

# Reversible Cross-Linking and De-Cross-Linking System of Polystyrenes Bearing the Monohydrate Structure of Vicinal Tricarbonyl Group through Water—Alcohol Exchange Reactions at Ambient Conditions

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# **Supporting Information**

**ABSTRACT:** We describe in this paper reversible crosslinking and de-cross-linking system based on a polystyrene derivative bearing monohydrate structure of vicinal tricarbonyl groups with 1,6-hexanediol utilizing the direct water—alcohol exchange reactions on the vicinal tricarbonyl groups. By employing diphenylpropanetrione as a unit model compound for the polymer, we have demonstrated that the water—alcohol exchange reactions could be carried out reversibly in both directions by changing solvents. Notably, the water—alcohol exchange reactions proceeded without any catalysts and under mild conditions. For example, an equimolar mixture of the hydrate of diphenylpropanetrione and benzyl alcohol in



chloroform (0.5 M) reached equilibrium after standing at ambient temperature within 48 h, where the content ratio of the benzyl alcohol adduct increased up to 49%. The reaction rate and the position of the equilibrium were highly affected by the concentrations of the substrates as well as the reaction temperature. By virtue of the above characteristic features of the water– alcohol exchange reactions, the polystyrene derivative bearing monohydrate structure of vicinal tricarbonyl group (2.0 M) was cross-linked with 1,6-hexanediol (0.2 equiv of OH group to the tricarbonyl unit) in acetone at ambient temperature for 5 days to afford the networked polymer in almost quantitative yield. On the other hand, the networked polymer was treated with an excess of water at ambient temperature for 3 days to afford the original linear polymer in high yield as a result of de-cross-linking through the water–alcohol exchange reaction. The cross-linking and de-cross-linking behavior was also evidenced by SEC analysis of the reaction mixture.

# INTRODUCTION

Vicinal tricarbonyl compounds, such as alloxan, 1,2,3indanetrione, dehydroascorbic acid, and diphenylpropanetrione (DPPT, 1), have by definition the three contiguous carbonyl groups, and are characterized by a highly electrophilic central carbonyl group, which is activated by the adjacent two carbonyls and significantly reactive toward various nucleophiles, such as water and alcohols (Scheme 1).<sup>1,2</sup> Hence, vicinal tricarbonyl compounds are usually obtained as their hydrated forms (2,2-gem-diol, DPPT-H<sub>2</sub>O, 2) as a result of hydration with moisture in air or solvents used during the isolation processes (Scheme 1a). These hydrates can be dehydrated to give pure free vicinal tricarbonyls (1) by heating under vacuum,<sup>3–5</sup> sublimation,<sup>5,6</sup> distillation,<sup>7–10</sup> crystallization,<sup>9</sup> azeotropic removal of water,<sup>10</sup> and utilization of dehydrating agents such as molecular sieves 4A or P2O5.6,10,11 This reversible hydration-dehydration nature of vicinal tricarbonyls enables us to utilize them as recyclable dehydrating agents.<sup>12</sup> Of particular interest is that the reversible hydration process is accompanied by disappearance and appearance of the distinctive yellow color due to the collapse and recovery of

the contiguous three carbonyl groups, respectively, hence being detectable by the naked eye.<sup>1,2</sup> The vicinal tricarbonyl compounds exhibit a similar behavior toward alcohols (Scheme 1b); the addition of alcohols readily proceeds at ambient temperature to form the corresponding alcohol adducts (hemiketal, DPPT-ROH, **3**) without any catalyst, being accompanied by disappearance of their distinctive color arising from the vicinal tricarbonyl structures. Conversely, the vicinal tricarbonyl compounds are obtained by heating under vacuum to remove the alcohols.

Motivated by the characteristic features of vicinal tricarbonyl compounds, we recently reported design and synthesis of a polystyrene derivative bearing acyclic vicinal tricarbonyl structures in the side chains (4) and detailed investigation of its reversible addition–elimination behavior of water and alcohols to the vicinal tricarbonyl polymer (Scheme 1c).<sup>13–16</sup> The vicinal tricarbonyl pendants of 4 readily reacted with water

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or alcohols to quantitatively yield the corresponding water or alcohol adduct polymer 5. On the other hand, heating 5 under vacuum afforded the original polymers with the vicinal tricarbonyl pendants 4 without deteriorating the polymer structure.

