Macromolecules **1997,** *30,* 2805−2807 **2805**

Synthesis of α-Carboxyl, ω-Amino Heterodifunctional Polystyrene and Its Intramolecular Cyclization

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Received December 17, 1996

Revised Manuscript Received February 20, 1997

The study of polymers with complex chain architecture will explore the role of chain topology on chemical and physical properties. The development of a polymerization technique has provided various macromolecular architectures including dendrimers,[1] hyperbranched polymers,[2] and star polymers.[3] The ring-shaped polymer is one such macromolecular architecture.

A possible approach for a ring polymer includes a bimolecular cyclization between a telechelic polymer and difunctional compound. Macrocyclic polystyrenes have been successfully prepared by the coupling reaction of a two-ended living polystyryl anion with a difunctional electrophile such as α,α′-dibromo-*p*-xylene,[4] α,α′-dichloro-*p*-xylene,[5] and dichlorodimethylsilane[6] under high dilution. Another strategy for a ring polymer is an intramolecular (unimolecular) cyclization of a linear α,ω-heterodifunctional polymer. Deffieux et al. prepared α-styrenyl, ω-acetal heterodifunctional poly(chloroethyl vinyl ether) by the living polymerization technique and carried out its ring-closure reaction in the presence of a Lewis acid to obtain cyclic polymers.[7] They prepared cyclic polystyrene by a similar method.[8]

We wish to report here the synthesis of cyclic polystyrene using α-carboxyl, ω-amino heterodifunctional polystyrene as a linear precursor.

The cyclic polystyrene **6** was prepared according to Scheme 1. The α-carboxyl, ω-amino heterodifunctional polystyrene **5** was derived from α-diethyl acetal, ω-amino heterodifunctional polystyrene **1**. To introduce the α-acetal functionality, which can be easily converted into a carboxyl group, the polymerization of styrene was initiated with 3-lithiopropionaldehyde diethyl acetal[9] in benzene in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) at room temperature according to the literature.[8] The molecular weight of the polymer was designed to be around 2000, since the low molecular weight simplifies the NMR analysis for the resulting structure. The ω-amino group was introduced by reacting the living polystyryllithium anion with 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane as an aminating agent.[10] In spite of the fact that this amination procedure was not quantitative (92%), it was possible to isolate pure amine-terminated polystyrene by chromatography. Quirk and Cheng reported that the terminal amino group on the polystyrene strongly interacts with SiO_2.[11] Figure 1a shows the ^1H NMR spectrum of **1**. The peaks at 4.2, 3.5−3.2, and 1.0 ppm are assigned to methine, methylene, and methyl protons of the head diethyl acetal moiety, respectively. Since aminated polystyrene is difficult to characterize directly by GPC,[10] the molecular weight of the polymer was determined from the peak area ratio of head diethyl acetal protons to aromatic protons. Before hydrolysis of the α-diethyl acetal function, the ω-amino group was protected with benzyloxycarbonyl chloride to obtain **2**. The benzyl carbamate was reported to be stable under acidic and oxidative conditions.[12] Figure 1b shows the ^1H NMR spectrum of **2**. The amounts of α-diethyl acetal and ω-benzyl carbamate groups were estimated from the peak areas of diethyl acetal and benzyl protons, respectively. It was found that the ratio of acetal head to carbamate end is 1.0, indicating the formation of a well-defined heterodifunctional polymer. The hydrolysis of the diethyl acetal moiety was carried out in THF containing aqueous hydrochloric acid under reflux to obtain **3**. The oxidation of the aldehyde group was carried out with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at room temperature to obtain **4**. Finally, the benzyloxycarbonyl group was removed by a conventional acidolysis reaction in glacial acetic acid containing 30 wt % of hydrobromide at room temperature. The structure of the α-carboxyl, ω-amino heterodifunctional polystyrene **5** was confirmed by its ^1H NMR spectrum, as shown in Figure 1c. The peaks at 7.3 and 5.1 ppm assignable to the benzyloxycarbonyl group disappeared completely. The peak around 5 ppm can be assigned to the protons of the terminal amino group.

