Novel Synthesis of Single- and Double-Cyclic Polystyrenes by Electrostatic Self-Assembly and Covalent Fixation with Telechelics Having Cyclic Ammonium Salt Groups[†]

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ABSTRACT: A novel telechelic polystyrene having moderately strained cyclic ammonium, i.e., six-membered bicyclic quinuclidinium salt groups, has been synthesized, and mono-, di-, and tetracarboxylate counteranions were introduced by the ion-exchange reaction. A monocarboxylate, i.e., benzoate, counteranion was found to cause a selective ring-opening reaction of the quinuclidinium salt end group by the heat treatment at 110 °C. A single-cyclic polystyrene **2** was then produced in a high yield from the polymer precursor carrying a dicarboxylate, i.e., terephthalate, counteranion by the heat treatment in a diluted (0.1 g/L) toluene solution. Furthermore, a double-cyclic (8-shaped) polystyrene **3** was produced relevantly from another precursor carrying a tetracarboxylate, i.e., tetrakis((4-carboxylatophenyl)oxymethyl)methane, counteranion.
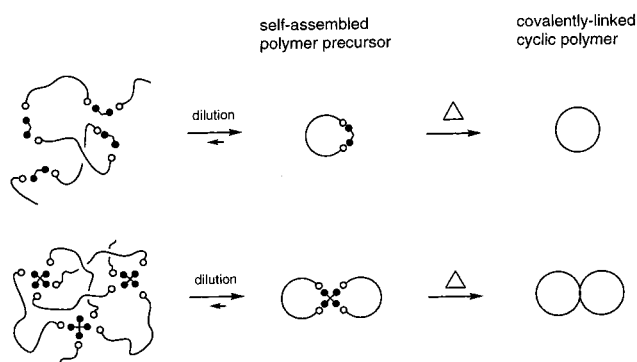
Introduction

Unconventional polymer architectures including large cyclic units have gained a growing interest in basic and applied polymer materials science.[1,2] In particular, cyclic polymers, due to the absence of end groups, have now realized unprecedented properties and functions unattainable by linear and branched counterpart. Moreover, the loop topology in cyclic polymers opens a unique opportunity to construct such unusual polymer architectures like mechanically linked catenanes and rotaxanes.[3-5] However, an efficient and practical means to construct cyclic polymer architectures remains to be a challenge, in contrast to remarkable achievements to synthesize such well-defined branched polymers having plural end groups as star polymers,[6] polymacromonomers,[7] hyperbranched polymers,[8] and dendrimers.[9]

We have recently developed an "electrostatic self-assembly and covalent fixation" process for an efficient construction of a variety of macromolecular architectures containing cyclic polymer units.[10] In this process, telechelic poly(THF)s having moderately strained cyclic ammonium salt groups, carrying a plurifunctional carboxylate counteranion, have been prepared as a key polymer precursor. To demonstrate a further applicability of this novel strategy, we report here an efficient synthesis of single- and double-cyclic polystyrenes by employing a newly prepared telechelic precursor having cyclic ammonium salt groups.

Cyclic polystyrenes have so far been prepared, in most cases, by an end-to-end linking reaction of a bifunctionally living polystyrene with a bifunctional end-linking reagent.[11-16] It should be noted, however, that this bimolecular reaction must be conducted under a strict molar balance between a polymer precursor and a low-molecular-weight coupling reagent. Moreover, the highly

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Scheme 1

diluted condition is required to promote the intramolecular process and to suppress the intermolecular process leading to the chain extension. This, in turn, substantially reduces the reaction rate due to the bimolecular, second-order kinetics of the reaction. An alternative means to improve efficiency in the polymer cyclization process includes a high dilution, but unimolecular, process by use of α,ω-heterobifunctional polystyrenes.[17-19] Nevertheless, the selective introduction of complementarily reactive groups at the opposite chain ends inherently requires multistep synthesis involving protection–deprotection processes, and thus its practical usefulness will be limited. An interfacial reaction by using a pair of immiscible liquids has also been applied.[20]

Our strategy is, as shown in Scheme 1, relied on an electrostatic self-assembly of telechelic polystyrenes having cyclic ammonium salt groups carrying pluricarboxylate counteranions in an organic medium. Upon dilution, a smallest assembly composed of polymer precursors and counteranions is predominantly formed from the ionically aggregated polymer precursors, with balancing the charges between cations and anions. The subsequent ring-opening reaction of cyclic ammonium salt end groups by the nucleophilic attack of carboxylate counteranions at appropriately elevated temperature

Table 1. Covalent Fixation of Electrostatically Self-Assembled Polystyrene Precursors Having Quinuclidinium Salt Groups[a]

run	precursor[a,b]	concn (g/L)	product[b]	yield (SEC)[c] (%)	M_p(SEC)[d] ($\times 10^3$)	M_p/M_p(**I**)	M_n(NMR)[e] ($\times 10^3$)	PDI[f]
1	**A**	4.0	**1**	100	5.8	1.0	5.5	1.09
2	**B**	4.0	**2**	65	4.6	0.79		
3	**B**	0.4	**2**	75 (52)	4.6	0.79	5.4[g]	1.06[g]
4	**B**	0.1	**2**	90	4.6	0.79		
5	**C**	4.0	**3**	30	9.1	1.57		
6	**C**	0.4	**3**	40	8.8	1.52		
7	**C**	0.2	**3**	50 (10)	8.8	1.52	11[g]	1.04[g]

