# A Novel Approach for the Chemical Recycling of Polymeric Materials: The Network Polymer ⇄ Bifunctional Monomer Reversible System

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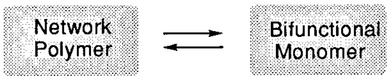
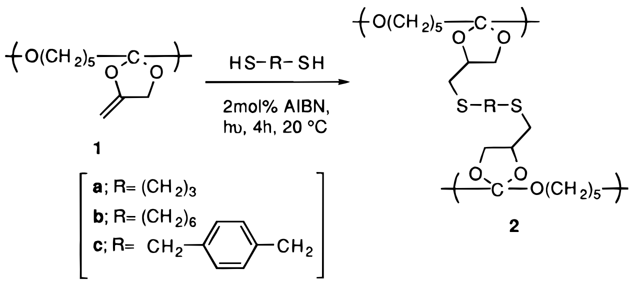
Development of an excellent method for recycle use of polymeric materials, i.e. plastics, is an extremely important subject in recent polymer science and technology.[1] Among the few technologies for recycle use, chemical recycle may be the most important and essential. Recycle use of thermosetting resins is regarded as one of the urgent problems to be settled because of its technological difficulty. To get over this problem, we have proposed a possible approach which consists of the introduction of the concept of equilibrium polymerization into chemical recycle of thermosetting resins. Namely, if we provide a bifunctional monomer having functional groups which can construct an equilibrium polymerization system, a curing−depolymerization system between the monomer and the corresponding cross-linked network polymer can be established as shown in Scheme 1. In this system, the curing and depolymerization can be controlled by simply changing the conditions of the system, suggesting that the cross-linked polymer reverts to the original bifunctional monomer by depolymerization. Several depolymerization systems such as poly(methyl methacrylate),[2] polylactones,[3] polylactides,[3] polybutadiene,[4] poly(chloroacetaldehyde),[5] and the polysaccharide xanthan[6] have been reported; however, no reversible system between bifunctional monomers and network polymers has been reported yet. This paper describes an idea of chemical recycle, i.e. the successful construction of a novel reversible system of network polymers between bifunctional monomers by utilizing the equilibrium polymerization system of a spiro orthoester which has been recently developed.[7]

Poly(cyclic orthoester) (**1**) ($\bar{M}_n = 4900$, $\bar{M}_w/\bar{M}_n = 2.13$) possessing an exo methylene group was prepared by the dehydrochlorination of poly(chloromethyl cyclic orthoester) with 3.0 equiv of *t*-BuOK in THF.[7] Radical addition of **1** with 1.0 equiv of dithiols such as 1,3-propanedithiol (**a**), 1,6-hexanedithiol (**b**), and *p*-xylene-α,α′-dithiol (**c**) was carried out at 20 °C in the presence of 2 mol % of AIBN under UV irradiation in benzene for 4 h (Scheme 2).[8] The radical addition efficiently proceeded to give the corresponding cross-linked poly(cyclic orthoester)s (yield: **2a**, 67%; **2b**, 70%; **2c**, 83%). The purification of **2a**−**c** was carried out by washing the reaction mixtures with dichloromethane using a Soxhlet extractor. **2a**−**c** were insoluble in various organic solvents (dichloromethane, chloroform, benzene, dimethyl sulfoxide, *N*,*N*-dimethylformamide), and the IR absorptions of the exo methylene group (1690 cm$^{-1}$) and the thiol group (2550−2600 cm$^{-1}$) were not observed at all in the polymers, suggesting that the reaction proceeded quantitatively. The quantitative introduction of dithiols to **1** was confirmed by elemental analyses.

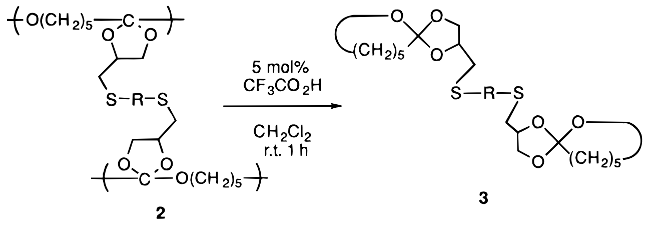
**Scheme 1**



**Scheme 2**



**Scheme 3**



A suspension of **2a** (34 mg, 0.076 mmol) in dichloromethane (3.4 mL) was treated with 5 mol % of trifluoroacetic acid at room temperature for 1 h to change to a homogeneous solution, from which dithiol-linked bifunctional spiro orthoester (**3a**, yield 66%, determined by GPC using monodisperse polystyrene as an internal standard) was obtained. Under similar conditions, the cross-linked polymers **2b** and **2c** depolymerized to the bifunctional monomers **3b** and **3c** in 69 and 82% yields, respectively (Scheme 3). In the GPC trace of the crude reaction mixture in the reaction from **2** to **3**, several small peaks derived from oligomers in addition to the peak of **3** were determined. The structures of **3a**−**c** were determined by their $^1$H, $^{13}$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 and the corresponding dithiols.[9] This depolymerization proceeded smoothly by various acids such as Lewis acids [anhydrous tin(IV) chloride, boron trifluoride etherate, or titanium(IV) chloride], or other protic acids (trichloroacetic acid, methanesulfonic acid), but weak acids like acetic acid did not promote the depolymerization.

