A Novel Network Polymer ⇄ Linear Polymer Reversible System. A New Cross-Linking System Consisting of a Reversible Cross-Linking–Depolymerization of a Polymer Having a Spiro Orthoester Moiety in the Side Chain

Takeshi Endo,[*] Takashi Suzuki, Fumio Sanda, and Toshikazu Takata[†]

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

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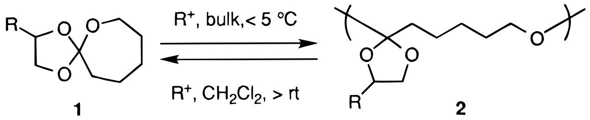
Bio- and photodegradable polymers have been widely studied for environmental protection.[1] Recyclable polymers are expected to be candidate polymers for overcoming a serious problem. Depolymerization is important in recycling of polymers, and many studies on depolymerization systems have been reported, e.g., poly(methyl methacrylate),[2] polysaccharide,[3] poly(chloroacetaldehyde),[4] poly(2,2-dialkyl-3-hydroxypropionic acid),[5] and poly(ϵ-caprolactone).[6] However, the degree of the depolymerization in these systems is low. Recently, we reported that the cationic polymerization of spiro orthoester **1** proceeds at low temperature via a single ring-opening process to give poly(cyclic orthoester) **2** (Scheme 1).[7] Since this polymerization is a typical equilibrium polymerization, the obtained polymer **2** can be readily converted to the original monomer **1** by treatment with acid catalyst. In the course of study of equilibrium polymerization of **1**, we have designed a new cross-linking system using the equilibrium polymerization. This communication demonstrates acid-catalyzed completely reversible cross-linking–depolymerization of a polymer having a spiro orthoester group in the side chain.

Scheme 1



Radical polymerization of 2-methylene-1,4,6-trioxaspiro[4.6]undecane (**3**)[8] with equivalent acrylonitrile (AN) initiated by 2,2′-azobis(isobutyronitrile) (AIBN, 2 mol %) in bulk at 60 °C for 24 h efficiently proceeded to afford the corresponding copolymer (**4**) as the methanol-insoluble part in 85% yield. **4** was soluble in dichloromethane, THF, and DMF. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of **4** were determined by gel permeation chromatography (GPC) to be 46 000 and 2.27, respectively. The structure of **4** was confirmed by the ^{1}H NMR spectrum.[9] The copolymerization content of **4** was estimated to be **3**:AN = 44:56 by the ^{1}H NMR spectrum besides elemental analysis.[10]

The reaction of **4** with trifluoroacetic acid (TFA, 5 mol %) in dichloromethane (4.2 M) was carried out at −10 °C for 1 h to afford cross-linked polymer **5** quantitatively. **5** was then treated with TFA at a low concentration (0.1 M) in dichloromethane at room temperature for 1 h to yield **4** in 97% yield (Scheme 2). The GPC profiles (Figure 1) before cross-linking and after depolymerization confirmed the acid-catalyzed reversible cross-linking–depolymerization of the polymer possessing the spiro orthoester group in the side chain.

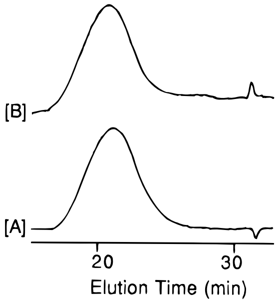
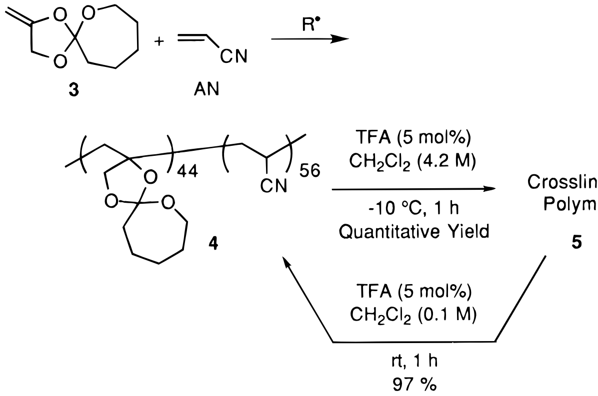


Figure 1. GPC profiles of **3** before cross-linking and after depolymerization: (A) before cross-linking, $\bar{M}_n = 46\,000$, $\bar{M}_w/\bar{M}_n = 2.27$; (B) after depolymerization, $\bar{M}_n = 54\,000$, $\bar{M}_w/\bar{M}_n = 2.21$.

Scheme 2



In conclusion, a new cross-linking system consisting of a reversible cross-linking–depolymerization of a polymer having a spiro orthoester moiety in the side chain has been explored. Further studies on the effects of concentration on the cross-linking and of temperature on the depolymerization are now under investigation.

References and Notes

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(8) Prepared by the reaction of epichlorohydrin and ϵ-caprolactone catalyzed by $BF_3{\cdot}OEt_2$, followed by dehydrochlorination with sodium methoxide. See: Endo, T.; Okawara, M.; Yamazaki, N.; Bailey, W. J. *J. Polym. Sci., Part A: Polym. Chem.* **1981**, *19*, 1283.
(9) ^{1}H NMR (δ CDCl$_3$, 90 MHz) 1.4–2.6 (m, 10 H for unit **3**, 2 H for AN), 2.7–3.4 (m, 1 H for AN, C*H*CN), 3.5–4.3 (m, 4 H for unit **3**, CH$_2$O). The copolymerization content was calculated from the integration ratio of the signals at 2.7–3.4 ppm and 3.5–4.3 ppm.
(10) The copolymerization content calculated by % N in the elemental analysis was **3**:AN = 45:55, which agreed well with that calculated from ^{1}H NMR.

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[*] To whom correspondence should be addressed.

[†] Present address: Department of Applied Chemistry, College of Engineering. University of Osaka Prefecture, Gakuen-cho, Sakai, Osaka 593, Japan.

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