[a] All polystyrene precursors (**A**−**C**) were prepared from the identical telechelic polystyrene having quinuclidinium salt groups. The ring-opening reaction of pyrrolidinium salt end groups was performed at reflux temperature in toluene for 5 h. Products were recovered quantitatively in all cases. [b] See Schemes 2 and 3. [c] Estimated from the SEC peak area of the crude product. Values in parentheses indicate isolated yields after purification by preparative TLC (SiO₂, EtOH/CH₂Cl₂/ET₃N = 5/90/5) (run 3) or after the fractionation by the preparative TLC followed by the SEC (run 7). [d] M_p: apparent peak molecular weight estimated by SEC with a calibration using polystyrene standards. [e] By ¹H NMR assuming quantitative chemical conversion of polymer end groups. [f] By SEC with a calibration using polystyrene standards. [g] For purified products.

has produced covalently linked single- and double-cyclic polystyrenes in good yields.

Experimental Section

Materials. Styrene was dried over CaH₂ and distilled just before use. Sodium naphthalene was prepared by a standard method.[21] 3-(*tert*-Butyldimethylsiloxy)propyldimethylchlorosilane was prepared as reported.[22] THF was dried over sodium benzophenone ketyl and distilled just before use. Benzene, toluene, and pyridine were distilled over CaH₂. Quinuclidine (Aldrich, 97%), sodium benzoate (Koso Chemical Co., Ltd.) and sodium terephthalate (Tokyo Kasei Kogyo Co., Ltd.) were used as received. A sodium salt of tetracarboxylic acid, tetrakis((4-carboxyphenyl)oxymethyl)methane, was prepared as reported.[23] Unless otherwise noted, materials were obtained from commercial sources.

Synthesis of a Telechelic Polystyrene Having Quinuclidinium Salt Groups. A bifunctional living polystyrene was produced by a "syringe-and-flask" technique detailed before.[24,25] The end-capping reaction of the living polystyrene was carried out by adding 3 times excess of a chlorosilane derivative having a protected hydroxy group, 3-(*tert*-butyldimethylsiloxy)propyldimethylchlorosilane. After 0.5 h, to the reaction mixture was added methanol containing 1.0 vol % hydrochloric acid. The solution was stirred at 20 °C for 15 h to promote the deprotection reaction. The mixture was then poured into cold methanol (−15 °C) to isolate the crude product by filtration. The product was purified by reprecipitation from the THF/methanol system and finally freeze-dried from a benzene solution to give a telechelic polystyrene having 3-hydroxypropyl groups (100% recovery yield with the quantitative introduction of the end group). Then, 1.8 g (3.6 × 10⁻⁴ mol) of the product was dissolved in 3 mL of pyridine, and 1.4 g (7.4 × 10⁻³ mol) of *p*-toluenesulfonyl (tosyl) chloride was added under a nitrogen atmosphere. The reaction mixture was stirred at 20 °C for 2 h and poured into cold methanol (−15 °C). The crude product, recovered by filtration, was purified by reprecipitation from the THF/methanol system and finally freeze-dried from a benzene solution to give a telechelic polystyrene having *p*-toluenesulfonate (tosylate) groups (86% recovery yield with the quantitative transformation of the end group). In a final step, 1.6 g (3.2 × 10⁻⁴ mol) of the telechelic polystyrene having tosylate groups was dissolved in 15 mL of toluene, and an excess amount of quinuclidine (9.6 × 10⁻³ mol) was added under a nitrogen atmosphere. The reaction was allowed to proceed at 90 °C for 15 h, and the solution was condensed by evacuation. The quaternized product was isolated (90% recovery yield with the quantitative quaternization of the end group) by precipitation of the THF solution into petroleum ether (−15 °C) and subsequently into water (5 °C) and finally freeze-dried from a benzene solution.

Ion-Exchange Reaction of a Telechelic Polystyrene Having Quinuclidinium Salt Groups. A procedure of the ion-exchange reaction was similar to that for a telechelic polystyrene having *N*-methylpyrrolidinium salt groups, re-

ported before.[24] The ion-exchange products **A**, **B**, and **C** (prepared by the reaction with sodium benzoate, sodium terephthalate, and sodium tetracarboxylate, respectively) were obtained in good-to-excellent yields (85−95%) by repetitious precipitation treatments of the telechelic polystyrene having quinuclidinium salt groups into a 50 vol % aqueous methanol solution containing an excess amount (10−20 equiv) of a sodium carboxylate at −15 °C.