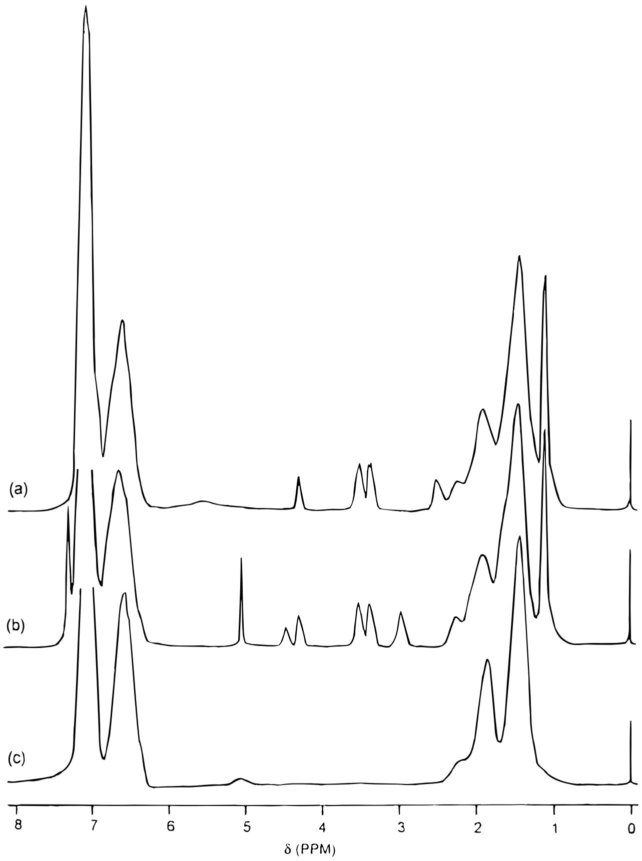


Figure 1. 270-MHz ^1H NMR spectra of (a) α-diethyl acetal, ω-aminopolystyrene **1** of M_n = 2240, (b) α-diethyl acetal, ω-[(benzyloxycarbonyl)amino]polystyrene **2** of M_n = 2360, and (c) α-carboxyl, ω-aminopolystyrene **5** of M_n = 2170. Solvent: $CDCl_3$.

The intramolecular cyclization of **5** was carried out in dichloromethane under reflux using 1-methyl-2-chloropyridinium iodide[13] as a coupling reagent. The

S0024-9297(96)01850-5 CCC: $14.00

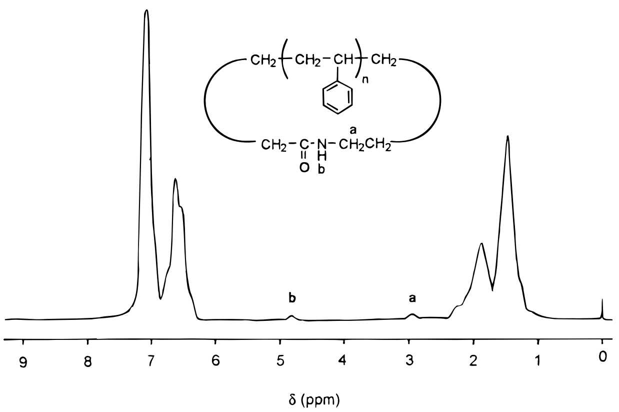


Figure 2. 270-MHz ^{1}H NMR spectrum of cyclic polystyrene **6** of $M_n = 2150$. Solvent: $CDCl_3$.

molecular weight of **5** was calculated from that of parent polymer **1**, assuming that the degree of polymerization remains unchanged during the reactions. The end-to-end ring closure is favored at low polymer concentrations. We carried out the intramolecular cyclization at a final α,ω-heterodifunctional polystyrene concentration of 1.4×10^{-4} mol/L. The reaction products were passed through a silica-gel column to obtain the cyclic polystyrene **6**.

The ^{1}H NMR spectrum of **6** is shown in Figure 2. The peaks at 4.9 and 3.0 ppm are assigned to protons of the amide group and methylene group adjacent to nitrogen, respectively. The ^{13}C NMR spectrum exhibited the amide carbonyl carbon at 172 ppm. The IR spectrum exhibited an absorption peak at 1643 cm^{-1} assigned to the amide group. The GPC curve of **6** is shown in Figure 3 together with that of its parent polymer **2**. The molecular weight of **2** was found to be 2250 as a polystyrene standard, which was close to the value (2360) calculated from NMR. On the other hand, the molecular weight of the cyclic polystyrene **6** (1790) obtained from GPC as a polystyrene standard was much lower than the calculated (true) value (2150) based on its parent polymer **1**. The change of the elution volume can be explained by the lower hydrodynamic volume of the cyclic structure than that of the linear one.[6] It is noteworthy that the obtained cyclic polystyrene **6** showed a unimodal peak without contamination of higher molecular weight products. The reason for the high purity of the cyclic product can be attributed to the easy isolation by silica-gel column chromatography because the linear chain-extended byproducts possess a terminal amine functionality which interacts with SiO_2.

