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Cyclic poly(dimethylsiloxane) via ring-closing dehydrocoupling of α,ω-dihydroxy-PDMS with α,ω-dihydrido-PDMS in dilute solution

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ABSTRACT

Cyclic poly(dimethylsiloxane) (PDMS) was prepared from commercially available linear α,ω-dihydroxy-PDMS by a platinum-catalyzed dehydrocoupling of its chain ends with α,ω-dihydrido-PDMS in dilute solution. Ring closing was verified by MALDI-ToF mass spectrometry along with GPC, IR, ^{1}H and ^{29}Si NMR spectroscopy. Purification of the cyclic PDMS was achieved by inclusion complexation of linear byproducts with γ-cyclodextrin. Cyclic yields are ≥ 50% and the average molecular weight (M) closely reflects that of the linear starting material. Yields of large cycles, $[(CH_3)_2SiO]_x$ where $x > 6$, are greater than those achieved by the traditional ring-chain equilibration route beginning with $[(CH_3)_2SiO]_4$ and $[(CH_3)_2SiO]_5$ [1], and the M is greater than that obtained for the cyclic product obtained from base-catalyzed cyclodepolymerization of the same α,ω-dihydroxy-PDMS precursor [2].

1. Introduction

Cyclic poly(dimethylsiloxane) (PDMS) was the first synthetic ring polymer prepared in sufficient quantities and molecular weights for comprehensive property measurements. In a series of papers published from 1969 [3] to 2005 [4], Semlyen and coworkers demonstrated how the properties of this cyclic polymer compared to its linear counterpart [5–8], thereby providing the most complete collection of data from which the effect of topology on polymer properties can be observed. These data, along with data on other cyclized polymers and basic theoretical developments, have provided significant insight [9,10]. Nevertheless, gaps exist in our fundamental understanding, including for example the description of cyclic dynamics above entanglement molecular weights [11]. With the increasing availability of more complex cyclic and multicyclic topologies [12], it is important that topological effects are understood for the simplest member of this nonlinear class.

Progress is restricted by the limited availability of cyclic polymers in sufficient quantities for physical studies. Semylen et al. prepared cyclic PDMS by base-catalyzed ring-chain equilibration of $[(CH_3)_2SiO]_x$ (D_x) in which $x = 4$ and 5. The resulting product is a thermodynamically controlled mixture with sharply decreasing concentration of rings with increasing ring size. Yields of all large ($x > 6$) cycles were 13% [1]. Significantly higher yields of large cycles (>70%) are available from the kinetically controlled cyclodepolymerization of α,ω-dihydroxy-PDMS by deprotonation in dilute solution [2,13]. Silanolate chain ends backbite to give rings of all sizes resulting in a cyclic product with a significantly broadened molecular-weight distribution and reduced average compared to the linear precursor [2].

To avoid backbiting and its consequences on the molecular weight, silanolate intermediates must be avoided. The approach described here, outlined in Fig. 1, is dehydrocoupling of α,ω-dihydroxy-PDMS with α,ω-dihydrido-PDMS. Dehydrocoupling polymerization of disilanols with bis-silanes has been reported for the preparation of a variety of siloxane polymers [14–16]. When conducted in dilute solution, ring closure should lead to cyclic PDMS. Advantages of this route include the commercial availability of starting materials with a range of molecular weights, and the preparation of a cyclic product that is pure PDMS. An alternative route might be the dilute-solution hydrosilylation of α,ω-diethenyl-PDMS with α,ω-dihydrido-PDMS, but this would give cyclic PDMS with two ethylene groups in its structure.

