Synthesis and Efficient Purification of Cyclic Poly(dimethylsiloxane)

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Received January 30, 2002
Revised Manuscript Received May 20, 2002

The synthesis of cyclic poly(dimethylsiloxane) (PDMS) was first achieved through ring-chain equilibration of siloxane oligomers in the presence of potassium silanolate.[1−5] The resulting product mixture contained both linear and cyclic species with broad size distributions which were separated and purified by repeated fractional precipitation and distillation. In addition to these involved workup procedures, limitations of this synthetic method include restriction to relatively low molar masses (reportedly <30 kg/mol) and the inability to directly compare the cyclic product with its linear precursor.[6] As pointed out by others,[6,7] these last two limitations are overcome with a synthetic method based on the ring closure of α,ω-end-functionalized linear polymers using a complementary difunctional coupling agent in dilute solution. This method has been successfully used to prepare cyclic poly(oxyethylene),[8−10] polystyrene,[6,11] poly(2-vinylpyridine),[12] and polystyrene-*block*-poly(dimethylsiloxane).[13] The product mixture still includes linear byproducts from chain extension or endcapping of the linear precursor at one or both ends by the coupling agent, which are removed with fractional precipitation,[4] preparative gel permeation chromatography,[14] or liquid chromatography at the critical condition.[6,7,15] Such purification steps typically reduce yields since the physical characteristics upon which they are based are similar for the cyclic polymers and their linear precursors. Tezuka has diminished the need for such purification steps by introducing a modification to the synthetic method in which the functional groups of both the polymer and coupling agent are charged.[16−18] Electrostatic self-assembly of the components is followed by covalent fixation to quantitatively yield a large variety of well-defined nonlinear polymer topologies.[19]

While the Tezuka method is quantitative, the appropriate electrostatic functional groups must be incorporated onto the ends of the linear precursors. Similarly, appropriate complementary functional groups must be introduced at chain ends when using those methods based on the intramolecular end-to-end coupling of α,ω-heterodifunctional linear polymers.[20] Commercially available α,ω-dihydroxy-functionalized polymers can be deprotonated, or vinyl monomers can be anionically polymerized to directly yield α,ω-dianion-functionalized polymers which are then cyclized simply by reaction with a difunctional electrophile. However, a more efficient purification scheme is needed to remove the linear byproducts without decreasing the yields of cyclic polymer. The methods currently in use are based on physical properties; to completely remove linear byproducts from cyclic polymers using methods based on physical properties, portions of the cyclic material will be removed as well. Here we propose a modification to the synthetic method by which the two species may be effectively separated by their chemical differences. This is demonstrated for the synthesis of cyclic poly(dimethylsiloxane) (PDMS) from a commercially available α,ω-dihydroxy-PDMS ($M_n \sim 2460$ g/mol).[21] The linear precursor is deprotonated using sodium hydride in dilute THF ($\leq 10^{-2}$ M) and then end-coupled using a dichlorosilane coupling agent. The uncyclized anionic linear precursors are then removed by a macroporous anion-exchange resin. The successful cyclization and purification is monitored by infrared (IR) and ^{29}Si nuclear magnetic resonance (^{29}Si NMR) spectroscopy, gel permeation chromatography (GPC), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS).

Experimental Section. a. Materials. All reagents were used as received. α,ω-Dihydroxypoly(dimethylsiloxane) ($M_n \sim 2460$ g/mol)[21] was purchased from Gelest. Sodium hydride (dry, 95%), dichlorodimethylsilane (99%), tetrahydrofuran (anhydrous, 99.9%), and toluene (HPLC grade, 99.8%) were purchased from Aldrich. The macroporous anion-exchange resin AG MP-1M (1 mequiv/mL, 0.7 g/mL, 100−200 mesh, chloride form) was purchased from Bio-Rad Laboratories and dried under vacuum prior to use.

