Synthesis of Comb Block Copolymers by ROMP, ATRP, and ROP and Their Assembly in the Solid State

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Received September 15, 2005; Revised Manuscript Received November 28, 2005

ABSTRACT: This article reports the synthesis of comb block copolymers with backbones from *exo*-norbornene esters via ring-opening metathesis polymerizations (ROMP) and arms composed of polystyrene and polylactide. These polymers represent an exciting new architecture of polymers that have applications in the fabrication of photonic materials and nanofluidic systems. The living polymerization of block copolymers by ROMP with degrees of polymerization up to 2000 units and polydispersities less than 1.2 are described. This result is important as it extends the range of block copolymers that can be synthesized by ROMP to include those with high molecular weights. Comb block copolymers were grown from these block copolymers as they displayed initiators for the ring-opening polymerization of lactide and the atom transfer radical polymerization of styrene. Comb block copolymers with polystyrene and polylactide arms were synthesized with molecular weights up to 63 000 000 g mol^{-1}. The polystyrene arms had narrow polydispersities and molecular weights in excess of 10 000 g mol^{-1}; this result showed that the polymerization of styrene was well controlled. The sizes and shapes of these comb polymers were characterized by multiangle laser light scattering and scanning probe microscopy and demonstrated that some of these polymers were shaped as rigid rods with lengths in excess of 300 nm. To demonstrate their potential as photonic materials, an example of a comb block copolymer was assembled in the solid state with domain sizes exceeding 100 nm and characterized by scanning electron microscopy.

Introduction

Comb polymers are an interesting architecture of hyperbranched polymers that have complex geometries and properties (Figure 1).[1−5] Comb polymers have polymeric arms regularly and densely spaced along a polymeric backbone. Steric crowding between these arms can cause the backbone to assume a mostly linear conformation and the entire polymer to be shaped as a rigid rod.[6] These polymers represent a new type of soft nanomaterial with nonspherical dimensions that have potential applications in the emerging field of nanoscience. These polymers offer the opportunity to control the spatial distribution of functional groups on single polymers with dimensions from tens to hundreds of nanometers. This point is particularly important as there are many methods to synthesize complex geometries of hard materials (such as metals, semiconductors, and insulators) but fewer methods to synthesize nanometer-sized, nonspherical geometries of polymers.

Most comb polymers are synthesized using free radical or atom transfer radical polymerizations (ATRP).[1,5,7] A few examples where cationic or anionic polymerizations were used have been reported, but relatively few reports of comb polymers synthesized using ring-opening metathesis polymerizations (ROMP) have been published.[4,8,9] Typically, ROMP was used to polymerize the backbones or arms, and the molecular weights of these polymers were approximately several hundreds of thousands of grams per mole. In a recent article, the Grubbs' first-generation catalyst was used to polymerize the backbone through ROMP and low molecular weight arms by ATRP.[10]

The relatively few examples of ROMP in the synthesis of comb polymers is somewhat surprising as it is a living polymerization, and the Grubbs' first-generation catalyst is stable to a wide variety of functional groups. ROMP can be carried out at room temperature with less stringent demands on atmosphere conditions and with higher functional group tolerance than radical or anionic polymerizations.[3,9,11−13] In addition, polymers synthesized from ROMP have low polydispersities and predictable molecular weights. Because of these advantages, ROMP is becoming an increasingly attractive method to synthesize polymers with reactive functional groups exposed along the backbone.[13]

The structures and compositions of most reported comb polymers have been very simple with all of the arms composed of one polymer with total molecular weights less than several million grams per mole. The complexities of these polymers are slowly changing as comb-on-comb, star-comb, and comb block copolymers have been recently reported that increase the types of polymers that can be envisioned (see Figure 1a).[14] These polymers are interesting for their unique compositions and architectures.

The synthesis of ultrahigh molecular weight comb polymers is challenging as side reactions tend to cause the polymers to cross-link. There are only a few reports of comb polymers with molecular weights exceeding 10 000 000 g mol^{-1}. These comb polymers are interesting as they are typically shaped as rigid rods with diameters of ∼10 nm and lengths of hundreds of nanometers. More methods to synthesize comb polymers that allow their sizes, shapes, and distribution of functional groups are needed.

In this publication we report the synthesis of both homopolymers and block comb copolymers and their self-assembly into arrays in the solid state (Figure 1). In these experiments we used ROMP catalyzed by the Grubbs' first-generation catalyst to synthesize the backbone with ATRP and ring-opening polymerizations (ROP) to synthesize the arms. We made several significant accomplishments during the course of this study. First, we report the ROMP of *exo*-norbornene-based monomers into block copolymers with low polydispersities and high degrees of polymerization (up to 2000). Previous work by others

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10.1021/ma052012g CCC: $33.50

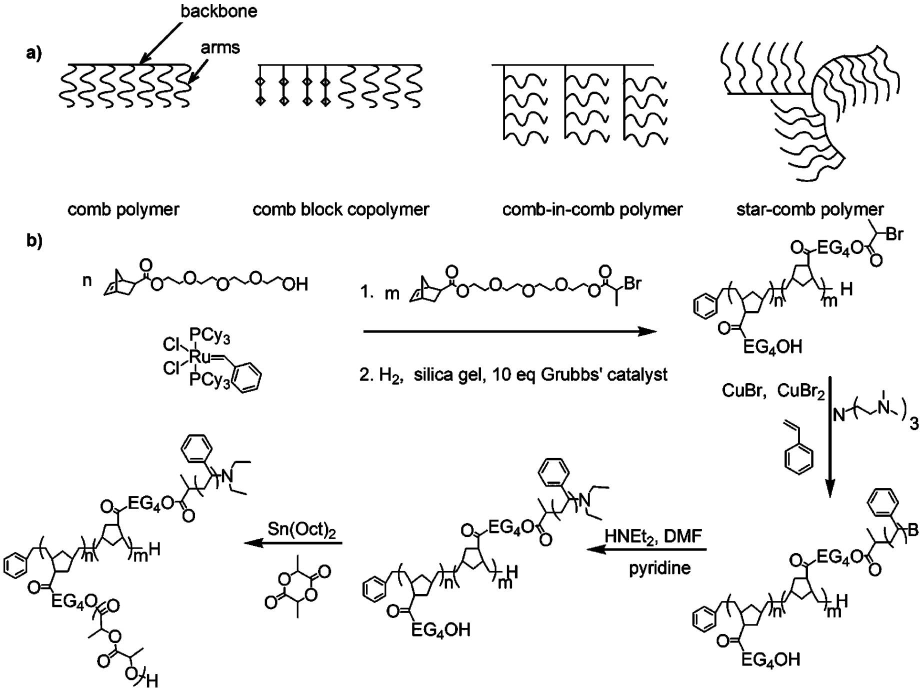


Figure 1. (a) Different architectures of comb polymers that were recently synthesized and reported in the literature. Here, the backbones are represented by straight lines and the arms by curvy lines or lines with diamonds. In this article we will describe the synthesis of ultrahigh molecular weight comb polymers of the first two types. (b) An outline of our synthetic method that shows how the comb block copolymers were synthesized.

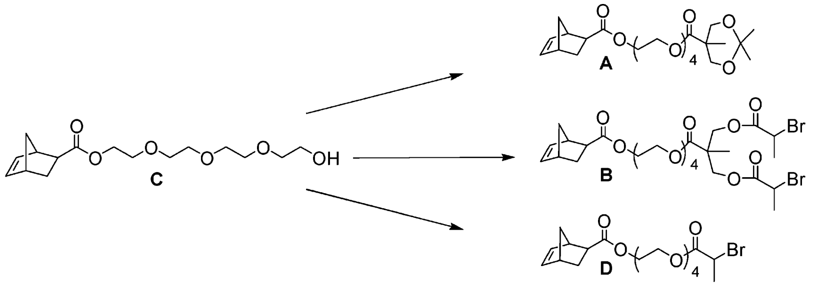


Figure 2. Monomers used for ROMP with the Grubbs' first-generation catalyst to synthesize the backbone of our comb polymers.

demonstrated that ROMP was living for polymers with several hundred monomer units; our work extends this range and increases the types and complexities of polymers that can be synthesized.[11,13,15−18] Second, these polymers were hydrogenated by decomposing the Grubbs' catalyst on silica gel in the presence of H_2. The polymerization and hydrogenation of the backbone were completed in one step. Third, we report the synthesis of new comb block copolymers with blocks composed of polystyrene and polylactide and with total molecular weights exceeding 10 000 000 g mol^{-1}. These polymers are exciting for their potential applications as photonic materials. Fourth, we report the assembly of these polymers into three-dimensional porous arrays in the solid state with dimensions greater than 100 nm. This result is significant as these arrays have dimensions on the size scale of light and form the basis for new photonic materials.