Polymer materials that can be reversibly cross-linked and decross-linked through covalent bonds have recently attracted much attention from the standpoint of chemical recycling as well as self-healing materials.<sup>17–19</sup> Taking advantage of the reversible nature of the alcohol addition to vicinal tricarbonyl groups, we developed a new reversible cross-linking system from the vicinal tricarbonyl polymers **4** and an  $\alpha,\omega$ -diol as the cross-linking reagent. However, the vicinal tricarbonyl polymer system has some drawback toward materials application; the de-cross-linking step utilizing the elimination of alcohols requires heating at around 100 °C under reduced pressure. In addition, the polymers bearing vicinal tricarbonyl pendants are susceptible to moisture and need to be preserved under dry conditions. Therefore, new processes or systems that can be reversibly cross-linked and de-cross-linked under mild conditions are desired to be developed.

Over the course of our study to develop new polymer materials based on the vicinal tricarbonyl structures, we noted that the two reversible reactions, the reversible addition of water and that of alcohol, indicated that the apparently direct exchange of water and alcohols on the vicinal tricarbonyls in situ is possible by way of vicinal tricarbonyl intermediates (Figure 1a). On the basis of this equilibrium, we envisaged that use of the gem-diol polymers would lead to a new system that can be reversibly cross-linked and de-cross-linked system under mild conditions through the direct water-alcohol exchange reaction (Figure 1b). However, no detailed study for such direct wateralcohol exchange reactions had been reported to date. Therefore, we started from the systematic study of the water-alcohol exchange reactions using a unit model compound, and then we went into the gem-diol polymers. Herein, we describe the reversible cross-linking and de-crosslinking system of polystyrene bearing the gem-diol structure of vicinal tricarbonyl group using an  $\alpha_{j}\omega$ -alcohol exploiting the direct water-alcohol exchange reaction along with the detailed investigation using a unit model compound.

# EXPERIMENTAL SECTION

**Materials.** Chloroform, chloroform-*d* (CDCl<sub>3</sub>) and dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) were distilled over molecular sieves 4A (MS 4A). Acetone and acetone- $d_6$  were distilled over CaCl<sub>2</sub>. Benzyl alcohol and 1-hexanol were distilled over CaH<sub>2</sub>. 1,4-Dioxane was distilled over sodium benzophenone ketyl. D<sub>2</sub>O (Merck KGaA, Germany), *n*-Hexane (Wako Pure Chemical Industries, Japan) and 1,6-hexanediol (Wako) were purchased and used without further purification. Diphenylpropanetrione monohydrate (**2**, DPPT-H<sub>2</sub>O),



Figure 1. Schematic illustrations of (a) water-alcohol exchange reaction on vicinal tricarbonyl groups and (b) reversible cross-linking and de-crosslinking of polymers bearing vicinal tricarbonyl pendants using  $\alpha_i \omega$ -diols through water-alcohol exchange reaction.

diphenylpropanetrione–benzyl alcohol adduct (**3a**, DPPT-BnOH) and polymer bearing monohydrate structure of vicinal tricarbonyl moieties **5a** were synthesized according to the literature.<sup>13</sup> The number-average molecular weight of **5a** was estimated to be  $1.5 \times 10^4$ with a polydispersity index (PDI) of 10.3 by size exclusion chromatography (SEC) based on PSt standards. Polymer **5a** with number-average molecular weight of  $3.8 \times 10^3$  with a PDI of 2.9 was prepared from the polymer synthesized by radical polymerization of 4vinyldibenzoylmethane with 20 mol % of 2,2'-azobis(isobutyronitrile) (AIBN) at 80 °C for 18 h.

Measurements. <sup>1</sup>H NMR spectra were measured on a IEOL JNM-ECS 400 spectrometer at a resonance frequency of 400 MHz with tetramethylsilane (TMS) as an internal standard. NMR chemical shifts were reported in delta unit ( $\delta$ ). IR spectra were recorded on a Thermo Scientific Nicolet iS10 spectrometer. UV-vis spectra were measured with a JASCO V-570 spectrophotometer in a 1-cm quartz cell. Number-average and weight-average molecular weights  $(M_n, M_w)$ and polydispersity indices  $(M_w/M_n)$  of the polymers were estimated by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as the eluent at a flow rate of 0.6 mL/min at 40 °C, performed on a Tosoh chromatograph model HLC-8320 system equipped with Tosoh TSKgel SuperHM-H styrogel columns (6.0 mm  $\phi \times 15$  cm, 3 and 5  $\mu$ m bead sizes), UV-vis detector (254 nm). The molecular weight calibration curve was obtained with polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Seiko Instrument Inc. TG-DTA 6200 with an aluminum pan under a 150 mL/min N<sub>2</sub> flow at a heating rate of 10 °C/min. The single crystal X-ray data for the benzyl alcohol adduct (3a) was collected on a Bruker Smart Apex CCD-based X-ray diffractometer with Mo–K $\alpha$  radiation ( $\lambda$  = 0.71073 Å).<sup>20</sup>

