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Controlled Depolymerization of Poly(5-ethyl-5-phenyl-1,3-dioxan-2-one): Selective Liberation of Cyclic Carbonate Monomer from Polymer Chain End

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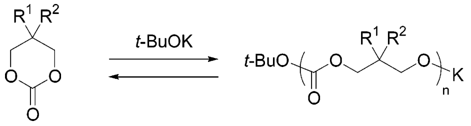
To date, there have been various studies on depolymerization of polymers. A small difference in enthalpy between monomer and polymer, which is often found in the case of polymerization of disubstituted olefins, leads to the equilibrium nature of the polymerization. On the basis of this equilibrium nature, the polymer can be depolymerized into its original monomer under appropriate conditions. In most cases, depolymerization proceeds with random scission of the polymer main chain to give a mixture of monomer and residual oligomers, which prevent the selective regeneration of the monomer. On the other hand, in some cases, depolymerization initiates selectively from the chain end of the polymer to release the monomer.[1−4] Such a so-called "unzipping" depolymerization is potentially as a highly effective method for chemical recycle of monomer. Furthermore, if the degree of unzipping can be well-controlled, it can be a powerful chisel for nanoscale control of figures and patterns of polymer materials.

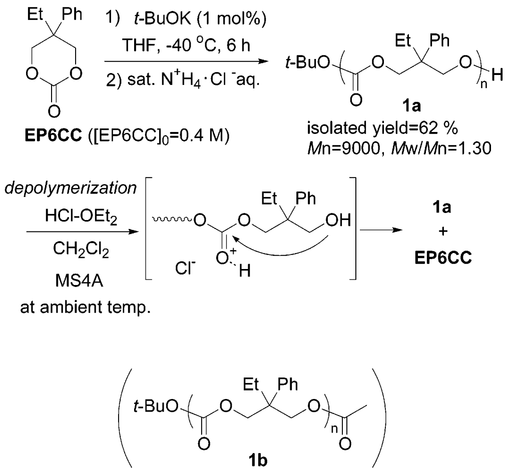
We have reported equilibrium polymerization behaviors of cyclic monomers.[5−9] For example, six-membered cyclic carbonates (6CC) undergo anionic polymerization, and on the basis of equilibrium nature, the formed polymer (poly6CC) undergoes anionic depolymerization (Scheme 1).[8] This equilibrium nature depends on the bulkiness of the substituents at the 5-position of the monomer: The more bulky the substituents are, the more easily depolymerization undergoes. In this anionic depolymerization system, a significant amount of oligomers are formed besides the monomer in the early stage of the depolymerization, suggesting that the main reaction involved in the system is a random attack of anionic species to the carbonate group in the main chain. During our efforts to control the depolymerization of poly(6CC), we found that a cationic system is capable of achieving a controlled unzipping depolymerization, which is the main subject of this Communication.[10]

Scheme 1



Scheme 2 illustrates the present polymerization−depolymerization system. For the polymerization, potassium *tert*-butoxide was employed as an anionic initiator, as previously reported.[8] The polymerization was carried out in tetrahydrofuran (THF) at −40 °C. By monitoring the polymerization reaction by ^{1}H NMR analysis, it was revealed that the conversion of the monomer was determined to be 32% at 1 h after the initiation, and then the conversion reached 77% at 6 h, which would be the equilibrium point under the conditions. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the resulting polymer, which were estimated by size exclusion chromatography (SEC) of the crude mixture *before* precipitation, were 9000 and 13 300, respectively. These values did not change after precipitation. The formed polymer **1a** was isolated in 62% yield as methanol-insoluble material. The presence of hydroxyl group at the polymer terminal was confirmed by its IR absorption at 3100 cm^{-1}.

Scheme 2



Thus, we examined the acid-promoted depolymerization of the obtained polycarbonate **1a** using HCl−OEt$_2$ as a promoter.[11] The time dependence of M_n and M_w/M_n of the polymer and that of yield of EP6CC for the depolymerization are shown in Table 1. As can be seen from these data, the yield of EP6CC increased with the elapse of time, and accordingly, M_n of the resulting polymer decreased by depolymerization. The time dependence of yield of EP6CC was not an exactly linear one but showed the tendency that the rate of depolymerization slightly declined upon elongation of time, suggesting the equilibrium nature of the polymerization. The previously reported monomer concentration at equilibrium in the anionic polymerization of EP6CC is 0.4 M (at 20 °C, the initial monomer concentration = 0.6 M, initiator = *t*-BuOK, in THF), which means that approximately $^2/_3$ of the repeating unit in the polymer can be depolymerized into EP6CC.[8] Thus, the monomer

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Table 1. Acid-Promoted Depolymerization of Poly(EP6CC)

	depolymerization of **1a**[a]		depolymerization of **3a**[b]
depolym time/h	M_n[c] (M_w/M_n)[c]	yield of recovered monomer/%[d]	yield of recovered monomer/%[e]
0	9000 (1.27)	(0)	(0)
3	nd[f]	nd[f]	3
6	9000 (1.30)	4	4
24	8300 (1.31)	9	9
48	7800 (1.31)	16	nd[f]
72	7100 (1.31)	20	14

