# Synthesis of Ultralarge Molecular Weight Bottlebrush Polymers Using Grubbs' Catalysts

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ABSTRACT: This paper describes two methods to synthesize bottlebrush polymers with molecular weights from 1 million to over 60 million g mol<sup>-1</sup> using Grubbs' first and second generation catalysts. In the first method, macromonomers of poly(L-lactide) were synthesized using tin(II) 2-ethylhexanoate and terminated on one end with a norbornyl group. Grubbs' first generation catalyst polymerized macromonomers with one poly(L-lactide) chain per norbornene, and Grubbs' second generation catalyst polymerized macromonomers with two poly(L-lactide) chains per norbornene. The predicted and measured molecular weights closely matched each other, and the polydispersities of the bottlebrush polymers were between 1.05 and 1.39. These examples are the first where Grubbs' second generation catalyst can be considered living for ROMP. In the second method, the backbone was polymerized first, and polylactide arms with molecular weights from 15 000 to 50 000 g mol<sup>-1</sup> were polymerized from the backbone. Polymers that were shaped as spheres or rigid rods were synthesized. The polymers were analyzed by GPC, MALLS, QELS, and <sup>1</sup>H NMR.

#### Introduction

The synthesis and applications of well-defined, soluble organic nanomaterials remain important areas of chemistry as nanoscience is recognized as a field that will have a large and wide impact in the next number of years.<sup>1</sup> Organic nanomaterials that assume the shape of spheres are well-known, yet only a few examples of the synthesis of more complex, soluble architectures have been reported.<sup>2-4</sup> Polymers have been self-assembled in solution and the solid state, cross-linked in an inorganic matrix, and synthesized in multiple steps to yield organic nanomaterials with unique architectures.<sup>2–4</sup> The synthesis of nonspherical, organic architectures remains an important goal that will have wide applications in nanotechnology. In this paper we will report our efforts to synthesize ultrahigh molecular weight bottlebrush polymers that are shaped as spheres and nanorods.

Bottlebrush polymers are a new architecture of polymers with regular and densely spaced arrangements of arms along a backbone (Figure 1).<sup>4-12</sup> Both the arms and backbones are polymers; thus, these polymers have ultrahigh molecular weights and may assume nonspherical shapes due to steric crowding between arms. For arms with medium to high molecular weights steric crowding between adjacent arms causes the backbone to assume a mostly linear conformation.<sup>7,10,13</sup> One consequence of this steric crowding is that bottlebrush polymers may be shaped as rigid rods with occasional bends and kinks.

Several excellent syntheses of bottlebrush polymers have been reported.<sup>4–11</sup> These polymers are typically synthesized using one of three methods. In the first method macromonomers are polymerized to yield bottlebrush polymers. This method has found widespread use as the physical properties of the arms can be characterized prior to the synthesis of the bottlebrush polymers, and a wide variety of polymer architectures are readily synthesized by the copolymerization of different macromonomers.<sup>8</sup> In the second method arms are polymerized from the backbone to yield bottlebrush polymers. This method is often challenging as small amounts of coupling between arms can lead to cross-linked, insoluble polymers. In addition, steric crowding between the arms will limit the concentration of arms along the backbone. Thus, the syntheses of the arms are typically run at high dilutions. In the third method, backbones and arms are polymerized separately and coupled in a final step. This method has the advantage that both the arms and backbones can be well characterized prior to their coupling. A disadvantage is that steric crowding may limit the number of arms that are ultimately coupled to a backbone.

These polymers offer challenges to their full characterization. As they may assume shapes from random coils to rigid rods, these polymers are not correctly characterized using standard size exclusion chromatography connected to a refractive index detector. These polymers must be characterized using light scattering to determine their molecular weights.<sup>5,14</sup> In addition, others have reported that these polymers have anomalous elution times and separations in SEC.<sup>10</sup>

The growth of living and controlled polymerizations over the past dozen years has yielded a series of methods that can be tailored to synthesize bottlebrush polymers.<sup>3,9,15–19</sup> One polymerization catalyst that is curiously absent from use in the synthesis of bottlebrush polymers despite its high activity and excellent tolerance of functional groups is Grubbs' catalyst. Only a few examples of Grubbs' first generation catalyst have been reported in the synthesis of bottlebrush polymers; no examples of Grubbs' second generation catalyst have been reported.<sup>11</sup> We wished to explore the use of Grubbs' first and second generation catalysts to synthesize bottlebrush polymers with molecular weights in excess of 10 million g mol<sup>-1</sup>.

\* Corresponding author: e-mail ned-bowden@uiowa.edu; Tel (319) 335-1198; Fax (319) 335-1270. Grubbs' first and second generation catalysts are wellstudied.<sup>15–18,20,21</sup> The first generation catalyst typically is used to synthesize polymers with small to medium



**Figure 1.** An example of a bottlebrush polymer that we synthesized and a schematic of the polymer beneath it. In (a) the polylactide (wavy line) is terminated on one end with a norbornyl group (square). The macromonomer is polymerized to yield a bottlebrush polymer as shown in (c). A macromonomer is a polymer with a polymerizable group on one end. (b) Lactide is polymerized from a backbone (connected squares) to yield a bottlebrush polymer. (c) The backbone is a polynorbornene and the arms are polylactides.

degrees of polymerization along the backbone (from tens to several hundred monomer units). We wished to study whether this catalyst could be used to synthesize welldefined polymers with degrees of polymerization in excess of 500 that could function as backbones for the synthesis of bottlebrush polymers. Grubbs' second generation catalyst is not described as a living catalyst as polymerizations with it are not well controlled.<sup>16,17,20</sup> Yet, this catalyst is one of the most active ring-opening metathesis polymerization (ROMP) catalysts that are commercially available.<sup>20</sup> In this paper we will report the polymerization of small molecule monomers and high molecular weight macromonomers with Grubbs' catalysts.

In this paper we will describe two approaches to synthesize bottlebrush polymers using ROMP and ringopening polymerizations (Figure 1). We synthesized bottlebrush polymers by polymerizing macromonomers of L-lactide terminated with norbornene and by polymerizing L-lactide onto backbones of polynorbornene. Polylactide is important as it is biologically compatible and easily degraded. Both methods yielded bottlebrush polymers, but each method had unique advantages and disadvantages. In addition, we will outline evidence based on light scattering that our highest molecular weight bottlebrush polymers are shaped as rigid rods.

#### **Experimental Section**

**Materials.** 1,12-Dodecanediol, *tert*-butyldimethylsilyl chloride, 1-hexadecanol, imidazole, oxalyl chloride, tetraethylene glycol, 4-(dimethylamino)pyridine, *p*-toluenesulfonic acid monohydrate, 1,3-dicyclohexylcarbodiimide, 1,1,1-tris(hydroxymethyl)ethane, 1-hexadecanol, 5-norborne-2-carboxylic acid (as an endo/exo mixture), tetrabutylammonium fluoride (1 M in THF), and DOWEX 50X2-400 were purchased from Aldrich or Acros Organics at their highest purity and used as received. The GPC solvent was HPLC grade chloroform and purchased from Acros Organics and used as received. All other solvents were reagent grade and purchased from Acros Organics.

