Synthesis and Cationic Polymerization of Bicyclo Orthoester-Based Poly(ϵ-caprolactone) Macromonomer and Depolymerization of the Obtained Graft Copolymer

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The macromonomer technique is one of the most efficient and simplest methods to obtain well-defined graft copolymers. Since the development of polystyrene-based macromonomers by Milkovich et al.,[1] a wide variety of graft copolymers have been synthesized by this method based on living polybutadiene, poly(vinylpyridine),[2] poly(methyl methacrylate),[3] poly(vinyl ether),[4] poly(ethylene oxide),[5] poly(hexamethyltrisiloxane),[6] poly(ϵ-caprolactone),[7] etc., some of which have found industrial applications such as rubber, elastomers, hydrogels, and gas permeation membranes.[8] Recent rapid progress of living radical polymerization is further developing the molecular design of macromonomers,[9] along with conventional living anionic and cationic polymerization.

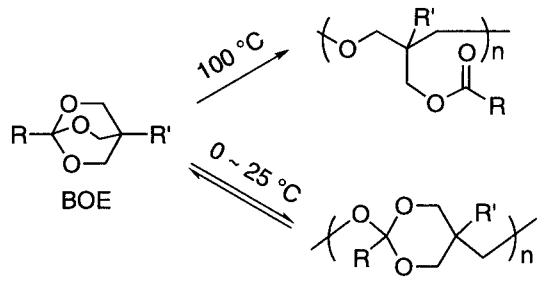
Bicyclo orthoesters (BOEs) undergo cationic double ring-opening polymerization to afford poly(ether ester)s (Scheme 1, top).[10] The most interesting feature of this polymerization is volume expansion during polymerization. Consequently, BOEs are expected for filling, adhesive, and curing materials, which can eliminate lowering of material properties caused by volume shrinkage.

In the course of our study on cationic ring-opening polymerization of BOEs, we have found that they undergo single ring-opening polymerization around 0 °C (Scheme 1, bottom), and this polymerization shows equilibrium character,[11] which is different from the double ring-opening isomerization polymerization around 100 °C (Scheme 1, top). The starting monomers can be recovered in high yields by treating the generated polymers in appropriate solvents at 25 °C. If we employed a BOE as a polymerizable group of a macromonomer, we might obtain a novel macromonomer undergoing reversible polymerization−depolymerization. This paper communicates the first example of synthesis and cationic polymerization of BOE-based poly(ϵ-caprolactone) macromonomer and depolymerization of the obtained graft copolymer.

The anionic polymerization of ϵ-caprolactone was carried out with a BOE-based Grignard reagent as an initiator in THF to obtain poly(ϵ-caprolactone) (Scheme 2, Table 1).[12] The polymer was obtained quantitatively at 20 °C (runs 1, 4, and 5), while it was obtained slightly at −30 and −78 °C (runs 2 and 3). The number-average molecular weight (M_n) increased according to the initial monomer/initiator ratio (runs 1, 4, and 5).[13] The incorporation of the BOE unit was confirmed by the ^{1}H NMR spectroscopic signals of the BOE moiety in the polymer as shown in Figure 1. The degree of polymerization was calculated by the integration ratio between the signals of the cyclic methylene protons *b* of BOE unit and methylene protons *h* of the poly(ϵ-caprolactone) unit. The degree of polymerization was larger than that expected from the monomer/initiator ratio, suggesting that the initiator efficiency was not quantitative.

The cationic polymerization of BOE-based poly(ϵ-caprolactone) macromonomers was carried out with BF_3·OEt_2 (10 mol % vs BOE unit) in CH_2Cl_2 with the macromonomer concentration of 1 M (per ϵ-caprolactone unit) at 0 or −78 °C for 72 h (Scheme 3). It was confirmed by GPC measurement that the macromonomers with the M_n's of 14 200 and 36 400 converted into the corresponding graft polymers in the polymerization at −78 °C, while no reaction took place at 0 °C, or in

Scheme 1



Scheme 2

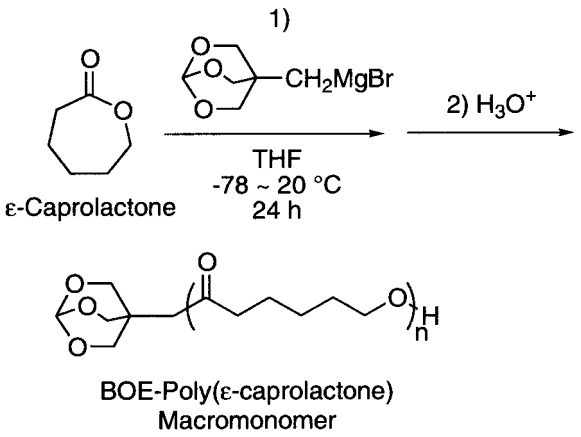


Table 1. Anionic Polymerization of ϵ-Caprolactone with a BOE-Based Grignard Reagent as an Initiator[a]

run	$[monomer]_0/[initiator]_0$	temp (°C)	conv[b] (%)	yield[c] (%)	M_n/DP[d] (^{1}H NMR)	M_n[e] (GPC)	M_w/M_n[e] (GPC)
1	200	20	98	90	28000/245	71300	1.86
2	200	−30	6	*f*	*f*	*f*	*f*
3	200	−78	3	*f*	*f*	*f*	*f*
4	125	20	96	95	17200/151	36400	1.21
5	50	20	100	95	6500/57	14200	1.28

[a] ϵ-Caprolactone 1.8 mmol, THF 1.8 mL, time 24 h. [b] Determined by ^{1}H NMR. [c] Methanol-insoluble part. [d] Determined by the integration ratio between cyclic methylene protons of BOE and methylene protons of poly(ϵ-caprolactone) unit in ^{1}H NMR. DP: degree of polymerization. [e] Estimated by GPC based on polystyrene standard samples eluted with THF. [f] Not determined.