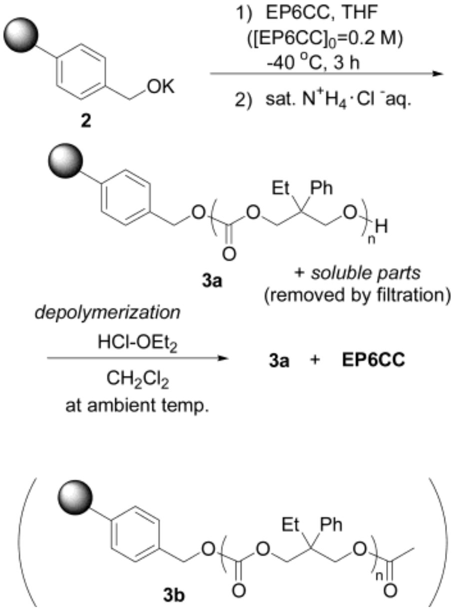
[a] Conditions: $[\text{polymer-OH}]_0 = 0.25$ M; $[\text{HCl-OEt}_2]_0 = 0.125$ M. [b] Conditions: $[\text{polymer-OH}]_0 = 0.17$ M; $[\text{HCl-OEt}_2] = 0.51$ M. [c] Estimated by SEC analysis (eluent: THF, calibrated with polystyrene standards) of the crude mixture. [d] Determined by ^{1}H NMR. [e] Determined by GC. [f] Not determined.

yield in the present depolymerization seems to be still much lower than the expected one from the potential depolymerizability of poly(EP6CC). This low monomer yield in the present depolymerization is presumably due to the following two reasons: (1) The acid-promoted depolymerization is much slower than that promoted by basic reagent, and thus the depolymerization did not reach its equilibrium yet. (2) Solvent should have strong effects on the equilibrium nature: Since highly electron donative THF was used for the previously reported anionic depolymerization while electron deficient dichloromethane was used in the present acidic depolymerization, the equilibrium monomer concentration should be different.

It is noteworthy that no formation of the corresponding oligomers was found by SEC analysis of the obtained mixture, suggesting that the mechanism of the depolymerization does not involve a random scission of the main chain but is a selective intramolecular attack of the terminal hydroxyl group to the carbonyl group of the main chain, which is activated by protonation. The polymer **1b**[12] having an acetylated terminal did not undergo depolymerization under the same conditions, indicating that the terminal hydroxyl group is indispensable for initiation of the depolymerization. During the depolymerization of **1a**, no significant change in M_w/M_n was observed, while ideal unzipping depolymerization of well-defined polymer obtained by living polymerization should have an intrinsic tendency of decrease in polydispersity. The change of polydispersity during the depolymerization is considered to significantly have reflected the change during the polymer growth in the polymerization: The polymer **1a**, formed by initiation with *t*-BuOK, should have a large polydispersity in the early stage of the polymerization because the initiation reaction is slower than the propagation. Thus, it can be considered that the polydispersity should increase with retracing the propagation to compensate the intrinsic tendency of decrease in polydispersity for an ideal well-controlled depolymerization process, finding no significant change in it.

Addition of molecular sieve (MS4A), which traps water, is essential to achieve well-controlled depolymerization: After the depolymerization for 72 h in the absence of MS4A, M_n of the resulting polymer decreased to 7500 with increase of M_w/M_n to 1.53, suggesting that random scission of the main chain would undergo by hydrolysis of the protonated carbonate group.

Scheme 3



The present polymerization−depolymerization system was successfully applicable to a solid-supported polycarbonate, i.e., poly(EP6CC) grafted on a cross-linked polystyrene (Scheme 3). Graft polymerization of EP6CC was carried out using a solid-supported anionic initiator **2**, which was prepared from cross-linked hydroxymethylated polystyrene beads by treatment with potassium hexamethyldisilazide ($\text{KN(SiMe}_3)_2$) in THF.[13] The polymerization came to equilibrium with the corresponding depolymerization at 3 h after the initiation, and the monomer conversion at this point was determined to be 76% by GC analysis of the mixture. The resulting beads **3a** were filtered and washed by THF to remove soluble parts. From the weight increase of the obtained beads, conversion of EP6CC to the grafted poly(EP6CC) was calculated to be 35%. IR analysis of the beads showed strong absorptions at 1753 and at 3120 cm^{-1}, which were attributable to acyclic carbonate group in the main chain of the grafted poly(EP6CC) and hydroxyl group at the chain end, respectively. The soluble parts consisted of the monomer (24%) and oligo- and poly(EP6CC) (total 41%), which would be formed by backbiting reaction of the propagating polymer and by intermolecular nucleophilic attack of the propagating polymer to the carbonate group of the other polymer chain. The beads **3a** were exposed to the conditions for acetylation to obtain the beads **3b**,[12] on which the immobilized poly(EP6CC) had a masked hydroxyl terminal by esterification. Complete masking of the terminal hydroxyl group was confirmed by disappearance of its IR absorption at 3120 cm^{-1}.