(3.S)-*cis*-3,6-Dimethyl-1,4-dioxane-2,5-dione (98%) was purchased from Aldrich. It was purified by recrystallization from ethyl acetate three times and stored under N<sub>2</sub> in a glovebox. Tin(II) 2-ethylhexanoate was purchased from Aldrich and used as received. The pure exo isomer of 5-norborne-2-carboxylic acid was synthesized according to a literature procedure.<sup>22</sup> 2-Methoxyethyl ether was dried over activated molecular sieves (type 3A) and stored in a Kontes flask. Three freeze–pump–thaw cycles were performed, and it was taken into the glovebox, poured over activated aluminum oxide, and stored. Isopropylidine-2,2-bis(methoxy)propionic acid was synthesized according to a literature procedure.<sup>23</sup> Geduran silica gel 60 was purchased from Fisher and used for all purifications.

**Instrumentation.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX 300 using CDCl<sub>3</sub>. The solvent signal was used as an internal standard. Size exclusion chromatography (SEC) using CHCl<sub>3</sub> as the mobile phase (1.0 mL min<sup>-1</sup>) was performed at room temperature. A Waters 515 HPLC pump was used for SEC. Four Waters columns (styragel HR2, HR4, HR4, and HR6) were used in series. The DAWN EOS 18 angle laser light scattering detector from Wyatt Corp., the Wyatt-QELS for quasi-elastic light scattering, and the Wyatt Optilab DSP for refractive index were used to measure the absolute molecular weights of the polymers. We used a value of  $6.59 \times 10^{-5}$  mol mL g<sup>-2</sup> for the second viral coefficient for the bottlebrush polymers in Tables 3 and 4. This value was the average of those measured for entries 1–3 in Table 4. For molecular weights of less than 10 million g mol<sup>-1</sup>, the molecular weights and polydispersities varied less than 20% when the second viral coefficient was changed from 0 to  $6.59 \times 10^{-5}$  mol mL g<sup>-2</sup>. For higher molecular weight polymers the changes in the molecular weights and polydispersities were more substantial.

Synthesis of Homopolylactide Using 1-Hexadecanol as the Initiator. The polymerizations in Table 1 were run from 2 to 24 h. We will describe the procedure for one polymerization as a representative example. 1-Hexadecanol (0.121 g, 0.5 mmol) was added to a glass vial and evacuated. L-Lactide (2.38 g, 16.5 mmol) was added to the vial. At an initiator-to-catalyst ratio of 50/1, tin(II) 2-ethylhexanoate (3.28  $\mu$ L, 1.0  $\mu$ mol) was added to the glass vial. The vial was evacuated and backfilled with N<sub>2</sub> five times. The vial was flame-sealed under vacuum and heated to 110 °C for 2 h. The vial was cooled in ice and opened, and the contents were dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The polymer was precipitated into methanol and filtered. It was dried under vacuum for 48 h.

Polylactide had a low value for dn/dc and did not scatter light well. We could not determine the absolute molecular weight of homopolylactide; thus, we investigated the molecular weights of the polylactides using polystyrene standards (purchased from Waters) and by end-group analysis from the <sup>1</sup>H NMR spectrum. To determine the molecular weight by NMR, the peaks at 1.3, 0.9, 5.1, and 1.6 ppm were integrated against each other. The triplet at 0.9 ppm corresponded to the methyl on the initiator. The broad peak at 1.3 ppm corresponded to 26 protons on the initiator. The quartet at 5.1 ppm corresponded to the CO-CH(CH<sub>3</sub>)-O peak. The doublet at 1.6 ppm corresponded to the CO–CH( $C\hat{H}_3$ )–O peak. We found the molecular weights of the polylactides by measuring the ratio of the integration of the peaks at 1.3 and 5.1 ppm. For polylactide with  $M_{\rm n} = 5200, 9500, 14\,000, \text{ and } 21\,000 \text{ g mol}^{-1},$ the ratio of the peak at 5.1 to 1.3 ppm was 2.6, 4.9, 7.3, and 11.1, respectively. The peaks at 0.9 and 1.6 ppm were used to find a second value for  $M_n$  that was checked against the first value.

**Synthesis of Macromonomers of Polylactide.** The synthesis of macromonomers followed the same general procedure as in the previous section. The molar ratio of alcohol to tin was 50/1, and the reactions were run from 2 to 24 h. We will describe the synthesis of exo-A-4300. A (0.644 g, 0.002 mol) was added to a glass vial. Next, L-lactide (9.36 g, 0.065 mol) was added. The vial was evacuated and backfilled with N<sub>2</sub> five times. Tin(II) 2-ethylhexanoate (13.0  $\mu$ L, 0.04 mmol) was added. The vial was evacuated and backfilled with N<sub>2</sub> five times. The glass vial was flame-sealed. The vial was placed in an oil bath at 110 °C for 2 h. The vial was cooled in ice and opened, and the contents were dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>.

The polymer was precipitated into 400 mL of methanol. The polymer was redissolved in  $CH_2Cl_2$  and precipitated into methanol three times. The polymer was isolated and dried under vacuum at room temperature for 48 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.58 (d, 3H, J = 7.1 Hz), 5.17 (q, 1H, J = 7.1 Hz).

ROMP of Macromonomers with Grubbs' First Generation Catalyst. The exo-A macromonomers in Table 2 were polymerized at the highest possible concentrations from 4 to 24 h. The macromonomers were polymerized in a glovebox under an atmosphere of N2. We will describe the synthesis of entry 2 in Table 3. The macromonomer (2.50 g) was dissolved in 6.68 mL of CH<sub>2</sub>Cl<sub>2</sub>. Grubbs' first generation catalyst was added to a vial and dissolved with CH<sub>2</sub>Cl<sub>2</sub> to a concentration of 1.00 mg mL<sup>-1</sup>. From this catalyst solution, 0.82 mL was added to the monomer. The reaction was allowed to run for 15 h. The reaction was removed from the glovebox, and ethyl vinyl ether (1 mL) was added. The reaction was stirred for 1 h, and the polymer was precipitated into 300 mL of methanol. The polymer was isolated by filtration, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, and precipitated into methanol. The polymer was dried under vacuum for 48 h.

**ROMP of Macromonomers with Grubbs' Second Generation Catalyst.** The exo-**B** macromonomers in Table 2 were polymerized from 0.5 to 2.0 h using the same procedure as described for the ROMP of macromonomers with Grubbs' first generation catalyst.

