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# Six-Membered Cyclic Carbonate Having Styrene Moiety as a Chemically Recyclable Monomer. Construction of Novel Cross-Linking−De-Cross-Linking System of Network Polymers

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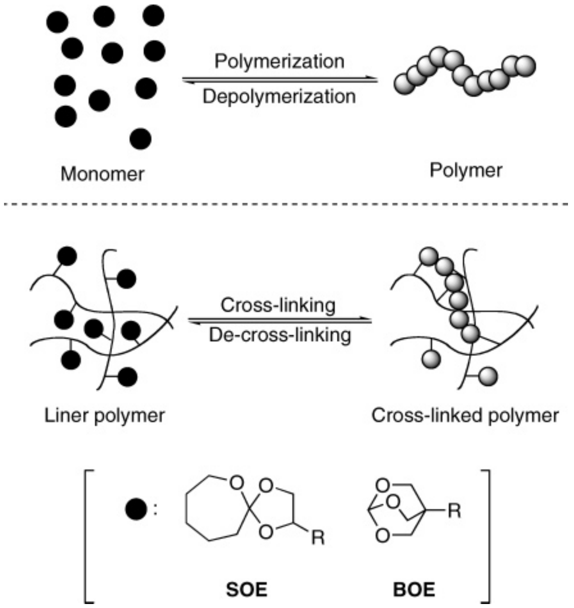
ABSTRACT: This article deals with (1) synthesis and anionic polymerization of a six-membered cyclic carbonate having styrene moiety, (2) anionic depolymerization of the obtained polymer, (3) radical cross-linking of the obtained polymer, and (4) anionic de-cross-linking of the cross-linked polymer. The monomer 5-ethyl-5-[(*p*-vinylphenyl) methoxymethyl]-1,3-dioxan-2-one (St6CC) underwent anionic polymerization with potassium *tert*-butoxide (*t*-BuOK) as an initiator in THF to afford the corresponding polycarbonate [poly(St6CC)]. It was confirmed that this polymerization was equilibrium polymerization by the relationships between the polymerization temperature and monomer conversion. Poly(St6CC) underwent anionic depolymerization with *t*-BuOK (5 mol % vs polymer repeating unit) as a catalyst in THF (0.1 M) at 20 °C for 24 h to recover St6CC in 60% yield. Treatment of poly(St6CC) with a radical initiator afforded the cross-linked polymer. Employment of styrene as the comonomer satisfactorily afforded the corresponding cross-linked polymer. It underwent anionic de-cross-linking with *t*-BuOK (10 mol % vs polymer repeating unit) in THF at 50 °C for 24 h to afford a THF-soluble polymer. The yield of the THF-soluble part increased as the styrene composition in the cross-linked polymer increased. It was suggested that the de-cross-linking efficiency depended on the cross-linking density.

## Introduction

Development of an excellent method for recycling use of polymeric materials is an issue of great importance in recent polymer science and technology.[1] Chemical recycling is the most important and essential among a few recycling methods of used polymers such as thermal recycling, material recycling, and chemical recycling because only this method can regenerate the original monomers from the polymers. Monomers undergoing equilibrium polymerization is applicable to chemical recycling of polymeric materials because depolymerization of the obtained polymers can afford the starting monomers. We have recently reported cationic equilibrium polymerization behavior of spiro orthoesters[2] (SOEs) and bicyclo orthoesters[3] (BOEs) and chemical recycling systems between linear polymers having SOE[4] or BOE[5] moieties and cross-linked polymers based on the cationic equilibrium polymerization of SOEs and BOEs (Scheme 1).

**Scheme 1**



Six-membered cyclic carbonates (6CCs) efficiently undergo ring-opening polymerization to afford the corresponding liner polycarbonates, especially under anionic conditions.[6] The most interesting feature of this polymerization is volume expansion during polymerization.[7] This volume expansion can be accounted for by the difference in strength of the intermolecular interaction between the monomers and polymers. That is, strong interactions (dipole−dipole) in the monomers and weak interactions in the polymers eventually cause the volume expansion. Höcker et al. have found that this polymerization shows equilibrium character[8] (Scheme 2). We have previously reported the substituent effect on the anionic equilibrium polymerization of 6CCs,[8b] i.e., the equilibrium between the monomer and polymer shifts to the monomer side with respect to the bulkiness of the monomer substituent. 6CCs are also applicable to chemical recycling of polymeric materials. If we employed 6CC as a polymerizable group in the side

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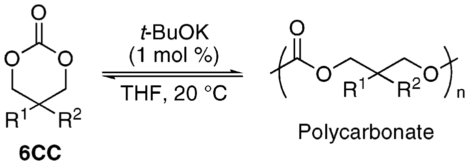
**Scheme 2**



chain, we might obtain a polymer undergoing reversible cross-linking–de-cross-linking. In this work, we wish to demonstrate a novel cross-linking–de-cross-linking system between linear polymers and network polymers based on equilibrium polymerization of 5-ethyl-5-[(*p*-vinylphenyl)methoxymethyl]-1,3-dioxan-2-one (St6CC).

