemical recycling, i.e., the successful construction of novel reversible systems of polymers and monomers utilizing the equilibrium polymerization system of cyclic monomers which have been recently developed.

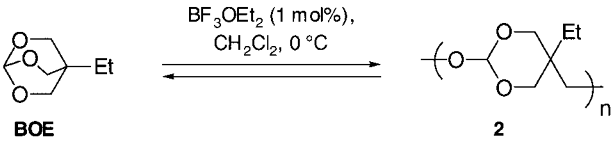
Spirocyclic and Bicyclic Monomers

Spiro orthoesters (**SOEs**) polymerize with cationic catalysts at 100 °C to yield poly(ether-ester)s via a double ring-opening process, and no shrinkage in volume is observed during this polymerization.[7] In contrast, we have recently found that **SOEs** polymerize with $SnCl_4$ as a catalyst at 0 °C to give poly(cyclic orthoester)s (**1**) via a selective single ring-opening of the seven-membered ether ring (Scheme 1).[8] During the study of the above-mentioned polymerization, we have found that the obtained polymers (**1**) can be converted into the starting monomers **SOEs** by the treatment with a catalytic amount of anhydrous HCl at room temperature in a diluted condition in 67–82 % yield. Temperature dependence of the conversion of **SOEs** in this polymerization show typical behavior of equilibrium polymerization, namely, the conversion decreases with increase of polymerization temperature. Further, since the linear relationship was observed between ln[M] and 1/T in the polymerization of **SOEs**, this polymerization may behave as an equilibrium polymerization.



Scheme 1

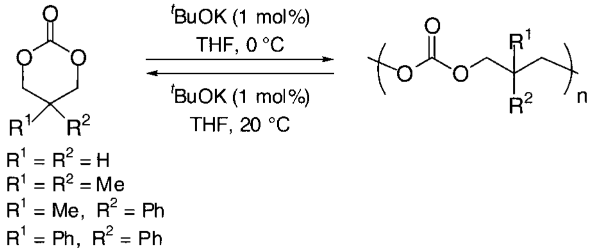
Furthermore, bicyclo orhoesters (**BOEs**) undergo cationic double ring-opening polymerization at 100 °C to show volume expansion on polymerization.[9] We have reported that **BOE** polymerizes with BF_3OEt_2 as a catalyst at 0 °C to afford the single ring-opened polymer (**2**) and this polymerization acted as equilibrium one (Scheme 2).[10] The obtained polymer can be converted into the starting monomer in 43 % yield under the conditions similar to those for the polymerization.



Scheme 2.

Cyclic Carbonates

It has been reported that anionic ring-opening polymerization of cyclic carbonates show equilibrium character,[11] however, there are few reports on the substituent effect on the equilibrium polymerization. We have found that the cyclic carbonates with bulky substituents show higher equilibrium monomer concentration in the anionic polymerization (Scheme 3),[12] which may suggest that the formation of a cyclic carbonate with more bulky substituents is more preferable than that of the linear polymer. The monomer recovered yiled in the anionic depolymerization well agreed with the equilibrium monomer one in the anionic ring-opening polymerization.



Scheme 3.

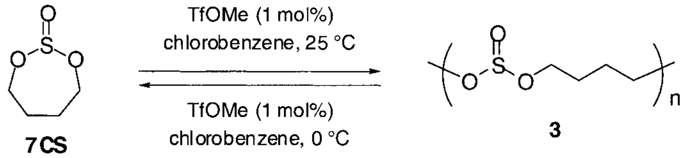
Table 1. Monomer Yield Recovered in the Depolymerization of Polycarbonates and Equilibrium Monomer Concentration.[a]

entry	polymer	$M_n(M_w/M_n)^b$	monomer recovered (%)^c	euilibrium monomer concentration (M)
1	poly(**1**)	54 000(1.4)	7	0.03
2	poly(**2**)	61 200(1.3)	19	0.08
3	poly(**3**)	25 300(1.5)	32	0.15
4	poly(**4**)	18 500(1.6)	71	0.32

[a] Conditions: initiator, ^{t}BuOK (1 mol%); solvent, THF (0.45 M); temperature, 20 °C; time, 24 h. [b] Estimated by SEC based on polystyrene standards. [c] Determined by ^{1}H NMR spectroscopy.