Experimental Section

Materials. Pyridine, 2-bromopropionyl bromide, 2,2-bis(hydroxymethyl)propionic acid, oxalyl chloride, 4-(dimethylamino)-pyridine (DMAP), styrene, *p*-toluenesulfonic acid monohydrate, copper(I) bromide, copper(II) bromide, formic acid, formaldehyde, tris(2-aminoethyl)amine, and diethylamine were purchased from Aldrich or Acros Organics at their highest purity and used as received. The GPC solvent was HPLC grade chloroform purchased from Acros Organics and used as received. All other solvents were reagent grade and purchased from Acros Organics.

Tin(II) 2-ethylhexanoate was purchased from Aldrich and used as received. (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_2 in a glovebox. The pure exo isomers of tetraethylene glycol bicyclo[2.2.1]hept-5-ene-2-carboxylate and monomer **A** in Figure 2 were prepared as described in the literature.[19] 2-Methoxyethyl ether and CH_2Cl_2 were dried over activated molecular sieves and stored in a Kontes flask. Three freeze−pump−thaw cycles were performed before being taken into the glovebox, poured over aluminum oxide, and stored. Geduran silica gel 60 was purchased from Fisher and used for all purifications.

Characterization. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 using $CDCl_3$ as the solvent and internal standard. Size exclusion chromatography (SEC) using $CHCl_3$ as the mobile phase (1.0 mL min^{-1}) was performed at room temperature. A Waters 515 HPLC pump and four Waters columns (Styragel HR 4, HR 5E, HMW 7, and HMW 7) were used in series. A DAWN EOS 18 angle laser light scattering detector from Wyatt Corp., a Wyatt-QELS detector to measure quasi-elastic light scattering, and a Wyatt Optilab DSP to measure changes in refractive index were used to measure absolute molecular weights of the polymers. We measured Zimm plots of the comb polymers and found second virial coefficients of 4.6×10^{-4} and 3.7×10^{-5} mol mL g^{-2} respectively for comb polymers composed of polystyrene and comb block copolymers of polystyrene and polylactide. Images from scanning probe microscopy were obtained with a Digital Instruments Nanosope III System. A 10 μm micromasch tip was used in tapping

Table 1. Synthesis and Hydrogenation of Polymers Synthesized by ROMP

				before hydrogenation		after hydrogenation			
entry	M[a]	M/C[b]	predicted $M_n \times 10^{-3}$ (g mol^{-1})[c]	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	Ru equiv added[d]	yield (%)[e]
1	A	500	235	215	1.01	218	1.02	0	>97
2	A	500	235	280	1.07	215	1.04	0	>97
3	A	500	235			210	1.09	0	>97
4	B	500	360	355	1.09	378	1.21	0	55
5	B[f]	500	360	370	1.07	366	1.17	0	70
6	B	500	360	359	1.09	377	1.21	0	90
7	B[g]	500	360	373	1.07	500	1.56	0	80
8	B	500	360	372	1.14	386	1.25	0	75
9	B	500	360			390	1.05	10	>97
10	D	500	225			213	1.05	1	75
11	D	500	225			238	1.04	5	>97
12	D	500	225			228	1.07	5	>97

[a] Monomer used for the polymerization. All of these polymerizations were run at room temperature for 1.5 h, and the hydrogenations were run in a Parr reactor for 10−15 h at 50 °C. [b] The monomer-to-catalyst ratio. [c] The predicted M_n was found by assuming all of the monomer was consumed. [d] This column describes if additional equivalents of Grubbs' catalyst were added after the polymerization but before the hydrogenation. [e] The yield for hydrogenation of olefins along the backbone. [f] Temperature for the hydrogenation was 45 °C. [g] Temperature for the hydrogenation was 60 °C.

mode in air. The drive amplitude ranged from 95 to 106 Hz, and the typical scan area was 3 × 3 μm^2.

Monomer (D). Tetraethylene glycol bicyclo[2.2.1]hept-5-ene-2-carboxylate (5.0 g, 15.9 mmol) and pyridine (2.52 g, 31.8 mmol) were dissolved in 65 mL of CH_2Cl_2 under N_2. The reaction was cooled to 0 °C before 2-bromopropionyl bromide (6.87 g, 31.8 mmol) was added. The reaction was warmed to 25 °C and stirred for 20 h. The reaction was diluted with 150 mL of CH_2Cl_2, and impurities were extracted with water. The organic phase was evaporated, and the product was purified by chromatography on silica gel, eluting with 40% ethyl acetate/60% hexane to give the product as a viscous pale yellow oil: 6.2 g (87%). ^{1}H NMR ($CDCl_3$): δ 1.32−1.40 (m, 2H), 1.51−1.54 (m, 1H), 1.82 (d, 3H, J = 6.9 Hz), 1.92 (d of t, 1H, J = 11.7 Hz and J = 4.2 Hz), 2.23−2.28 (m, 1H), 2.92 (m, 1H), 3.04 (m, 1H), 3.65−3.74 (m, 12H, CH_2O), 4.23−4.26 (m, 2H, CH_2−O−CO), 4.30−4.33 (m, 2H), 4.39 (q, 1H, O−COCHBrCH$_3$), 6.08−6.15 (m, 2H, $CH{=}CH$). ^{13}C NMR ($CDCl_3$): δ 21.24, 29.92, 39.56, 41.21, 42.60, 45.87, 46.22, 63.01, 64.55, 68.31, 68.79, 70.13, 70.21, 70.26, 135.31, 137.62, 169.63, 169.64, 175.55.

2,2-Bis(methyl-2-bromopropanoate)propanoic Acid. 2,2-Bis(hydroxymethyl)propionic acid (4.98 g, 37 mmol) was partially dissolved in 150 mL of CH_2Cl_2 at 0 °C. Bromopropionyl bromide (16.03 g, 74 mmol) was added and allowed to stir for 30 min before pyridine (5.87 g, 74 mmol) was added. The reaction was warmed to 25 °C and stirred for 15 h. The reaction was diluted with 75 mL of CH_2Cl_2, and impurities were extracted with water. The organic layer was evaporated to give a viscous yellow oil: (13.75 g, 92%). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 3H), 1.80 (d, 6H), 4.25−4.45 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 17.66, 17.69, 17.76, 21.38, 21.43, 21.47, 39.43, 39.47, 39.51, 46.39, 65.73, 65.83, 65.86, 65.93, 169.53, 169.55, 169.56, 169.58, 178.55, 178.59, 178.63.