Ring-Opening Reaction of Cyclic Ammonium Salt Groups in Telechelic Polystyrenes. Telechelic polystyrenes carrying a series of carboxylate counteranions (0.02−0.5 g) were dissolved in toluene at the prescribed concentration (0.1−10 g/L) and were heated at 110 °C for 5 h under vigorous stirring. The covalently converted products were quantitatively recovered by simply evaporating the solvent and were subjected to spectroscopic and chromatographic analysis. The recovered crude cyclic polystyrene (run 3 in Table 1) was subjected to the further purification, by means of a preparative thin-layer chromatography technique (SiO₂, EtOH/CH₂Cl₂/Et₃N = 5/90/5), to give a major fraction (R_f = 0.2−0.3) in 52% isolated yield and a minor fraction (R_f = 0.3−0.4) in 20% yield. A purified double-cyclic polystyrene (run 7 in Table 1) was collected by the subsequent fractionation with an analytical SEC apparatus in 10% total yield.

Measurements. SEC measurements were performed using a Tosoh model CCPS equipped with a refractive index detector model RI 8020 and a UV detector model UV 8020 at 254 nm and with a column of TSK G3000HXL. An eluent was either THF or THF with 5.0 vol % of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) at a flow rate of 1.0 mL/min. In particular, the latter was employed for polystyrene samples containing amino groups, by which one can avoid any elution delay, which occurred in the absence of TMEDA due to the interaction between amino groups of the obtained polystyrene and SEC gel beads surfaces.[26] IR spectra were taken on a JASCO FT/IR-410 infrared spectrometer by casting the sample from the chloroform solution on a NaCl plate. ¹H NMR spectra were recorded with a JEOL JNM-AL300 apparatus in CDCl₃ at 40 °C.

Results and Discussion

1. Synthesis of a Telechelic Polystyrene Having Quinuclidinium Salt Groups. In our previous studies,[10] telechelic poly(THF)s having *N*-phenylpyrrolidinium salt groups, carrying pluricarboxylate counteranions, have been successfully used for the construction of unusual polymer architectures, such as single- and double-cyclic (8-shaped) poly(THF)s. We have reported also on the synthesis of branched and network polystyrenes[24] and poly(dimethylsiloxane)s[27] of well-defined structures by the ion-coupling reaction of the relevant polymer precursors having another cyclic ammonium, i.e., *N*-methylpyrrolidinium salt groups. It has been

Scheme 2

A

B

C
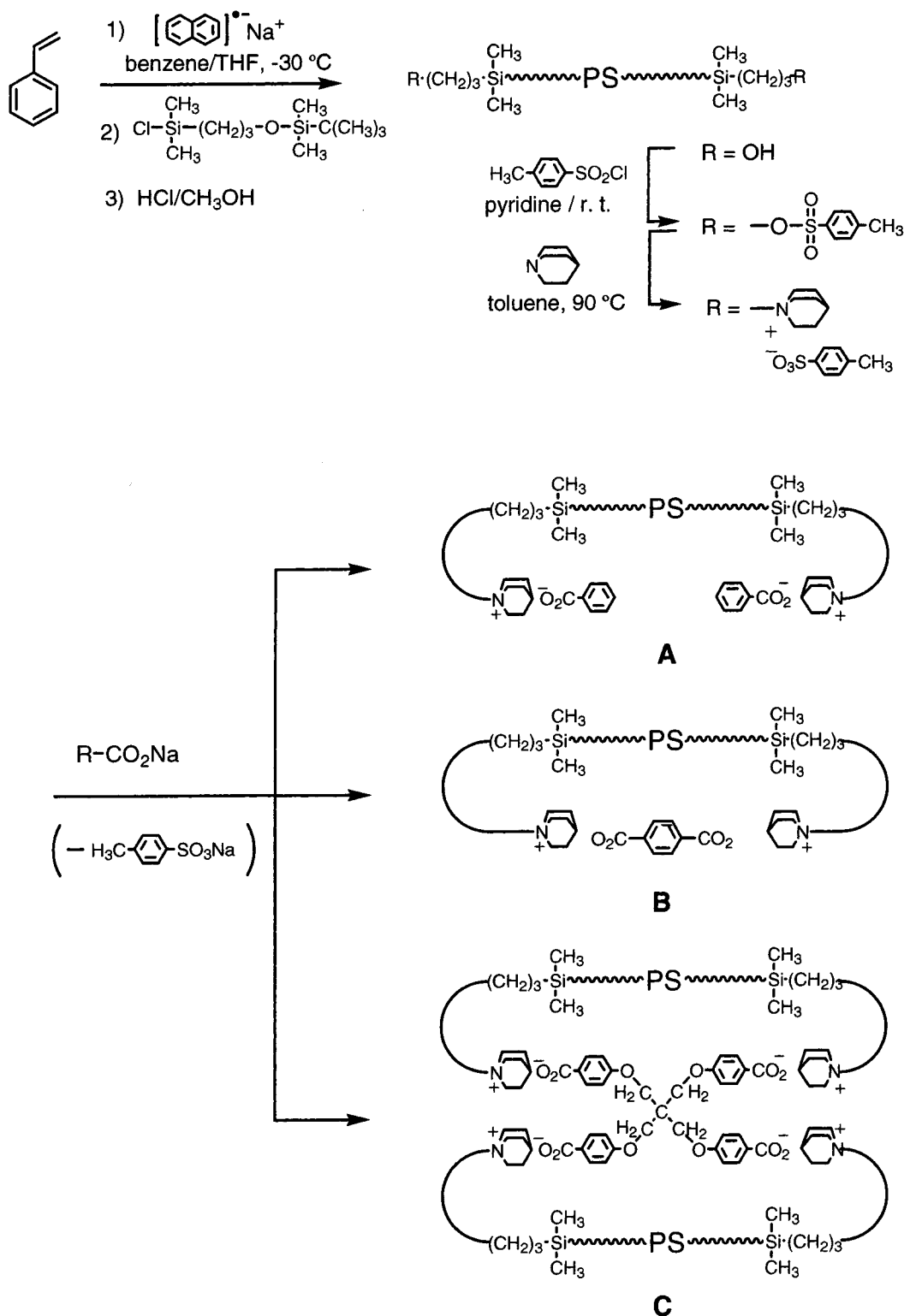
shown that *N*-methylpyrrolidinium salt groups can be introduced readily by the quaternization reaction of polymer precursors having tosylate end groups, which is produced through the stepwise derivatization of the corresponding living polymers (Scheme 2). On the other hand, the quaternization of the tosylate end groups by *N*-phenylpyrrolidine was circumvented, apparently due to its substantially weaker nucleophilic reactivity (pK_a = 3.45) than *N*-methylpyrrolidine (pK_a = 10.3).