The reaction scheme shown in Fig. 1 includes the formation of linear species, which must be removed to obtain pure cyclic PDMS. For routes that proceed through silanolate end groups, linear byproducts are effectively removed by quenching the reaction with a macroporous anion exchange resin [2,13]. Since the linear species shown in Fig. 1 are not charged, they must be removed from the product mixture by another method. One approach is the use of cyclodextrins (CD), which selectively thread linear polymers to give inclusion complexes that precipitate from solution. Cyclodextrins (α-CD) have been successfully employed to remove linear

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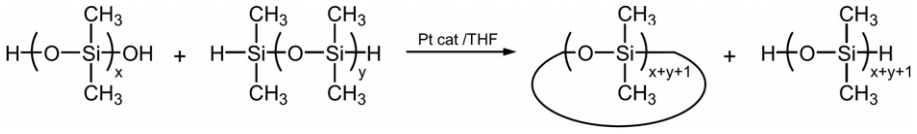

Fig. 1. Pt-catalyzed dehydrocoupling of linear α,ω-dihydroxy-PDMS with α,ω-dihydrido-PDMS. When conducted in dilute solution, the major product is cyclic PDMS.

byproducts from cyclic poly(oxyethylene) [17], and are known to thread linear PDMS (γ-CD) to form inclusion complexes [18,19]. Here we demonstrate their use in purifying cyclic PDMS.

2. Experimental section

2.1. Materials

All reagents were used as received. α,ω-Dihydroxy-PDMS (45–85 cSt, 0.96 g/mL, $M \sim 2$–3.5 kg/mol, $M_n \sim 2.5$ kg/mol [13]; 700–800 cSt, $M \sim 18$ kg/mol) and α,ω-dihydrido-PDMS (2–3 cSt, 0.90 g/mL, $M \sim 400$–500 g/mol) were purchased from Gelest. Hydrogen hexachloroplatinate(IV) hexahydrate (≥37.5% as Pt), methanol (99%), tetrahydrofuran (anhydrous, 99.9%), and toluene (HPLC grade, 99.8%) were purchased from Aldrich. γ-Cyclodextrin (γ-CD) was received from Wacker.

2.2. Instrumentation

Samples for gel permeation chromatography (GPC) were prepared in a 1 wt.% solution of toluene and filtered through a 0.45-μm nylon filter, with an eventual injection volume of 100 μL. GPC was conducted in toluene (1 mL/min) at 303 K on three Waters Styragel columns (5-μm beads: HR 0.5; HR 1; HR 3) that were connected to a Waters 2690 separations module and 2410 differential refractive index detector. A calibration curve was computed by fitting a third-order polynomial to the log M versus retention time plot prepared from polystyrene standards. Universal calibration was employed using the following Mark-Houwink constants: $k_{PS} = 0.0075$ [(mL/g)(mol/g)^a], $a_{PS} = 0.75$ [20], $k_{PDMS} = 0.0042$ [(mL/g)(mol/g)^a], and $a_{PDMS} = 0.83$ [1]. For cyclic PDMS, the k is the same and $a_{cPDMS} = 0.77$ [1].

MALDI-ToF mass spectrometry was carried out on a Micromass TofSpec 2E operated in linear mode with α-cyanohydroxycinnamic acid as matrix. Samples were prepared from THF solutions. Ambient sodium ions or NaI were used for ionization and spectra were smoothed to reduce noise levels. IsoPro 3.0 was used to simulate isotopic distributions of peak assignments.

NMR spectra were acquired on a Bruker AMX-400 spectrometer operated at 79.5 (^{29}Si) or 400.1 (^{1}H) MHz. Samples were prepared as solutions in $CDCl_3$: 80% (w/v) for ^{29}Si and 5% (w/v) for ^{1}H NMR. ^{29}Si NMR spectra were collected with inverse gated ^{1}H decoupling, 64 k data points, 33-kHz spectral width, 12-s recycle time, and 1 k (linear precursors) or 4 k (cyclic products) scans. ^{1}H NMR spectra were measured with 64 k data points, 8.3-kHz spectral width, 3-s recycle delay and 128 scans.