Cyclic Sulfites

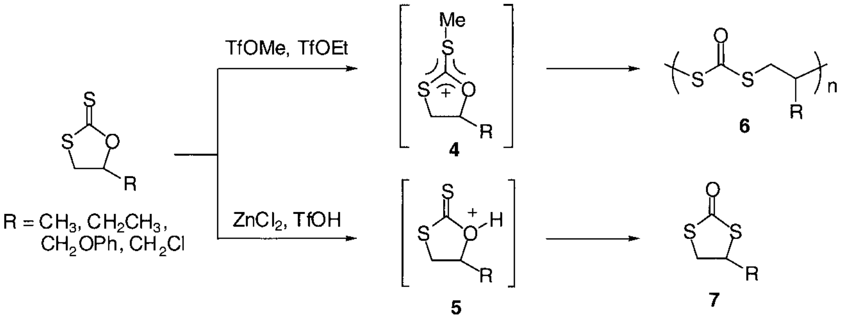
Cyclic sulfites, sulfur analogs of cyclic carbonates, undergo cationic ring-opening polymerization to give polysulfites (Scheme 4).13) In the cationic polymerization of seven-membered cyclic sulfite (**7CS**), the conversion of **7CS** decreased as the polymerization temperature increased, suggesting that this polymerization might behave an equilibrium one.14) The equilibrium monomer concentration at 25 °C was estimated as 2.4 *M*. The obtained polymer (**3**) can be depolymerized with TfOMe as a catalyst to regenerate the starting monomer **7CS** in 52 % yield.



Scheme 4.

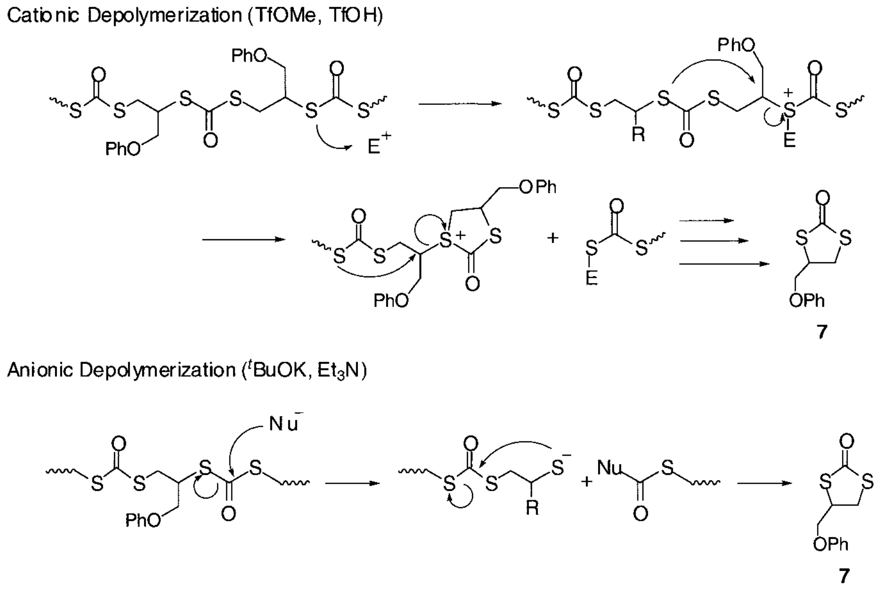
Cyclic Dithiocarbonates

Selectivity of reaction pathways is extremely important, however, no successful report on catalytic control of polymerization and isomerization has been reported so far. We have found that alkyl triflates predominantly polymerize five-membered cyclic dithiocarbonates, whereas Lewis and protonic acids selectively isomerize the dithiocarbonates into the corresponding 1,3-dithiolane-2-one derivatives (7) (Scheme 5).[15] The formation of cyclic carbenium cation (4) and cyclic oxonium cation (5) was confirmed in the reactions of dithiocarbonate with TfOMe and TfOH, respectively.[16] The selectivity of the cationic polymerization and isomerization of dithiocarbonate is attributable to the different intermediates depending on the catalysts.



Scheme 5.