## Experimental Section

**Materials.** Unless stated otherwise, all chemicals and reagents were obtained commercially and used without further purification. Tetrahydrofuran (THF) was dried over sodium benzophenone and distilled under nitrogen before use. *N*,*N*-Dimethylformamide (DMF) was used after distillation over calcium hydride and stored over molecular sieves (4A).

**Measurements.** $^1$H NMR and $^{13}$C NMR spectra were recorded with a JEOL Lambda-300 spectrometer in chloroform-*d* ($CDCl_3$) using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer. Number-average molecular weights ($M_n$) and polydispersities ($M_w/M_n$) were estimated by size exclusion chromatography (SEC) on a Tosoh HPLC HLC-8120 system equipped with two consecutive polystyrene gel columns (TSK gels G4000HXL and G2500HXL), refractive index, and ultraviolet detectors using THF as an eluent with a flow rate of 1.0 mL/min, by polystyrene calibration at 30 °C. Thermogravimetric analyses (TGA) were performed on a Seiko TG/DTA6000 (EXSTER 6000) instrument. Differential scan calorimetry (DSC) measurements were performed on a Seiko DSC-220 instrument under a nitrogen atmosphere.

**Monomer Synthesis. Synthesis of 5-Ethyl-5-hydroxymethyl-2,2-dimethyl-1,3-dioxane (1).** Trimethylolpropane (53.7 g, 400 mmol), acetone (120 mL, 1.6 mol), petroleum ether (120 mL), and *p*-toluenesulfonic acid monohydrate (1.8 g) were fed in a 300 mL flask equipped with a water separator (Dean–Stark trap). The mixture was refluxed overnight until water was no more collected in the Dean–Stark trap. The mixture was cooled in an ice–water bath, and anhydrous sodium carbonate (1.8 g) was added to the mixture, followed by stirring for 30 min. The mixture was then filtered, and petroleum ether and excess amount of acetone were removed from the mixture by evaporation. The residual liquid was distilled under a reduced pressure to obtain **1** as a colorless liquid; yield 53.0 g (76%), bp 117 °C/10 mmHg (lit.[9] 80–90 °C/0.2 mmHg). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 3.66 (dd, $J = 5.1$ and 11.2 Hz, 4H, $-CH_2O$), 3.60 (s, 2H, $-CH_2OH$), 3.35 (t, $J = 5.1$ Hz, 1H, $-CH_2OH$), 1.41 (d, $J = 11.2$ Hz, 6H, $-CH_3$), 1.34 (q, $J = 7.5$ Hz, 2H, $-CH_2CH_3$), 0.84 ppm (t, $J = 7.5$ Hz, 3H $-CH_2CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 98.0, 64.9, 61.9, 36.8, 26.9, 23.5, 20.3, 6.9 ppm. IR (neat): $\nu$ (cm$^{-1}$) = 3438, 2968, 2881, 2247, 1655, 1477, 1455, 1373, 1348, 1257, 1202, 1155, 1091, 1048, 983, 919, 832, 733.

**Synthesis of 2-Ethyl-2-[(*p*-vinylphenyl)methoxymethyl]-1,3-propanediol (2).** Sodium hydride (60% dispersion in mineral oil, 13.5 g) was added to a solution of DMF (40 mL) and THF (200 mL) with stirring under a nitrogen atmosphere. A solution of **1** (53.3 g, 306 mmol) in THF (60 mL) was added dropwise to the resulting mixture at 10 °C. After the addition was completed, the reaction mixture was warmed to room temperature and stirred until hydrogen gas was no more generated (1.5 h). Then the reaction mixture was cooled to 10 °C again, and then *p*-chloromethylstyrene (46.9 g, 307 mmol) was added dropwise to the mixture. After the addition was completed, the reaction mixture was warmed to room temperature, followed by stirring overnight. The mixture was put into ice-cold water (1 L), and the mixture was extracted by diethyl ether (200 mL × 3). The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Methanol (200 mL) was added to the residual liquid (121.9 g), and then concentrated HCl (34.8 mL, 420 mmol) was added dropwise to the resulting solution at 10 °C with stirring. Then the reaction mixture was warmed to room temperature, followed by stirring for 1 h. Then the reaction mixture was cooled in an ice bath again; triethylamine (43.6 g, 431 mmol) was added dropwise to the mixture. The mixture was extracted with benzene (300 mL × 3). The combined organic layers were evaporated after dryness with anhydrous magnesium sulfate. The crude solid was recrystallized from diethyl ether to obtain **2** as a white crystal. Yield: 54.7 g (219 mmol, 72%); mp 59–61 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.39 (d, $J = 8.1$ Hz, 2H, $-C_6H_4-$), 7.26 (d, $J = 8.1$ Hz, 2H, $-C_6H_4-$), 6.70 (dd, $J = 11.0$ and 17.6 Hz, 1H, $-CH{=}CH_2$), 5.75 (dd, $J = 0.75$ and 17.6 Hz, 1H, $-CH{=}CH_2$), 5.25 (dd, $J = 0.75$ and 11.0 Hz, 1H, $-CH{=}CH_2$), 4.48 (s, 2H, $-OCH_2C_6H_4-$), 3.71 (d, $J = 11.0$ Hz, 2H, $-CH_2OH$), 3.65 (d, $J = 11.0$ Hz, 2H, $-CH_2OH$), 3.46 (s, 2H, $-CH_2O-$), 2.71 (brs, 2H, $-OH$), 1.33 (q, $J = 7.5$ Hz, 2H, $-CH_2CH_3$), 0.82 ppm (t, $J = 7.5$ Hz, 3H, $-CH_2CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 137.4, 137.1, 136.4, 127.8, 126.3, 114.0, 73.7, 73.4, 65.9, 42.9, 23.0, 7.48 ppm. IR (KBr): $\nu$ (cm$^{-1}$) = 3430, 2970, 2935, 2883, 2867, 2250, 1910, 1630, 1570, 1513, 1463, 1406, 1381, 1364, 1090, 1062, 1018, 990, 909, 828, 733. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.68. Found: C, 71.78; H, 8.62.