2.3. Synthesis

After drying at 120 °C for 12 h, a 250-mL round-bottom 2-neck flask with magnetic stir bar, condenser, and stopcock was sealed with a rubber septum and cooled while evacuating and then backfilled with dry N_2. Under positive nitrogen pressure, the septum was removed and hydrogen hexachloroplatinate(IV) hexahydrate (previously vacuum-dried) was transferred to the flask using a spatula. The flask was then evacuated and 200-mL THF was charged by cannula, giving an orange solution with Pt concentration of 1 mM. After ~ 5 min, α,ω-dihydroxy-PDMS (1.125 mL) and α,ω-dihydrido-PDMS (0.6 mL) were added sequentially with syringes to give a combined PDMS concentration between 7.5 and 10 g/L. For ring closure, the PDMS concentration should be below the overlap concentration [21], $c^* = 1/kM^a$, where M, k and a are the molecular weight and Mark-Houwink constants, respectively, of the linear PDMS precursor.

The solution was stirred and refluxed for 18 h. The solvent was removed by rotary evaporation, and the crude product dissolved in toluene, washed with distilled water (×2), and dried over magnesium sulfate. The mixture was filtered and solvent removed by rotary evaporation yielding 1.9 g (98%) of oil. Crude product (50 mg) was added to 5 mL of a saturated solution of γ-CD in distilled water (0.04 g/mL) at room temperature. The mixture was ultrasonically agitated for 90 min and allowed to stand overnight. The cloudy suspension was centrifuged to collect the γ-CD and complexed linear PDMS at the bottom of the centrifuge tube [17]. The cyclic PDMS was decanted from the top of the mixture and subjected to the purification procedure 2 more times. The cyclic PDMS was dissolved in toluene, washed with distilled water (×2) and dried over magnesium sulfate. The mixture was filtered and solvent removed by rotary evaporation affording 25 mg (50% gravimetric yield) of clear oil.

3. Results and discussion

Platinum-catalyzed dehydrocoupling of α,ω-dihydroxy-PDMS with α,ω-dihydrido-PDMS is depicted in Fig. 1. According to the scheme, intermolecular reactions are required to prepare both cyclic and linear PDMS, although the cyclic PDMS is ultimately formed by a subsequent intramolecular reaction. In our implementation, the α,ω-dihydrido-PDMS is smaller and might be considered the coupling agent for cyclization of the α,ω-dihydroxy-PDMS. The reaction was performed by adding α,ω-dihydrido-PDMS to a solution containing α,ω-dihydroxy-PDMS and Pt catalyst. During the course of the addition, the molar ratio of dihydrido-PDMS to dihydroxy-PDMS proceeds from a shortage to an excess of the stoichiometric ratio. We varied the rate of α,ω-dihydrido-PDMS addition from several hours, using a syringe pump (pseudo-high dilution conditions), to seconds, with manual injection, and observed no significant change in product molecular weight or yield.

The ratio of cyclic and linear PDMS in the product depends on the PDMS concentration in solution. The overlap concentration (c^*) for α,ω-dihydroxy-PDMS (45–85 cSt) with a reported molecular weight range of 2–3.5 kg/mol is 430–270 g/L, or 360 g/L for the measured average molecular weight of 2.5 kg/mol [13]. The reaction was carried out at 8 and 64 g/L total PDMS, both of which are well below the overlap concentration. The GPC traces of the starting materials and products obtained at 8 and 64 g/L are shown in Fig. 2. At 8 g/L, the major product has the same average molecular weight as the starting α,ω-dihydroxy-PDMS. From this result, combined with the spectroscopic data to be presented below, we conclude that the major product is cyclic PDMS. At 64 g/L, even though we are still below the overlap concentration by a factor of about 5, chain extension clearly occurs to give a product with a higher average molecular weight. While some of this product may be larger cyclic PDMS, we did not characterize this mixture further. Our focus was directed to the detailed characterization of the product obtained from the reaction conducted at 8 g/L PDMS.