b. Instrumentation. Gel permeation chromatography was conducted in toluene (1 mL/min) at 303 K on three Waters Styragel columns (5 μm beads: HR 1, 100 Å; HR 3, 1000 Å; HR 4, 10 000 Å) that were connected to a Waters 2690 separations module and Waters 2410 refractive index detector. MALDI−TOF mass spectrometry was carried out on a Micromass TofSpec 2E with dithranol serving as the matrix and silver trifluoroacetate used for ionization. ^{29}Si NMR spectra were measured on a Bruker AMX 400 in chloroform-*d* ($CDCl_3$).

c. Synthesis. Glassware was dried at 120 °C overnight; all liquid transfers occurred via gastight syringes unless otherwise noted. Round-bottom flasks with stir bars were sealed with rubber septa and a stopcock adapter and cooled while evacuating and then backfilling with dry N_2. THF (200 mL) was charged by cannula to a 250 mL three-neck flask. Under positive nitrogen flow, a septum was removed and sodium hydride (0.1124 g, 4.4 mmol) was added. Immediately, α,ω-dihydroxy-PDMS (4.00 mL, 2 mmol based on the number-average molecular weight) was added, and the mixture was stirred overnight or until all solid particulates had dissolved. Once dissolution was established, a dilute solution of dichlorodimethylsilane (0.28 mL, 2.3 mmol) in THF (10 mL) was added to the reaction vessel. The solution was stirred for another 24 h before quenching with AG MP-1M anion-exchange resin (4.8 g). The mixture was stirred gently for 4 h to ensure complete ion exchange before filtering.[22] The solvent was removed by rotary evaporation, and the solid crude material was dissolved in toluene (200 mL), washed with distilled water (200 mL × 3) to remove salts, and dried over magnesium sulfate. The mixture was filtered and the solvent removed by rotary evaporation. The product was finally concentrated as a slightly viscous clear oil (3.03 g, 77% yield) by removing low-molecular-weight byprod-

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10.1021/ma0255027 CCC: $22.00
Published on Web 06/06/2002

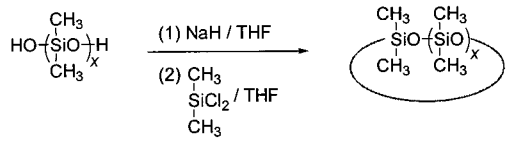

Figure 1. Synthetic scheme for cyclization of linear α,ω-dihydroxy-PDMS.

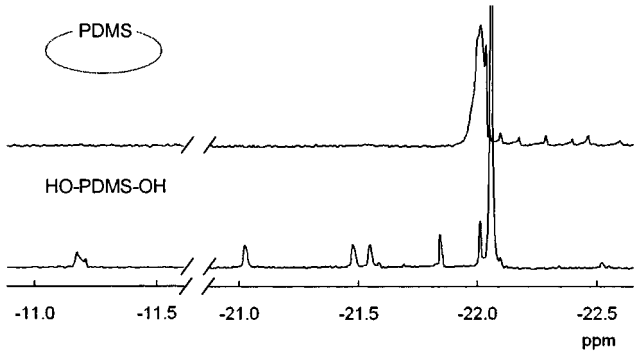

Figure 2. ^{29}Si NMR spectra comparing linear α,ω-dihydroxy-PDMS starting material with the product of the cyclization scheme shown above, demonstrating the disappearance of the silanol end groups.

ucts through vacuum distillation (T = 170 °C, P = 400 mTorr).

Results and Discussion. Silanol-terminated linear PDMS was converted to the corresponding silanolate-terminated species and then reacted with dichlorodimethylsilane as depicted in Figure 1. End-to-end coupling was promoted over chain extension by conducting the reaction in dilute solution ($\leq 10^{-2}$ M). The reaction was followed by the disappearance of the hydroxy end groups with IR spectroscopy. The IR spectrum of the linear PDMS reveals a broad −OH peak from 3120 to 3470 cm^{-1} that is not present in the product. Disappearance of the end groups was also apparent from ^{29}Si NMR (see Figure 2). The spectrum of the starting material contains a major peak at −22.1 ppm due to internal silicons and downfield peaks due to silicons adjacent to hydroxy end groups (e.g., at −11.2 ppm).[23] These downfield peaks are completely absent in the product spectrum. The major peak in the product spectrum has been assigned to PDMS rings containing ≥15 repeat units, and the small upfield peaks have been attributed to smaller cycles (x_n = 5−14).[24]