Thus, we have first examined our "electrostatic self-assembly and covalent fixation" process with a telechelic

polystyrene having *N*-methylpyrrolidinium salt groups carrying benzoate counteranions by subjecting it to the heat treatment in a toluene solution. Although the nucleophilic reaction of the benzoate anion on the *N*-methylpyrrolidinium salt end group was found to occur at 90 °C, slightly lower temperature than that reported in bulk,[24] it was noticed that not only the *endo*-methylene position of the pyrrolidinium salt group but also the *N*-methyl position was attacked to cause the concurrent demethylation up to 20%. On the other hand, no reaction at the *exo*-methylene position was detected.[28]
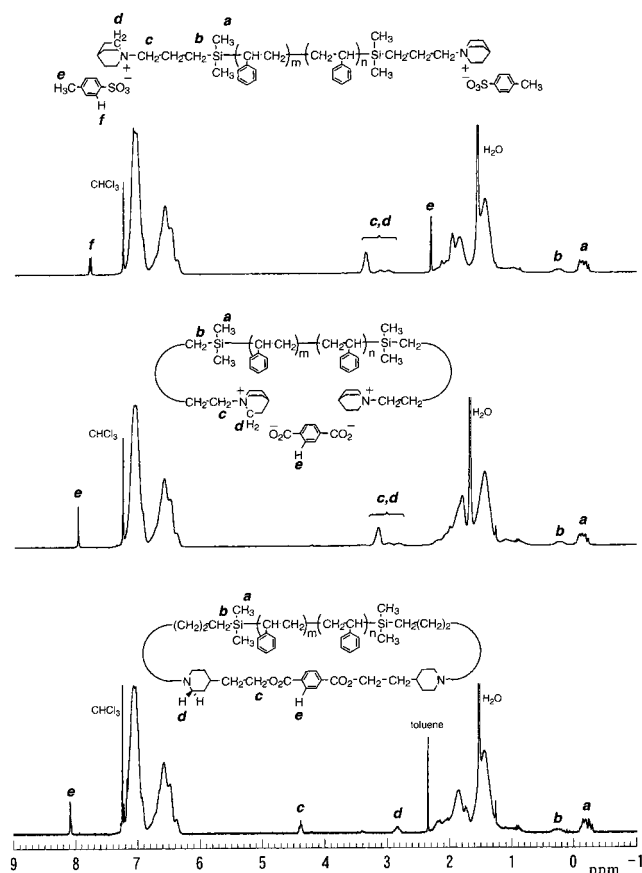
Figure 1. The 300 MHz ^{1}H NMR spectra of a telechelic polystyrene having quinuclidinium salt groups (top) and the ion-exchange product with sodium terephthalate before (**B**; middle) and after (**2**; bottom) the heat treatment (sample: run 3 in Table 1, CDCl$_3$, 40 °C).

Accordingly, we have employed a novel telechelic polystyrene having six-membered bicyclic quinuclidinium salt groups. The nucleophilic attack of the carboxylate counteranion on the quinuclidinium salt group can take place only at the *endo*-methylene position to cause the ring-opening reaction of a strained azabicyclo unit, and a reaction at the alternative *exo*-methylene position will be excluded. And, it was shown previously that the quinuclidinium salt group introduced at the end of a telechelic poly(THF) underwent a selective ring-opening reaction by a benzoate counteranion, while a higher temperature at 130 °C was required than in the case of the *N*-methylpyrrolidinium salt group (at 90 °C).[29]

Thus, the synthesis of a telechelic polystyrene having quinuclidinium salt groups has been performed by the following process. First, a bifunctionally living polystyrene, prepared by sodium naphthalene as an initiator, was terminated with a chlorosilane derivative having a protected hydroxy group. A telechelic polystyrene having 3-hydroxypropylsilyl groups was obtained after the deprotection with acidic methanol. The hydroxy groups were then quantitatively tosylated with tosyl chloride in pyridine at 20 °C to give a telechelic polystyrene with tosylate groups. The tosylate groups were finally converted into a six-membered bicyclic ammonium salt group, i.e., a quinuclidinium salt by the reaction with an excess amount (30 equiv) of quinuclidine in a toluene solution at 90 °C. The ^{1}H NMR spectrum (Figure 1, top) confirms the presence of the quinuclidinium salt end group from signals due to the

endo-cyclic ammonium methylene protons at 3.26–3.42 ppm and signals at 2.90–3.24 ppm due to the diastereotopic *exo*-cyclic ammonium methylene protons.