**Polymerization of A.** A (1.10 g, 3.4 mmol) was taken into the glovebox.  $CH_2Cl_2$  (1.06 mL) was added to the monomer. Grubbs' first generation catalyst (27.4 mg) was added to 3.8 mL of  $CH_2Cl_2$ . From this catalyst solution, 0.94 mL was added to the monomer, and the reaction was allowed to proceed for 4 h. The reaction was removed from the glovebox, and ethyl vinyl ether (1 mL) was added. The reaction was stirred for 1 h before being precipitated into 20 mL of hexanes. The polymer was dissolved in THF and precipitated into methanol; this procedure was repeated three times. The polymer was isolated and dried under vacuum for 48 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.05–1.20 (br, m, 17H), 1.41–1.65 (br, m, 6H), 1.82–2.10 (br, m, 2H), 2.41–3.18 (br, m, 3H), 3.57 (br, m, 2H), 4.02 (br, m, 2H), 5.18–5.42 (br, m, 2H). GPC:  $M_n = 143\ 000\ g\ mol^{-1}$ , PDI = 1.02.

Polymerization of D. D (0.800 g, 1.86 mmol) was added to a vial in the glovebox.  $CH_2Cl_2$  (1.5 mL) was added to **D**. Grubbs' first generation catalyst (21.0 mg) was added to 3.4 mL of CH<sub>2</sub>Cl<sub>2</sub>. From this catalyst solution, 0.50 mL was added to the monomer. The reaction was stirred for 1.5 h and removed from the glovebox. Ethyl vinyl ether (1 mL) was added, and the reaction was stirred for 1 h. The reaction was filtered through a plug of silica gel, and the polymer was precipitated into diethyl ether. The polymer was redissolved in minimal CH<sub>2</sub>Cl<sub>2</sub> and precipitated into diethyl ether. This procedure was repeated two times. The polymer was isolated and dried under vacuum for 48 h. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.01– 1.20 (br, m, 4H), 1.62 (br, s, 1H), 1.82-2.05 (br, m, 2H), 2.41-3.18 (br, m, 3H), 3.20 (br, s, 2H), 3.57-3.90 (br, m, 16H), 4.10-4.38 (br, m, 4H), 5.10–5.41 (br, m, 2H). GPC:  $M_n = 226\ 000$ g mol<sup>-1</sup>, PDI = 1.12.

**Synthesis of Arms of Poly(L-lactide) from the Backbone.** The same procedure was followed for all entries in Table 4. We will describe the synthesis of entry 5 in Table 4 as an example. Poly-**D** (41.4 mg, 96.1  $\mu$ mol) and L-lactide (2.84 g, 19.7 mmol) were added to a Schlenk flask in the glovebox. 2-Methoxyethyl ether (4.26 mL) was added to the flask. The flask was sealed, removed from the glovebox, and attached to a N<sub>2</sub> line. It was heated at 110 °C for 20 min to dissolve all of the polymer. Tin(II) 2-ethylhexanoate (6.2  $\mu$ L, 19.2  $\mu$ mol) was added under a positive pressure of N<sub>2</sub>. The polymerization was allowed to run for 2 h at 110 °C and then cooled in ice. The polymer was dissolved in CHCl<sub>3</sub> and precipitated into methanol. This process was repeated three times. The polymer was dried under vacuum for 48 h. Yield = 2.65 g (92%). The <sup>1</sup>H NMR was identical to that of homopolylactide.

(*tert*-Butyldimethylsilyloxy)dodecanol. 1,12-Dodecanediol (15.00 g, 74.1 mmol) and imidazole (6.31 g, 92.7 mmol) were dissolved in 75 mL of warm DMF, and the reaction mixture

was cooled to room temperature. tert-Butyldimethylsilyl chloride (5.587 g, 37.1 mmol) was added, and the reaction mixture was stirred for 18 h at room temperature. Water (150 mL) was added to the reaction mixture, and the product was extracted with four portions of CH<sub>2</sub>Cl<sub>2</sub>. After the solvent had been removed under reduced pressure, the product was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> and extracted with four portions of water (100 mL). The crude product was purified by liquid chromatography on silica gel, eluting with 3:97 ethyl acetate/hexane gradually increasing to 15:85 ethyl acetate/hexane to give (tertbutyldimethylsilyloxy)dodecanol as a colorless viscous oil: 4.568 g, yield = 39%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  -0.06 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.78 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.11-1.16 (m, 16H), 1.31-1.43 (m, 4H), 3.13 (s, 1H, OH), 3.47 (m, 4H, CH<sub>2</sub>O).<sup>13</sup>C NMR  $(CDCl_3): \delta -5.56, 13.89, 18.07, 20.65, 25.47, 25.58, 25.62,$ 25.71, 29.23, 29.30, 29.41, 29.44, 32.51, 32.62, 60.12, 62.24, 63.03, 170.85. HRMS: Calcd for C<sub>18</sub>H<sub>40</sub>O<sub>2</sub>Si + H<sup>+</sup>: 317.2876. Found: 317.2892.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 12-(tert-Butyldimethylsilyloxy)dodecyl Ester. 5-Norborne-2-carboxylic acid (1.635 g, 11.9 mmol) was dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 30 min. Oxalyl chloride (4.07 mL, 47.4 mmol) was added. The temperature was raised to 25 °C, and the reaction was allowed to react for 6 h. The  $CH_2Cl_2$  was evaporated, and a slightly yellow viscous oil was obtained. The oil was dissolved in 12 mL of THF at 0  $^\circ C$  under  $N_2.$  The mixture was stirred at 0 °C for 30 min, and then (tertbutyldimethylsilyloxy)dodecanol (4.50 g, 14.2 mmol) and pyridine (3.83 g, 47.4 mmol) were added. The temperature was raised to 25 °C, and the reaction was allowed to run overnight. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude product was purified by liquid chromatography on silica gel, eluting with 2:98 ethyl acetate/hexane to give bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 12-(tert-butyldimethylsilyloxy)dodecyl ester as a colorless viscous oil: 4.543 g (88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ −0.03 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>), 0.83 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.21-1.31 (m, 18H) 1.39-1.48 (m, 3H), 1.52-1.58 (m, 2H), 1.86 (m, 1H), 2.14 (m, 1H), 2.83 (m, 1H), 2.96 (m, 1H), 3.52 (t, 2H, J= 6.6 Hz, CH<sub>2</sub>O), 4.00 (d of t, 2H, J = 0.6 Hz and J = 6.8 Hz, CH<sub>2</sub>-O-CO-), 6.04 (m, 2H, CH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ -5.42, 18.16, 25.68, 25.83, 28.58, 29.13, 29.31, 29.39, 29.42,29.44, 29.51, 30.15, 32.74, 41.48, 43.00, 46.17, 46.46, 63.04, 64.29, 135.58, 137.79, 175.85. HRMS: Calcd for C<sub>26</sub>H<sub>48</sub>O<sub>3</sub>Si + Na+: 459.3270. Found: 459.3261.

Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 12-Hydroxydodecyl Ester (A). Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 12-(tert-butyldimethylsilyloxy)dodecyl ester (4.543 g, 10.4 mmol) was dissolved in 11 mL of THF at room temperature under a nitrogen atmosphere. Tetrabutylammonium fluoride (31.2 mL, 31.2 mmol) was added, and the reaction mixture was stirred for 22 h at room temperature. Water was added to the reaction mixture, and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The crude product was purified by liquid chromatography on silica gel, eluting with 25:75 ethyl acetate/hexane to give A as colorless viscous oil: 3.219 g (96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.22–1.34 (m, 18H), 1.45–1.59 (m, 5H), 1.86 (t of d, 1H, J = 3.9 Hz and J = 11.8 Hz), 2.15 (d of d, 1H, J = 4.5Hz and J = 10.2 Hz), 2.24 (s, 1H, OH), 2.85 (s, 1H), 2.97 (br, s, 1H), 3.54 (t, 2H, J = 6.6 Hz, CH<sub>2</sub>O), 4.01 (t, 2H, J = 6.8 Hz, CH<sub>2</sub>–O–CO), 6.06 (m, 2H, CH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 25.63, 25.77, 28.51, 29.06, 29.29, 29.32, 29.36, 29.38, 29.43, 30.13, 32.59, 41.46, 43.05, 46.19, 46.44, 62.62, 64.44, 135.59, 137.83, 176.20. HRMS: Calcd for  $C_{20}H_{35}O_3 + Na^+$ : 323.2586. Found: 323.2584.

**(B)**. 5-Norborne-2-carboxylic acid (4.00 g, 29.0 mmol) was dissolved in 35 mL of  $CH_2Cl_2$  at 0 °C under a nitrogen atmosphere. The mixture was stirred at 0 °C for 30 min before oxalyl chloride (9.96 mL, 116 mmol) was added. The temperature was raised to 25 °C, and the reaction was allowed to react for 6 h. The  $CH_2Cl_2$  was evaporated, and a slightly yellow viscous oil was obtained. The oil was dissolved in 25 mL of THF under a nitrogen atmosphere. 1,1,1-Tris(hydroxymethyl)-ethane (6.96 g, 58 mmol) was dissolved in 90 mL of warm THF and added to the reaction mixture. Pyridine (4.69 mL, 57.9

mmol) was added, and the reaction was allowed to reach completion overnight. The product was extracted from water (50 mL) with four portions of CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic phase was evaporated, and the crude product was purified by liquid chromatography on silica gel, eluting with 40:60 ethyl acetate/hexane gradually increasing to 50:50 ethyl acetate/hexane to give **B** as white crystals: 3.76 g (56%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.84 (s, 3H, CH<sub>3</sub>), 1.11 (br, s, 1H), 1.35–1.43 (m, 2H), 1.47–1.50 (m, 1H), 1.91 (m, 1H), 2.26 (m, 1H), 3.04 (m, 3H), 3.53 (d of d, 4H, J = 11.4 Hz and J = 18.3 Hz, CH<sub>2</sub>O), 4.18 (d of d, 2H, J = 11.4 Hz and J = 17.4 Hz, CH<sub>2</sub>–O–CO), 6.12 (d of d, 2H, J = 3 Hz and J = 5.4 Hz, CH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.80, 30.41, 40.83, 41.59, 43.24, 46.37, 46.67, 66.39, 67.43, 67.48, 135.55, 138.08, 177.41. HRMS: Calcd for C<sub>13</sub>H<sub>21</sub>O<sub>4</sub> + Na<sup>+</sup>: 241.1440. Found: 241.1431.

Tetraethylene Glycol Bicyclo[2.2.1]hept-5-ene-2-carboxylate. 5-Norborne-2-carboxylic acid (4.00 g, 29 mmol) was dissolved in 35 mL of  $CH_2Cl_2$  at 0 °C under  $N_2$ . The reaction was stirred at 0 °C for 30 min before oxalyl chloride (9.96 mL, 116 mmol) was added. The temperature was raised to 25 °C, and the reaction was allowed to react for 6 h. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated, and a slightly yellow viscous oil was obtained. The oil was dissolved in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C under a nitrogen atmosphere. Tetraethylene glycol (20.0 mL, 115 mmol) was dissolved in 25 mL of  $CH_2\check{Cl}_2$  and added to the reaction mixture. Pyridine (4.69 mL, 57.9 mmol) was added, and the reaction was allowed to reach completion overnight at room temperature. Water (100 mL) was added to the reaction mixture, and the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was evaporated, and the crude product was purified by liquid chromatography on silica gel, eluting with 100% ethyl acetate to give tetraethylene glycol bicyclo[2.2.1]hept-5-ene-2-carboxylate as a colorless viscous oil: 7.198 g (80%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.33–1.40 (m, 2H), 1.53 (m, 1H), 1.91–1.96 (m, 1H), 2.24–2.28 (m, 1H), 2.37 (br, s, 1H, OH), 2.92 (s, 1H), 3.05 (m, 1H), 3.59-3.74 (m, 14H, CH<sub>2</sub>O), 4.25 (m, 2H, CH<sub>2</sub>-O-CO), 6.12 (m, 2H, CH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  16.88, 30.11, 41.40, 42.82, 46.06, 46.43, 49.50, 63.12, 63.23, 66.72, 68.55, 68.96, 70.15, 70.25, 70.33, 135.47, 137.84, 175.30, 176.00. HRMS: Calcd for  $C_{11}H_{21}O_6$  (parent peak minus cyclopentadiene): 249.1338. Found: 249.1328.

(C). Tetraethylene glycol bicyclo[2.2.1]hept-5-ene-2-carboxylate (5.00 g, 15.9 mmol), isopropylidine-2,2-bis(methoxy)propionic acid (3.87 g, 22.2 mmol), 4-(dimethylamino)pyridine (555 mg, 4.54 mmol), and *p*-toluenesulfonic acid monohydrate (605 mg, 3.18 mmol) were mixed in 75 mL of CH<sub>2</sub>Cl<sub>2</sub> under a nitrogen atmosphere. DCC (5.91 g, 28.6 mmol) was added. The reaction was stirred at room temperature for 15 h. The DCU was filtered with a glass frit and washed with a small volume of CH<sub>2</sub>Cl<sub>2</sub>. The crude product was purified by liquid chromatography on silica gel, eluting with 60:40 ethyl acetate/hexane to give C as colorless viscous oil: 4.96 g (66%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.15 (s, 3H, CH<sub>3</sub>), 1.21 (m, 1H), 1.29–1.43 (m, 8H), 1.90-1.94 (m, 1H), 2.27 (m, 1H), 2.92 (s, 1H), 3.04 (s, 1H), 3.60-3.72 (m, 14H, CH<sub>2</sub>O), 4.21-4.32 (m, 6H), 6.12 (m, 2H, CH=CH).<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  18.65, 23.04, 24.19, 30.32, 41.61, 41.74, 41.99, 43.01, 46.26, 46.65, 63.43, 63.83, 65.90, 68.99, 69.23, 70.52, 70.57, 70.60, 98.01, 135.68, 138.05, 174.10, 176.18. HRMS: Calcd for C<sub>24</sub>H<sub>38</sub>O<sub>9</sub> + Na<sup>+</sup>: 493.2414. Found: 493.2404.