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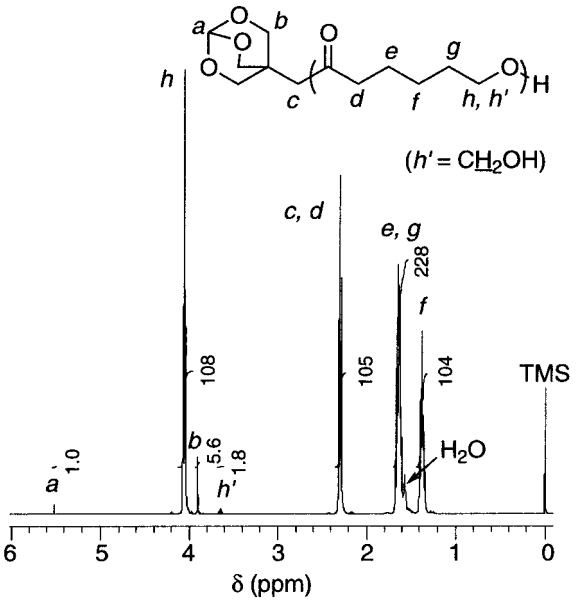
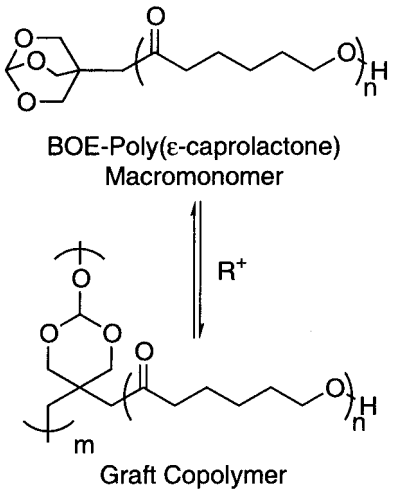


Figure 1. ^{1}H NMR spectrum (solvent $CDCl_3$, 500 MHz) of poly(ϵ-caprolactone) obtained by the polymerization initiated with a BOE-based Grignard reagent. M_n 14 200, M_w/M_n 1.28, run 5 in Table 1.

Scheme 3



the case of the macromonomer with the M_n of 71 300. These results would be understandable from the equilibrium character of BOE polymerization; i.e., the monomer conversion increased with increase of monomer concentration and decrease of reaction temperature.[11] Figure 2 depicts the GPC profiles before (A) and after (B) the polymerization of the macromonomer. The peak top shifted toward the higher molecular weight region, clearly indicating the progress of macromonomer polymerization. The degree of polymerization was estimated as 3−4 from the peak top molecular weights before and after the polymerization. However, the reaction mixture seemed to contain a partial amount of the macromonomer, which did not participate in the polymerization, because the residual peak was observed at the original molecular weight area.

Next, cationic depolymerization of the obtained graft polymers was carried with BF_3·OEt_2 (10 mol % vs BOE unit) in CH_2Cl_2 with the graft polymer concentration of 1 or 0.1 M (per ϵ-caprolactone unit) at 0 or −78 °C for 72 h (Scheme 3). The original BOE−poly(ϵ-caprolactone) macromonomer was quantitatively recovered

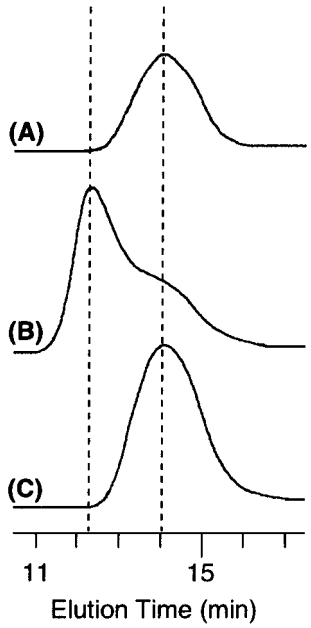


Figure 2. GPC profiles of (A) poly(ϵ-caprolactone) macromonomer (run 5 in Table 1), M_n 14 200, M_w/M_n 1.28; (B) graft copolymer obtained by the polymerization of the poly(ϵ-caprolactone) macromonomer with BF_3·OEt_2 (10 mol % vs BOE unit) in CH_2Cl_2 with the macromonomer concentration of 1 M (per ϵ-caprolactone unit) at −78 °C for 72 h, M_n 30 900, M_w/M_n 1.98; and (C) poly(ϵ-caprolactone) macromonomer recovered by the depolymerization of the graft copolymer with BF_3·OEt_2 (10 mol % vs BOE unit) in CH_2Cl_2 with the reagent concentration of 0.1 M (per ϵ-caprolactone unit) at 0 °C for 72 h, M_n 14 300, M_w/M_n 1.29.

in every case, whose structure was confirmed by ^{1}H, ^{13}C NMR, and IR spectroscopy, which also indicated no depolymerization of the poly(ϵ-caprolactone) unit into ϵ-caprolactone. As shown in Figure 2C, the GPC profile of the recovered macromonomer exhibited almost the same pattern as that of the original one before polymerization (A).

In summary, we could demonstrate the first example of polymerization of bicyclo orthoester (BOE)-based poly(ϵ-caprolactone) macromonomer, and depolymerization of the obtained graft copolymer, based on the cationic equilibrium polymerization of BOE. This approach may explore new fields of macromonomer polymerization and equilibrium polymerization.

Supporting Information Available: Experimental details of the macromonomer synthesis, polymerization, and depolymerization of the obtained graft copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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