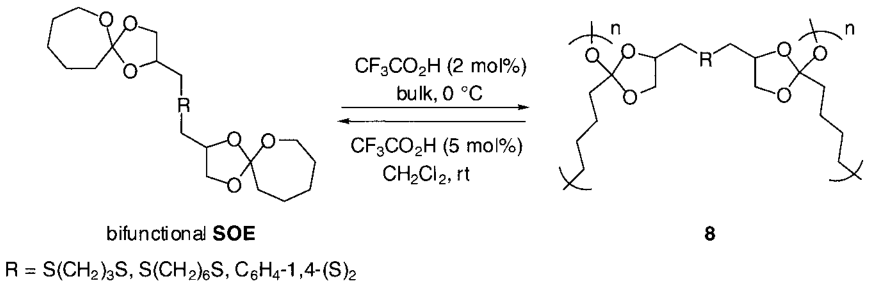
In the cationic polymerization and isomerization of the dithiocarbonate, increase of isomer content was observed as the elongation of reaction time. This means that depolymerization of a polymer into an isomer of the monomer takes place. Cationic reagents depolymerize the polydithiocarbonate obtained from 5-phenoxymethyl 1,3-oxathiolane-2-thione to produce the isomer (7) in 35–83 %. Anionic reagents are more effective to afford the isomer, which can be recovered quantitatively when potassium *tert*-butoxide is used.[17] The plausible reaction mechanism is illustrated in Scheme 6.



Scheme 6.

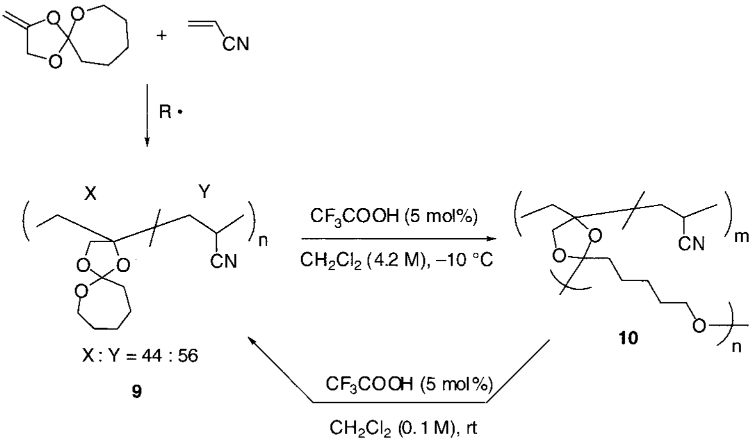
Crosslinking-decrosslinking system

Chemical recycling of network polymers is much difficult compared with that of linear polymers, because of their infusibility and insolubility in solvents based on network structure. If we can develop a decrosslinking system of network polymers, it may demonstrate a novel field of polymer recycling. With a bifunctional monomer having functional groups which can construct an equilibrium polymerization system, a crosslinking-decrosslinking system between the monomer and the corresponding crosslinked polymer can be established. The dithiol-linked bifunctional **SOE**s were prepared by the radical additions of dithiols to **SOE** possessing exomethylene group.[18] The bifuncitional **SOE**s could undergo the cationic polymerization with CF_3COOH as a catalyst at 0 °C to afford the corresponding crosslinked polymers (**8**) in 19–53 % yields (Scheme 7). Decrosslinking of the crosslinked polymers efficiently proceed to recover the original bifunctional **SOE**s in 66–82 % yields at room temperature.



Scheme 7.

Further, an acid-catalyzed reversible crosslinking-decrosslinking of a polymer bearing **SOE** moiety in the side chain was developed.[19] The copolymer (**9**) obtained by the radical copolymerization of **SOE** possessing exomethylene group with acrylonitrile was treated with CF_3COOH in CH_2Cl_2 at −10 °C to afford the corresponding crosslinked polymer (**10**) quantitatively (Scheme 8). The crosslinked polymer was then treated with CF_3COOH in CH_2Cl_2 at room temperature to give the original polymer in 97 % yield.



Scheme 8.

Conclusion

In this article, we reviewed our recent works on chemical recycling of the polymers and the crosslinked polymers utilizing the equilibrium polymerization system. The recycling systems consisting of polymerization–depolymerization and crosslinking–decrosslinking can be controlled by changing the concentration of the reagents and temperature. The novel equilibrium polymerization for chemical recycling demonstrated in this study would be significant in the field of polymer science, environmental issue, and so on.

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