Water–Alcohol Exchange Reaction of DPPT–H<sub>2</sub>O, 2, with Alcohols. A typical experimental procedure was as follows. 2 (64.1 mg, 0.250 mmol) was dissolved in 0.50 mL of CDCl<sub>3</sub> under an argon atmosphere. To the solution was added BnOH (26.2  $\mu$ L, 0.250 mmol), and the solution was transferred to an NMR tube. The reaction progress was monitored by <sup>1</sup>H NMR.

Water–Alcohol Exchange Reaction of DPPT–BnOH, 3a, with Water. DPPT–BnOH (7.81 mg, 0.025 mmol) was dissolved in 0.50 mL of a mixture of  $D_2O$  and acetone- $d_6$  (1/9, v/v) under an argon atmosphere, and the solution was transferred to an NMR tube. The reaction progress was monitored by <sup>1</sup>H NMR.

Water–Alcohol Exchange Reaction of Polystyrene Derivative 5a with Alcohols. A typical experimental procedure was as follows. Polymer 5a (282 mg, 1.00 mmol) was dissolved in chloroform (5.0 mL). To the solution was added 1-hexanol (374  $\mu$ L, 3.00 mmol), and the reaction mixture was stirred at ambient temperature under argon atmosphere for 3 days. The resulting mixture was precipitated with *n*-hexane and filtered to obtain polymer 6 (298 mg, 94%) as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>, 298 K):  $\delta$  8.17– 5.20 (br, aromatic-*H*, –O*H*), 3.70–3.30 (br, –OC*H*<sub>2</sub>–), 2.40–0.50 (br, aliphatic-*H*) ppm. IR (ATR) 3415 (O–H), 2929 (C–H), 1721 (central C=O), 1682 (side C=O) cm<sup>-1</sup>.

Recovery of Polymer 5a from Polymer 6 through Water– Alcohol Exchange Reaction with Water. Polymer 6 (151 mg, 0.469 mmol) was dissolved in 10 mL of a mixture of water and acetone (1/9, v/v), and the resultant solution was stirred at ambient temperature for 3 days. The resulting mixture was precipitated with a large amount of water and filtered to obtain polymer 5a (127 mg, 96%) as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ , 298 K): see Supporting Information, Figure S4.

Cross-Linking of Polystyrene Derivative 5a through the Water–Alcohol Exchange Reaction with 1,6-Hexanediol. To a solution of polymer 5a (282 mg, 1.00 mmol) in acetone (0.50 mL) was added 1,6-hexanediol (11.8 mg, 0.100 mmol), and the reaction mixture was stirred at ambient temperature under argon atmosphere for 5 days. The resultant highly viscous mixture was filtered and washed with acetone (5.0 mL). The insoluble part was dried *in vacuo* at room temperature to afford the networked polymer 7 (292 mg, 99%) as a yellow solid. IR (ATR): 3392 (OH), 2932 (C–H), 1721 (central C=O), 1674 (side C=O) cm<sup>-1</sup>.

Recovery of Polymer 5a by De-Cross-Linking of Networked Polymer 7 through the Water–Alcohol Exchange Reaction with Water. A pea-sized piece of networked polymer 7 (168 mg) was immersed in 10 mL of water–acetone (1/9, v/v) and the mixture was gently stirred at room temperature. The polymer swelled gradually and then completely dissolved within 2 days. The resultant solution was stirred for one more day, and then mixture was reprecipitated with a large amount of water and filtered to obtain polymer 5a (149 mg, 0.527 mmol, 91%) as a pale yellow solid. <sup>1</sup>H NMR (400 MHz, acetone- $d_{6}$ , 298 K): see Supporting Information, Figure S5.