**Synthesis of 5-Ethyl-5-[(*p*-vinylphenyl)methoxymethyl]-1,3-dioxan-2-one (St6CC).** Ethyl chloroformate (41.6 mL, 437 mmol) and triethylamine (60.7 mL, 437 mmol) were added dropwise to a solution of **2** (54.7 g, 219 mmol) in THF (500 mL) at 10 °C. After that, the reaction mixture was warmed to room temperature and stirred overnight. Precipitated triethylamine·HCl salt was filtered off, and the solvent was removed from the mixture by distillation under a reduced pressure. The crude solid was recrystallized from diethyl ether to obtain St6CC as white crystal. Yield: 39.6 g (143 mmol, 66%); mp 48–50 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.40 (d, $J = 8.2$ Hz, 2H, $-C_6H_4-$), 7.25 (d, $J = 8.2$ Hz, 2H, $-C_6H_4-$), 6.71 (dd, $J = 10.9$ and 17.6 Hz, 1H, $-CH{=}CH_2$), 5.76 (d, $J = 17.6$ Hz, 1H, $-CH{=}CH_2$), 5.26 (d, $J = 10.9$ Hz, 1H, $-CH{=}CH_2$), 4.48 (s, 2H, $-OCH_2C_6H_4-$), 4.33 (d, $J = 11.0$ Hz, 2H, $-CH_2OCO-$), 4.13 (d, $J = 11.0$ Hz, 2H, $-CH_2OCO-$), 3.42 (s, 2H, $-CH_2O-$), 1.53 (q, $J = 7.5$ Hz, 2H, $-CH_2CH_3$), 0.88 ppm (t, $J = 7.5$ Hz, 3H, $-CH_2CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 148.5, 137.3, 136.9, 136.3, 127.8, 126.3, 114.1, 73.7, 72.7, 68.2, 35.4, 23.3, 7.3 ppm. IR (KBr): $\nu$ (cm$^{-1}$) = 2971, 2926, 1756, 1471, 1405, 1179, 1115, 766. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.26; H, 7.07.

**Anionic Ring-Opening Polymerization of St6CC.** Typical procedure: All glass vessels were heated in vacuo before use, filled with dry nitrogen, and handled in a stream of dry nitrogen. A solution of St6CC (276 mg, 1 mmol) in toluene (1 mL) was prepared and stored over molecular sieves (4A) overnight. 1.0 M solution of potassium *tert*-butoxide in THF (10 $\mu$L, 0.01 mmol) was quickly added to the monomer solution in a glass tube equipped with a three-way stopcock, and the resulting mixture was stirred at a set temperature for 24 h. The reaction was quenched by the addition of a solution of methanol/phosphoric acid (v/v = 9:1, 10 $\mu$L). The resulting mixture was poured into a large amount of methanol to precipitate the polymer. It was collected as colorless gum by filtration and dried under vacuum.

**Poly(St6CC).** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.34 (d, $J = 8.1$ Hz, 2H, $-C_6H_4-$), 7.22 (d, $J = 8.1$ Hz, 2H, $-C_6H_4-$), 6.67 (dd, $J = 10.9$ and 17.5 Hz, 1H, $-CH{=}CH_2$), 5.71 (d, $J = 17.5$ Hz, 1H, $-CH{=}CH_2$), 5.21 (d, $J = 10.9$ Hz, 1H, $-CH{=}CH_2$), 4.42 (s, 2H, $-OCH_2C_6H_4-$), 4.10 (s, 4H, $-CH_2OCO-$), 3.33 (s, 2H, $-CH_2O-$), 1.47 (q, $J = 7.7$ Hz, 2H, $-CH_2CH_3$), 0.82 ppm (t, $J = 7.7$ Hz, 3H, $-CH_2CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 155.1, 137.8, 136.9, 136.5, 127.6, 126.2, 113.7, 73.1, 69.6, 67.7, 41.9, 22.6, 7.5 ppm. IR (KBr): $\nu$ (cm$^{-1}$) = 2970, 1750, 1630, 1513, 1462, 1405, 1238, 1110, 989, 827, 788. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.60; H, 7.10.