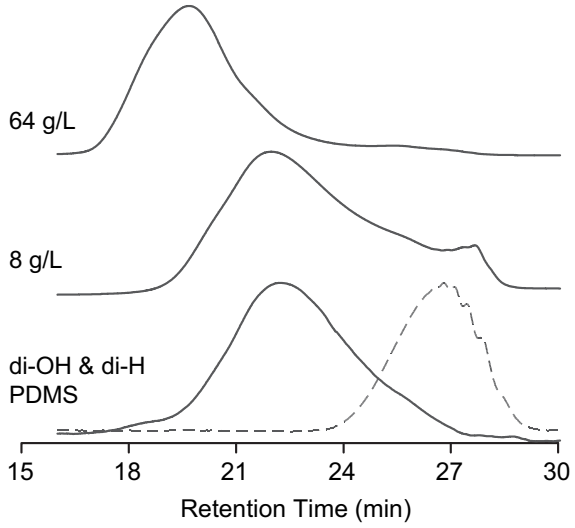

Fig. 2. GPC traces of α,ω-dihydroxy-PDMS (di-OH, M_n ~ 2.5 kg/mol, solid line), α,ω-dihydrido-PDMS (di-H, M ~ 400–500 g/mol, dashed line), and their dehydrocoupled products when total PDMS concentration is 8 g/L and 64 g/L. The major product at the lower concentration is cyclic PDMS.

The reaction product was purified by inclusion complexation and removal of the linear byproducts with γ-cyclodextrin (γ-CD). According to NMR spectra (see Figs. 3 and 4), end groups indicative of linear species are no longer present in the purified product. The ^{1}H NMR spectra (cf. Fig. 3) of both linear starting materials contain a major peak at 0.08 ppm due to methyl protons on internal silicons, and a smaller peak to its left attributed to methyl protons on silicons near the end groups. End-group protons appear at 2.5 ppm for the α,ω-dihydroxy-PDMS and at 4.7 ppm for the α,ω-dihydrido-PDMS. These peaks completely disappear in the NMR spectra of the crude and purified product indicating disappearance of the silanol and silane end groups below the detection threshold for ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of the reaction product contains a single major peak at 0.08 ppm. These data are consistent with the ^{29}Si NMR spectra shown in Fig. 4. Peaks due to Si–OH (−10.7 ppm) and Si–H end groups (−7 ppm) in the starting materials are absent in the product spectrum, which contains a single peak at −22 ppm due to internal dimethyl-substituted silicons.

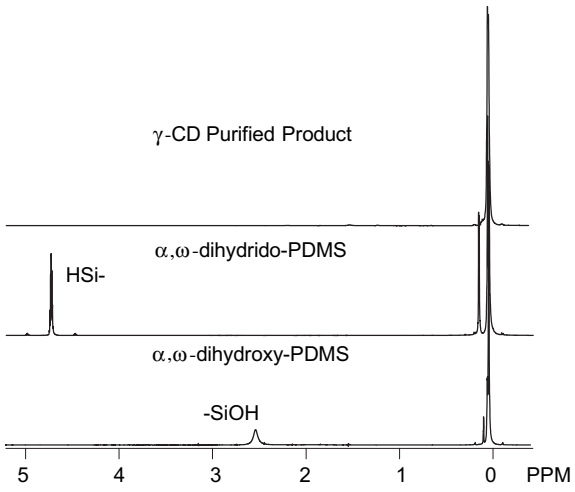

Fig. 3. ^{1}H NMR spectra of α,ω-dihydroxy-PDMS (M_n ~ 2.5 kg/mol), α,ω-dihydrido-PDMS (M ~ 400–500 g/mol), and the γ-CD-purified product of their dehydrocoupling reaction in dilute solution (total PDMS concentration ~ 8 g/L).