## RESULTS AND DISCUSSION

**Reversible Water–Alcohol Exchange Reaction of Monohydrate of Diphenylpropanetrione with Alcohols.** We chose the monohydrate of diphenylpropanetrione 2 (DPPT–H<sub>2</sub>O) as a unit model compound for polystyrene bearing monohydrate structure of vicinal tricarbonyl group and investigated its water–alcohol exchange reaction in detail. Before investigating the model reaction, we prepared the benzyl alcohol adduct of diphenypropanetrione 3a (DPPT–BnOH) according to our previous report.<sup>15</sup> Single crystals of **3a** suitable for X-ray analysis were grown from a solution in benzyl alcohol. The X-ray analysis revealed that the benzyl alcohol was added to the central carbonyl group, and the central carbon atom adopted the tetrahedral configuration (Figure 2).<sup>20</sup> We



Figure 2. ORTEP structure of 3a with thermal ellipsoids at 50% probability. Selected data: bond lengths =  $O1-C7 \ 1.214 \ \text{Å}, \ O2-C15 \ 1.208 \ \text{Å}, \ O3-C8 \ 1.407 \ \text{Å}, \ O4-C8 \ 1.394 \ \text{Å}; \ angles = O3-C8-O4 \ 113.36^\circ, \ C7-C8-C15 \ 110.12^\circ; \ dihedral \ angles = O1-C7-C8-O3 \ -133.36^\circ, \ O2-C15-C8-O3 \ -129.29^\circ.$ 

monitored the water-alcohol exchange reaction of **2** with benzyl alcohol in CDCl<sub>3</sub> by <sup>1</sup>H NMR. Figure 3 shows the time dependence of partial <sup>1</sup>H NMR spectra in the aromatic region of an equimolar mixture of **2** and benzyl alcohol ( $[2]_0 =$  $[BnOH]_0 = 0.5$  M) after mixing at ambient temperature, indicating that three species, i.e., **2**, and diphenylpropanetrione (DPPT, **1**), and BnOH adduct (DPPT-BnOH, **3a**) were involved in the equilibrium. The existence of **1** was also evidenced by the naked-eye observation that the reaction mixture took on the distinctive yellow color due to the contiguous three carbonyl groups.<sup>1,13-15</sup> The *ortho*-proton signals of the benzene rings of **1**, **2**, and **3a** appeared as three clearly separated ones at around 8 ppm, with which we estimated the content ratios of the three species. The contents of the three species were plotted against the reaction time as



Figure 3. <sup>1</sup>H NMR spectra of the reaction mixture of DPPT-H<sub>2</sub>O 2 with equimolar benzyl alcohol in  $CDCl_3$  at ambient temperature after (a) 10 min, (b) 1 h, (c) 12 h, and (d) 48 h (400 MHz, 298 K).  $[2]_0 = [BnOH]_0 = 0.5$  M.

shown in Figure 4A. At an early stage of the reaction (10 min, Figure 3a), the major part of the mixture was 2, and a small amount of 1 with a trace amount of 3a were detected after 1 h (Figure 3b). The content of 1 reached maximum a few hours later, and the content of 3a gradually increased with time, while 1 and 2 decreased monotonously (Figure 3c). The mixture reached equilibrium within 48 h, at which the content ratios of 1, 2, and 3a were 18%, 33%, and 49%, respectively (Figure 3d). The initial concentration of the starting materials and the reaction temperature markedly affected the reaction rate as well as the position of the equilibrium of the water—alcohol exchange reaction. When the initial concentrations of 2 and BnOH were set to 0.1 M, the reaction became significantly slow and 4 days were required for reaching equilibrium at ambient temperature, where the content ratios of 1, 2, and 3a were 38%,

34%, and 28%, respectively (Figure 4B). In contrast, the rate of the exchange reaction became much higher at 50 °C than that at ambient temperature and the equilibrium state was achieved within half a day. The position of the equilibrium state was also shifted to a certain extent toward the free tricarbonyl 1; the contents of 1, 2, and 3a at equilibrium were 49%, 15%, and 36%, respectively at 50 °C (Figure 4C).

Next, we investigated the effect of solvent on the wateralcohol exchange reaction (Figure 5). We chose 1-hexanol



**Figure 5.** Changes in the content ratios of **3a** and **3b** upon mixing with BnOH in CDCl<sub>3</sub> (a), and with 1-hexanol in CDCl<sub>3</sub> (b), in DMSO- $d_6$  (c), and in acetone- $d_6$  (d) at ambient temperature.  $[\mathbf{2}]_0 = [1\text{-hexanol}]_0 = 0.5 \text{ M}.$ 

instead of benzyl alcohol, because the BnOH adduct showed poor solubility and insufficient peak separation of the <sup>1</sup>H NMR spectra in acetone and DMSO. In CDCl<sub>3</sub>, the exchange reaction with 1-hexanol exhibited a similar behavior to that with benzyl alcohol and the mixture reached equilibrium within 48 h, at which the content ratios of **1**, **2**, and **3b** were estimated to be 11%, 21%, and 68% by using the integrals of the <sup>1</sup>H NMR spectrum. The content of the 1-hexanol adduct **3b** at equilibrium was much higher than that of **3a** in CDCl<sub>3</sub> probably because of the less steric hindrance of the hydroxyl group in 1-hexanol than that of benzyl alcohol. In contrast, the exchange reaction rate slowed very much in DMSO-*d*<sub>6</sub> and it took *ca*. 120 h until equilibrium was attained. The content of **3b** was as low as 23% at equilibrium, which was much lower than that in CDCl<sub>3</sub>. This is consistent with our previously reported