**Table 1. Radical Cross-Linking of Poly(St6CC) with Styrene**[a]

| run | feed ratio (mol %) carbonate[b]:styrene | yield (%)[c] | polymer composition[d] carbonate[b]:styrene (molar ratio) | $T_{d5}$[e] (°C) | $T_g$[f] (°C) |
|---|---|---|---|---|---|
| 1 | 100:0 | 83 | 100:0 | 305 | *g* |
| 2 | 50:50 | 64 | 38:62 | 333 | *g* |
| 3 | 33:67 | 85 | 29:71 | 307 | 102 |
| 4 | 20:80 | 56 | 22:78 | 319 | 112 |
| 5 | 11:89 | 56 | 11:89 | 325 | 103 |
| 6 | 6:94 | 82 | 7:93 | 336 | 102 |
| 7 | 3:97 | 76 | 5:95 | 343 | 97 |

[a] Conditions: initiator BPO (1 mol %), solvent DMF (2 M), 80 °C, 3 h. [b] Molar ratio per St6CC repeating unit. [c] THF-insoluble part. [d] Estimated by elemental analysis. [e] Determined by TGA under nitrogen. [f] Determined by DSC under nitrogen. [g] Not determined.

**Anionic Depolymerization of Poly(St6CC).** *t*-BuOK in THF (1.0 M, 50 $\mu$L, 0.05 mmol) was added to a solution of poly(St6CC) (276 mg, 1 mmol per repeating unit) in THF (10 mL) at 20 °C under a nitrogen atmosphere. After the mixture was stirred at the temperature for 24 h, the reaction was quenched by the addition of a solution of methanol/phosphoric acid (9:1 = v/v, 20 $\mu$L). St6CC was isolated from the mixture by preparative high-performance liquid chromatography on a Japan Analytical Industry LC-908 system equipped with two polystyrene gel columns (JAI gels H1 and H2) with chloroform as an eluent at a flow rate of 3.8 mL/min. The yield of St6CC was 166 mg (60%).

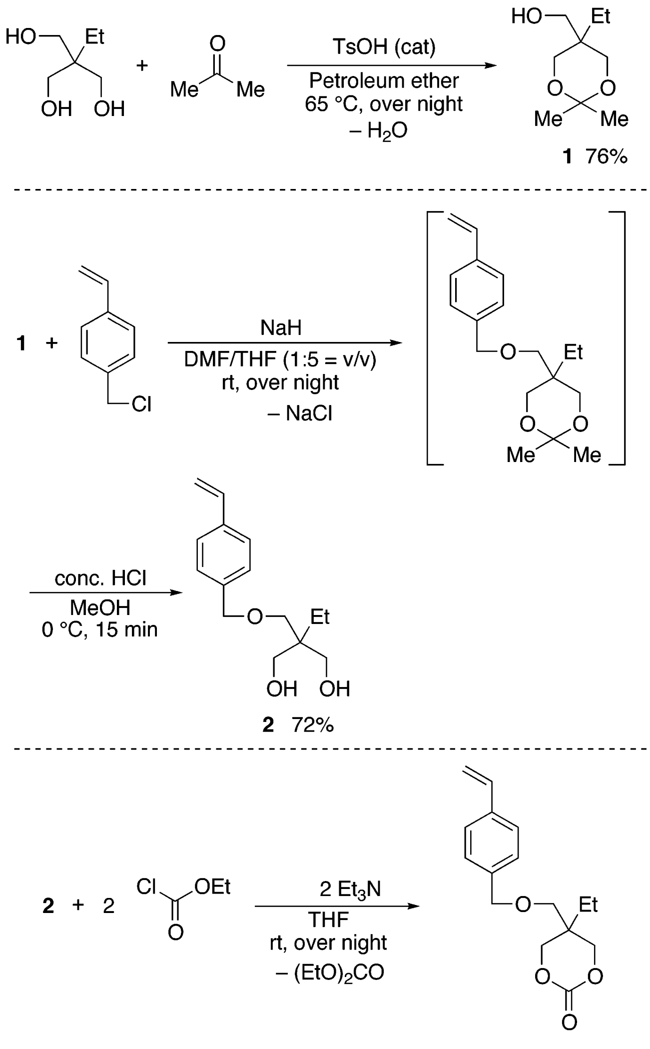
**Radical Cross-Linking of Poly(St6CC)**. Typical procedure: Benzoyl peroxide (BPO, 5 mg, 0.02 mmol, 1 mol %) and subsequently styrene, if required, were introduced to a solution of poly(St6CC) (552 mg, 2 mmol per repeating unit) in DMF (1 mL, 2 M) in a polymerization tube. The tube was cooled, degassed, sealed off, and heated at 80 °C for 3 h. The resulting residue was rinsed using a Soxhlet extractor and dried under a reduced pressure. The yield of the cross-linked polymer was 458 mg (83%). Spectral data and elemental analysis of the cross-linked polymer obtained in run 1 in Table 1 are as follows. IR (KBr): $\nu$ (cm$^{-1}$) = 3444, 3083, 3060, 3026, 2919, 2850, 2313, 1943, 1871, 1752, 1602, 1493, 1453, 1365, 1269, 1233, 1096, 1069, 1028, 907, 757, 539. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.61; H, 7.17.