2. Ion-Exchange and Ring-Opening Reactions of Quinuclidinium Salt Groups in Telechelic Polystyrene. The tosylate counteranions accompanied by the quinuclidinium salt group of the telechelic polystyrene were then quantitatively replaced by benzoate anions, through a simple precipitation treatment into a 50 vol % aqueous methanol solution (−15 °C) containing an excess amount of sodium benzoate (Scheme 2). The obtained ion-exchange product **A** was subjected to a heat treatment in a toluene solution (5 g/L) to cause a ring-opening reaction of the quinuclidinium salt group by a nucleophilic attack of the benzoate anion, leading to a covalently converted product **1** (Scheme 3). The reaction was monitored by means of ^{1}H NMR and IR, as in the case of the *N*-methylpyrrolidinium salt end group reported before.[24] ^{1}H NMR analysis showed that, after the ion-exchange reaction, signals at 2.31 and 7.78 ppm due to the tosylate protons were replaced by those due to the benzoate protons visible at 7.24–7.30 and 8.05–8.08 ppm, and after the heat treatment, signals due to α-methylene protons on the quinuclidinium salt group at 2.90–3.60 ppm were replaced by those at 4.37 ppm due to the ester methylene protons (see Supporting Information). Consequently, it was confirmed that the quinuclidinium salt groups underwent a selective ring-opening reaction by the benzoate counteranions in toluene at 110 °C. The required temperature was found to be somewhat lower than for the previous telechelic poly(THF) having quinuclidinium salt groups in bulk, where the temperature at 130 °C was required.

3. Synthesis of Single- and Double-Cyclic Polystyrenes. The polymer cyclization was conducted with the telechelic polystyrene having quinuclidinium salt groups, carrying a terephthalate counteranion, which was introduced by the ion-exchange reaction shown above. The balance of the charges between the quinuclidinium cations and the terephthalate anions (as in Scheme 2) was confirmed to be retained by the ^{1}H NMR spectroscopic analysis (Figure 1, middle). Then, this ionically linked polymer precursor **B** was subjected to a heat treatment, to cause a ring-opening reaction of the quinuclidinium salt end group by a nucleophilic attack of the terephthalate anion, in a toluene solution under various concentrations. The soluble products were recovered in almost quantitative yields irrespective of the solution concentration.

The ring-opening reaction was found to proceed at each concentration. Thus, IR spectrum of the product exhibits an absorption at 1720 cm^{-1} assignable to the ester carbonyl groups of the ring-opening products (see Supporting Information). Besides, the ^{1}H NMR spectrum of the product (Figure 1, bottom) showed a triplet at 4.40 ppm due to ester methylene protons after the heat treatment. The visible signals in the spectrum are totally assignable and the signal intensities for the linking group (signals a, b, c, d, and e) are consistent with the expected structure. It was observed, at the same time, that those intensities are slightly smaller than those expected from the main-chain signal intensities. Consequently, it was concluded that, while the ring opening occurred with as high as 90% selectivity, concurrent minor side reactions, including that causing the carbon–silicon bond cleavage,[30] were not completely eliminated.