Monomer B. 2,2-Bis(methyl-2-bromopropanoate)propanoic acid (25.1 g, 62 mmol) was dissolved in 350 mL of THF under N_2. Oxalyl chloride (31.54 g, 248 mmol) was added, and the reaction was heated at 45 °C for 8 h. THF was then evaporated to yield a yellow oil. The oil was added to tetraethylene glycol bicyclo[2.2.1]hept-5-ene-2-carboxylate (7.81 g, 25 mmol) dissolved in 270 mL of CH_2Cl_2 at 0 °C under N_2 and allowed to stir for 20 min. Pyridine (7.86 g, 99 mmol) and DMAP (0.61 g, 5 mmol) were then added, and the reaction was warmed to 25 °C and stirred for 15 h. The reaction was diluted with 100 mL of CH_2Cl_2, and impurities were extracted with water. The organic layer was evaporated, and the product was purified by chromatography on silica gel, eluting with 40% ethyl acetate/60% hexane to give the product as a pale yellow oil (5.5 g, 31%). ^{1}H NMR ($CDCl_3$): δ 1.29−1.37 (m, 5H), 1.49−1.51 (m, 1H), 1.78 (d, 6H, J = 6.9 Hz), 1.90 (d of t, 1H, J = 11.4 Hz and J = 4.5 Hz), 2.21−2.26 (m, 1H), 2.89 (s, 1H), 3.02 (m, 1H), 3.61−3.70 (m, 12H, CH_2O), 4.20−4.43 (m, 10H), 6.06−6.13 (m, 2H, $CH{=}CH$). ^{13}C NMR ($CDCl_3$): δ 18.6, 22.99, 24.15, 30.27, 41.54, 41.70, 42.96, 46.21, 46.55, 46.59, 63.38, 63.78, 65.85, 68.94, 69.17, 70.47, 70.52, 70.55, 70.56, 97.95, 135.63, 137.99, 174.03, 176.11.

***N,N,N′,N′,N″,N″*-Hexamethyltriethylenetetraamine.** We followed a literature procedure for this synthesis.[20] Tris(2-aminoethyl)amine (4.44 g, 30 mmol) was dissolved in 4.5 mL of H_2O at 0 °C. Formic acid (18.18 g, 0.395 mol) and then formaldehyde (8.21 g, 0.273 mol) were added; the flask was fit with a condenser and heated to 80 °C. The reaction proceeded for 20 h before the pH was adjusted to 14 with aqueous KOH. The product was then extracted with CH_2Cl_2 and evaporated to give a yellow oil. The product was purified by distillation. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 18H), 2.35−2.40 (m, 6H), 2.58−2.63 (m, 6H).

^{1}H NMR Kinetics for the ROMP of *exo*-Monomers. In an NMR tube monomer **A** from Figure 2 (0.1 g, 0.21 mmol) was dissolved in 0.85 mL of CD_2Cl_2. Grubbs' first-generation catalyst (19.9 mg, 0.024 mmol) was dissolved in 8.5 mL of CD_2Cl_2, from which 0.150 mL (0.350 mg, 0.425 μmol) was withdrawn and added to the monomer. The reaction was monitored by conversion of the olefin hydrogens in **A** at 6.04 ppm to the olefin hydrogens in the polymer at 5.13−5.3 ppm.

Typical ROMP Polymerization. In a glovebox, monomer **B** from Figure 2 (0.5 g, 0.697 mmol) was dissolved in 4.6 mL of CH_2Cl_2. Grubbs' first-generation catalyst (24.3 mg, 29.5 μmol) was dissolved in 8.45 mL of CH_2Cl_2. 0.4 mL of the Grubbs' catalyst solution (1.15 mg, 1.40 μmol) was added to the monomer. The polymerization proceeded 1.5 h before ethyl vinyl ether (1 mL) was added. After stirring for 45 min, the polymer was filtered through silica gel and crashed into hexanes. The polymer was purified by precipitation once more to yield poly**B**. ^{1}H NMR ($CDCl_3$): δ 1.16 (m, 1H), 1.32 (s, 3H), 1.65 (m 1H), 1.81 (d, 6H, J = 6.9 Hz), 1.93−2.10 (m, 2H), 2.53−3.09 (m, 3H), 3.64−3.72 (m, 12H), 4.14−4.46 (m, 10H), 5.31−5.36 (m, 2H, $HC{=}CH$).

Typical Hydrogenation of Olefins along the Polymer Backbone. We followed the polymerization described above. After the polymerization was complete we added 4 mL of the Grubbs' catalyst solution (11.5 mg, 14.0 μmol) prepared above followed by 250 mg of silica gel. The polymerization was placed in a metal Parr reactor, pressurized to 1500 psi, and heated to 50 °C. After 16 h the reactor was cooled to 0 °C. The polymer was then filtered through silica gel and precipitated into hexanes. The polymer was dissolved and precipitated into hexanes to yield entry 7 in Table 1. ^{1}H NMR ($CDCl_3$): δ 0.7 (m, 1H), 1.25 (m, 3H), 1.32 (s, 3H), 1.43−1.49 (2H), 1.81 (d, 6H, J = 6.9 Hz), 1.89−2.06 (m, 4H), 2.38 (m, 1H), 3.65−3.75 (m, 12H), 4.21−4.44 (m, 10H).

Typical Block Copolymerization. In a glovebox, monomer **A** from Figure 2 (0.328 g, 0.698 mmol) was dissolved in 2.8 mL of CH_2Cl_2. Grubbs' catalyst (32.2 mg, 38.8 μmol) was dissolved in 14.0 mL of CH_2Cl_2. 0.5 mL of the Grubbs' catalyst solution (1.15 mg, 1.40 μmol) was added to the monomer solution. The polym-

Table 2. Synthesis and Hydrogenation of Block Copolymers by ROMP

				before hydrogenation		after hydrogenation			
entry	M_1:M_2[a]	M_1:M_2:C[b]	predicted $M_n \times 10^{-3}$ (g mol^{-1})[c]	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	Ru equiv added[d]	yield (%)[e]
1	A:B	500:500:1	595	519	1.04	570	1.10	0	75
2	A:B	500:500:1	595	600	1.01	596	1.12	0	75
3	A:B	500:500:1	595			475	1.19	10	>97
4	A:B	1000:500:1	832			800	1.12	10	90
5	A:B	1000:1000:1	1200			1100	1.48	20	>97
6	C:D	500:1000:1	610	690	1.26	865	1.48	10	>97
7	C:D	500:1000:1	610			650	1.68	3	82
8	C:D	500:1000:1	610			720	1.50	0	33
9	A:D	250:1000:1	570			660	1.13	15	95

[a] This column lists the identities of the first, M_1, and second, M_2, monomers. [b] The ratios of M_1:M_2:catalyst. [c] M_n was predicted assuming complete initiation of the catalyst and consumption of the monomers. [d] Additional equivalents of the Grubbs' catalyst were added after the polymerizations but before the hydrogenations. [e] Yields for hydrogenations.

Table 3. Synthesis of Polystyrene Comb Polymers

		polystyrene arms		comb polymer					
entry	M_1:M_2:C[a]	measured M_n (g mol^{-1})[b]	PDI	predicted $M_n \times 10^{-3}$ (g mol^{-1})[c]	measured $M_n \times 10^{-3}$ (g mol^{-1})[d]	PDI	R_z (nm)	R_h (nm)	R_z/R_h
1[e]	500B:1	14 000	1.04	14 000	18 000	1.07	89.4	42.4	2.11
2[e]	500B:1	16 000	1.05	16 000	23 000	1.10	102.9	59.7	1.73
3[f]	500A:500B:1	13 000	1.02	13 000	13 000	1.43	99.6	44.5	2.23
4[f]	500A:500B:1	25 000	1.05	25 000	21 000	1.17	96.7	45.3	2.13
5[g]	500C:1000D:1	28 000	1.05	28 000	17 000	1.32	93.5	61.2	1.52
6[h]	500C:1000D:1	18 000	1.02	18 000	18 000	1.35	139.7	76.7	1.82
7[h]	500C:1000D:1	25 000	1.01	25 000	19 000	1.42	149.9	86.4	1.73

[a] The backbone polymers were synthesized by block copolymerizing monomers M_1 and M_2. This column shows the molar ratio of M_1, M_2, and catalyst. [b] The polystyrene arms were cleaved from the backbone as described in the text. [c] The predicted molecular weights were found by multiplying the M_n of the polystyrene arms by the number of arms along the backbone. [d] Measured with light scattering and refractive index detectors using an A_2 value of 4.6×10^{-4} mol mL g^{-2}. [e] This backbone polymer was from entry 9 in Table 1. [f] The backbone polymer was from entry 3 in Table 2. [g] Backbone polymer had M_n = 500 000 g mol^{-1}, PDI 1.34. [h] Backbone polymer had M_n = 555 000, PDI = 1.08.