**Anionic De-Cross-Linking of the Cross-Linked Polymer.** Typical procedure: The cross-linked polymer (2 mmol per repeating unit) was fed in a 50 mL flask equipped with a three-way stopcock and dried under a reduced pressure at 100 °C for 1 h. After it was cooled to 50 °C, THF (20 mL) was added to the dried cross-linked polymer under a nitrogen atmosphere, followed by stirring for 1 h to swell the cross-linked polymer. *t*-BuOK in THF (10 mol % vs carbonate repeating unit) was added to the mixture. After the mixture was stirred at 50 °C for 24 h, the reaction was quenched by the addition of a solution of methanol/phosphoric acid (9:1 = v/v, 40 $\mu$L). The reaction mixture was filtered. The filtrate was concentrated and poured into a large amount of *n*-hexane to precipitate the polymer. Spectral data of the polymer obtained in run 2 in Table 1 are as follows. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.26−6.21 (m, 9H, $-C_6H_4-$ and $-C_6H_5$), 4.41 (brs, 2H, $-C_6H_4OC\mathit{H}_2-$), 4.30 (brs, 2H, $COOCH_2$), 4.11 (brs, 2H, $COOCH_2$), 3.40 (brs, 2H, $OCH_2C$), 2.17−1.08 (m, 8H, $-C\mathit{H}_2C\mathit{H}Ar-$ and $-C\mathit{H}_2CH_3$), 0.85 ppm (brs, 3H, $-CH_2C\mathit{H}_3$). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 148.5, 144.8, 134.8, 127.6, 73.4, 72.8, 68.3, 40.4, 35.5, 32.2, 23.4, 7.5 ppm. IR (KBr): $\nu$ (cm$^{-1}$) = 3084, 3058, 3026, 2970, 2924, 2861, 1758, 1602, 1513, 1494, 1472, 1453, 1406, 1385, 1251, 1177, 1115, 1019, 910, 821, 765, 701.

## Results and Discussion

**Monomer Synthesis.** Scheme 3 illustrates the synthetic routes of St6CC, the six-membered cyclic carbonate having a styrene moiety. It was synthesized by the reaction of ethyl chloroformate with the diol **2**, which was prepared by acetalization of trimethylolpropane with acetone, etherification of **1** with *p*-chloromethylstyrene, and subsequent alcoholysis catalyzed with HCl.

**Scheme 3**



**Anionic Ring-Opening Polymerization of St6CC.** Anionic ring-opening polymerization of St6CC was carried out with 1 mol % potassium *tert*-butoxide (*t*-BuOK) in toluene with an initial monomer concentration of 1 M at 0 °C for 24 h (Scheme 4) to obtain polycarbonate [poly(St6CC)] with $M_n$ 14 000 in 80% yield. The structure of poly(St6CC) was determined by $^1$H NMR, $^{13}$C NMR, and IR spectroscopy. Figure 1 depicts the $^1$H and $^{13}$C NMR spectra of St6CC and poly(St6CC). The $^1$H NMR spectrum of poly(St6CC) (Figure 1B) showed three signals assignable to the vinylic protons of styrene moiety at 5.21, 5.71, and 6.67 ppm. The $^{13}$C NMR spectrum of poly(St6CC) (Figure 1D) showed two signals assignable to the vinylic carbon atoms at 113.7 and 136.9 ppm. It was confirmed that St6CC selectively underwent anionic ring-opening polymerization at the 6CC moiety without the polymerization of the styrene moiety.