**Figure 4.** Changes in the content ratio of 1, 2, and 3a upon mixing DPPT-H<sub>2</sub>O 2 and BnOH in  $CDCl_3$ : (A)  $[2]_0 = [BnOH]_0 = 0.5$  M, room temperature, (B)  $[2]_0 = [BnOH]_0 = 0.1$  M, room temperature, and (C)  $[2]_0 = [BnOH]_0 = 0.5$  M, 50 °C.

result that the addition of alcohol to **1** is slowed in polar solvents,<sup>15</sup> thus indicating that the rate-determining step for the water—alcohol exchange reaction is most likely to be the addition of the alcohol. The reaction rate was even lowered in acetone- $d_6$  than in DMSO- $d_6$  and it required more than 240 h to achieve equilibrium, although the content of **3b** was higher than that in DMSO- $d_6$  at the final equilibrium state.

We demonstrated the back reaction directly from 3a to 2 exploiting the water–alcohol exchange reaction in a similar way to that for the hydration of 1 according to our previous report.<sup>13</sup> The isolated 3a was dissolved in a mixture of  $D_2O$  and acetone- $d_6$  (1/9, v/v) at ambient temperature, and the exchange reaction was monitored by <sup>1</sup>H NMR (Scheme 2).

Scheme 2. Water-Alcohol Exchange Reaction of DPPT-BnOH 3a with D<sub>2</sub>O



After 3 days, an almost quantitative water–alcohol exchange was achieved with generation of 2' (DPPT–D<sub>2</sub>O) in 97% yield confirmed by <sup>1</sup>H NMR (Figure 6A). Similarly to the forward reaction, the backward reaction was accelerated by heating at 50 °C, so that 2' was generated in 97% yield (<sup>1</sup>H NMR) within 24 h (Figure 6B).

Reversible Water-Alcohol Exchange Reaction of Polystyrene Derivative 5a with 1-Hexanol. On the basis of the results of the model reactions, we investigated the reversible water-alcohol exchange reaction of the polystyrene bearing monohydrate structure of vicinal tricarbonyl group 5a with 1-hexanol (Table 1). The polymer with gem-diol structure **5a**  $(M_{\rm p} = 1.5 \times 10^4, \text{PDI} = 10.3)$  was prepared according to our previous report.<sup>13</sup> 1-Hexanol was added to a solution of 5a in  $CHCl_3$  ([5a]<sub>0</sub> = 0.2 M) and the reaction mixture was stirred at ambient temperature and took on a yellow color, which suggested the existence of vicinal tricarbonyl units. After 3 days, the resulting mixture was precipitated with *n*-hexane to obtain 1-hexanol adduct of the polymer 6 in 91-96% yield. The IR spectrum showed a weak but distinctive absorption peak at  $1721 \text{ cm}^{-1}$  assignable to the three contiguous carbonyl groups, indicating that 6 contained vicinal tricarbonyl unit along with