Table 4. Characterization of Comb Polymers of Polylactide

		measured by light scattering/GPC					measured by SPM[a]		
entry	predicted $M_n \times 10^{-3}$ (g mol^{-1})[b]	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	R_z (nm)	R_h (nm)	R_z/R_h	length (nm)	width (nm)	height (nm)
1	15 800	18 300	1.03	110	53	2.1	*c*	*c*	*c*
2	31 600	36 100	1.21	131	65	2.0	395.7 ± 52.2	91.4 ± 7.6	1.5 ± 0.2
3	52 300	64 000	*d*	243	*d*	*d*	262.7 ± 47.1	59.5 ± 7.0	1.8 ± 0.4

[a] Measured from 15 samples. [b] The predicted molecular weight was determined by assuming the polymerization of lactide went to 100% conversion. [c] This polymer was not characterized by SPM. [d] This polymer was too large for the GPC columns.

erization stirred for 2.5 h before monomer **B** from Figure 2 (0.5 g, 0.698 mmol) dissolved in 5 mL of CH_2Cl_2 was added. After 2.5 h the polymer was hydrogenated as described above to yield entry 3 in Table 2. ^{1}H NMR ($CDCl_3$): δ 0.69−0.74 (m, 2H), 1.21−1.31 (m, 12H) 1.39 (s, 3H), 1.42 (s, 3H) 1.47 (m, 4H) 1.81 (d, 6H, J = 6.9 Hz), 1.85−2.01 (m, 8H), 2.37 (m, 2H), 3.62−3.72 (m, 26 H), 4.17−4.46 (m, 16H).

Typical Deprotection of the Diol in PolyA. Entry 3 from Table 2 (0.16 g) was dissolved in 50 mL of THF and 90 mL of methanol. *p*-Toluenesulfonic acid monohydrate (29.2 mg, 0.15 mmol) was added, and the reaction was allowed to stir for 3 h at 25 °C. Pyridine (36.4 mg, 0.46 mmol) was added, and the solvent was evaporated. The polymer was redissolved in a minimum amount of CH_2Cl_2 and precipitated in 1:1 hexane:diethyl ether to yield a white polymer 0.08 g (50%). ^{1}H NMR ($CDCl_3$): δ 0.71−0.74 (m, 2H), 1.12 (s, 3H), 1.248 (m, 6H) 1.32 (s, 3H), 1.43−1.47 (m, 4H), 1.81 (d, 6H, J = 6.9 Hz), 1.88−2.03 (m, 8H), 2.34−2.39 (m, 2H), 2.86 (m, 2H, OH), 3.64−3.83 (m, 26H), 4.17−4.46 (m, 16H).

Polymerization of Styrene from Backbone Polymers. CuBr (24.8 mg, 0.17 mmol), $CuBr_2$ (15.4 mg, 0.069 mmol), and a stir bar were placed in a 500 mL Schlenk flask and backfilled with N_2 twice. Styrene (173 g, 1.66 mol) was poured over aluminum oxide to remove inhibitor and added to the flask. *N*,*N*,*N*′,*N*′,*N*″,*N*″-Hexamethyltriethylenetetraamine (0.061 g, 0.26 mmol) was then added, and the flask was freeze−pump−thawed three times. Entry 7 from Table 1 (0.062 g, 0.17 μmol) was dissolved in 20 mL of styrene and added under positive N_2 pressure. The polymerization was heated to 90 °C for 3 h, then cooled to 0 °C and precipitated into methanol, redissolved in minimum CH_2Cl_2, and precipitated into methanol to yield a comb polymer, entry 3 from Table 3, as a white polymeric powder.

Reaction of Alkyl Bromides on the Ends of Polystyrene with Diethylamine. Entry 5 from Table 3 (0.5 g, 0.025 μmol) was dissolved in 25 mL of DMF, degassed twice, and placed under N_2. Diethylamine (55.1 mg, 0.75 mmol) and pyridine (0.178 g, 2.25 mmol) were added. The reaction was stirred at 25 °C for 48 h. The reaction was then precipitated into methanol, redissolved in CH_2Cl_2, and precipitated into methanol four more times.

Typical Lactide Polymerization. In a glovebox entry 5 from Table 3 (0.1 g, 5.0 nmol), lactide (1 g, 6.9 mmol), and diglyme (1 mL) were added to a 10 mL Schlenk flask. The flask was removed from the glovebox, attached to a Schlenk manifold, and heated to 110 °C. Sn(II) 2-ethylhexanoate (4.05 mg, 0.01 mmol) was added, and the reaction was stirred under N_2 for 2.5 h and then cooled to 0 °C, upon which it solidified. The polymer was redissolved in minimum CH_2Cl_2 and precipitated into 100 mL of methanol to yield 0.33 g of entry 3 in Table 5, of white polymeric powder (yield = 30%). ^{1}H NMR ($CDCl_3$): δ 1.34−1.89 (m, 17H), 5.16 (q, 4.7H), 6.57 (m, 2H), 7.07 (m, 3H).

Assembly of Comb Block Copolymers. Entry 4 in Table 5 was dissolved in CH_2Cl_2 at a concentration of 1.5 mg mL^{-1}. This solution was allowed to slowly evaporate at room temperature; it was then annealed for 4 days at 110 °C. The polymer film was immersed in 1 M aqueous NaOH at 65 °C for 12 h. The sample

Table 5. Polymerization of Lactide from Polystyrene Comb Polymers To Yield Comb Block Copolymers

	predicted		measured				
entry	M_n for each polylactide arm (g mol^{-1})[a]	M_n for comb block copolymer (g mol^{-1})[a]	M_n of comb block copolymer (g mol^{-1})[b]	PDI of comb polymer	R_z (nm)	R_h (nm)	R_z/R_h
1[c]	110 600	72 300 000	59 000 000	1.54	138.1	95.3	1.45
2[c]	58 800	46 000 000	39 000 000	1.36	160.3	120.0	1.33
3[c]	105 900	69 900 000	58 000 000	2.35	188.0	133.5	1.41
4[d]	40 400	38 000 000	36 000 000	2.08	216.9	112.1	1.93

[a] The value for M_n for each polylactide arm was found from the composition of the backbone polymer, the value for M_n for the polystyrene arms, and the ratio of polystyrene to polylactide from ^{1}H NMR. [b] The M_n was measured by GPC equipped with light scattering and refractive index detectors. The value for A_2 was measured from Zimm plots to be 3.7×10^{-5} mol mL g^{-2}. [c] Polylactide was grown from the polymer described in entry 5 of Table 3. [d] Polylactide was grown from the polymer described in entry 6 of Table 3.

was rinsed, coated with Au/Pd, and imaged with a Hitachi 4000 field emission scanning electron microscope (SEM) at an accelerating voltage of 5 kV.

Results and Discussion

Choice of ROMP to Synthesize Backbones of Comb Block Copolymers. We choose to use ROMP catalyzed by the Grubbs' first-generation catalyst to synthesize the backbones of our comb polymers as it is living, is mild and compatible with a wide range of functional groups, and polymerizes strained olefins. The latter point is important as ROMP is used to polymerize *mechanistically incompatible* monomers from ATRP which is an extremely useful method to polymerize styrenes, acrylates, methacrylates, and acrylamides.[21] Because ROMP and ATRP can polymerize mechanistically incompatible monomers, we could combine elements of each of these reaction techniques on one monomer. For instance, in Figure 2 we show norbornene monomers (**B** and **D**) that can be polymerized with ROMP through the strained olefins and used as initiators for ATRP. Also, monomers **A** and **C** can be polymerized with ROMP and used as initiators for ROP of lactide. Although others have shown that the Grubbs' catalyst promotes ATRP at elevated temperatures, we carried out ROMP reactions at room temperature where it is inactive toward ATRP.[10,22] These polymerization techniques are compatible with each other, and their combination allows for the synthesis of complex, functional materials.