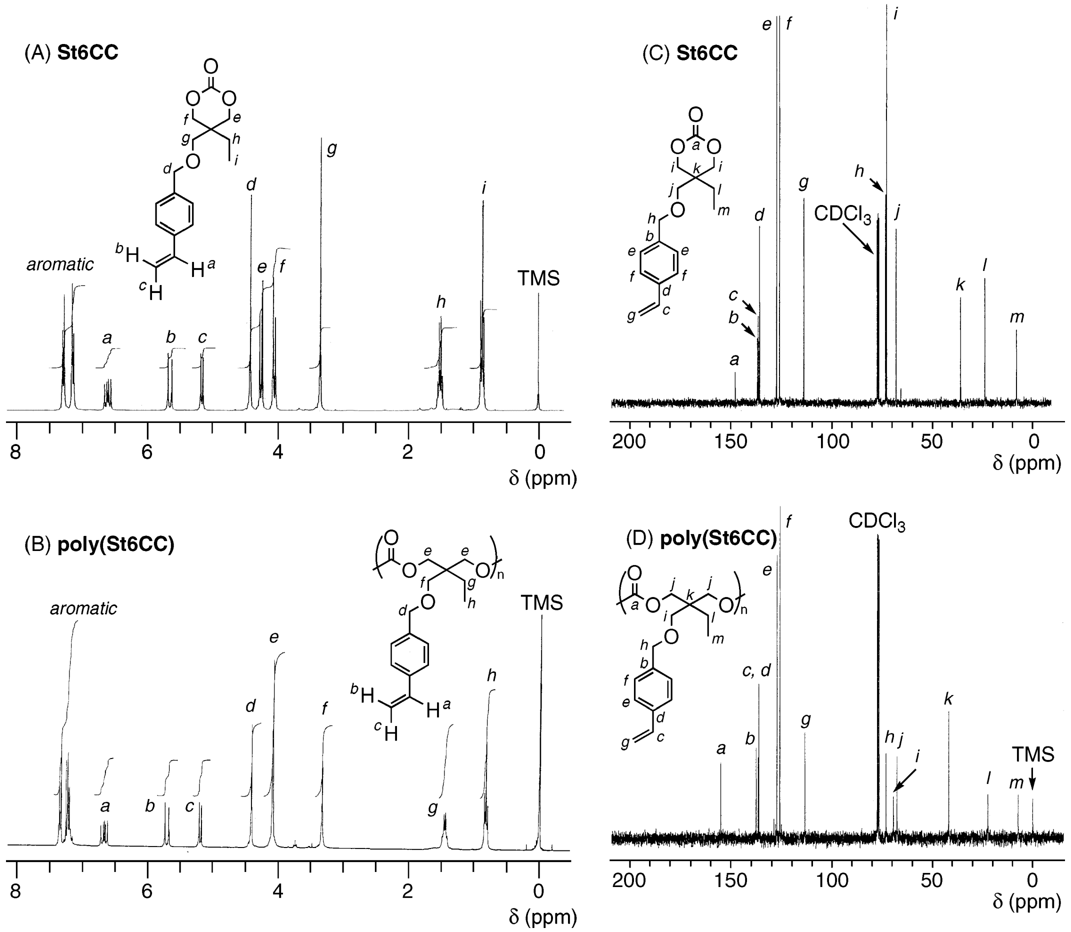
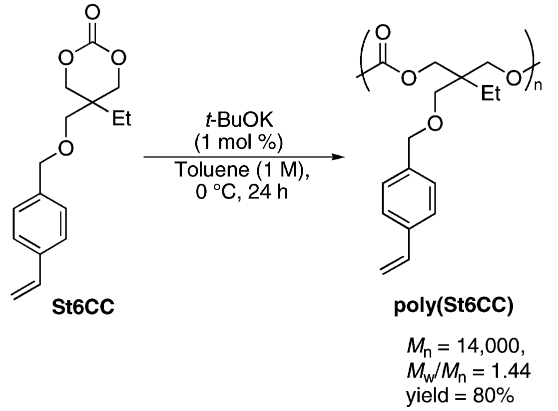


**Figure 1.** $^1$H NMR spectra (solvent; CDCl$_3$, 300 MHz) of (A) St6CC and (B) poly(St6CC) obtained in the polymerization with *t*-BuOK (1 mol %) as an initiator at 0 °C for 24 h; $^{13}$C NMR spectra (solvent; CDCl$_3$, 75 MHz) of (C) St6CC and (D) poly(St6CC) obtained in the polymerization with *t*-BuOK (1 mol %) as an initiator at 0 °C for 24 h.

**Scheme 4**



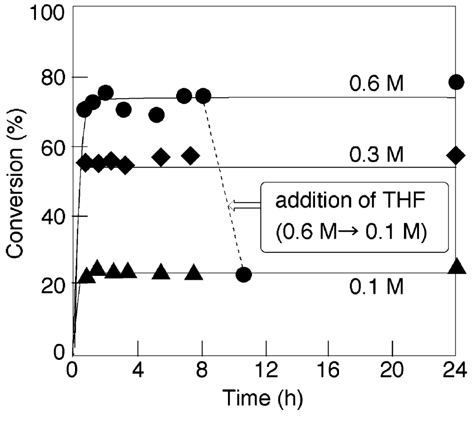


**Figure 2.** Time–conversion relationships in the anionic ring-opening polymerization of St6CC with *t*-BuOK (1 mol %) in THF with the initial monomer concentration of 0.1, 0.3, and 0.6 M at 20 °C.

Equilibrium behavior was examined in the anionic ring-opening polymerization of St6CC. Figure 2 depicts the time–conversion relationships in the anionic ring-opening polymerization of St6CC at 20 °C with the initial monomer concentration of 0.1, 0.3, and 0.6 M. It was confirmed that the St6CC conversion reached a constant after 1 h in every case, whose value decreased according to the initial monomer concentration ([M]$_0$). The equilibrium monomer concentrations ([M]$_e$) were estimated as 0.08 M ([M]$_0$ = 0.1 M), 0.14 M ([M]$_0$ = 0.3 M), and 0.15 M ([M]$_0$ = 0.6 M), respectively. After the St6CC conversion reached a constant, the monomer was regenerated by the addition of THF to dilute the monomer concentration from 0.6 to 0.1 M. These results support strongly that there is an equilibrium between poly(St6CC) and St6CC.

Figure 3 depicts the time–conversion relationships in the anionic ring-opening polymerization of St6CC with the initial monomer concentration of 0.3 M at 0, 20, and 40 °C. The conversions of St6CC reached a constant after 1 h in every case. It was confirmed that the monomer conversion decreased with raising the polymerization temperature, as typically observed in equilibrium polymerization. Dainton's equation can be applied to this type of equilibrium polymerization,

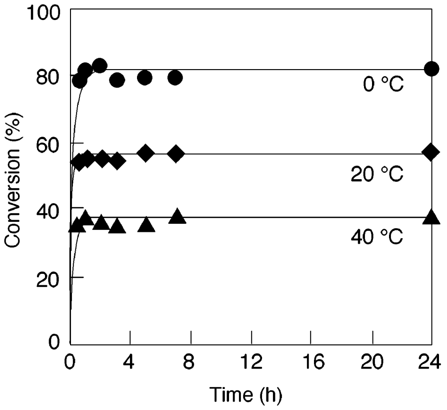


**Figure 3.** Time−conversion relationships in the anionic ring-opening polymerization of St6CC with *t*-BuOK (1 mol %) in THF with the initial monomer concentration of 0.3 M at 0, 20, and 40 °C.