gem-diol and hemiketal units (Figure S2, Supporting Information). A weak but distinctive absorption peak at 455 nm observed in the UV/vis spectrum also the existence of the vicinal tricarbonyl unit in the polymer **6** (Figure S3, Supporting Information).<sup>1,13-15</sup> The hemiketal structure in **6** was confirmed by the appearance of a broad signal between 3.3 and 3.7 ppm in the <sup>1</sup>H NMR spectra that corresponds to that of alkoxymethylene protons of the hemiketal side chain (Figure S4, Supporting Information). The contents of gem-diol, tricarbonyl, and hemiketal structures were estimated by using the integrals of the <sup>1</sup>H NMR spectra. When equimolar 1hexanol was used, the contents of the three units were 39%. 27%, and 34% for gem-diol, vicinal tricarbonyl, and hemiketal units, respectively. The content of the hemiketal unit (34%) halved when compared to that of the equilibrium solution of an equimolar mixture of 2 and 1-hexanol in CDCl<sub>3</sub> (68%, vide infra). This could be attributed to the lowered total concentration as well as the steric hindrance of the polymer backbones. The content of hemiketal unit in 6 increased with an increase in the feed ratio of 1-hexanol, and it reached 62% when 10 equiv of 1-hexanol was used. The thermogravimetric analysis (TGA) profile of 6 was consistent with the <sup>1</sup>H NMR results (Figure 7). Only a negligible weight loss was observed up to 220 °C for the tricarbonyl polymer 4 (dehydrated form of 5a) upon being heated from 30 °C at a rate of 10 °C/min under nitrogen flow. In contrast, the gem-diol polymer 5a showed a weight loss of 6 wt % up to 200 °C, which was in good agreement with the weight of water that can be released potentially from 5a. The TGA profile of 6 (obtained with 3 eq of 1-hexanol) had two-step weight loss at around 100 and 200 °C, which probably correspond to the releases of water and 1hexanol, respectively. The weight loss up to 250 °C coincides with the combined weight of water and 1-hexanol incorporated in 6 that was estimated by the <sup>1</sup>H NMR analysis.

We also examined the recovery of the *gem*-diol polymer **5a** directly from the hemiketal polymer **6** in the same manner as that for the unit model system (Scheme 3). Being stirred at ambient temperature, a mixture of **6** in water-acetone (1/9, v/v) became homogeneous and colorless. After 3 days, the mixture was reprecipitated with water to afford **5a** in 96% yield. The <sup>1</sup>H NMR spectrum of the obtained polymer **5a** agreed completely with that of the original *gem*-diol polymer **5a** (Figure S4, Supporting Information).

Reversible Cross-Linking and De-Cross-Linking of Polystyrene Derivative 5a through the Water–Alcohol



**Figure 6.** Change in the content ratio of DPPT (1), DPPT–D<sub>2</sub>O (2') and DPPT–BnOH (3a) upon mixing 3a in D<sub>2</sub>O/acetone- $d_6$  (1/9, v/v) at (A) ambient temperature and (B) at 50 °C. [3a]<sub>0</sub> = 0.05 M.

Table 1. Water-Alcohol Exchange Reaction of 5a with 1-Hexanol and Compositions of Resulting Polymers



		content ratio / 70			
entry	hexanol/equiv <sup>a</sup>	gem-diol	tricarbonyl	hemiketal	yield <sup>c</sup> /%
1	1	39	27	34	91
2	3	38	16	46	94
3	10	24	14	62	96

<sup>a</sup>Versus gem-diol moieties of 5a. <sup>b</sup>Determined by integral ratios on <sup>1</sup>H NMR spectra. <sup>c</sup>Isolated yield.



Figure 7. TG profiles of 4, 5a, 6, and 7 (heating rate 10  $^\circ\text{C/min},$  under  $N_2$  flow).

#### Scheme 3. Recovery of Polymer 5a



Exchange Reaction with 1,6-Hexanediol. We investigated the reversible cross-linking-de-cross-linking of the gem-diol polymer 5a through the water-alcohol exchange reaction by using 1,6-hexanediol as a bifunctional cross-linking reagent (Figure 8). We used acetone for the solvent, because it is a good solvent for 5a so that we could achieve a high concentration of 5a, which is advantageous for the crosslinking reaction. A small amount of 1,6-hexanediol (0.2 equiv of OH group relative to the gem-diol moiety of 5a) was added to a concentrated solution of 5a ( $M_n = 1.5 \times 10^4$ , PDI = 10.3) in acetone (2.0 M). After 1 day at ambient temperature, the magnetic stirring had been stopped because of significantly increased viscosity of the mixture. The mixture displayed an orange color, which indicated the existence of vicinal tricarbonyl units. The highly viscous mixture was allowed to stand for 4 more days and washed with acetone. The insoluble

part was dried in vacuo at room temperature to afford the networked polymer 7 in 99% yield as a yellow solid. In the IR spectrum of the obtained networked polymer, a peak due to methylene moiety of 1,6-hexanediol and a weak peak originating from the vicinal tricarbonyl structure were observed at 2932 cm<sup>-1</sup> and 1721 cm<sup>-1</sup>, respectively (Figure S2, Supporting Information).<sup>1,13–15</sup> The TGA profile of 7 showed a weight loss of 9 wt % up to ca. 250 °C, which agreed well with the combined weight of water and 1,6-hexanediol covalently attached to the polymer side chain (Figure 7). Figure 8 shows the photographs for the polymer mixture before (a) and after (b) the cross-linking. While the solution of 5a in acetone exhibited high fluidity as solution, a transparent self-standing gel was formed after the cross-linking with 1,6-hexanediol. The scanning electron microscopy (SEM) images of the fracture surface of the networked polymer are shown in Figure S6 (Supporting Information). The morphology of the networked polymer 7 showed smooth and homogeneous surface, and no phase-separated morphology was observed in the micrometric scale.