Others have used the Grubbs' first-generation catalyst to synthesize block copolymers with low polydispersities.[13] These polymers typically have degrees of polymerizations up to several hundred monomers, but block copolymers with higher degrees of polymerization are not known. This is somewhat surprising as the Grubbs' catalyst is very active toward strained monomers, and low polydispersities have been observed for polymers with several hundred monomer units. It is important to learn what the upper limit for degree of polymerization of block copolymers synthesized by ROMP with the Grubbs' first-generation catalyst is for these monomers. Here, we will report the synthesis of block copolymers with degrees of polymerization up to 2000 that extend the range of block copolymers that can be synthesized with this important catalyst.

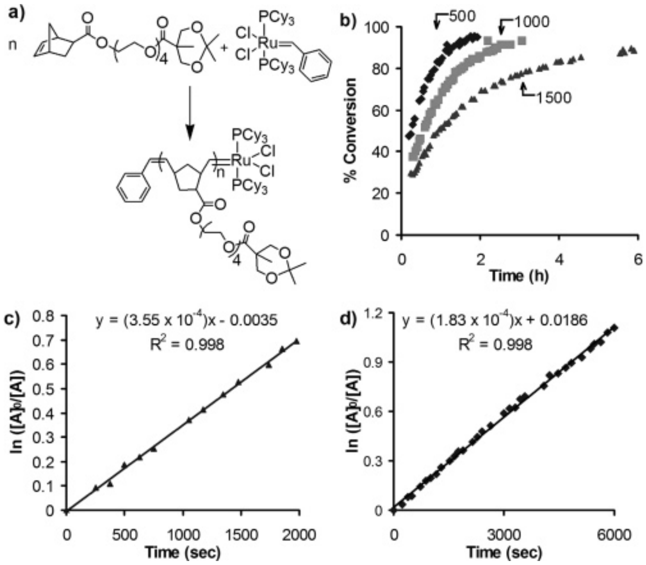
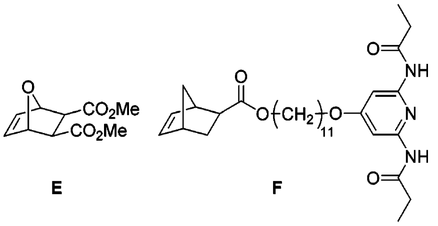


Figure 3. (a) Representative polymerization of **A** used in kinetic experiments. (b) The conversion of monomer **A** as a function of time showed first-order kinetics in concentration of monomer. The numbers in the graph in (b) refer the equivalents of **A** relative to the Grubbs' catalyst used in each polymerization. In (c) and (d) we monitored the conversion of **A** as a function of time by ^{1}H NMR and plotted the data assuming a first-order equation in [**A**]. The rate constants for monomer/catalyst ratios of (c) 500/1 and (d) 1000/1 were found by assuming that all of the catalyst had initiated.

Scheme 1. *exo*-Monomers E and F Had Similar Rate Constants as Our Monomers



Living Polymerization of Monomers by ROMP into Polymers with High Degrees of Polymerization. Because we wished to synthesize comb block copolymers with high molecular weight backbones, we first studied how to synthesize block copolymers with degrees of polymerization greater than 500. We studied the rate and conversion of monomer **A** at monomer to catalysts loadings of 500/1, 1000/1, and 1500/1 in CD_2Cl_2 by ^{1}H NMR (Figure 3). Methylene chloride was chosen as we observed that the Grubbs' catalyst decomposed within 10 h in chloroform even after extensive cleaning including distillation over P_2O_5 and passing over activated alumina. Deuterated and nondeuterated CH_2Cl_2 were good solvents for this catalyst as it was still active for over 24 h.

These polymerizations followed first-order kinetics and yielded rate constants of 0.84, 0.86, and 0.92 L mol^{-1} s^{-1} at monomer/catalyst ratios of 500/1, 1000/1, and 1500/1. Our values are very similar to those found by Weck et al. for the polymerization of **F** (0.57 L mol^{-1} s^{-1}) in $CDCl_3$ and France et al. for the polymerization of **E** (0.116 L mol^{-1} s^{-1}) in $CDCl_3$ (Scheme 1).[16,18] These values are ~15 times larger than the rate constants for the polymerization of endo/exo mixtures of these monomers.[16,17] In addition to the values for the rate constants, our reactions described how long each polymerization took to reach high conversions. We learned that polymerizations at

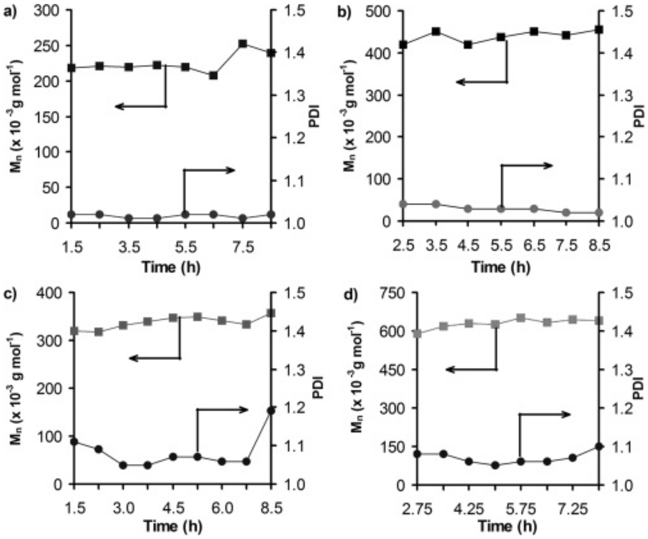


Figure 4. Values for M_n and PDI for the polymerization of **A** at monomer/catalyst ratios of (a) 500/1 and (b) 1000/1 and the polymerization of **B** at monomer/catalyst ratios of (c) 500/1 and (d) 1000/1. These polymerizations were complete after 1.5 h (M/C ratios of 500/1) and 3.0 h (M/C ratios of 1000/1).

monomer/catalyst loadings of 500/1 and 1000/1 took 1.5 and 3.0 h to reach >97% conversion. Monomer/catalyst loadings of 1500/1 took 6.0 h to reach 90% conversion; we choose to use this loading for the second block of our copolymers.

One important consideration in the synthesis of block copolymers is the competition between ROMP and cross-metathesis of olefins along the backbone and ruthenium catalysts at the ends of the polymers. Cross-metathesis will broaden the polydispersities and not allow for clean synthesis of block copolymers. To address this issue, we first studied how molecular weights and PDI's varied with time after >97% of the monomer had been consumed. In Figure 4, we show that the values for M_n and PDI are nearly constant for hours after the polymerizations are complete. These results indicate that we may allow these polymerizations to go to completion and still obtain narrow polydisperse polymers.

One test of a living polymerization is the ability to predict the molecular weight of the polymer based on the monomer/initiator loading. We polymerized **A** with different loadings of the Grubbs' first-generation catalyst and found a linear relationship between the measured molecular weight and the monomer/catalyst loading (Figure 5a). In addition, the molecular weights were measured using a Wyatt light scattering detector which allows for the absolute molecular weight to be found. At each monomer/catalyst loading, the predicted molecular weight was within 5% of the measured molecular weight.

To further learn whether these polymerizations were living, we synthesized block copolymers. In Figure 5b,c we show GPC traces of the block copolymerization of monomers using ROMP. In each of these polymerizations we polymerized the first monomer to completion before removing a small aliquot for GPC. Next, we added the second monomer and polymerized it to completion before quenching the reaction with ethyl vinyl ether. Figure 5c shows poly**A** (500 units of **A**) and a block copolymer of poly**A**−**B** that was synthesized by adding 1000 units of **B** to poly**A**. The GPC traces of the polymers were monomodal and suggest that the all of poly**A** was converted to the block copolymer. As these peaks overlapped, we also polymerized 100 units of **A** followed by 1000 units of **D** (Figure 5b). These peaks were well separated by GPC and showed the clean conversion of all of poly**A** to a block copolymer.