The dithiol-linked bifunctional spiro orthoester (**3a**), which was prepared from a spiro orthoester possessing an exo methylene group by the radical addition of 1,3-propanedithiol, could undergo the polymerization with 2 mol % of trifluoroacetic acid as a catalyst in bulk condition to give the cross-linked polymer (**2a**) (Scheme 4, path A). The yields of **2a** depended upon the reaction temperature. At 0 °C, **2a** was isolated in 52% yield. At 15 and 30 °C, the equilibrium on the polymerization of **3a** was shifted to the side of **3a** rather than the case of 0 °C. Consequently, **2a** was obtained in lower yields (43 and 19%, respectively). Depolymerization of **2a** prepared from **3a** efficiently proceeded by trifluoroacetic acid in dichloromethane to obtain the bifunctional

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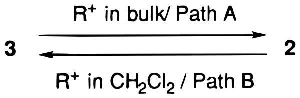
**Scheme 4**



monomer (**3a**) at room temperature in 82% yield without remaining the cross-linked polymer (Scheme 4, path B).

In conclusion, depolymerizations of cross-linked poly(cyclic orthoester)s linked by a covalent bond with dithiols to bifunctional spiro orthoesters were accomplished by acid catalysts, and the reversible cross-linking–depolymerization system was controlled by changing temperature. Our approach has demonstrated that even cross-linked polymers can be depolymerized to bifunctional monomers under equilibrium polymerization conditions.

## References and Notes

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(9) **3a**: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 1.15–1.95 (m, 18 H), 2.10–2.97 (m, 8 H), 3.52–4.55 (m, 10 H). $^{13}$C NMR (22.5 MHz, $C_6D_6$) $\delta$ 23.09, 23.17, 29.42, 29.46, 29.79, 31.03, 31.09, 31.29, 31.44, 35.47, 36.65, 37.69, 37.75, 64.00, 68.58, 69.23, 75.52, 77.04, 124.73, 124.90. IR (neat) 2924, 1474, 1439, 1366, 1240, 1178, 1132, 1044, 922, 847, 767, 663 cm$^{-1}$. Anal. Calcd for $C_{21}H_{36}O_6S_2$: C, 56.22; H, 8.09; S, 14.29. Found: C, 55.90; H, 8.41; S, 14.30. **3b**: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 1.02–1.78 (m, 24 H), 2.10–3.05 (m, 8 H), 3.53–4.53 (m, 10 H). $^{13}$C NMR (22.5 MHz, $C_6D_6$) $\delta$ 23.11, 23.19, 28.57, 29.46, 29.90, 31.04, 31.13, 32.59, 32.72, 35.60, 36.82, 37.75, 37.82, 64.05, 68.69, 69.36, 75.63, 77.13, 124.77, 124.95. IR (neat) 2932, 2857, 1439, 1366, 1240, 1179, 1132, 1036, 963 cm$^{-1}$. Anal. Calcd for $C_{24}H_{42}O_6S_2$: C, 58.74; H, 8.63; S, 13.07. Found: C, 58.80; H, 8.46; S, 13.30. **3c**: $^1$H NMR (90 MHz, $C_6D_6$) $\delta$ 1.15–1.82 (m, 16 H), 2.08–2.92 (m, 4 H), 3.46–4.50 (m, 14 H), 7.09–7.17 (m, 4 H). $^{13}$C NMR (22.5 MHz, $C_6D_6$) $\delta$ 23.09, 23.17, 29.44, 29.49, 31.03, 31.11, 34.41, 35.69, 36.28, 36.34, 37.71, 64.00, 68.52, 69.06, 75.46, 76.91, 124.75, 124.90, 129.40, 137.47. IR (neat) 2928, 2857, 1510, 1474, 1437, 1366, 1238, 1179, 1132, 1073, 961, 847, 772, 666 cm$^{-1}$. Anal. Calcd for $C_{24}H_{38}O_6S_2$: C, 61.15; H, 7.50; S, 12.56. Found: C, 60.90; H, 7.55; S, 12.30.

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