Synthesis and Copolymerization of Cyclic Macromonomer Based on Cyclic Polystyrene: Gel Formation via Chain Threading

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Received February 20, 2002; Revised Manuscript Received April 29, 2002

ABSTRACT: A well-defined cyclic macromonomer based on a cyclic polystyrene was prepared, and its radical copolymerizations with vinyl monomers were carried out. The copolymerization with *tert*-butyl acrylate in benzene at 70 °C gave an insoluble cross-linked polymer with a good swelling property. The insoluble material was converted to soluble polymers by the cleavage of cyclic polystyrene from the backbone chain, suggesting a mechanically cross-linking process due to the threading of the cyclic polystyrene by a segment of another polymer chain during the copolymerization.

Introduction

Over the past several years there has been an increasing interest in the synthesis of mechanically cross-linked polymers in which there is no covalent bond among the chains.[1] Gibson et al. carried out polycondensations involving a macrocyclic dicarboxylic acid[2] or macrocyclic diol[3] to obtain insoluble polymeric materials. They proposed the threading of a main chain through the macrocyclic cavity of another chain to form a mechanically linked network. Several synthetic routes have been developed to prepare mechanically linked networks of vinyl polymers using large macrocyclic compounds as nonbond cross-linking agents. Zada et al. demonstrated that the copolymerizations of 29−32-membered crown ether derivatives carrying one polymerizable double bond with vinyl monomers gave cross-linked polymers.[4−6] Oike et al. also reported a network formation by a radical copolymerization of methacrylate-functionalized cyclic poly(tetrahydrofuran) with methyl methacrylate (MMA).[7] Since the movement of the chain segment is easy in a nonbond type network, these cross-linked polymers are expected to exhibit good impact strength as well as a high degree of swelling.[6]

In the course of our research on the preparation of a well-defined cyclic polystyrene by the intramolecular cyclization of an α-carboxyl, ω-amino heterodifunctional polystyrene, we became interested in creating various macromolecular architectures using a cyclic polystyrene as a starting material.[8−10] The cyclic polystyrene possesses an amide linkage that is thought to be a useful functional group for chemical modification. In this paper we synthesized a well-defined cyclic macromonomer based on a cyclic polystyrene and carried out its copolymerization with vinyl monomer to obtain a mechanically cross-linked polymer due to chain threading.

Experimental Section

Instrumentation. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with JEOL EX-270 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G2500H and G3000H columns using tetrahydrofuran (THF) and standard polystyrenes as an eluent and references, respectively. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) was performed using a Kratos Kompact II spectrometer using dithranol and silver trifluoroacetate as a matrix and cationization reagent, respectively. The degree of swelling was determined by comparing the weight of the dry gel with that of the swollen gel after immersion in a solvent at room temperature for 24 h.

Cyclic Polystyrene (2). Into a suspension of lithium aluminum hydride (0.10 g, 2.6 mmol) in 30 mL of THF was added cyclic polystyrene **1**[10] (M_n = 3200) (0.45 g, 0.14 mmol) and the mixture was heated under reflux for 5 h. The reaction mixture was cooled to 0 °C, and saturated magnesium sulfate solution was added dropwise to the solution. The mixture was extracted with dichloromethane. The organic layer was dried with magnesium sulfate and placed under reduced pressure to remove the solvent to give 0.39 g (87%) of **2** as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.1−2.3 (m, C*H* and CH_2), 4.6 (brs, N*H*), 6.3−7.2 (phenyls).

Cyclic Macromonomer (3). A mixture of cyclic polystyrene **2** (M_n = 3600) (0.23 g, 0.06 mmol), vinyl benzyl chloride (60 mg, 0.4 mmol), powdered KOH (40 mg, 0.7 mmol), dichloromethane (2 mL), and dimethyl sulfoxide (DMSO) (2 mL) was stirred at room temperature for 24 h. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using dichloromethane as the eluent. After the first band was collected to remove the excess vinyl benzyl chloride, the eluent was changed to ethyl acetate and the second band was collected to give 0.14 g (58%) of **3** as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.1−2.3 (m, C*H* and CH_2), 3.32 (brs, NCH_2-Ar), 5.2−5.3 (m, CH_2═CH), 5.7−5.8 (m, CH_2═CH), 6.3−7.4 (phenyls and CH_2═C*H*).