Scheme 3
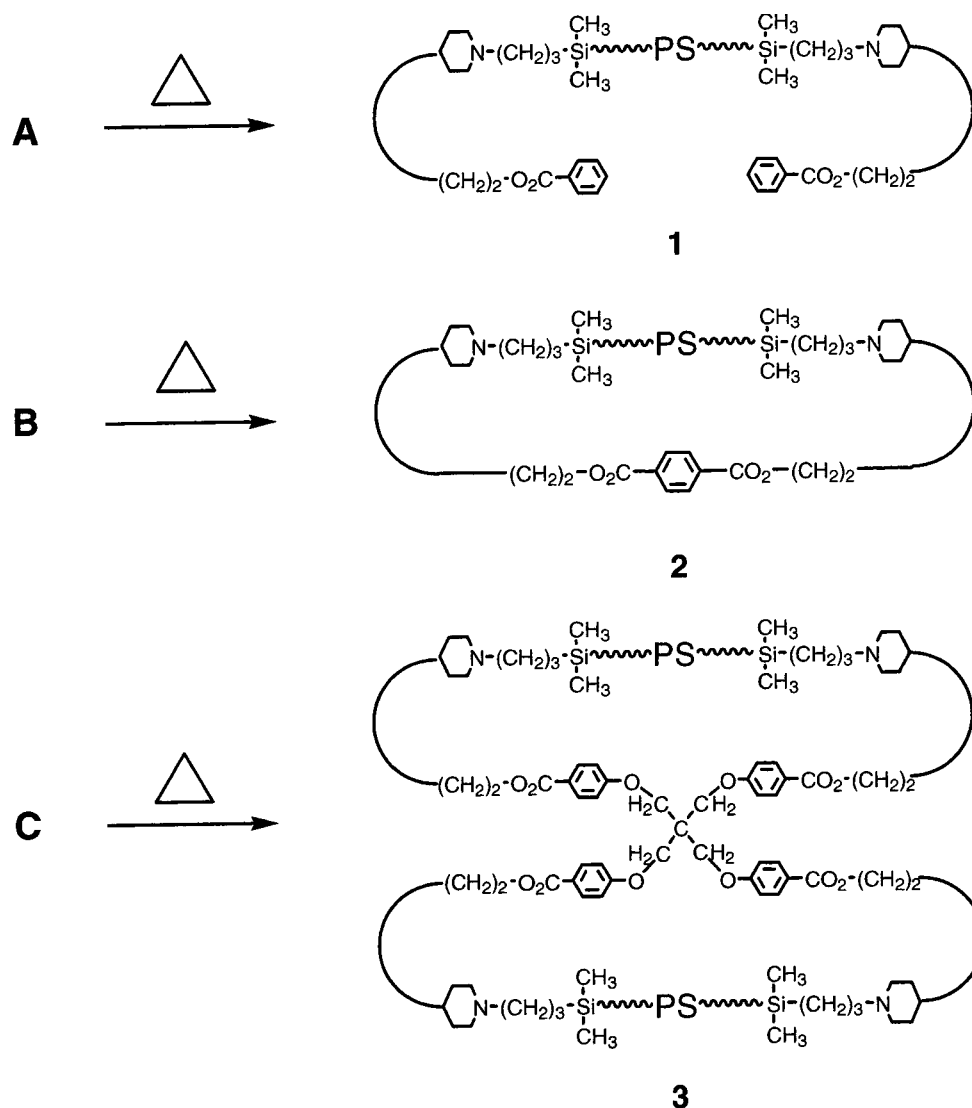
SEC profiles of a series of covalently converted products obtained under different concentrations are compared in Figure 2. It is shown evidently that a fraction at the lower molecular weight region possesses a narrow size distribution irrespective of the reaction solution concentrations, and its relative content increases up to 90% upon dilution, toward 0.1 g/L (run 4 in Table 1). This agrees with that a precursor comprising single polymer unit is predominantly formed under dilution from the ionically aggregated polymer precursors, while retaining the balance between cations and anions, and is subsequently converted to the covalently linked product by the heat treatment (Scheme 1).

The recovered product after the heat treatment of the solution at the concentration of 0.4 g/L was subjected to the further purification by means of silica gel chromatography, and the purified product was isolated in 52% yield (run 3 in Table 1), by separating a minor fraction. The SEC (Figure 3, bottom: solid line) showed the purified product **2** possesses a narrow size distribution and a notably smaller hydrodynamic volume than that of the linear analogue **1** (Figure 3, bottom: broken line), independently prepared from the identical polystyrene precursor carrying benzoate counteranions as described in the previous section.

Then, the absolute molecular weight of the linear analogue **1** (M_n = 5800) was estimated by SEC measurement and was consistent with that of the polystyrene precursor (M_n = 5400) having tosylate end groups. The absolute molecular weights (thus corresponding to their total chain length) of the cyclic **2** and of the linear **1** determined independently by the ^{1}H NMR technique were also consisted with each other as shown in Table 1. On the other hand, the ratio of the hydrodynamic volumes between the cyclic **2** and the linear **1**, estimated also by SEC from the apparent peak molecular weights of **2** and **1**, $\langle G \rangle = M_{pC}/M_{pL}$, was found to be 0.79, which is in a good agreement with previously reported ones for cyclic and linear polymers.[15−19]