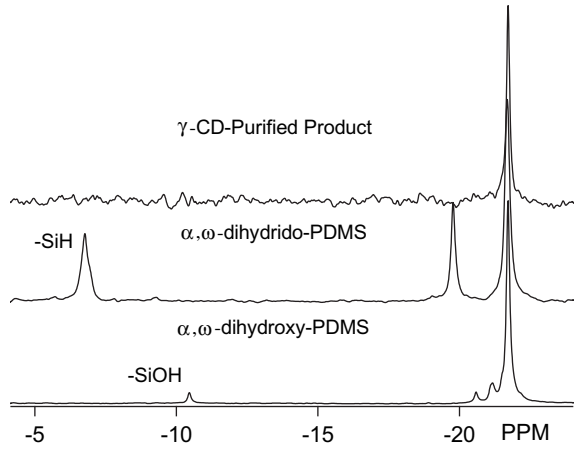

Fig. 4. ^{29}Si NMR spectra of α,ω-dihydroxy-PDMS (M_n ~ 2.5 kg/mol), α,ω-dihydrido-PDMS (M ~ 400–500 g/mol), and the γ-CD-purified product of their dehydrocoupling reaction in dilute solution (total PDMS concentration ~ 8 g/L).

Increased sensitivity is possible with IR spectroscopy. IR spectra of the linear starting materials, crude product, and γ-CD-purified product are shown in Fig. 5. Silanol end groups appear as a broad peak from 3120 to 3470 cm^{-1}, characteristic of intermolecular hydrogen-bonded hydroxyls, and as a sharper series of peaks around 3700 cm^{-1}, attributed to isolated hydroxyls. Silane end groups appear as a sharp absorption at 2120 cm^{-1}. Absorptions due to Si–H and hydrogen-bonded Si–OH groups are significantly diminished in the IR spectrum of the crude product, while peaks for isolated hydroxyl groups remain. This indicates the crude product contains linear species but the end groups are much less concentrated than in the linear starting materials. The IR spectrum of the γ-CD-purified product reveals the complete disappearance of the Si–H and hydrogen-bonded Si–OH groups, consistent with the NMR data. There appears to be a very slight absorption due to free hydroxyls in the IR spectrum of the γ-CD-purified product, but the intensity of this absorption is nearly the same as that observed in the IR spectrum of the α,ω-dihydrido-PDMS starting material. In general, these IR spectra show that end groups are removed by the Pt-catalyzed

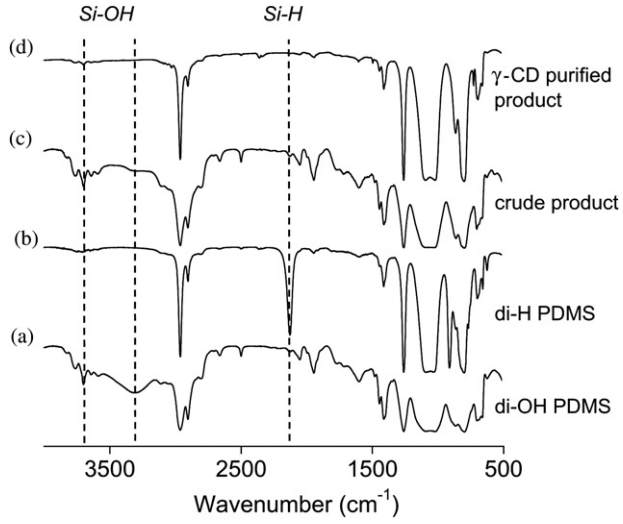

Fig. 5. IR spectra of (a) α,ω-dihydroxy-PDMS (di-OH PDMS, M_n ~ 2.5 kg/mol), (b) α,ω-dihydrido-PDMS (di-H PDMS, M ~ 400–500 g/mol), and their dehydrocoupled reaction product before (c) and after (d) purification using γ–cyclodextrin (γ-CD) to complex and remove linear byproducts.