(D). C (4.06 g, 10.5 mmol) was dissolved in 80 mL of methanol. One teaspoon of DOWEX 50X2-400 was added, and the reaction mixture was stirred for 7 h at room temperature. DOWEX 50X2-400 was filtered and carefully washed with methanol. The filtrate was evaporated, and the crude product was purified by liquid chromatography on silica gel, eluting with 100% ethyl acetate to give **D** as a colorless viscous oil: 3.85 g (85%). <sup>1</sup>H NMR (CDČl<sub>3</sub>): δ 1.17 (s, 3H, CH<sub>3</sub>), 1.25-1.31 (m, 2H), 1.44 (m, 1H), 1.83 (m, 1H), 2.17 (m, 1H), 2.83 (s, 1H), 2.96 (m, 1H, OH), 3.19 (s, 2H), 3.58-3.73 (m, 16H, CH<sub>2</sub>O), 4.16 (m, 2H, CH<sub>2</sub>-O-CO), 4.24 (m, 2H, CH<sub>2</sub>-O-CO), 6.03 (m, 2H, CH=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 16.88, 30.11, 41.40, 42.82, 46.06, 46.43, 49.50, 63.12, 63.23, 66.72, 68.55, 68.96, 70.15, 70.25, 70.33, 135.47, 137.84, 175.30, 176.00. HRMS: Calcd for C<sub>16</sub>H<sub>29</sub>O<sub>9</sub> (parent peak minus cyclopentadiene): 365.1812. Found: 365.1803.

Scheme 1. Synthesis of Homopolyactide from a Small Molecule Initiator



Table 1. Molecular Weights of Polylactides Synthesized in Scheme 1

predicted M <sub>n</sub> (g mol <sup>-1</sup> )	$M_{\rm n}$ from <sup>1</sup> H NMR (g mol <sup>-1</sup> )	$M_{\rm n}{}^a$ from GPC (g mol <sup>-1</sup> )	M <sub>n</sub> (GPC)/ M <sub>n</sub> (NMR)	PDI					
5 000	5 200	8 600	1.7	1.04					
10 000	9 500	17 000	1.8	1.06					
15 000	14 000	25 000	1.8	1.06					
20 000	21 000	36 000	1.7	1.11					
40 000	b	70 000	b	1.14					
50 000	b	80 400	b	1.16					
75 000	b	114 000	b	1.09					

<sup>a</sup> Calibrated against polystyrene standards. <sup>b</sup> The molecular weights of the three highest molecular weight polylactides could not be determined by <sup>1</sup>H NMR.

### **Results and Discussion**

Bottlebrush Polymers from the ROMP of Poly-(L-lactide) Macromonomers. In this section we will describe the synthesis and polymerization of macromonomers of polylactide terminated on one end with a norbornyl group, as shown in Figure 1a. Before we synthesized the macromonomers, we studied the polymerization of L-lactide to investigate the molecular weights and polydispersities of the polymers that we could synthesize (Scheme 1 and Table 1). The polymerizations of L-lactide were initiated from 1-hexadecanol, catalyzed by a Sn(II) catalyst, and run for 2-24 h. Each polymerization went to >95% conversion as judged by the amount of polymer isolated at the end of the reaction. These conditions were chosen as others have shown that the polymers have narrow polydispersities and predictable molecular weights.<sup>24</sup>

These polymers scattered light poorly; thus, we could not determine their absolute molecular weights using multiangle laser light scattering. Instead, we used two techniques to measure their molecular weights. In one method we used gel permeation chromatography (GPC) with a refractive index detector to measure the molecular weights against polystyrene standards. In the second method we calculated the molecular weights from <sup>1</sup>H NMR using end-group analysis as described in the Experimental Section.

From the results in Table 1 we see that the predicted molecular weights closely matched those measured by <sup>1</sup>H NMR. These polymerizations were well controlled as shown by the narrow polydispersities for all molecular weights measured and the close agreement between the predicted molecular weights and the molecular weights measured by <sup>1</sup>H NMR. The ratio of the molecular weights measured by <sup>1</sup>H NMR. The ratio of the molecular weights measured by <sup>1</sup>H NMR. The ratio of the molecular weights measured by <sup>1</sup>H NMR were close to 1.7 and can be understood by differences in hydrodynamic volume for polystyrene relative to polylactide.<sup>25</sup> These experiments demonstrated that we synthesized high molecular weight polylactide with low polydispersities.

*Synthesis of the Macromonomers.* We choose norbornene-based monomers for the synthesis of the backbone for three reasons (Figure 2). First, these monomers have large ring strains and are readily polymerized by



**Figure 2.** Synthesis of monomers **A**, **B**, and **D** that we used in this study. The full synthetic procedures are described in the Experimental Section.

 
 Table 2. Macromonomers That Were Synthesized Using Lactide and Tin(II) 2-Ethylhexanoate

initiator <sup>a</sup>	macromonomer	<i>M</i> <sub>n</sub> <sup><i>c</i></sup> from GPC (g mol <sup>-1</sup> )	PDI from GPC	duration of polymeri- zation <sup>b</sup> (h)
exo- A	exo-A-4300	4 300	1.06	4
exo-A	exo-A-19000	19 000	1.08	15
exo-B	exo- <b>B</b> -9800	9 800	1.09	10
exo-B	exo- <b>B</b> -52000	52 000	1.09	24
endo/exo- <b>B</b>	endo/exo- <b>B</b> -11000	11 000	1.19	12

<sup>a</sup> The prefix "exo" refers to norbornenes that are solely the exo isomer. The prefix "endo/exo" refers to norbornenes that are approximately 80% endo and 20% exo. <sup>b</sup> The yields of the polymerizations based on isolated polymer were greater than 90%. <sup>c</sup> The molecular weights were measured against polylactide standards. Macromonomers initiated from exo-**B** had two arms with *combined* molecular weights of the values reported.

Grubbs' catalysts at room temperature. Second, these monomers are synthesized in a few steps. Third, the pure exo monomer can be isolated. The exo monomer is more active than the endo monomer toward polymerization; thus, the choice of monomers can tune the rate of polymerization.

Norbornenes with one or two alcohols were used as initiators for the synthesis of the macromonomers. In our synthesis each alcohol becomes an arm; thus, we could vary the density of arms along the backbone through our choice of macromonomer. In Table 2 we show the results of the synthesis of our macromonomers.

To characterize these polymers, we used the polylactide standards that were synthesized in Table 1 and the molecular weights found using <sup>1</sup>H NMR spectroscopy to calibrate the GPC. Although the molecular weights found using <sup>1</sup>H NMR spectroscopy are values for the number-average molecular weight,  $M_n$ , rather than the molecular weight at the top of the peak,  $M_p$ , the values for  $M_n$  and  $M_p$  will be close to one another due to the narrow polydispersities of these polymers. We sacrificed a small amount of error in the value for  $M_p$  to use polylactide standards rather than polystyrene standards. Each macromonomer was synthesized with a low polydispersity, including those synthesized from an initiator with two alcohols.