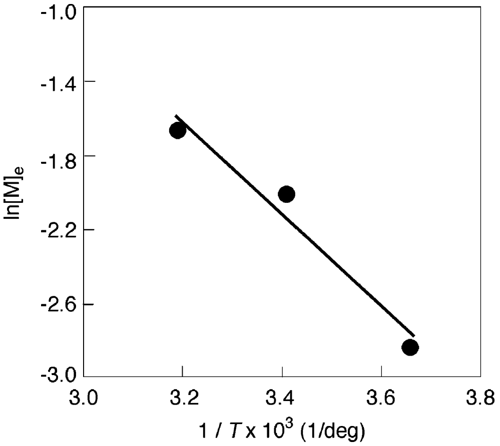


**Figure 4.** ln $[M]_e$−$1/T$ relationship in the anionic ring-opening polymerization of St6CC with *t*-BuOK (1 mol %) in THF for 24 h.

where $T$, $[M]_e$, $\Delta H_{SS}$, and $\Delta S_{SS}$ denote the polymerization temperature, monomer concentration at equilibrium, standard enthalpy, and standard entropy change for the polymerization of cyclic carbonate in a solution, respectively (eq 1).[10]

$$\ln\,[M]_e = \Delta H_{SS}/RT - \Delta S_{SS}/R \qquad (1)$$

Figure 4 replots the data in Figure 3 in conjunction with the logarithm of $[M]_e$ vs the reciprocal of the polymerization temperature ($1/T$). The liner relationships clearly indicate that the polymerization of St6CC obeys Dainton's equation, confirming the equilibrium character of the polymerization. Thermodynamics parameters calculated from the plots were $\Delta H_{SS} = -4.99$ kcal/mol, $\Delta S_{SS} = -12.76$ cal/(mol K), and $\Delta G_{SS} = -1.25$ kcal/mol (at 20 °C).

**Depolymerization of Poly(St6CC).** We next examined the depolymerization of poly(St6CC) with *t*-BuOK (5 mol % vs polymer repeating unit) as a catalyst in THF (reagent concentration = 0.1 M per polymer repeating unit) at 20 °C for 24 h. The starting monomer was recovered in 60% yield (Scheme 5). The original polymer was completely consumed, producing an oligomer along with the monomer, as shown in the SEC profiles before and after depolymerization (Figure 5). Figure 6 shows the time courses of St6CC formation and $M_n$ of the remaining polymer in the depolymerization of poly(St6CC). The anionic depolymerization of poly(St6CC) underwent rapidly to form St6CC, and the formation reached a constant after 1 h. The $M_n$ of the polymer decreased ≈10% of the initial one for 30 min.

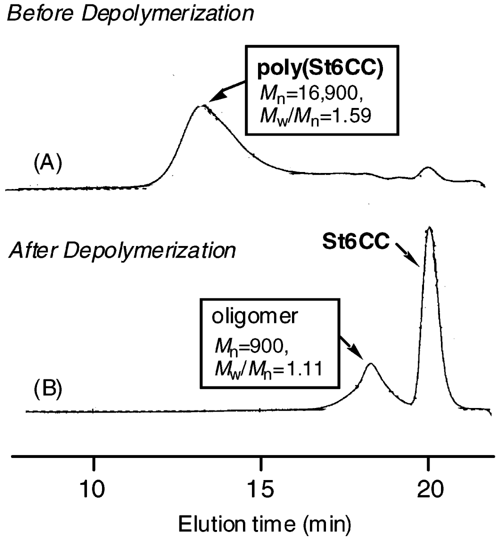


**Figure 5.** SEC profiles before and after the depolymerization of poly(St6CC) ($M_n$ = 17 000, $M_w/M_n$ = 1.59). The depolymerization was carried out with *t*-BuOK (5 mol % vs polymer repeating unit) as a catalyst in THF (the initial reagent concentration = 0.1 M per polymer repeating unit) at 20 °C for 24 h.

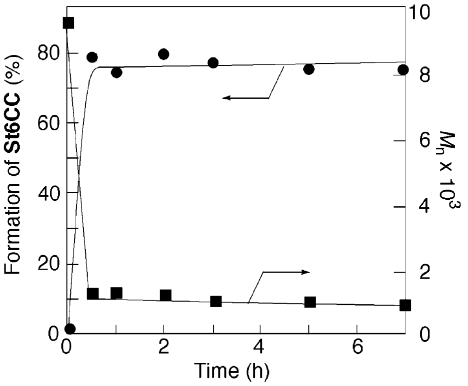
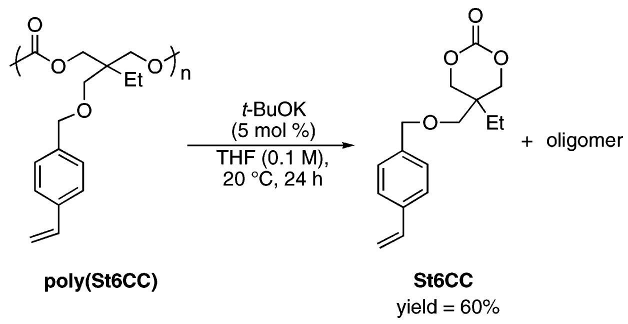