Copolymerization. Given amounts of cyclic macromonomer **3**, comonomer, 2,2′-azobisisobutyronitrile (AIBN), and the solvent were placed in an ampule that was degassed completely by the freeze−thaw method and sealed. The ampule was placed in a bath at 70 °C for 5 h. In the case of gel formation, the gel was recovered and soaked in a large excess of THF for 1 day to extract the unlinked polymers. Then, the swollen gel was placed under reduced pressure to remove volatile materials. Otherwise, the reaction mixture was dissolved in a small amount of THF and poured into methanol to precipitate the polymer.

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10.1021/ma020282i CCC: $22.00
Published on Web 06/21/2002

Table 1. Copolymerizations[a] of Cyclic Macromonomer 3 with Vinyl Monomers

run	**3**, mg	vinyl monomer, g	[vinyl monomer]/[**3**]	benzene, mL	yield, g (%)	$M_n \times 10^{-3}$ [b]
1	20	St, 1.0	1700	0.5	81	12
2	50	St, 1.0	700	0.5	75	10
3	20	St, 1.0	1700		96	34
4	20	MMA, 1.0	1800	0.5	98	35
5	20	^{t}BuA, 1.0	1400	0.5	97	gelation
6	15	^{t}BuA, 1.0	1800	0.5	96	gelation
7	20	^{t}BuA, 1.0	1400	5.0	98	56
8	20[c]	^{t}BuA, 1.0	1400[c]	0.5	76	99

[a] Conditions: AIBN = 15 mg, temp = 70 °C, time = 5 h. [b] Determined by GPC based on polystyrene standards. [c] Cyclic polystyrene **1** was used instead of **3**.

Benzyl-Substituted Cyclic Polystyrene (4). A mixture of cyclic polystyrene **2** (M_n = 3100) (0.34 g, 0.11 mmol), powdered KOH (60 mg, 1.1 mmol), benzyl chloride (70 mg, 0.6 mmol), dichloromethane (2 mL), and DMSO (2 mL) was stirred for 12 h at room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The residue was charged on a silica gel column using dichloromethane as the eluent. After the first band was collected to remove the excess benzyl chloride, the eluent was changed to a mixture of dichloromethane and ethyl acetate (1:1 by volume) and the second band was collected to give 0.20 g (54%) of **4** as a white powder: ^{1}H NMR ($CDCl_3$, δ) 1.2−2.3 (m, C*H* and CH_2), 3.32 (brs, PhCH_2N), 6.3−7.2 (m, phenyls).

Debenzylation of 4. Into a solution of benzyl-substituted cyclic polystyrene **4** (M_n = 3000) (0.20 g, 0.07 mmol) in 7 mL of dichloromethane was added 1-chloroethyl chloroformate (20 mg, 0.14 mmol), and the mixture was stirred for 24 h at room temperature. Into the reaction mixture was added 10 mL of methanol and the mixture was heated under reflux for 2 h. The reaction mixture was placed under reduced pressure to remove the solvents. The residue was freeze-dried to give 0.19 g of white powder: ^{1}H NMR ($CDCl_3$, δ) 1.1−2.3 (m, C*H* and CH_2), 4.6 (brs, N*H*), 6.3−7.2 (phenyls).

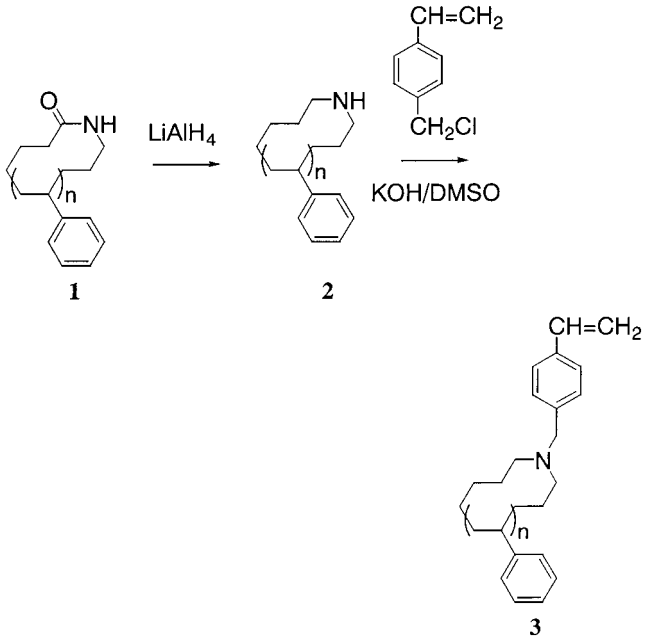
Degradation of Gel. A 0.8 g portion of cross-linked polymer (obtained from run 5, Table 1) was introduced into 20 mL of dichloromethane and the mixture was stirred at room temperature. After 3 h, 1-chloroethyl chloroformate (0.3 g, 2.0 mmol) was added, and the mixture was heated under reflux for 24 h. The swollen gel gradually dissolved in dichloromethane and finally formed a homogeneous clear solution. Then, 2-methyl-2-propanol (5 mL) was added and the mixture was heated under reflux for 12 h. The mixture was placed under reduced pressure to remove the solvents. The residue was charged on a silica gel column using dichloromethane as the eluent to give 56 mg of white solid (fraction A). Then, the eluent was changed to ethyl acetate and the second band was collected to give 14 mg of white solid (fraction B).