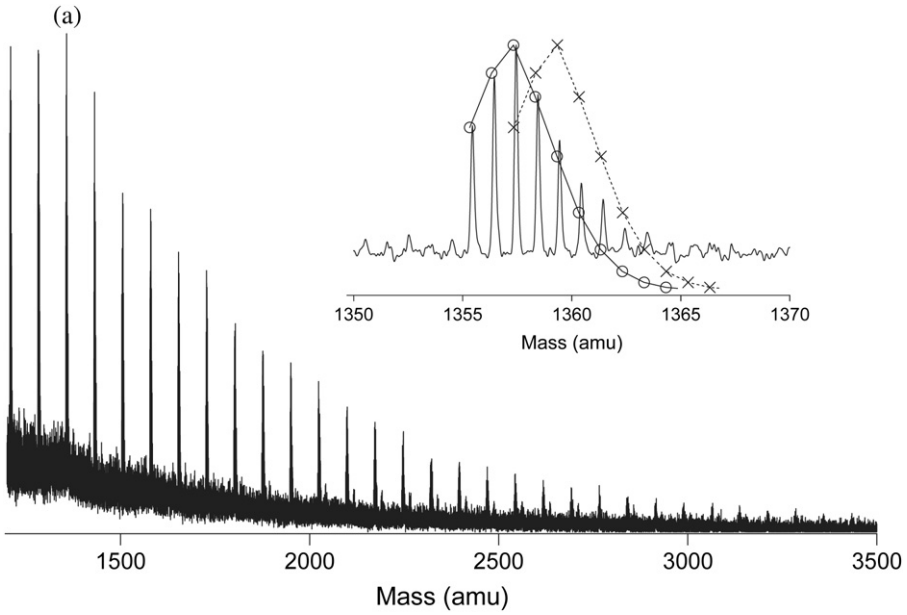

Fig. 6. MALDI-ToF mass spectrum of the γ-cyclodextrin-purified reaction product from dehydrocoupling of α,ω-dihydroxy-PDMS (M_n ~ 2.5 kg/mol) with α,ω-dihydrido-PDMS (M ~ 400–500 g/mol). Each peak in the major series is separated by 74 amu, the repeat-unit molecular weight of $[(CH_3)_2SiO]_x$, and represents sodium-cationized cyclic PDMS. The peak marked (a) at 1357.6 amu is due to $Na^+/[(CH_3)_2SiO]_{18}$ and is shown expanded in the inset along with spectral simulations that illustrate distributions of isotope combinations: ○ = Na^+/cyclic PDMS with 18 repeat units, × = Na^+/linear PDMS with 17 repeat units and $H/(CH_3)_2Si$–OH end groups.

dehydrocoupling scheme outlined in Fig. 1, and γ-CD is effective at removing linear byproducts from the crude product mixture.

The presence or absence of end groups in each homologue of polydisperse samples such as the ones examined here can be determined using MALDI-ToF mass spectrometry. The MALDI-ToF mass spectrum of the γ–cyclodextrin-purified product, shown in Fig. 6, contains a single series of signals separated by 74 amu, the repeat-unit molecular weight of PDMS. The most intense peak of the spectrum (Fig. 6a) appears at 1357.6 amu and corresponds to a sodium-cationized cyclic PDMS species containing 18 dimethylsiloxy repeat units [22]. Peaks due to cyclic PDMS decrease smoothly in intensity with increasing molecular weight and disappear into the noise above 3500 amu. The GPC chromatogram of Fig. 2 suggests a much higher relative concentration of cyclic PDMS homologues between 2 and 3.5 kg/mol than that shown in the MALDI-ToF spectrum of Fig. 6. This is explained by the reported discrimination against high-molecular-weight species in polydisperse samples by MALDI-ToF [23], and the particularly inefficient ionization of cyclic PDMS that contain no polar end groups [2]. Just above 2000 amu, low-intensity peaks appear 18 amu to the right of the major series of peaks and correspond to residual linear α,ω-dihydroxy-PDMS in low concentration, consistent with indications from IR data (cf. Fig. 5d). This is also consistent with the reported decrease in yield for γ-CD inclusion complex formation with increasing PDMS molecular weight above 750 g/mol [18].