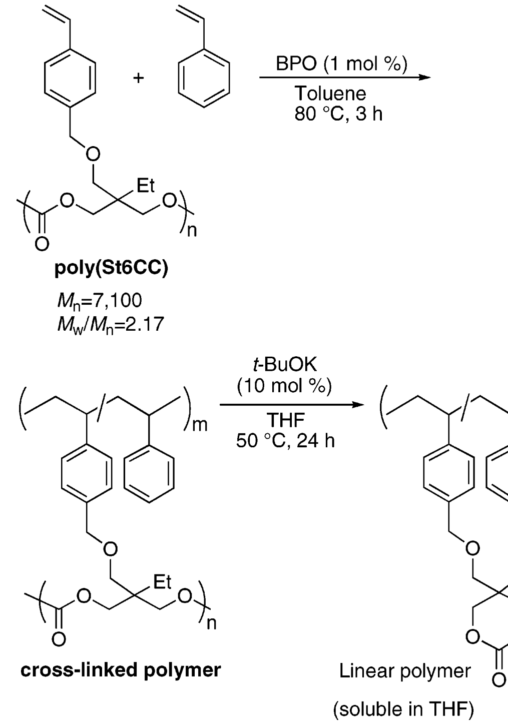
**Figure 6.** Time courses of the formation of St6CC and $M_n$ of the remaining polymer in the depolymerization of poly(St6CC) with *t*-BuOK (5 mol % vs polymer repeating unit) as a catalyst in THF (the initial reagent concentration = 0.1 M per polymer repeating unit) at 20 °C.

### Scheme 5



**Radical Cross-Linking of Poly(St6CC).** Radical cross-linking of poly(St6CC) was carried out in the absence and presence of styrene with BPO (1 mol %) as an initiator in DMF at 80 °C for 3 h to afford the solvent-insoluble cross-linked polymers in 56−85% yields (Scheme 6 and Table 1). The compositions of St6CC and

**Scheme 6**



styrene units in the cross-linked polymers were determined by elementary analysis. There values were in good agreement with the feed ratios, except for the case of equimolar feed ratio (run 2 in Table 1). This is probably due to the gelation time shorter than that required for complete conversion of poly(St6CC) unit. Furthermore, thermal properties of the cross-linked polymers were estimated by both TGA and DSC measurements in order to investigate the possibility of the cross-linked polymers for some applications (Table 1). TGA revealed that all the cross-linked polymers are stable below ca. 250 °C ($T_{d5}$ > 305 °C). The glass transition temperature ($T_g$) ranging from 97 to 112 °C was estimated by DSC measurement, except for the samples that the carbonate unit content exceeds 38% (runs 1 and 2 in Table 1). It is thought that thermal properties of the cross-linked polymers depend on a polystyrene unit that may originate from the different flexibility of the cross-linking unit. However, it is under examination about the details.

**Anionic De-Cross-Linking of the Cross-Linked Polymer.** We further examined the anionic de-cross-linking of the cross-linked polymer with *t*-BuOK (10 mol % vs polymer repeating unit) in THF at 50 °C for 24 h to obtain a THF-soluble polymer (Scheme 6). Table 2 summarizes the results of the de-cross-linking. The yield of the THF-soluble part increased as the styrene composition in the cross-linked polymer increased. It may be confirmed clearly that the efficiency of de-cross-linking depends on the cross-linking density. The $M_w/M_n$ of the THF-soluble polymer obtained was somewhat large (~3.19), presumably due to chain transfer reaction during radical cross-linking process, along with residual of non-depolymerized 6CC unit, although the amount should be small.

**Table 2. De-Cross-Linking of the Cross-Linked Polymer**[a]

| | cross-linked polymer | THF-soluble part obtained by the de-cross-linking the cross-linked polymer | |
|---|---|---|---|
| run | composition ratio[b] (St6CC: **St**) | yield (%) | $M_n$ ($M_w/M_n$)[c] |
| 1 | 100:0 | 23 | 800 (1.10) |
| 2 | 50:50 | 14 | 1700 (1.97) |
| 3 | 37:63 | 34 | 5100 (1.58) |
| 4 | 22:78 | 50 | 14000 (2.43) |
| 5 | 16:84 | 80 | 11000 (3.19) |

[a] Conditions: initiator *t*-BuOK (10 mol %), solvent THF (0.1 M: based on repeating unit of the polymer), 50 °C, 24 h. [b] Estimated by elemental analysis. [c] Estimated by SEC based on polystyrene standards, eluent THF.

In summary, we could demonstrate a novel cross-linking–de-cross-linking system based on the anionic depolymerization of a novel cyclic carbonate with a styrene moiety, St6CC. We believe that our approach will develop a new field of polymer recycling method for thermosetting resins as well as thermoplastics.

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