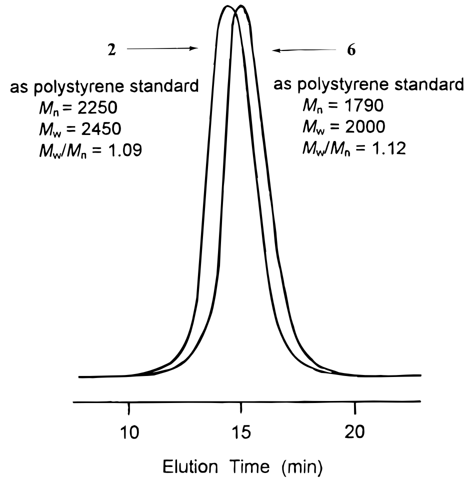
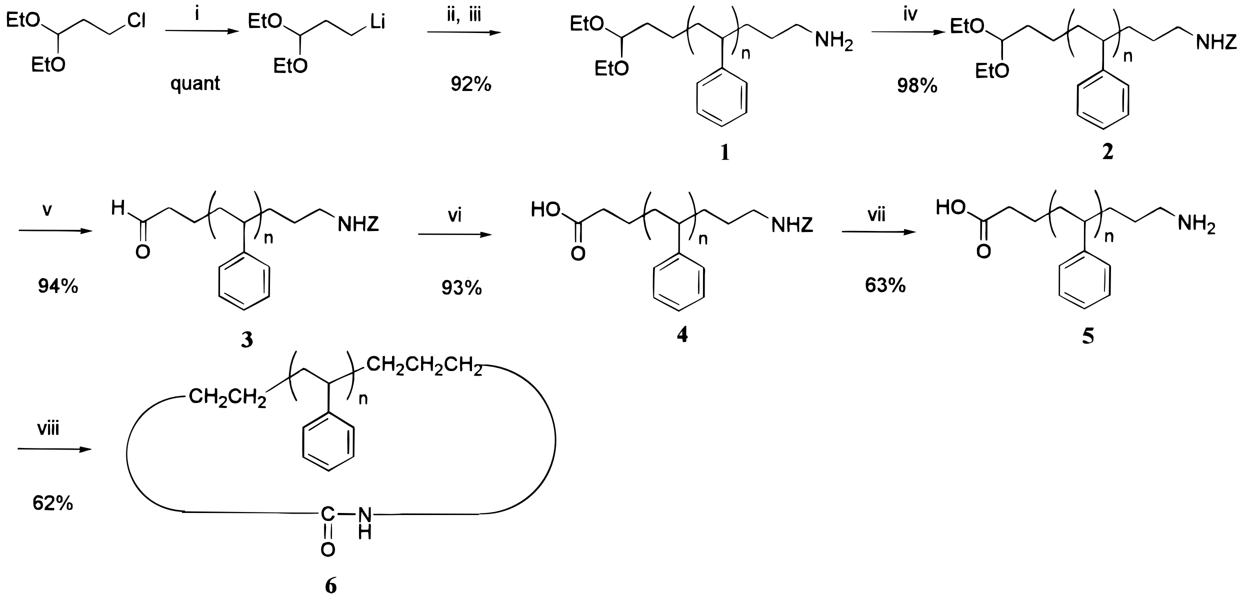


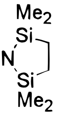
Figure 3. GPC curves of linear α-diethyl acetal, ω-[(benzyloxycarbonyl)amino]polystyrene **2** (M_n = 2360) and cyclic polystyrene **6** (M_n = 2150).

Further investigation is under progress to extend our cyclic polystyrene to various architectures since the amide moiety on the cyclic polymer chain is thought to be a useful functional group for chemical modification.

Scheme 1. Synthesis of Cyclic Polystyrene



i, Li; ii, St/TMEDA; iii, $BrCH_2CH_2CH_2N$



$(SiMe_2CH_2CH_2SiMe_2)$; iv, $C_6H_5CH_2OCOCl$ (ZCl) ; v, H^+; vi, MCPBA;

vii, HBr/AcOH; viii, high dilution, 1-methyl-2-chloropyridinium iodide/NBu_3

References and Notes

(1) Tomalia, D. A.; Durt, H. D. *Top. Curr. Chem.* **1993**, *165*, 193. Newkome, G. R. *Advances in Dendritic Macromolecules*; JAI: Greenwich, Ct, 1993; Vol. 1, p 1.

(2) Hawker, C. J.; Chu, F.; Pomery, P. J.; Hill, D. J. T. *Macromolecules* **1996**, *29*, 3831 and references cited therein.

(3) Rein, D.; Rempp, P.; Lutz, P. J. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 237. Roovers, J.; Zhou, L.-L.; Toporowski, P. M.; Van der Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324. Fukui, H.; Deguchi, T.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1996**, *29*, 1131.

(4) Hild, G.; Kohler, A.; Rempp, P. *Eur. Polym. J.* **1980**, *16*, 525. Vollmert, B.; Huang, J.-X. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 333.

(5) Geiser, D.; Höcker, H. *Macromolecules* **1980**, *13*, 653.

(6) Roovers, J.; Toporowski, P. M. *Macromolecules* **1983**, *16*, 843.

(7) Schappacher, M.; Deffieux, A. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 447. Deffieux, A.; Schappacher, M.; Rique-Lubet, L. *Polymer* **1994**, *35*, 4562.

(8) Rique-Lubet, L.; Schappacher, M.; Deffieux, A. *Macromolecules* **1994**, *27*, 6318.

(9) Wagener, K. B.; Linert, J. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, No. 1, 178.

(10) Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.

(11) Quirk, R. P.; Cheng, P. L. *Macromolecules* **1986**, *19*, 1291.

(12) Greene, T. W. *Protective Groups in Organic Synthesis*; John Wiley & Sons: New York, 1981.

(13) Bald, E.; Saigo, K.; Mukaiyama, T. *Chem. Lett.* **1975**, 1163.

MA961850V