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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) in THF 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 orthoesters² (SOEs) and bicyclo orthoesters³ (BOEs) and chemical recycling systems between linear polymers having SOE⁴ or BOE⁵ moieties and cross-linked polymers based on the cationic equilibrium polymerization of SOEs and BOEs (Scheme 1).

Six-membered cyclic carbonates (6CCs) efficiently undergo ring-opening polymerization to afford the corresponding linear polyesters, 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 interac-
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. Purification. Tetrahydrofuran (THF) was dried over sodium methoxide and stored over molecular sieves (4A).

Measurements. 1H NMR and 13C NMR spectra were recorded with a JEOL Lambda-300 spectrometer in chloroform-d (CDCl3) using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer. Number-average molecular weights (Mn) and polydispersities (Mw/Mn) were estimated by size exclusion chromatography (SEC) on a Tosoh HPLC HLC-8120 system equipped with two consecutive polystyrene gel columns (TSK gels G4000HQ 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). Trichloromethylpropene (53.7 g, 400 mmol), acetonitrile (120 mL, 1.6 mol), potassium chloride (120 mL), and p-toluene sulfonic 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 longer collected in the Dean–Stark trap. The mixture was cooled in an ice water bath, and anhydrous sodium carbonate (7.8 g) was added to the mixture, followed by stirring for 30 min. The mixture was then filtered, and petroleum ether (300 mL) was prepared and stored over molecular sieves (4A) 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 added dropwise to a solution of 1 (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 48.6 °C. 1H NMR (300 MHz, CDCl3): δ 6.69 (d, J = 8.2 Hz, 2H, −CH2OH), 3.36 (s, 2H, −CH3), 5.71 (d, J = 11.7 Hz, 1H, −CH=CH2), 5.26 (d, J = 10.9 Hz, 1H, −CH=CH2), 4.84 (s, 2H, −OCH2CH2OCH3), 4.33 (d, J = 11.0 Hz, 2H, −CH2OOCO−), 4.13 (d, J = 11.0 Hz, 2H, −CH2OOCO−), 3.42 (s, 2H, −CH2O−), 1.53 (q, J = 7.5 Hz, 2H, −CH2CH2), 0.88 ppm (t, J = 7.5 Hz, 3H, −CH3CH2). 13C NMR (75 MHz, CDCl3): δ 148.5, 137.6, 137.6, 127.8, 126.3, 126.3, 126.3, 127.7, 67.8, 68.2, 35.4, 22.2 ppm. IR (KBr): ν (cm−1) = 2971, 2926, 1756, 1471, 1405, 1179, 1115, 766. Anal. Calcd for C15H22O3: C, 69.54; H, 7.30. Found: C, 69.60; H, 7.10. Analytical 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 μL, 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 2 h.

The reaction was quenched by the addition of a solution of methanol/phosphoric acid (v/v = 9:1, 10 μL). 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.

PolySt6CC (H). 1H NMR (300 MHz, CDCl3): δ 7.34 (d, J = 8.1 Hz, 2H, −CH3−), 7.22 (d, J = 8.1 Hz, 2H, −CH3−), 6.67 (dd, J = 10.9 and 17.5 Hz, 1H, CH−CH=), 5.71 (d, J = 17.5 Hz, 1H, CH−CH=), 5.21 (d, J = 10.9 Hz, 1H, CH−CH=), 4.42 (s, 2H, −OCH2CH2OCH3), 4.10 (s, 4H, −CH2OOCO−), 3.33 (s, 2H, −CH2O−), 1.47 (q, J = 7.5 Hz, 2H, −CH2O−), 0.82 ppm (t, J = 7.5 Hz, 3H, −CH3). 13C NMR (75 MHz, CDCl3): δ 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): ν (cm−1) = 2970, 1750, 1630, 1513, 1462, 1405, 1238, 1110, 989, 827, 788. Anal. Calcd for C21H24O3: C, 69.54; H, 7.30. Found: C, 69.60; H, 7.10.
Table 1. Radical Cross-Linking of Poly(St6CC) with Styrene

<table>
<thead>
<tr>
<th>run</th>
<th>carbonate:a:styrene</th>
<th>yield (%)</th>
<th>polymer composition</th>
<th>carbonate:a:styrene (molar ratio)</th>
<th>$T_{d^*}$ (°C)</th>
<th>$T_d$ (°C)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
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<td>100:0</td>
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<td>305</td>
<td>8</td>
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<td>2</td>
<td>50:50</td>
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<td>38:62</td>
<td>333</td>
<td>333</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>33:67</td>
<td>85</td>
<td>29:71</td>
<td>307</td>
<td>102</td>
<td>8</td>
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<td>20:80</td>
<td>56</td>
<td>22:78</td>
<td>319</td>
<td>112</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>11:89</td>
<td>56</td>
<td>11:89</td>
<td>325</td>
<td>103</td>
<td>8</td>
</tr>
<tr>
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<td>6:94</td>
<td>82</td>
<td>7:83</td>
<td>330</td>
<td>102</td>
<td>8</td>
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<td>76</td>
<td>5:95</td>
<td>345</td>
<td>97</td>
<td>8</td>
</tr>
</tbody>
</table>

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

**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.

**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 vinyl 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 vinyl 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.
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 t-BuOK (1 mol %) in THF with the initial monomer concentration of 0.1, 0.3, and 0.6 M at 20 °C.
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

$$\ln [M]_e = \frac{\Delta H_{SS}}{RT} - \frac{\Delta S_{SS}}{R}$$

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 linear 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 $\sim 10\%$ of the initial one for 30 min.

**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...
stereoregular polystyrene containing non-depolymerized 6CC unit, although the amount should be small.

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.

References and Notes


Table 2. De-Cross-Linking of the Cross-Linked Polymer

<table>
<thead>
<tr>
<th>run</th>
<th>composition ratio  (St6CC: St)</th>
<th>cross-linked polymer</th>
<th>THF-soluble part obtained by the de-cross-linking the cross-linked polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100:0</td>
<td>23</td>
<td>yield (%)</td>
</tr>
<tr>
<td>2</td>
<td>50:50</td>
<td>14</td>
<td>M_w (M_n)</td>
</tr>
<tr>
<td>3</td>
<td>37:63</td>
<td>34</td>
<td>5100 (1.58)</td>
</tr>
<tr>
<td>4</td>
<td>22:78</td>
<td>50</td>
<td>14000 (2.45)</td>
</tr>
<tr>
<td>5</td>
<td>16:84</td>
<td>80</td>
<td>11000 (3.19)</td>
</tr>
</tbody>
</table>

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

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 stereoregularity 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.