Chemically Cross-Linked P^{t}BuA Gel. Into an ampule were introduced *tert*-butyl acrylate (^{t}BuA) (1.0 g, 7.8 mmol), AIBN (15 mg), 1,4-divinylbenzene (DVB) (10 mg, 0.08 mmol), and benzene (0.5 mL). It was degassed completely by the freeze−thaw method, sealed, and placed in a bath at 70 °C for 5 h. The obtained gel was recovered and soaked in a large excess of THF for 1 day to extract the unlinked polymers. Then, the swollen gel was placed under reduced pressure to remove the volatile materials.

Results and Discussion

Cyclic Macromonomer 3. The cyclic macromonomer **3** was prepared from a well-defined cyclic polystyrene **1**[10] in two steps according to Scheme 1. To simplify the NMR analysis for the resulting structure, the molecular weight of **1** was designed to be around 3000. Moreover, it is a ring of, on average, ca. 70 atoms, just large enough for linear polymers to thread through. We reduced the amide linkage of the cyclic polystyrene **1**

Scheme 1



to introduce an amine functionality in the chain. The transformation of **1** to macrocyclic amine **2** was confirmed by ^{13}C NMR and IR. The absorption peak at 173 ppm in the ^{13}C NMR spectrum due to the amide carbonyl carbons disappeared completely. The IR spectrum did not exhibit an amide carbonyl peak at 1643 cm^{-1}, which was present in macrocyclic amide **1**.

To introduce polymerizable group into the macrocyclic amine **2**, the condensation of **2** with vinylbenzyl chloride was carried out in a mixture of DMSO and dichloromethane in the presence of potassium hydroxide at room temperature. The reaction products were passed through a silica gel column to obtain the cyclic macromonomer **3**, since the unreacted cyclic polystyrene **2** possesses an amine functionality that strongly interacts with SiO_2. The structure of **3** was confirmed by ^{1}H and ^{13}C NMR, IR, and MALDI-TOF MS. The ^{1}H NMR spectrum of cyclic macromonomer **3** is shown in Figure 1. In addition to the signals due to polystyrene, there were absorption peaks at 5.2 and 5.8 ppm arising from vinyl protons. The peak at 3.3 ppm can be assigned to benzyl protons. The ^{13}C NMR spectrum exhibited absorption peaks at 136.4 and 113.9 ppm assignable to vinyl groups. Finally, the structure of **3** was confirmed by MALDI-TOF MS, as shown in Figure 2. The spectrum showed the presence of only one peak series of polymer. Each peak in the spectrum represents a cyclic macromonomer **3**, which was cationized by the attachment of silver cation. The spacing between the peaks was 104.1 Da, corresponding to the molar mass of styrene. The observed

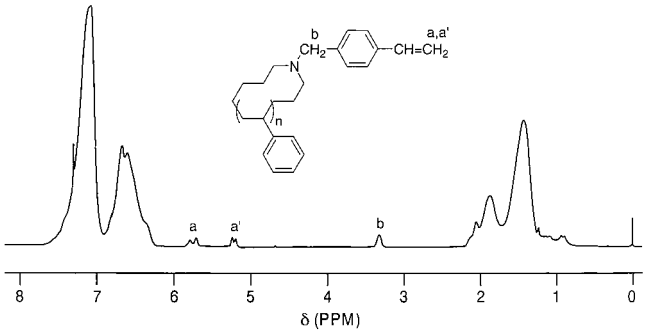


Figure 1. ^{1}H NMR spectrum of cyclic macromonomer **3** of M_n = 3400 (in $CDCl_3$).