These results demonstrate that the Grubbs' first-generation catalyst promotes the living polymerization of *exo*-norbornene esters with degrees of polymerization up to 2000. This result is exciting as it expands the size of polymers that can be cleanly synthesized by ROMP and opens up new avenues to synthesize large molecular weight polymers with narrow polydispersities and well-defined compositions.

Hydrogenation of Olefins along the Backbone. We wished to grow polystyrene from the backbones and assemble comb block copolymers in the solid state into ordered arrays. Olefins along the backbone may present trouble with the synthesis of polystyrene by ATRP as they may react with the carbon radicals to terminate the polymerization of an arm of polystyrene and, possibly, cross-link comb polymers. Thus, we wished to hydrogenate the backbones of these polymers.

Our hydrogenation method was inspired by work done by others where the Grubbs' catalyst was used as the hydrogenation catalyst. Grubbs et al. reported that the addition of 150 psi of H_2 after a polymerization by ROMP was complete resulted in hydrogenation of 75% of the backbone olefins after 8 h at 65 °C.[22] Wagner et al. reported that the addition of silica gel and H_2 after a polymerization is complete resulted in 100% hydrogenation.[23] We observed similar results as hydrogenations without added silica gel did not completely hydrogenate olefins along the backbone, but the presence of silica gel resulted in quantitative hydrogenation.

We hydrogenated polymers derived from **A**, **B**, and **D** by adding silica gel and H_2 (1500 psi) at the end of the polymerization (Figure 6, Table 1). Poly**A** was completely hydrogenated after 10 h at 50 °C. The molecular weights and polydispsersities before and after the hydrogenations were similar and agreed well with predicted values. Poly**B** and poly**D** were more challenging to hydrogenate. An excess of the Grubbs' catalyst had to be added at the end of the polymerization to completely hydrogenate these polymers. In these experiments we waited until the polymerizations were complete, and then we added silica gel and an additional amount of Grubbs' catalyst before heating the reaction. Poly**D** was completely hydrogenated in the presence of an additional 5-fold excess of Grubbs' catalyst, and poly**B** required a 10 fold excess of catalyst. Similar to poly**A**, the molecular weights for pre- and post-hydrogenated poly**B** and poly**D** were similar and the polydispersities remained low.

It is important to note that the polymerizations and hydrogenations were mild and did not affect the functional groups on the polymers. The alkyl bromides on poly**B** and poly**D** were not affected as we did not observe a change in protons near the bromides in the ^{1}H NMR spectra before or after hydrogenation. Also, these functional groups are ATRP-active in the presence of the Grubbs' catalyst at elevated temperatures, but no cross-linking or side reactions were observed. Further evidence that these bromides were present will be presented shortly when we report the synthesis of polystyrene arms from these polymers.

Deprotection of PolyA to Expose Alcohols along the Backbone. We polymerized **A** as our attempts to polymerize monomer **G** (Scheme 2) resulted in polymers with high molecular weight humps on the GPC spectra and broad polydispersities (PDI > 1.5). This result was not entirely surprising as others have shown that alkoxides can replace the chlorides on the Grubbs' catalyst to form an inactive catalyst.[24] Although **G** was not deprotonated, the presence of a diol that can coordinate twice to ruthenium prevented the clean polymerization of this monomer. Polymerizations of monomers such as **C** with only one alcohol or monomers such as **A** with a

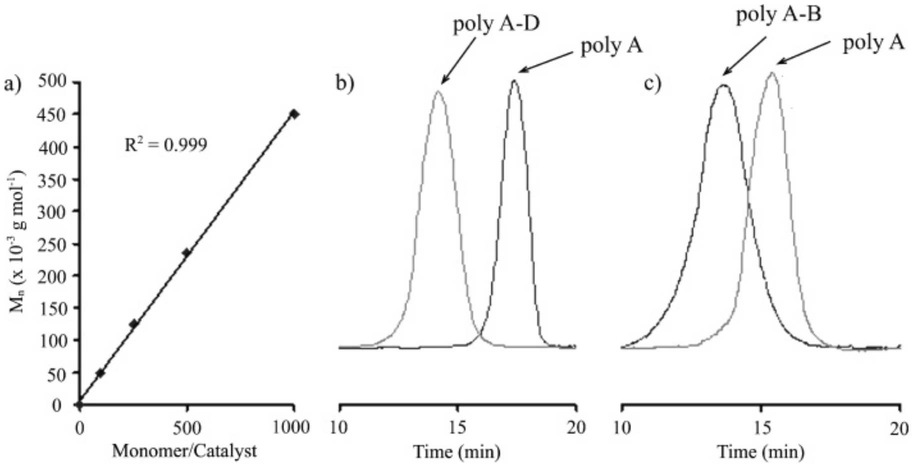


Figure 5. (a) Measured values for M_n for the polymerization of monomer **A** vs the monomer/catalyst ratio. The data follow a straight line and indicate that the polymerization is living. (b) GPC traces of poly**A** (monomer/catalyst ratio of 100/1) followed by the block copolymerization of 1000 units of **D**. These GPC traces show a clean conversion of all of poly**A** to the block copolymer. (c) GPC traces of a poly**A** (monomer/catalyst ratio of 500/1) followed by the block copolymerization of 1000 units of **B**. These peaks are monomodal but overlap slightly. These GPC traces indicate that poly**A** converted cleanly to the block copolymer.

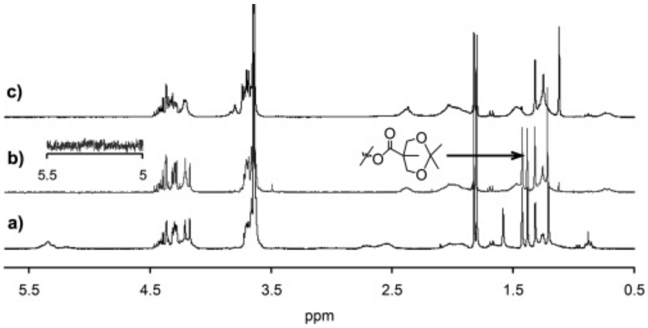
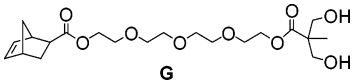


Figure 6. ^{1}H NMR spectra of entry 3 from Table 2. (a) The bottom spectrum shows the polymer before hydrogenation, and (b) the middle spectrum shows the polymer after hydrogenation. The olefinic region is enlarged to show the lack of peaks in this area. (c) The top spectrum shows the polymer after the diol was deprotected. The two methyl resonances are missing from the top spectrum.

Scheme 2. This Monomer Did Not Polymerize Well by the Grubbs' First-Generation Catalyst



G

protected diol proceeded smoothly with no apparent loss of reactivity of the Grubbs' catalyst.

The diols on poly**A** were deprotected with dilute acid. The deprotected polymers had similar molecular weights and polydispersities as those from poly**A** which indicated that no cross-linking occurred. The yield of the deprotection was cleanly followed by ^{1}H NMR and is shown in Figure 6. The two peaks due to the methyls on poly**A** disappeared after reaction in dilute *p*-toluenesulfonic acid monohydrate.

Block Copolymerization of Monomers by ROMP. In Table 2 the results of block copolymerizations and hydrogenations of *exo*-norbornene ester monomers are reported. The molecular weights of these polymers agreed with the predicted values and the polydispersities were generally low. The first monomer was polymerized to completion before the addition of a second monomer, and the entire polymerization was completed before the addition of H_2 gas and silica gel to hydrogenate the backbone.

Hydrogenation of Block Copolymers. To completely hydrogenate the olefins along the backbone, an additional amount of Grubbs' catalyst had to be added prior to the addition of H_2. This is not surprising as the catalyst was more dilute in the block copolymerizations than the homopolymerizations. We added up to 20 equiv of the Grubbs' catalyst with little effect on the molecular weights or polydispersities of the polymers. It is notable that we hydrogenated polymers with degrees of polymerization up to 2000 with an additional amount of Grubbs' catalyst (entry 5 in Table 2).