Depolymerization of the grafted poly(EP6CC) was examined under similar conditions to those adopted for the linear polymer. Figure 1 illustrates the apparatus used, which was designed so that GC analysis of the solution phase can be easily performed with the aid of temporary removal of the beads by filtration under a nitrogen atmosphere. In this depolymerization system for the grafted poly(EP6CC), the amount of HCl-OEt_2 complex was increased to 3 equiv to the terminal hydroxyl group because 0.5 equiv of the complex did not sufficiently promote the depolymerization, presumably due to some steric effects arisen by cross-linked polystyrene. As shown in Table 1, the monomer was gradually released from the beads by the depolymerization. SEC analysis of the solution phase revealed that elution

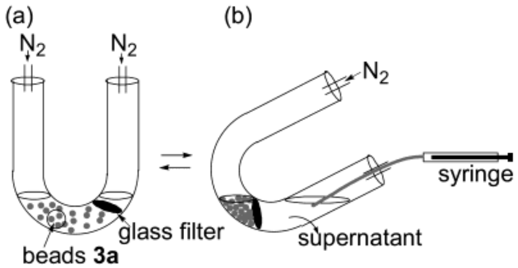


Figure 1. Apparatus for depolymerization of the solid-supported poly(EP6CC): (a) for reaction; (b) for sampling for GC analysis.

of polymeric and oligomeric products was negligible, indicating that selective depolymerization successfully proceeded without random scission of the main chain of the beads-supported poly(EP6CC), similarly to the depolymerization of the free poly(EP6CC). In addition, the terminal hydroxyl group of the grafted poly(EP6CC) was found to be indispensable for successful depolymerization: When **3b**, of which chain end was capped by acetylation, was exposed to the depolymerization conditions, only a negligible amount of EP6CC (<2%) was liberated from the beads even after 72 h.

In summary, poly(EP6CC) undergoes controlled depolymerization with releasing the monomer EP6CC selectively from the chain end in the presence of the HCl−OEt$_2$ complex, regardless of whether it is in a solution state or it is grafted on an insoluble cross-linked polymer. More detailed investigations on equilibrium behaviors of the polymerizations of EP6CC and other cyclic carbonates on various material surfaces are currently underway.

References and Notes

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(9) For the recent work by the other authors, see: Kanoh, S.; Nishimura, T.; Senda, H.; Ogawa, H.; Motoi, M.; Tanaka, T.; Kano, K. *Macromolecules* **1999**, *32*, 2438.
(10) Enzymatic degradation of polycarbonate is also of recent great interest. For example, see: Tsutsumi, C.; Nakagawa, K.; Shirahama, H.; Yasuda, H. *Macromol. Biosci.* **2002**, *2*, 223.
(11) HCl−OEt$_2$ has been found to be an effective promoter in polymerizations of cyclic lactones and cyclic carbonates using alcohol as an initiator; see: Shibasaki, Y.; Sanada, H.; Yokoi, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 4316.
(12) **1b** was obtained by acetylation of hydroxyl group at the terminal of **1a**: **1a** (200 mg) was treated with acetic anhydride (2 mL) and pyridine (4 mL) at room temperature for 24 h. The mixture was poured into methanol (30 mL) to obtain precipitates, which were redissolved in THF and were reprecipitated with methanol to obtain **1b** (191 mg, 95%), of which SEC-estimated M_n and M_w/M_n were identical with those of **1a**. For acetylation of the solid-supported polymer **3a**, dichloromethane and 4-(dimethylamino)pyridine (DMAP) were additionally used as a solvent and a catalyst, respectively.
(13) The procedure: To a THF dispersion (5 mL) of hydroxymethylated cross-linked polystyrene beads (purchased from Novabiochem Co., Ltd.; 0.87 mmol of −OH per 1 g; 115 mg, [−OH] = 0.10 mmol), a THF solution of KN(TMS)$_2$ (0.5 M; 0.20 mL, 0.10 mmol) was added at 0 °C under N$_2$. The mixture was shaken at 0 °C for 30 min. The beads were filtered and washed with THF (5 mL) twice under N$_2$ and swelled in THF (3 mL). To this THF dispersion of the beads, a THF solution (2 mL) of EP6CC (206 mg, 1.0 mmol) was added. The mixture was shaken at −40 °C for 3 h. The reaction was quenched by addition of saturated aqueous solution of ammonium chloride/methanol (1/9 (v/v), 0.1 mL). The beads were filtered, washed by THF and methanol, and dried under vacuum to give **3a** (187 mg).

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