Polymerization of Macromonomers Using Grubbs' Catalysts. We investigated the polymerization of macromonomers with one polylactide per norbornene using Grubbs' first generation catalyst (**E** in Scheme 2). Exo-**A**-4300 polymerized well with Grubbs' first generation



**Figure 3.** (a) GPC of exo-A-4300. (b) GPC of a bottlebrush polymer synthesized from exo-A-4300 with a macromonomer-to-catalyst ratio of 580/1 (entry 2 in Table 3). (c) GPC of a bottlebrush polymer synthesized from exo-A-4300 with a macromonomer-to-catalyst ratio of 1160/1 (entry 3 in Table 3). The conversion of macromonomer to the bottlebrush polymer was greater than 95%.

Scheme 2. Grubbs' First, E, and Second, F, Generation Catalysts



catalyst to greater than 95% conversion (Figure 3 and Table 3). Small high and low molecular weight shoulders were seen for the peaks, as shown in Figure 3b,c. Despite these shoulders, the polydispersities of the polymers were low. The polymerizations in Table 3 were run from 4 to 24 h, and extended reaction times did not significantly diminish the small amount of unreacted macromonomer that was present. Our polymers had high degrees of polymerization along the backbone, and the measured molecular weights matched the predicted molecular weights well. We note that this catalyst has been described as living for polymerizations of low molecular weight monomers, but we do not make this claim for polymerizations of macromonomers. More work would be needed to show that this catalyst is living for the ROMP of macromonomers.

We polymerized exo-A-4300 with Grubbs' second generation catalyst (entry 4 in Table 3). This polymerization resulted in greater than 95% conversion of macromonomer to bottlebrush polymer, but the measured molecular weight was significantly higher than the predicted molecular weight. This result was consistent with the high rate of propagation relative to the rate of initiation for Grubbs' second generation catalyst.<sup>16–18</sup>

We wished to test the limits of this method by polymerizing macromonomers with high molecular weights. One possible limitation to the polymerization of high molecular weight macromonomers was the high dilution necessary to completely dissolve the macromonomer. For example, in the ROMP of exo-**A**-4300 the concentration of **E** was approximately 0.11 mg mL<sup>-1</sup>. This concentration may be compared to the ROMP of monomers **A** and **D** as described in the Experimental Section where the concentration of **E** was 3.4 and 2.4 mg mL<sup>-1</sup>. To polymerize macromonomers with molecular weights greater than 4300 g mol<sup>-1</sup>, the concentration of **E** was less than 0.11 mg mL<sup>-1</sup>. Thus, we expected the polymerizations of high molecular weight macromonomers to be slow. Experiments to polymerize exoScheme 3. Macromonomers with One Polylactide Chain per Norbornene Polymerized Well with E, but Polymerizations with F Were Uncontrolled; Macromonomers with Two Polylactide Chains per Norbornene Polymerized Very Slowly with E, but Polymerizations with F Proceeded Rapidly and Resulted in Polymers with Narrow Polydispersities and Predicted Molecular Weights



Table 3. Synthesis of Bottlebrush Poly	ymers from Macromonomers
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entry	macromonomer	catalyst	macromonomer/ catalyst <sup>a</sup>	predicted M <sub>n</sub> (g mol <sup>-1</sup> )	measured $M_n^b$ (g mol <sup>-1</sup> )	PDI	time <sup>c</sup> (h)
	ovo A 1300	F	200/1	1 250 000	1 800 000	1.05	1
2	exo-A-4300	Ē	580/1	2 500 000	2 700 000	1.07	15
3	exo-A-4300	Ē	1160/1	5 000 000	5 200 000	1.19	23
4	exo-A-4300	F	1160/1	5 000 000	13 000 000	1.30	1.8
5	exo- <b>A</b> -19000	Ε	660/1	12 500 000	6 400 000	1.25	22
6	exo- <b>B</b> -9800	Е	51/1	500 000	430 000	1.03	4
7	exo- <b>B</b> -9800	Ε	1020/1	9 800 000	1 000 000	1.07	25
8	exo- <b>B</b> -9800	F	255/1	2 500 000	1 900 000	1.39	1
9	exo- <b>B</b> -9800	F	510/1	5 000 000	4 700 000	1.22	1
10	exo- <b>B</b> -9800	F	1020/1	10 000 000	12 000 000	1.17	1
11	endo/exo- <b>B</b> -11000	F	230/1	2 500 000	940 000	1.13	1.5
12	endo/exo- <b>B</b> -11000	F	460/1	5 000 000	520 000	1.08	1.5

<sup>*a*</sup> The ratio of macromonomer to Grubbs' catalyst. <sup>*b*</sup> Measured by GPC and MALLS. <sup>*c*</sup> The duration of the polymerizations. The yields for recovery of macromonomer and bottlebrush polymer were greater than 90% for each reaction.

**A**-19000 with **E** resulted in low conversions at long reaction times. For example, in entry 5 exo-**A**-19000 polymerized to 51% conversion after 22 h. Attempts to polymerize this macromonomer with **F** resulted in polymers with several peaks in the GPC.

We next investigated the polymerizations of macromonomers with two polylactide arms per norbornene. We attempted to polymerize exo-B-9800 with E, but the conversions were low. For example, in entry 7 in Table 3 the polymerization went to 10% conversion after 25 h. To investigate whether the concentration of the norbornene ends of the macromonomer and catalyst were responsible for the slow polymerization, we lowered the ratio of macromonomer to catalyst to 51/1 as shown in entry 6. The concentrations of the norbornene chain ends and the catalyst were higher than that in entry 1, yet this polymerization went to only 86% conversion after 4 h. Similar polymerizations with exo-A-4300 went to greater than 95% conversion in 4 h. Thus, **E** was found to be a slow and ineffective catalyst for the polymerization of norbornene with two polylactide arms.

It is well-known that F is a more active catalyst than E.<sup>16,18,20</sup> Despite its superior activity, F is rarely used as a ROMP catalyst as the polymerizations are not living. Two proposed reasons for the lack of living character of this catalyst are that it has a high value for the ratio of rate of propagation,  $k_{\rm p}$ , to rate of initiation,  $k_{\rm i}$ , and the catalyst chain transfers to olefins along the backbone of the polymers.<sup>16,18,20</sup> We hypothesized that our macromonomers would address these two problems due to their unique characteristics. First, steric crowding develops between macromonomers as they are added to the growing bottlebrush polymer. This steric crowding only occurs after multiple macromonomers have been added to the polymer. Thus, we expect that the steric crowding will affect  $k_p$  more than  $k_i$  and lower the ratio of  $k_p/k_i$ . Second, access to the olefins along the backbone is sterically hindered by the



**Figure 4.** (a) GPC of exo-**D**-9800. (b) GPC of a bottlebrush polymer synthesized from exo-**D**-9800 (entry 9 in Table 3).

polylactide arms. This hindrance may prevent the catalyst from reacting with these olefins.