Synthesis and Characterization of Comb Block Copolymers. We synthesized block copolymers by ROMP with initiators for ATRP and ROP decorated along the backbone. In this section we will describe the synthesis and characterization of comb polymers with polystyrene and polylactide arms along the backbone.

Polymerization of Styrene from Initiators Decorating Backbone Polymers. ATRP is well studied and has been described as living or controlled.[5] In these polymerizations a small molecule serves as an initiator for a radical polymerization that is mediated by the addition of metals. Typical ATRP conditions proceed to 20−80% conversions of monomer and yield polymers with low polydispersities, well-defined molecular weights, and predicted end groups.

We used polymers with ATRP initiators along the backbone to grow polystyrene. Polymerizations of styrene at even modest conversions of 20% resulted in cross-linked polymers that did not dissolve and were not characterized. To minimize cross-linking, we diluted these polymerizations with excess styrene and limited conversions to ∼3% to yield soluble comb polymers (Table 3). We believe that the origin of cross-linking was radical coupling between two comb polymers. By diluting the polymerization and adding $CuBr_2$ (0.4 equiv of $CuBr_2$ for every equivalent of CuBr) to slow the reaction, soluble comb polymers were obtained. With these conditions, we grew soluble polystyrene comb polymers even if the backbone was not hydrogenated. When the conversions were between 20 and 80%, the comb polymer was cross-linked regardless of whether the backbone was hydrogenated.

We first grew polystyrene arms from homopolymers of **B** that had degrees of polymerization of 500 (entries 1 and 2 in Table 3) and block copolymers with one block composed of either monomer **B** or **D** (entries 3−7 in Table 3). To characterize the arms, we cleaved them from the backbone in refluxing methanol and KOH. These conditions cleaved the ester bonds along the backbone and released the polystyrene arms. It is important to note that the molecular weights of the arms were from 13 000 to 28 000 g mol^{-1} and the PDI's were low (<1.1). These results indicate that the ATRP of styrene was well controlled even though the polymerizations were very dilute.

We measured the molecular weights, polydispersities, and sizes of the comb polymers by GPC. It is important to note that we used light scattering and refractive index detectors from Wyatt Technology to find the absolute molecular weights of our comb polymers. We and others have shown when the molecular weights of comb polymers were found using only refractive index detectors and calibration curves from linear polystyrene standards, the measured values for the molecular weights underestimate the true molecular weights of comb polymers by up to a factor of 10.[1−5] Thus, a different approach must be used for comb polymers. The combination of a light scattering detector and a refractive index detector allows absolute molecular weights to be found without using polystyrene standards and provide information about the sizes and shapes of the polymers.

Because of the ultrahigh molecular weights of these comb polymers, we measured values for the second viral coefficient (A_2) from Zimm plots and used these numbers to find the molecular weights and polydispersities. For typical polymers with molecular weights below 1 000 000 g mol^{-1}, A_2 values can be safely ignored. For polymers with molecular weights above that threshold, A_2 values are necessary to find the absolute molecular weights of polymers.

We predicted the molecular weights of the comb polymers from the composition of the backbone polymers and the molecular weight of the arms. We found that the measured and predicted molecular weights for the comb polymers agreed with each other while the polydispersities of these polymers were low.

We found values for the root-mean-square radius (R_z) and hydrodynamic radius (R_h) for each of the comb polymers. These numbers are interesting for two reasons. First, they indicate that we synthesized polymers with sizes in excess of 90 nm. Second, the ratio of R_z/R_h describes the shape of a polymer. Others have shown that for values less than 1.5 the polymer is shaped as a random coil or sphere, but values of 2.0 indicate that the polymer is shaped as a rigid rod.[25] In this discussion a polymer that assumes the shape of a rigid rod is defined as possessing a cylindrical shape that may have bends and kinks. The ratios of R_z/R_h indicate that some of these polymers are shaped as rigid rods. The highest values for R_z/R_h are found for polymers with **B** along the backbone, and the lowest values are found for polymers with **D** along the backbone. This result is not surprising as comb polymers assume the shape of rigid rods due to steric crowding between arms along the backbone. Poly**B** has two polystyrene arms per repeat unit of norbornene and poly**D** has only one polystyrene arm per repeat unit of norbornene. These values for R_z/R_h only provide one piece of evidence for the sizes and shapes of these polymers; we will describe the shapes of comb polymers with polylactide arms that were characterized by scanning probe microscopy.

Polymerization of Lactide from Initiators Decorating Backbone Polymers. We reported the polymerization of lactide from poly**B** that was deprotected to expose alcohols along the backbone in a recent publication; in this publication we will report the characterization of these polymers by scanning probe microscopy (SPM).[19] The polymerization of lactide from small molecule initiators is typically done in molten lactide at 110 °C with an initiator/catalyst ratio of 50/1.[26] Comb polymers synthesized under these conditions were cross-linked and insoluble as the backbone polymer never fully dissolved before lactide was polymerized. We added 2-methoxyethyl ether to the reaction mixture to dissolve the backbone and increased the initiator/catalyst ratio to 10/1. The conversions of these polymerizations was greater than 90%, and the comb polymer was soluble.

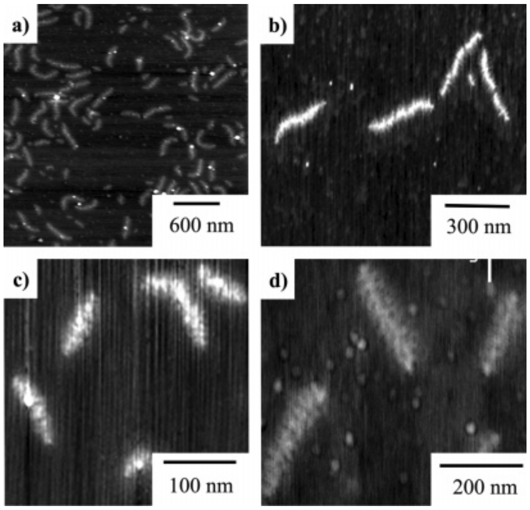


Figure 7. (a, b) SPM images of comb polymers from entry 2 in Table 4. (c, d) SPM images of comb polymers from entry 3 in Table 4.

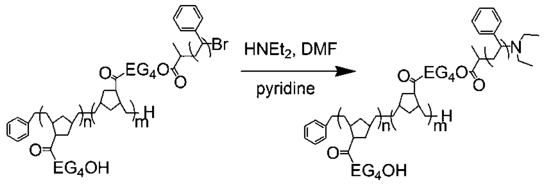


Figure 8. Diethylamine reacted with alkyl bromides at the ends of the polystyrene arms.

These polymers were characterized by light scattering using the Wyatt QELS and Optilab detectors (Table 4). The R_z/R_h ratios indicated that these polymers were shaped as rigid rods rather than spherical polymers. We examined two sets of these polymers by SPM (Figure 7) by casting a dilute solution of polymers on a silicon wafer and allowing the solvent to evaporate. The results of these measurements clearly indicate that these polymers are shaped as rigid rods with occasional kinks along the backbone. The backbone of these polymers had a degree of polymerization of 530; if the backbone is fully extended, its length will be ∼265 nm. The lengths of these polymers agreed well with these predictions. Interestingly, the heights of these polymers were less than 2.0 nm; we attribute this small value to spreading of the polymer on the surface upon evaporation of the solvent.