We demonstrated the de-cross-linking of the obtained networked polymer 7 through water–alcohol exchange reaction. A pea-sized piece of 7 was immersed in water-acetone (1/9, v/v) and the mixture was gently stirred at ambient temperature. The polymer swelled gradually and then completely dissolved within 2 days. The resultant solution was stirred for one more day and became colorless. After reprecipitation with water, the water-insoluble part was dried *in vacuo* at ambient temperature to afford the *gem*-diol polymer **5a** in 91% yield, of which the <sup>1</sup>H NMR spectrum was completely identical to that of the original polymer **5a** (Figure S5, Supporting Information).

Finally, we attempted SEC analysis of the reaction mixture prior to the gel point, in order to visualize the cross-linking–decross-linking behavior of 5a.<sup>21</sup> To this end, we prepared polymer 5a with a lower molecular weight ( $M_n = 3.8 \times 10^3$ , PDI = 2.9) and allowed to react with 1,6-hexanediol in the same manner. The SEC analysis of the reaction mixture showed an increase in molecular weight as well as PDI after 24 h ( $M_w = 4.5 \times 10^3$ , PDI = 5.0) and after 48 h ( $M_n = 4.6 \times 10^3$ , PDI = 8.5), indicating the formation of network polymer via cross-linking (Figure 9a–c). Upon treatment of the resulting partially networked polymer with excess amount of water at ambient temperature for 3 days, the SEC profile of the polymer ( $M_n = 3.4 \times 10^3$ , PDI = 2.9) showed good accordance with that of the



Figure 8. Photographs of before (a) and after (b) cross-linking of the polystyrene derivative 5a through water-alcohol exchange reaction on its vicinal tricarbonyl moieties.



Figure 9. SEC profiles of polymer 5a (a) as-prepared, (b) after crosslinking for 48 h, (c) after cross-linking for 96 h, and (d) after de-crosslinking.

original polymer **5a** as-prepared (Figure 9d), indicating that the de-cross-linking was completed.

## CONCLUSION

We have thus demonstrated here that the direct water-alcohol exchange reactions on the vicinal tricarbonyl compounds can be carried out reversibly in both directions by changing solvents, exploiting the reversible nature of the addition of alcohols to vicinal tricarbonyl compounds as well as that of the elimination of alcohols from the alcohol adducts. It should be noted here that the water-alcohol exchange reactions proceed without any catalysts and under mild conditions such as ambient temperature. By virtue of the above characteristic features of the water-alcohol exchange reactions on vicinal tricarbonyl compounds, the polystyrene derivative bearing monohydrate structure of vicinal tricarbonyl group can be networked with 1,6-hexanediol at ambient temperature through the wateralcohol exchange reaction to afford the networked polymer in almost quantitative yield. On the other hand, the treatment of the networked polymer with water affords the original polymer in high yield as a result of de-cross-linking through the wateralcohol exchange reaction. Thus, we believe that the crosslinking and de-cross-linking system based on the water—alcohol exchange reactions on vicinal tricarbonyl compounds is promising for development of new chemical recycling and self-healing materials because of its reversible nature as well as the feasibility under mild conditions.

# ASSOCIATED CONTENT

## **S** Supporting Information

Detailed X-ray crystal data of **3a**, IR, UV–vis, and <sup>1</sup>H NMR spectra of the polymers, and SEM images of 7. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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# REFERENCES

- (1) (a) Rubin, M. B.; Gleiter, R. Chem. Rev. 2000, 100, 1121–1164.
  (b) Rubin, M. B. Chem. Rev. 1975, 75, 177–202.
- (2) Wasserman, H. H.; Parr, J. Acc. Chem. Res. 2004, 37, 687-701.

(3) Hirama, M.; Fukazawa, Y.; Ito, S. Tetrahedron Lett. 1978, 19, 1299–1302.

(4) Moubasher, R.; Othman, A. M. J. Am. Chem. Soc. 1950, 72, 2667–2669.

(5) Lepley, A. R.; Thelman, J. P. Tetrahedron 1966, 22, 101-110.