We investigated the polymerization of exo-**B**-9800 with **F** at various ratios of macromonomer to catalyst (entries 8-10 in Table 3). These polymerizations went to greater than 95% conversion within 2 h (Figure 4 and Scheme 3). The agreement between the predicted molecular weight and the measured molecular weight was excellent, and the polydispersities decreased as the macromonomer-to-catalyst ratio was raised.

To study whether we could polymerize high molecular weight macromonomers with two polylactide arms per norbornyl group, we investigated the polymerization of exo-**B**-52000 with **F**. These polymerizations were not well controlled. At a macromonomer-to-catalyst ratio of 250/1 the polymerization went to completion, but there were several broad peaks in the GPC. Thus, the polymerization of the macromonomers with two polylactide arms per norbornene is limited to those with molecular weights lower than 52 000 g mol<sup>-1</sup>.



**Figure 5.** We polymerized norbornyl monomers to yield well-defined backbone polymers. Polylactides were synthesized from the alcohols on the backbone.

		predicted $M_{\rm n}$ for each arm <sup>b</sup>	predicted <i>M</i> <sub>n</sub> for bottlebrush polymer	measured for bottlebrush polymer				
entry	backbone <sup>a</sup>	(g mol <sup>-1</sup> )	(g mol <sup>-1</sup> )	$\overline{M_{ m w}{}^c}$ (g mol $^{-1}$ )	$\mathbf{PDI}^d$	$R_z^c$ (nm)	$R_{\rm h}{}^d$ (nm)	$R_z/R_{\rm h}$
1	poly-A	15 000	4 700 000	4 990 000	1.05	62	48	1.3
2	poly-A	30 000	9 400 000	8 920 000	1.02	64	54	1.2
3	poly-A	50 000	15 700 000	13 600 000	1.02	80	55	1.5
4	poly- <b>D</b>	15 000	15 800 000	18 300 000	1.03	110	53	2.1
5	poly- <b>D</b>	30 000	31 600 000	36 100 000	1.21	131	65	2.0
6	poly- <b>D</b>	50 000	52 300 000	64 000 000	e	243	e	

<sup>*a*</sup> Poly-**A** had a  $M_n = 143\ 000\ \text{g mol}^{-1}$ ; PDI = 1.02; degree of polymerization = 444. Poly-**D** had a  $M_n = 226\ 000\ \text{g mol}^{-1}$ ; PDI = 1.12; degree of polymerization = 525. <sup>*b*</sup> We assumed a 100% conversion of lactide to calculate the  $M_n$  for each arm. For poly-**D** each *alcohol* was treated as a separate arm. <sup>*c*</sup> Measured from a Zimm plot. <sup>*d*</sup> Measured with a GPC and a multiangle laser light spectrometer. <sup>*e*</sup> This polymer was too large to pass through the GPC columns.

We investigated the polymerization of endo/exo-**B**-11000 with **F** (entries 11 and 12 in Table 3). The polymerizations were slow and went to 40% and 10% conversions for macromonomer-to-catalyst ratios of 230/1 and 460/1 after 1.5 h. For comparison, the polymerizations of exo-**B**-9800 with **E** were run for 1 h and resulted in conversions of greater than 95%.

**Bottlebrush Polymers by Polymerizing Lactide from Backbone Polymers.** We developed a second method to synthesize bottlebrush polymers (Figure 5). In this method we synthesized the backbone first and grafted polylactide arms onto it in the next step. We wished to study whether this method would yield higher molecular weight bottlebrush polymers than were synthesized using the macromonomer approach.

We first investigated the polymerizations of **A**, **B**, and **D** (Figure 2). Polymers synthesized from **A** were soluble in methylene chloride and chloroform. The polymerizations of **A** proceeded smoothly at all concentrations we attempted. Notably, we synthesized a polymer with a molecular weight of 1 240 000 g mol<sup>-1</sup> and a polydispersity of 1.13. This polymer has a degree of polymerization of 4000 and may be used to synthesize bottlebrush polymers with long backbones. We investigated monomers structurally related to **A** but synthesized using 1,6-hexanediol and 1,10-decanediol. Polymers synthesized from these monomers were insoluble in methylene chloride and chloroform and not pursued.

Polymers synthesized from **B** were insoluble in methylene chloride, so we developed a short synthesis of **D**. This monomer yielded polymers with narrow polydispersities (PDI < 1.2) and degrees of polymerization up to 1500 along the backbone. Monomers synthesized in an analogous manner to **D** but with triethylene glycol resulted in polymers that were insoluble in  $CH_2Cl_2$  and were not pursued.

*Polymerization of L-Lactide.* We investigated the polymerization of L-lactide from the backbone. Typically, L-lactide polymerizations are run neat at 110 °C for

1-24 h.<sup>24</sup> When we attempted to grow polylactide from the backbone polymers under these conditions, the bottlebrush polymers were insoluble. The backbone polymer never dissolved in the molten lactide, and extensive cross-linking occurred.

To dissolve the backbone polymer, we added 2-methoxyethyl ether as a solvent to the polymerization. In addition, we changed the ratio of initiator to catalyst from 50/1 for neat polymerizations to 10/1 for polymerizations with 2-methoxyethyl ether. Polymerizations with an initiator-to-catalyst ratio of 50/1 using 2-methoxyethyl ether were slow, and conversions were low. Polymerizations with solvent and a 10/1 initiator-tocatalyst ratio yielded excellent results, as shown in Table 4. Under these conditions the polymer dissolved in the lactide and solvent prior to the addition of the tin catalyst. We synthesized bottlebrush polymers with ultrahigh molecular weights and narrow polydispersities. The polydispersities were narrow even for the highest molecular weight polymer that passed through the GPC columns. In addition, one should note the ratio of  $R_z/R_h$ , where  $R_z$  (m) is the root-mean-square radius and  $R_{\rm h}$  (m) is the hydrodynamic radius. For values of less than 1.5, this ratio indicates that the polymer is a random coil or a sphere.<sup>25</sup> For values of 2.0, this ratio indicates that the polymer is shaped as a rigid rod.<sup>25</sup> Thus, our initial results indicate that we synthesized bottlebrush polymers shaped as rigid rods and spheres.

In Figure 6, we show the Zimm plot of entry 6 in Table 4. The molecular weights of the bottlebrush polymers were ultralarge so the assumptions used to measure their molecular weights using GPC/MALLS were not valid. In particular, the second viral coefficient,  $A_2$ , is set equal to zero in GPC/MALLS systems so the absolute molecular weights of polymers can be measured.<sup>14</sup> This assumption is valid for polymers with molecular weights below approximately 1 million g mol<sup>-1</sup>, but our polymers had molecular weights that were much higher. We measured the Zimm plots for the polymers in Table 4



**Figure 6.** Zimm plot of entry 6 in Table 4. We show this plot as this polymer has the highest molecular weight in Table 4. The Zimm plots were increasingly difficult to plot as the molecular weight increased. The 5245 in the *x* axis is a stretch factor that is used to put the data in a clear format. The data were fitted to a quadratic equation.

as these plots report the values for  $M_w$ ,  $R_g$ , and  $A_2$  independent of any assumptions about  $A_2$ . We then used the values for  $A_2$  from the Zimm plots to measure polydispersities of the polymers from the GPC spectra.