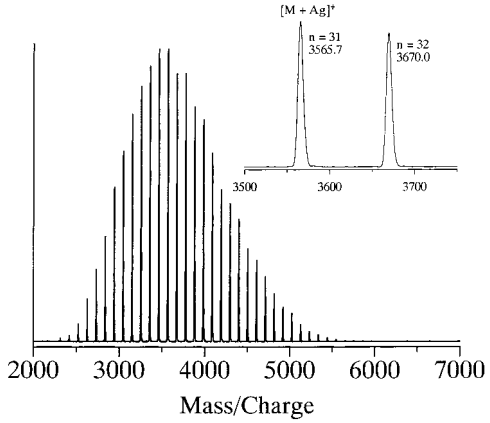
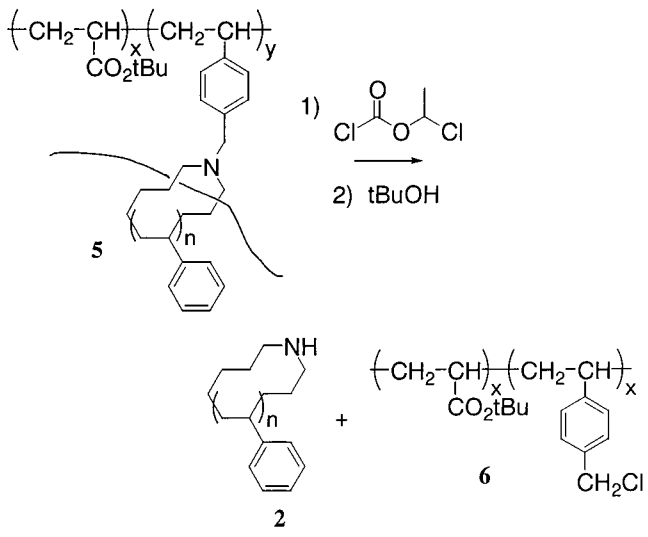


Figure 2. MALDI-TOF MS of cyclic macromonomer **3** of M_n = 3400.

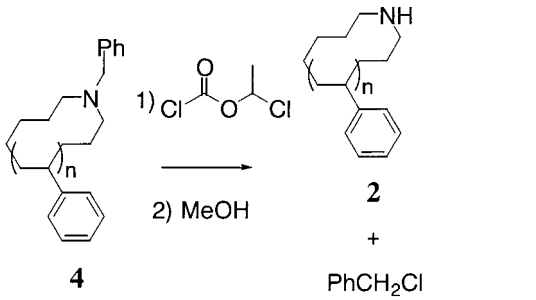
peak masses were in full agreement with the calculated masses for the proposed structure **3**. For example, the peak observed at 3565.7 Da was due to the cyclic macromonomer **3** with a degree of polymerization of 31 (calculated molar mass, 3565.9 Da). The M_n and M_w/M_n of **3** obtained by MALDI-TOF MS was 3400 and 1.02, respectively. The GPC trace exhibited a monomodal peak with M_n of 2990 (M_w/M_n = 1.08) as a polystyrene standard. The value of M_n obtained by GPC was lower than that obtained from mass analysis. This can be explained by the lower hydrodynamic volume of the cyclic structure of **3** than that of linear one.[11]

Copolymerization. The radical copolymerization of the macromonomer **3** with vinyl monomers was carried out at 70 °C using AIBN as an initiator. Table 1 summarizes the results of the copolymerization. When styrene (St) and MMA were employed as a comonomer, the polymerizations proceeded in a homogeneous state to give soluble polymers even in bulk polymerization (run 1−4). Gel formation took place when *tert*-butyl acrylate (^{t}BuA) was employed as a comonomer (run 5,6). It was noteworthy that the gelation was observed in the early stage of copolymerization, suggesting that a small fraction of threading of high molecular weight polymer is enough for network formation. On the other hand, the copolymerization with ^{t}BuA under a more diluted condition gave a soluble polymer (run 7). Further, no gelation took place in the copolymerization with ^{t}BuA in the presence of cyclic polystyrene **1** instead of **3** (run 8), indicating that the existence of the polymerizable group on the cyclic polystyrene is necessary for gel formation. These experimental results indicate that side reactions such as a covalent cross-linking by chain-transfer reaction are not responsible for the gelation. Therefore, one may conclude that the threading of the cyclic polystyrene by a segment of another polymer chain during the copolymerization resulted in the formation of nonbonded, cross-linked network. The reasons why gelation took place only in the copolymerization with ^{t}BuA are not known. In addition to the miscibility of the polymers, another interaction may play a role for chain threading.