While NMR and IR spectroscopy clearly indicated that the hydroxy end groups disappeared, they did not provide independent evidence that cyclization had occurred. For this, GPC and MALDI−TOF mass spectrometry were used. GPC chromatograms and selected portions of MALDI−TOF spectra are shown in Figure 3 for the linear starting material (a), purified product (c), and also for a product prepared using the previously standard procedure of quenching the reaction with methanol (b). For both the resin-quenched (c) and methanol-quenched products (b), the data of Figure 3

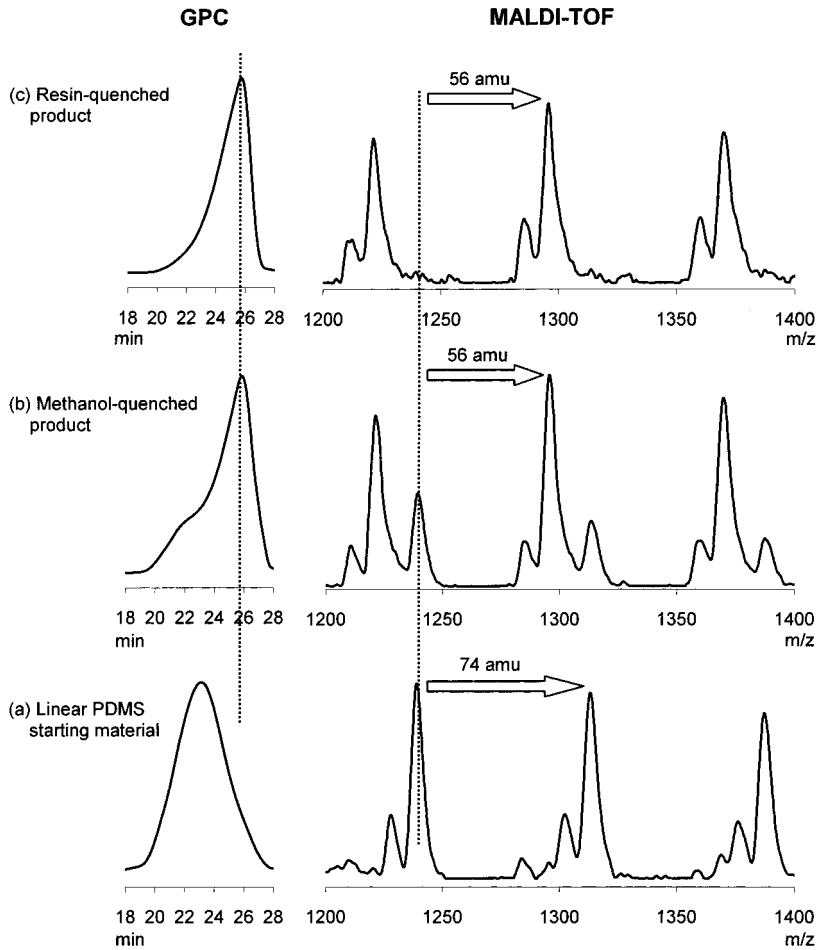

Figure 3. GPC chromatograms and selected regions of MALDI-TOF mass spectra for (a) α,ω-dihydroxy-PDMS linear starting material, (b) methanol-quenched product, and (c) resin-quenched product of cyclization scheme shown in Figure 1. For both products, data shown were collected following vacuum distillation as described in the Experimental Section. The 56 amu shift in the MALDI-TOF spectra is due to incorporation of the coupling agent via cyclization.

were collected after vacuum distillation of the product mixture as described in the Experimental Section. Vacuum distillation is used to remove the low-molecular-weight byproducts resulting from polymerization of the dichlorodimethylsilane coupling agent and from backbiting reactions of the end group silanolates.