In addition to α,ω-dihydroxy-PDMS, other possible linear species include α,ω-dihydrido-PDMS and α-hydrido-ω-hydroxy-PDMS (H/OH end groups), which is formed by reaction of α,ω-dihydrido-PDMS with one end of α,ω-dihydroxy-PDMS in the first step of this bimolecular cyclization. Peaks due to α,ω-dihydrido-PDMS would appear 14 amu to the left of the main series of peaks attributed to cyclic PDMS. None are clearly apparent in Fig. 6 in any significant amount. Peaks due to α-hydrido-ω-hydroxy-PDMS would appear 2 amu to the right of the main series of peaks attributed to cyclic PDMS. An expanded view of the most intense peak at 1357.6 amu is shown in the inset of Fig. 6 along with spectral simulations illustrating distributions of isotope combinations for sodium-cationized (○) cyclic PDMS with 18 repeat units, and (×) linear PDMS with 17 repeat units and $H/(CH_3)_2Si$–OH end groups (i.e., the precursor to the 18-repeat-unit cyclic PDMS). The simulated spectra confirm the assignment of the major series of peaks to cyclic PDMS and the absence of appreciable amounts of linear α-hydrido-ω-hydroxy-PDMS.

In mass spectra of the crude product, clear evidence for significant amounts of linear species with hydride end groups is not observed. This suggests that once a dihydrido-functionalized oligomer reacts with a dihydroxy-functionalized oligomer, the resulting species is a short-lived intermediate that rapidly cyclizes rather than remain in solution or further react with other linear material. In other words, the intermolecular reaction of α,ω-dihydroxy-PDMS with α,ω-dihydrido-PDMS is the rate-determining step in this bimolecular cyclization.

The GPC data of Fig. 2 (8 g/L) show that the product of the reaction scheme shown in Fig. 1 has approximately the same peak molecular weight as the starting material. The NMR (cf. Figs. 3 and 4), IR (cf. Fig. 5), and MALDI-ToF (cf. Fig. 6) data show that Si–H and Si–OH end groups are no longer present in the γ-CD-purified product. Thus, ring-closing dehydrocoupling of α,ω-dihydroxy-PDMS with α,ω-dihydrido-PDMS in dilute solution leads to cyclic PDMS. The procedure was also applied on a larger commercially available α,ω-dihydroxy-PDMS (700–800 cSt, M ~ 18 kg/mol) using the same low-molecular-weight α,ω-dihydrido-PDMS. The GPC trace of the dehydrocoupled product closely matched that of the linear α,ω-dihydroxy-PDMS starting material in peak position and polydispersity. This is in significant contrast to GPC data of the cyclic product obtained from base-catalyzed cyclodepolymerization of the same 18-kg/mol α,ω-dihydroxy-PDMS, which exhibited a considerable overall molecular weight reduction and polydispersity increase [2].

4. Conclusions

Commercially available α,ω-dihydroxy-PDMS and α,ω-dihydrido-PDMS were dehydrocoupled in dilute solution using a platinum catalyst to prepare cyclic PDMS in yields ≥ 50%. Linear

byproducts were successfully precipitated from the crude product by inclusion complexation with γ-cyclodextrin. As opposed to other routes to cyclic PDMS [1,2,13], this dehydrocoupling procedure avoids the formation of silanolate intermediates that backbite to reduce molecular weight and increase polydispersity. The achievable yields and predictable molecular weight characteristics should make this a useful technique for preparing cyclic PDMS for continuing fundamental and practical studies.

Acknowledgments

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