Scheme 2



Scheme 3



Debenzylation of Model Compound 4. The degradation of mechanically linked polymer network into soluble polymers can be possible if the pendant cyclic polystyrene units are detached from the backbone segment, as shown in Scheme 2. This will be achieved by C−N bond cleavage, since the benzyl moiety is often used as a protecting group for secondary amines.[12]

Before carrying out the degradation reaction, the debenzylation reaction of a benzyl-substituted cyclic polystyrene **4** was investigated as a model reaction (Scheme 3). The model compound **4** was prepared by the reaction of cyclic polystyrene **2** with benzyl chloride by a similar method for the preparation of the cyclic macromonomer **3**. The structure of **4** was confirmed by ^{1}H NMR and MALDI-TOF MS. The debenzylation reaction of **4** was carried out using 1-chloroethyl chloroformate, which was reported to be a mild and selective debenzylation agent of tertiary amines by Yang et al.[13] Figure 3 shows the MALDI-TOF MS spectra of the reaction products (solid line) together with that of starting material **4** (dotted line). Although small peaks due to **4** were still present, the masses of the main peaks were lower than those of **4** by 90. The decreased mass (90 Da) was in good agreement with the molecular weight difference between **2** and **4** (90.12), indicating an effective debenzylation. It was expected that 1-chloroethyl chloroformate treatment would be useful for the

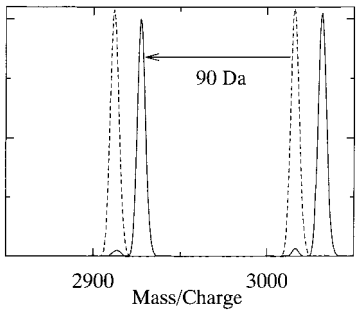


Figure 3. MALDI-TOF MS of (a) reaction mixture after debenzylation reaction (solid line) and (b) starting material **4** (dotted line).

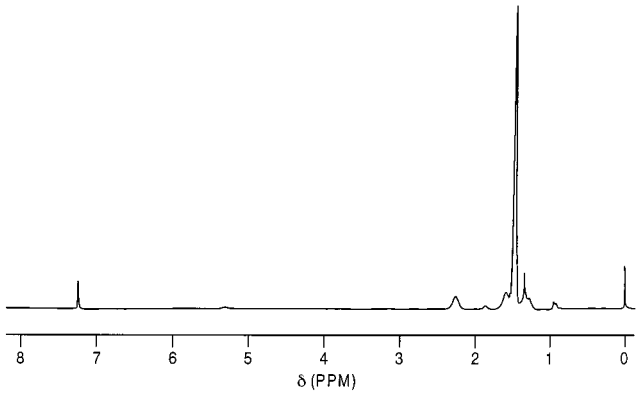


Figure 4. ^{1}H NMR spectrum of fraction A (in $CDCl_3$).

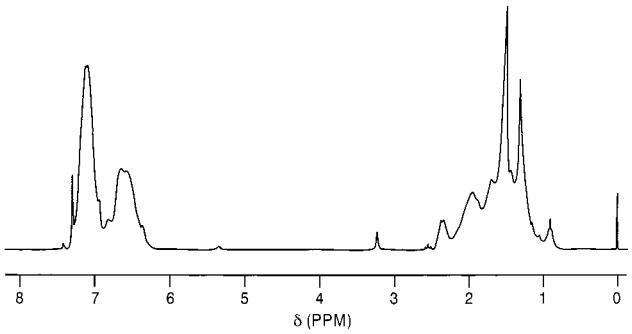


Figure 5. ^{1}H NMR spectrum of fraction B (in $CDCl_3$).

C−N bond cleavage to detach cyclic polystyrenes from the backbone chain.

Degradation of the Network. The cross-linked polymer was subjected to the C−N bond cleavage according to the above-mentioned method. After the gel was swollen in dichloromethane, 1-chloroethyl chloroformate was added and the mixture was heated under reflux. The gel gradually dissolved, and finally the reaction mixture turned to a homogeneous clear solution after 12 h, suggesting the degradation of the network structure into soluble polymers (Scheme 2).