The GPC spectra of entries 4-6 in Table 4 were unique. The peaks were broad and monomodal and had confusing retention times. The retention times of the peaks ranged from 40 to 65 min. For comparison, the retention times of small molecules (such as monomer) had retention times of 42-44 min in our GPC, and linear polymers had retention times from 22 to 35 min. Despite these characteristics, the peaks exhibited a strong dependence for light scattering intensity as a function of angle of detection (see Figure 7), and values for the molecular weights and  $R_{\rm g}$  were constant over the entire peak. The polymers had narrow polydispersities despite their broad appearance. We do not offer an explanation of this result but merely point it out. We only observed this result for the last three entries in Table 4 where light scattering data indicate the polymers were shaped as rigid rods.

One method to determine the shape of the polymer is to measure the Kuhn length from GPC and MALLS data. The Kuhn length is the distance between kinks in the polymer; thus, polymers with large Kuhn lengths are mostly linear and shaped as rigid rods. To determine the Kuhn length, a plot of  $R_g$  vs  $M_w$  must be modeled using different values for the Kuhn length. As our bottlebrush polymers had narrow polydispersities, the plot of  $R_g$  vs  $M_w$  did not cover a range large enough to find a value for the Kuhn length.

In Figure 7 we show light scattering data from the peak corresponding to entry 5 in Table 4. This figure demonstrates two important points. First, the GPC peak is monomodal and lacks high or low molecular weight humps. High molecular weight humps would indicate that the bottlebrush polymers are cross-linking. Low molecular weight humps would indicate that homopoly-lactide is being synthesized. Thus, the bottlebrush polymers are free of homopolylactide and not cross-linked. Second, the light scattering data show a strong angle dependence that indicates that the polymer has a high molecular weight.

**Comparison of the Two Methods To Synthesize Bottlebrush Polymers.** In the first method we polymerized polylactide macromonomers to yield bottlebrush polymers with degrees of polymerization up to 1160 along the backbone and narrow polydispersities. This method worked well for macromonomers with low to



**Figure 7.** Relationship between the intensity and scattering angle for the GPC/MALLS trace of entry 5 in Table 4. The strong dependence of angle on the scattering intensity indicates that the polymer has an ultrahigh molecular weight.

medium molecular weights (up to 9800 g mol<sup>-1</sup>). At higher molecular weights the polymerizations of the macromonomers were not well controlled and had low conversions, or multiple peaks were seen in the GPC.

During the course of this work we discovered the first example where Grubbs' second generation catalyst may be considered "living" as applied toward the synthesis of polymers using ROMP. As mentioned previously, this catalyst is not considered living as its rate of initiation is slow relative to its rate of propagation, and it reacts with olefins along the polymer backbone. In our work we used Grubbs' second generation catalyst to synthesize polymers with narrow polydispersities and molecular weights that were predicted on the basis of the ratio of macromonomer to catalyst. These results strongly suggest, but do not prove, that polymerizations of macromonomers with Grubbs' second generation catalyst were living.

We hypothesize that at least three factors contributed to the success of these polymerizations with Grubbs' second generation catalyst. First, the polymerizations were run at much lower concentrations than typical ROMP experiments. The concentrations may have an as yet unexplored effect on these polymerizations. Second, steric interactions between an incoming macromonomer and those already polymerized should lower the rate of polymerization but have little effect on the rate of initiation. Third, the rate of chain transfer to polymer may be slowed due to the steric crowding of the polylactide arms along the backbone.

One piece of evidence that supports our hypothesis is the comparison of the ROMP of exo-A-4300 and exo-**B**-9800. These macromonomers had similar values for the molecular weights of the polylactide arms but differed in the number of arms per norbornene (exo-B-9800 had two arms of average  $\hat{M}_n$  of 4900 g mol<sup>-1</sup> and exo-**A**-4300 had one arm with  $M_n$  of 4300 g mol<sup>-1</sup>). The steric crowding of polymerizing exo-A-4300 should be less than the steric crowding of polymerizing exo-B-9800. The polymerization of exo-A-4300 with Grubbs' second generation catalyst was uncontrolled, and the measured molecular weight was much higher than the predicted molecular weight. This result is consistent with a low value for  $k_i/k_p$ . The polymerization of exo-B-9800 with Grubbs' second generation catalyst was well controlled, and the measured molecular weights matched the predicted molecular weights. These results are consistent with the hypothesis that steric crowding may influence the reactivity of the catalyst but does not prove it. More experiments are needed to determine the reasons behind the success of these macromonomers with Grubbs' second generation catalyst.

In our second method to synthesize bottlebrush polymers we polymerized lactide from a backbone. This method was more versatile than the first method. We synthesized backbones with degrees of polymerization up to 4000. For our experiments we used polymers with degrees of polymerization of approximately 500 so the final molecular weights of the bottlebrush polymers would be within a range that we could easily characterize. We demonstrated that lactide could be polymerized from the backbone with little or no cross-linking between the bottlebrush polymers. In addition, we were able to synthesize arms with molecular weights up to approximately 50 000 g mol<sup>-1</sup>. The arms of the bottlebrush polymers synthesized using this method were of much higher molecular weight than those synthesized using the macromonomer method.

One disadvantage of this method is that we lacked an opportunity to directly measure the molecular weights or polydispersities of the arms. Thus, the arms were not fully characterized, and we must be careful when interpreting these results. We expect that the polydispersities of the arms were narrow on the basis of two related experiments. First, the polydispersities of homopolylactide were narrow as shown in Tables 1 and 2. Second, we polymerized L-lactide using 1-hexadecanol in 2-methoxyethyl ether at the same concentrations as used to synthesize the bottlebrush polymers. These homopolylactides had narrow polydispersities (PDI's from 1.11 to 1.28) for molecular weights from 5000 to  $50\ 000\ {\rm g\ mol}^{-1}$ .

# Conclusions

We report two methods to synthesize bottlebrush polymers using ROMP of norbornene-based monomers and ROP of L-lactide. The polymers had several characteristics. First, they had medium to high degrees of polymerization for the arms and backbones. Second, they were synthesized from L-lactide and are biologically compatible. Third, the polymers were shaped as spheres or cylinders as determined by light scattering.

What is the impact of this work? We synthesized ultrahigh molecular weight bottlebrush polymers with narrow polydispersities and biocompatible arms. These polymers are among the highest molecular weight bottlebrush polymers synthesized. We also described the first ROMP experiments where Grubbs' second generation catalyst may be described as living. The polymers offer an excellent opportunity to synthesize controlled organic nanomaterials that are shaped as spheres or rigid rods and may be integrated with inorganic nanomaterials.

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