The GPC chromatograms are shown in Figure 3 as signal intensity (differential refractive index) vs elution time. The hydrodynamic volumes of cyclic polymers are smaller than those of analogous linear polymers (i.e., same repeat-unit structure and molecular weight).[1] In GPC, decreased hydrodynamic volumes lead to increased retention times, which is exactly what is observed in Figure 3 for the reaction product. Thus, the product has been cyclized. Note in Figure 3b that a short-retention-time shoulder on the chromatogram for the methanol-quenched product signifies the presence of linear byproducts. The chromatogram for the resin-quenched product does not contain this broad shoulder, thereby signifying a much cleaner cyclic product. Several attempts were made to remove the linear byproducts in the methanol-quenched product by repeated fractional precipitations using acetone−methanol solvent mixtures; these were unsuccessful. Attempts were also made to decrease the fraction of linear byproducts in the crude product mixture by (1) increasing the stoichiometric excess of NaH, (2) increasing the stoichiometric excess of the dichlorosilane coupling agent, or (3) decreasing the concentration of starting material to 10^{-4} M; these were also unsuccessful.

In fact, the MALDI−TOF spectral regions of Figure 3 clearly show that all linear anionic species are efficiently removed by ion-exchange reactions with the macroporous anion-exchange resin. A very small number of α,ω-dichlorodimethylsilylated linear species are formed that get converted to α,ω-dihydroxy-PDMS (with two more repeat units than the linear material from which they are derived) during the workup. These are not removed by the anion-exchange resin but do not appear in the ^{29}Si NMR spectrum; they are detected in the IR spectrum as a narrow peak at 3691 cm^{-1} due to free hydroxy groups. These linear species can be removed by conversion to α,ω-disilanolates using sodium hydride followed again by addition of the anion-exchange resin.

The full MALDI−TOF spectra from which the regions of Figure 3 are selected contain the characteristic envelope of peaks representative of polydisperse synthetic polymers. However, the molecular weight distribution of the starting material is slightly broader than that of the cyclic product, which does not contain some of the higher-molecular-weight species. From GPC, the polydispersity indices are 1.88 for the starting material and 1.35 for the cyclic product. Either the low-molecular-weight PDMS is cyclized more efficiently than the longer chains, or some siloxane bonds are cleaved by the end group silanolates, or both. The asymmetric GPC chromatogram of Figure 3c presumably results from these effects, perhaps coupled with some loss of lower-molecular-weight cycles during the vacuum distillation step.

The MALDI−TOF spectral region containing the most intense peak of the distribution is shown in Figure 3a for the linear starting material. This peak appears at 1239 amu and corresponds to a silver-cationized α,ω-dihydroxy-PDMS species containing 15 dimethylsiloxy repeat units.[25] The minor peak just to the left of the most intense peak represents a sodium-cationized[26] α,ω-dihydroxy-PDMS species.[27] The three major peaks shown in Figure 3a (and also the three minor peaks) are separated by 74 amu, which is the mass of a PDMS repeat unit.

Peaks due to linear starting material appear in the MALDI−TOF spectral region of Figure 3b for the methanol-quenched product but not in the spectrum for the resin-quenched product shown in Figure 3c. Thus, resin quenching is an efficient means to remove linear byproducts. For both the methanol-quenched and resin-quenched products, the most intense peak in the spectra appears at 1295 amu, which is a molecular weight increase of 56 amu from the most intense peak for the linear starting material. This increase (56 amu) corresponds to the mass of the dehalogenated coupling agent (58 amu) incorporated into a deprotonated α,ω-dihydroxy-PDMS (minus 2 amu).[28] The major product is clearly cyclic PDMS. The methanol-quenched product contains cyclic PDMS as well as linear byproducts, as indicated by the overlapping sets of peaks in its mass spectrum. The resin-quenched product contains peaks due to the cyclic PDMS only, each separated from its subsequent homologue by 74 amu.

Acknowledgment. This work was supported by the Office of Naval Research (N00014-99-1-0757) and the NSF-REU program. We gratefully acknowledge partial stipend support from the Georgia Tech Molecular Design Institute, under prime contract N00014-95-1-1116 from the Office of Naval Research. The MALDI−TOF spectra were collected by David Bostwick of Georgia Tech.

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MA0255027