By the chromatographic separation process noted above, a minor fraction due to concurrent side reactions could be recovered. The SEC analysis showed this fraction comprises two parts (Figure 3, middle): namely one possessing a narrow size distribution with the molecular weight close to twice of the linear telechelic polystyrene precursor and another with the molecular weight close to that of the linear telechelic precursor. The ^{1}H NMR analysis of this fraction (as a mixture) suggests elimination reactions involving quinuclidinium/amino−ester end groups took place, as stated before.
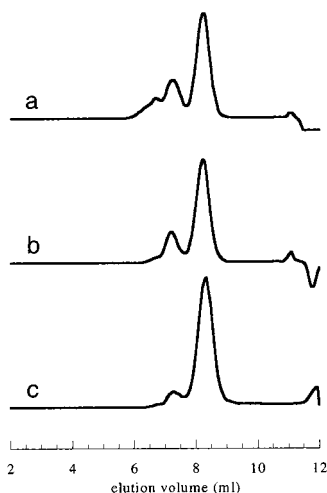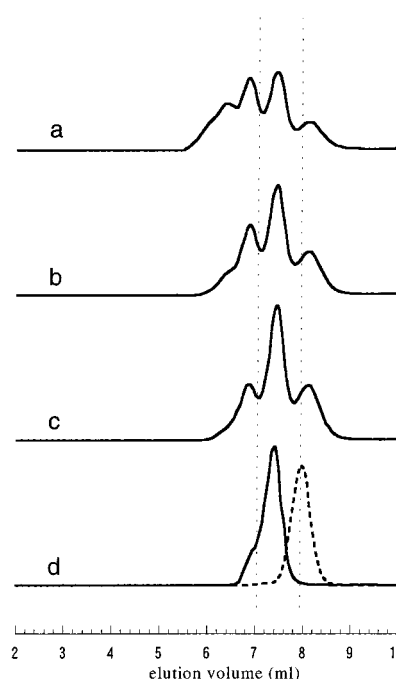
Figure 2. SEC traces (RI) of the quantitatively recovered product after the heat treatment of electrostatically self-assembled polymer precursor **B** at various concentrations. Concentration of the precursor **B** in toluene: a, 4.0 g/L; b, 0.4 g/L; c, 0.1 g/L (samples: runs 2, 3, and 4 in Table 1; column: TSK G3000HXL; eluent: THF/TMEDA = 95/5, 1.0 mL/min).
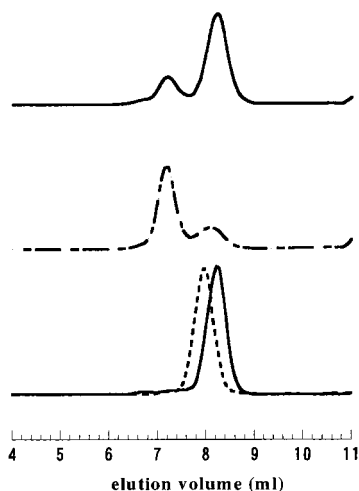
Figure 3. SEC traces (RI) of the covalently converted product by heating of electrostatically self-assembled polymer precursor **B** before (top) and after the preparative TLC separation (the purified single-cyclic polystyrene **2**: bottom solid line, and minor side products: middle) and of the linear analogue **1** (bottom, broken line) (sample: runs 1 and 3 in Table 1, column: TSK G3000HXL, eluent: THF/TMEDA = 95/5, 1 mL/min).

Finally, the synthesis of a double-cyclic polystyrene[31−33] has been performed by reference to the previous system with telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups (Scheme 3). The ionically linked polystyrene precursor **C** carrying a tetracarboxylate anion was thus prepared and subjected to the heat treatment in toluene under various concentrations (0.2−4.0 g/L) at 110 °C for 5 h. The reaction solution was homogeneous throughout the process at above concentrations, while a partial gelation took place when the reaction was conducted at higher concentrations. The crude product recovered quantitatively by evaporating the solvent was then studied by the spectroscopic and chromatographic techniques. The ^{1}H NMR spectrum showed that the quinuclidinium salt groups underwent the ring-opening reaction by the heat treatment to produce amino−ester groups, as in the cases for terephthalate as well as benzoate counteranions (see Support-

Figure 4. SEC traces (RI) of the quantitatively recovered product after the heat treatment of the electrostatically self-assembled polymer precursor **C** in various concentrations (a−c), of the purified double-cyclic polystyrene **3** (d, solid line) by SEC separation technique, and of the linear precursor analogue **1** (d, broken line). Concentration of the precursor **C** in toluene: a, 4.0 g/L; b, 0.4 g/L; c, 0.2 g/L (samples: runs 5, 6, and 7 in Table 1; column: TSK G3000HXL; eluent: THF/TMEDA = 95/5, 1.0 mL/min).

ing Information). From the integration of the relative signal intensities, the ring-opening reaction was confirmed to occur at around 80% yield.

SEC (Figure 4) revealed that the crude reaction product comprises three fractions: namely a main fraction tentatively corresponding to a double-cyclic polymer **3**, as well as the two minor fractions—one at the higher molecular weight region and another at the lower molecular weight region. The relative yield of the main fraction reached to 50 % along the dilution of the reaction solution toward 0.2 g/L. The apparent molecular weight, i.e., the measure of the hydrodynamic volume, of the main fraction is significantly higher than that of its linear precursor analogue **1** but lower than the twice of it, i.e., $M_p(\mathbf{3})/M_p(\mathbf{1}) = 1.52$ (Table 1). This indicates that the ratio of the apparent molecular weight of double-cyclic **3** against the linear polymer analogue possessing the same molecular weight is 0.76, and this value agrees with the reported ones (0.68−0.81).[10,31−33] Finally, the double-cyclic polystyrene having narrow size distribution was successfully isolated by the SEC separation technique, and ^{1}H NMR showed that the absolute molecular weight is close to twice of that of the starting precursor **1**. These results again demonstrate that an ionically linked polymer precursor, composed of the two units of the telechelic polystyrene having quinuclidinium salt groups and one unit of the tetracarboxylate anion, has been produced predominantly under dilution, and the subsequent heat treatment converted it to the covalently linked double-cyclic polymer product. The relative content of the fraction at the higher molecular weight region decreased with dilution, and this is indicative that this fraction comprises excess

units of polymer precursors and tetracarboxylate counteranions.