We analyzed the degradation products, which were separated by silica gel column chromatography (see Experimental Section). Figure 4 shows the ^{1}H NMR spectrum of the fraction A, which was eluted with dichloromethane. The signals were assignable to poly(*tert*-butyl acrylate) (P^{t}BuA). Since the monomer feed ratio of [^{t}BuA]/[**3**] in the copolymerization was above 1000, the ^{1}H NMR signals of the copolymer **6** are thought to be almost identical with those of P^{t}BuA. Figure 5 shows the ^{1}H NMR spectrum of the fraction B, which was eluted with ethyl acetate. Main signals

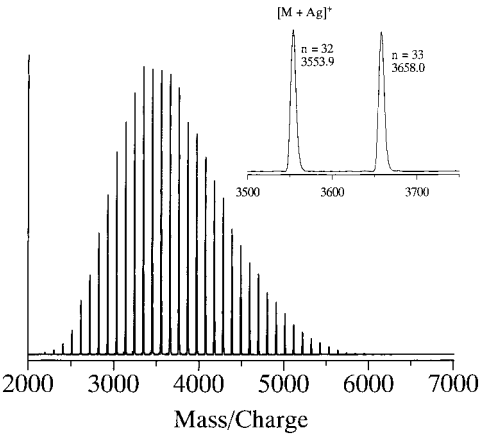


Figure 6. MALDI-TOF MS of fraction B.

can be attributed to cyclic polystyrene **2**, which was generated by the cleavage of the C−N bond. As one can see from the absorption at 1.4 ppm due to *tert*-butyl groups, it is conceivable that the fraction is contaminated with the copolymer **6**. Another possibility may be the rotaxane-type polymer products due to an insufficient dethreading. We carried out GPC analysis of fraction B to observe broad peaks with tailing. It has been pointed out that polystyrenes with amine functionalities are difficult to analyze by GPC because of physical absorption effects.[14] Finally, we carried out MALDI-TOF MS analysis of fraction B, as shown in Figure 6. All peaks corresponding to the structure of **2** were clearly observed. Namely, each peak presents a cyclic polystyrene **2** that was cationized by the attachment of silver cation. The observed peak masses were in full agreement with the calculated masses for the structure **2**.

Although quantitative isolation of the cleavaged cyclic polystyrene **2** with high purity was not successful, the treatment of the network polymer with 1-chloroethyl chloroformate resulted in formation of soluble polymers that consist of the backbone P^{t}BuA (fraction A) and cyclic polystyrene **2** (fraction B). These observations reveal that the chain threading of the cyclic polystyrene by another chain is responsible for the gelation to form a mechanically cross-linked polymer.

Swelling Property. The swelling property of the mechanically cross-linked P^{t}BuA gel (obtained from run 5, Table 1) was evaluated by soaking the sample in different polar and nonpolar solvents such as THF, dichloromethane, and benzene until an equilibrium weight was achieved (24 h). The percentage swelling was calculated according to the following relationship[15]

$$\% \text{ swelling} = (w_s - w_d)/w_d \times 100$$

where w_s and w_d are the weight of swollen gel and of dry gel, respectively. The swelling property was compared with that of chemically cross-linked P^{t}BuA gel that was prepared by the radical polymerization of ^{t}BuA in the presence of 1 mol % of DVB as a cross-linking agent. The results are summarized in Table 2. Although the exact degree of cross-linking is unknown for our mechanically cross-linked P^{t}BuA gel, mechanically cross-linked P^{t}BuA gel exhibited a better swelling property than chemically cross-linked P^{t}BuA gel. There are two possible explanations for the good swelling property. The first possibility may be its easy chain movement in the network structure in which intermolecular covalent

Table 2. Percent Swelling of P^{t}BuA Gels in Various Solvents

	% swelling		
P^{t}BuA gel sample	THF	dichloromethane	benzene
mechanically cross-linked[a]	1900	2700	2300
chemically cross-linked[b]	500	800	700

[a] Obtained from run 5 (Table 1). [b] DVB (1 mol %) was used as a cross-linking agent.

bonding is not present. The second possibility may be a very low degree of cross-linking. The molar ratio of cyclic macromonomer to ^{t}BuA was less than 1/1000.

Further investigation on the effects of ring size of the cyclic polystyrene, the molar ratio of cyclic macromonomer to vinyl comonomer, and the volume of the system is under progress.

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MA020282I