To graft polylactide to the backbone of polymers with polystyrene arms, we needed to alter the polymerizations slightly. The bromides on the ends of the polystyrene arms had to be removed as repeated attempts to polymerize lactide in their presence failed. Comb polymers with polystyrene arms were reacted with diethylamine, as shown in Figure 8 and described in the Experimental Section.[27]

When we attempted the polymerization of lactide from comb polymers of polystyrene, the comb polymers did not completely dissolve in 1-methoxymethyl ether at concentrations that were successful for previous polymerizations of lactide from backbone polymers. We added more solvent, but this resulted in polymerizations with conversions of less than 10%. The amount of solvent was decreased, and a 10 fold excess of lactide was

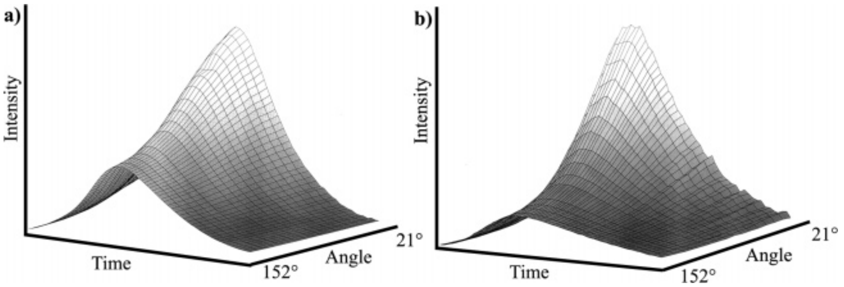


Figure 9. (a) Multiangle laser light scattering from a GPC trace of entry 5 in Table 3 and (b) entry 3 in Table 5 show the dependence of intensity with the scattering angle for these high molecular weight polymers.

added; these polymerizations were stopped when they became solid. The conversions were still low—approximately 10%—but the arms had average molecular weights in the tens of thousands (Table 5).

We predicted the molecular weights of the comb block copolymers from the starting molecular weight of the comb polymer of polystyrene and the ratio of polylactide to polystyrene for the final comb block copolymer. For instance, for entry 4 in Table 5 the starting molecular weight for the comb polymer of polystyrene was 18 000 000 g mol^{-1}. From the ^{1}H NMR of the comb block copolymer we found a mole ratio of polystyrene to polylactide of 1.62. This yielded an average molecular weight for each polylactide arm of 40 400 g mol^{-1} (there were twice as many arms of polystyrene along the backbone as polylactide) and a molecular weight for the comb block copolymer of 36 000 000 g mol^{-1}. It is important to note that the predicted and measured molecular weights for the comb block copolymers were close.

To measure the molecular weights of the comb polymers, we characterized them by GPC equipped with light scattering detectors (Figure 9). In Figure 9a we show an example of light scattering from the GPC trace of entry 5 in Table 3. This polymer was used to synthesize the comb block copolymers in Table 5. This figure shows a strong dependence between intensity and the angle of the detector as expected for polymers with ultrahigh molecular weights, and it shows that the peak was monomodal. In Figure 9b we show the light scattering from the GPC trace of entry 3 in Table 5. This figure shows an even greater dependence on intensity and the angle of the detector as expected for the higher molecular weight of the comb block copolymer as compared to the homopolystyrene comb polymer imaged in Figure 9a. Both traces show that the peaks were monomodal.

These results are interesting as we synthesized ultrahigh molecular weight comb block copolymers. These polymers are some of the highest molecular weight copolymers that have been reported in the literature. In the next section we will describe one application of these polymers.

Self-Assembly of Comb Block Copolymers in the Solid State. Many examples of linear block copolymers—including those composed of polystyrene and polylactide—have been assembled in the solid state by others.[28] These polymers have been assembled into a variety of arrays with domain sizes from several to tens of nanometers. The assembly of ordered arrays from block copolymers with domain sizes greater than 100 nm would be prohibitive because of the required ultrahigh molecular weights of the polymers and the long time periods needed for their assembly.

A few examples of block copolymers that assembled into arrays with domain sizes larger than 100 nm have been reported.[29−31] In most of these examples low molecular weight homopolymers were used to "swell" the domain sizes of arrays of block copolymers. This method was useful but limited as the homopolymers tended to assemble separately from block copolymers and decrease the order of the arrays. In other examples, colloids were used to swell each polymer layer such that the domain sizes were in excess of 100 nm.[30] In these previous examples it was shown that organic diblock polymers can function as photonic materials with visible light if the separation between blocks is greater than 100 nm and the spacing is regular.[29,30,32]

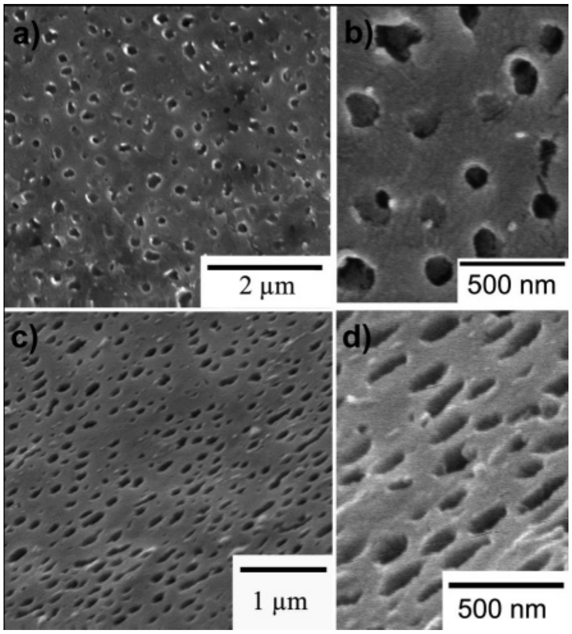


Figure 10. SEM micrographs of entry 4 in Table 5 that was assembled in the solid state and treated with NaOH. These micrographs are (a, b) perpendicular from the surface and (c, d) at an angle from the surface. The open pits were observed on the surface and on sections of the polymer that had been cut to reveal the interior.

Our comb block copolymers are a new architecture of polymer with ultrahigh molecular weights, and we predicted that they would assemble into arrays with domain sizes greater than 100 nm. To test this prediction, we assembled entry 4 from Table 5 in the solid state by dissolving the polymer in CH_2Cl_2 at a concentration of 1.5 mg mL^{-1} and allowing the solvent to slowly evaporate. We thermally annealed the polymer by heating it at 110 °C for 96 h. After assembly, the polylactide was dissolved in aqueous NaOH. The polymer was imaged by SEM, as shown in Figure 10.

From these SEM micrographs we conclude that these polymers assemble into arrays with large domain sizes but with some disorder. The images showed a series of holes in the surface of the samples. To find out whether these holes were present in the rest of the polymer, we cut the polymer slabs and imaged similar holes in the interior of the slabs. As SEM micrographs taken without treating the samples in NaOH did not show the holes throughout the surface, we believe that the holes are due to etched polylactide. Before assembly these polymers were white solids; after their assembly they were blue. In future work we will report the assembly of more ordered arrays and thoroughly characterize the morphology and optical characteristics of these arrays.

Conclusions

This article describes the synthesis, characterization, and assembly of ultrahigh molecular weight block copolymers. To synthesize these polymers, we first demonstrated that block copolymers with degrees of polymerization up to 2000 could be synthesized by ROMP catalyzed by the Grubbs' first-generation catalyst. This result is important as ROMP is an important polymerization technique, and it extends the molecular weight of block copolymers that can be envisioned and synthesized. In addition to their synthesis, we described a simple, general method to hydrogenate these polymers in the same "pot" as the polymerization.

We also demonstrated methods to graft polystyrene and polylactide onto the block copolymers to synthesize comb block copolymers. These polymers were thoroughly characterized by GPC, light scattering, and SPM to reveal their sizes, molecular weights, and, in some cases, their shapes. This work is critical as these are the highest molecular weight comb polymers that have been synthesized. Why does one wish to synthesize these polymers? One exciting application of these polymers is their assembly in the solid state into arrays with domain sizes exceeding 100 nm. This size range is important as these polymers may have applications in photonics and the synthesis of porous three-dimensional arrays. They extend the size range of arrays that can be assembled from linear block copolymers to size ranges that open up new applications in nanofluidics and photonics. We are pursuing some of these applications and will report them in future publications.

Acknowledgment. We thank the University of Iowa, Research Corporation, MPSF Program, Carver Scientific Research Initiative Grants Program, and ACS-PRF for funding.

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MA052012G