(6) (a) Netto-Ferreira, J. C.; Silva, M. T.; Puget, F. P. J. Photochem. Photobiol. A: Chem. 1998, 119, 165–170. (b) Silva, M. T.; Braz-Filho, R.; Netto-Ferreira, J. C. J. Braz. Chem. Soc. 2000, 11, 479–485.

(7) Mahran, M. R.; Abdou, W. M.; Sidky, M. M.; Wamhoff, H. Synthesis 1987, 5, 506-508. (8) Sharp, D. B.; Hoffman, H. A. J. Am. Chem. Soc. 1950, 72, 4311–4313.

(9) Roberts, J. D.; Smith, D. R.; Lee, C. C. J. Am. Chem. Soc. 1951, 73, 618–625.

- (10) Gill, G. B.; Idris, M. S. H.; Kirollos, K. S. J. Chem. Soc., Perkin Trans. 1 1992, 2355–2365.
- (11) Schönberg, A.; Singer, E. Chem. Ber. 1970, 103, 3871-3884.

(12) Endo, T.; Okawara, M. Bull. Chem. Soc. Jpn. 1979, 52, 2733-2734.

(13) Dei, T.; Morino, K.; Sudo, A.; Endo, T. J. Polym. Sci., Part A: Polym. Chem. 2011, 49, 2245–2251.

(14) Dei, T.; Morino, K.; Sudo, A.; Endo, T. J. Polym. Sci., Part A: Polym. Chem. 2012, 50, 2619–2625.

(15) Morino, K.; Sudo, A.; Endo, T. *Macromolecules* **2012**, *45*, 4494–4499.

(16) For a polymer bearing cyclic tricarbonyl moiety, see: Endo, T.; Fujiwara, E.; Okawara, M. J. Polym. Sci.: Polym. Chem. Ed. **1981**, 19, 1091–1099.

(17) For selected reviews on networked polymers, see: (a) Uyama, H.; Kobayashi, S. Curr. Org. Chem. 2003, 7, 1387. (b) Funaoka, M. Macromol. Symp. 2003, 201, 213. (c) Takeichi, T.; Kawauchi, T.; Agag, T. Polym. J. 2008, 40, 1121. (d) Yagci, Y.; Kiskan, B.; Ghosh, N. N. J. Polym. Sci., Part A: Polym. Chem. 2009, 47, 5565. (e) Suyama, K.; Shirai, M. Prog. Polym. Sci. 2009, 34, 194. (f) Tillet, G.; Boutevin, B.; Ameduri, B. Prog. Polym. Sci. 2010, 36, 191.

(18) For selected reviews on polymer recycling, see: (a) Sanda, F.; Endo, T. Polym. Recycl. **1998**, 3, 159–163. (b) Endo, T.; Nagai, D. Macromol. Symp. **2005**, 226, 79–86. (c) Takata, T. Polym. J. **2006**, 38, 1–20. (d) Nishida, H. Polym. J. **2011**, 43, 435–447.

(19) For selected reviews on self-healing polymers, see: (a) Hager, M. D.; Greil, P.; Leyens, C.; van der Zwaag, S.; Schubert, U. S. Adv. Mater. 2010, 22, 5424. (b) Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. Macromolecules 2010, 43, 2643. (c) Guimard, N. K.; Oehlenschlaeger, K. K.; Zhou, J.; Hilf, S.; Schmidt, F. G.; Barner-Kowollik, C. Macromol. Chem. Phys. 2012, 213, 131. (d) Urban, M. W. Nat. Chem. 2012, 4, 80.

(20) Crystal data for **3a**:  $C_{22}H_{18}O_4$ : FW = 346.36, monoclinic, space group  $P2_1/n$  (no. 14), a = 12.031(3) Å, b = 17.789(5) Å, c = 9.608(3)Å,  $\beta = 121.262(18)^\circ$ , V = 1.757.8(8) Å<sup>3</sup>, Z = 4,  $D_x = 1.309$ , 4135 reflections measured, 2718 unique reflections, 2542 observations ( $I > 2.0\sigma(I)$ ), R = 0.0324 ( $I > 2.0\sigma(I)$ ),  $R_w = 0.0893$  ( $I > 2.0\sigma(I)$ ). CCDC 885018. For more detail on the data, see Supporting Information.

(21) Inglis, A. J.; Nebhani, L.; Altintas, O.; Schmidt, F. G.; Barner-Kowollik, C. *Macromolecules* **2010**, *43*, 5515–5520.