On the other hand, the fraction at the lower molecular weight region, whose elution volume is close to that of a single-cyclic polymer, remained to be present despite the dilution of the reaction solution. This is in contrast to the relevant process with a telechelic poly(THF) having *N*-phenylpyrrolidinium salt groups, where a double-cyclic poly(THF) was produced in an almost quantitative yield.[10] The relatively high temperature (110 °C) required for the present covalent conversion process might have caused concurrent side reactions, although the detailed mechanism is obscure at present.[30] Further optimization with respect to the type of cyclic ammonium salt groups as well as plurifunctional carboxylates and to the covalent conversion condition will be a subject of future study.

Conclusion

A unique polymer cyclization process through the electrostatic self-assembly and covalent fixation strategy has been demonstrated with telechelic polystyrenes having quinuclidinium salt groups. This process will provide further opportunities to design a variety of cyclic polystyrenes having functional groups and a variety of polystyrene-based multicyclic architectures having other polymer segments. The studies toward these directions are now in progress in our laboratory.

Supporting Information Available: ^{1}H NMR spectra of ionic polystyrene precursors **A** and **C** and covalently converted polystyrenes **1** and **3** (double-cyclic polystyrene) as well as telechelic polystyrenes having hydroxy and tosylate groups; IR spectra of the telechelic polystyrene having quinuclidinium salt groups and the ion-exchange product with sodium terephthalate before (**B**) and after (**2**) the heat treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Gan, Y.; Dahai, D.; Carlotti, S.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **2000**, *122*, 2130−2131.
(2) Klein, J. *Macromolecules* **1986**, *19*, 105−118.
(3) Walba, D. M. *Tetrahedron* **1985**, *41*, 3161−3212.
(4) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2752−2828.
(5) Gibson, H. W.; Marand, H. *Adv. Mater.* **1993**, *5*, 11−21.
(6) Angot, S.; Taton, D.; Gnanou, Y. *Macromolecules* **2000**, *33*, 5418−5426.
(7) Tsukahara, Y.; Tsutumi, K.; Yamashita, Y.; Shimada, S. *Macromolecules* **1990**, *23*, 5201−5208.
(8) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505−2525.
(9) Fréchet, J. M. J. *Science* **1994**, *263*, 1710−1715.
(10) Oike, H.; Imaizumi, H.; Mouri, T.; Yoshioka, Y.; Uchibori, A.; Tezuka, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9592−9599.
(11) Geiser, D.; Höcker, H. *Macromolecules* **1980**, *13*, 653−656.
(12) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525−527.
(13) Hild, G.; Strazielle, C.; Rempp, P. *Eur. Polym. J.* **1983**, *19*, 721−727.
(14) Vollmert, B.; Huang, J.-X. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 467−472.
(15) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843−849.
(16) Hogen-Esch, T. E.; Sundararajan, J.; Toreki, W. *Makromol. Chem., Macromol. Symp.* **1991**, *47*, 23−42.
(17) Rique-Lurbet, L.; Schappacher, M.; Deffieux, A. *Macromolecules* **1994**, *27*, 6318−6324.
(18) Deffieux, A.; Schappacher, M. *Macromol. Symp.* **1995**, *95*, 103−119.
(19) Kubo, M.; Hayashi, T.; Kobayashi, H.; Tsuboi, K.; Itoh, T. *Macromolecules* **1997**, *30*, 2805−2807.
(20) Ishizu, K.; Shen, X. X. *Polymer* **1999**, *40*, 3251−3254.
(21) Richards, D. H.; Williams, R. L. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 89−104.
(22) Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. *J. Am. Chem. Soc.* **117**, 3380−3388.
(23) Oike, H.; Imamura, H.; Imaizumi, H.; Tezuka, Y. *Macromolecules* **1999**, *32*, 4819−4825.
(24) Tezuka, Y.; Imai, H.; Shiomi, T. *Macromol. Chem. Phys.* **1997**, *198*, 627−641.
(25) Tezuka, Y.; Araki, A. *Makromol. Chem.* **1993**, *194*, 2827−2837.
(26) Pispas, S.; Pitsikalis, M.; Hadjichristidis, N.; Dardani, P.; Morandi, F. *Polymer* **1995**, *36*, 3005−3011.
(27) Tezuka, Y.; Iwase, T.; Shiomi, T. *Macromolecules* **1997**, *30*, 5220−5226.
(28) Oike, H.; Hatano, H.; Tezuka, Y. *React., Funct. Polym.* **1998**, *37*, 57−63.
(29) Tezuka, Y.; Shida, T.; Shiomi, T.; Imai, K.; Goethals, E. J. *Macromolecules* **1993**, *26*, 575−580.
(30) A polystyrene with (aminoalkyl)silyl end groups was detected after the chromatographic separation of the crude products **2** and **3**. On the other hand, no Hoffman elimination products were detected at all.
(31) Antonietti, M.; Fölsch, K. J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 423−430.
(32) Schappacher, M.; Deffieux, A. *Macromolecules* **1995**, *28*, 2629−2636.
(33) Kubo, M.; Hayashi, T.; Kobayshi, H.; Itoh, T. *Macromolecules* **1988**, *31*, 1053−1057.