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Article

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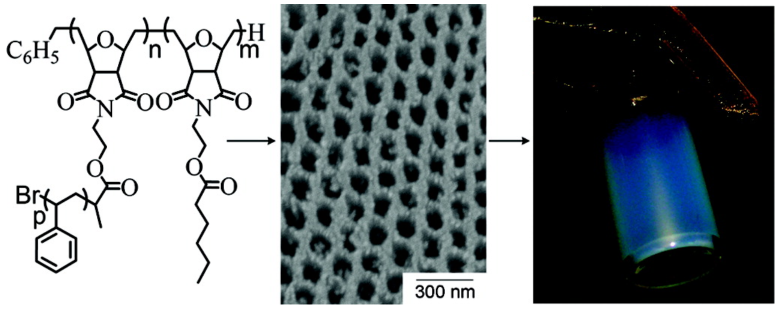

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Synthesis of High Molecular Weight Comb Block Copolymers and Their Assembly into Ordered Morphologies in the Solid State

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Abstract: This Article describes a simple two-step synthesis of comb block copolymers with molecular weights exceeding 1 000 000 g mol^{-1} and their assembly into ordered morphologies in the solid state. This work is exciting because these polymers assembled into morphologies with domain sizes exceeding 100 nm and, in some examples, 200 nm without the use of additives. These materials reflected selected wavelengths of visible light, and these wavelengths could be affected by swelling with methylene chloride vapor. A comparison between the structures of comb block copolymers and linear block copolymers is presented with a discussion of important parameters affecting their assembly in the solid state. This Article will first describe the synthesis of comb block copolymers using ring opening metathesis polymerization and atom transfer radical polymerization and their subsequent characterization. The comb block copolymers, backbone polymers, and polystyrene arms were all characterized independent of each other and had low polydispersities. The comb block copolymers were assembled by dissolving in methylene chloride and allowing the solvent to evaporate. After thermal annealing, the polymers were characterized by scanning electron and optical microscopy. These polymers assembled into spherical, lamellar, and cylindrical arrays with domain sizes from 132 to 258 nm. This work extends the molecular architectures of polymers that can be assembled in the solid state, the molecular weights of block copolymers that were assembled, and the domain sizes that can be realized without the use of additives.

Introduction

The self-assembly of block copolymers into ordered morphologies in the solid state is critically important for materials research as these ordered structures provide access to soft materials patterned in three dimensions with sizes from several to a hundred nanometers that are exciting test beds to study self-assembly and form scaffolds for new opportunities in nanoscience and optics.[1−45] Block copolymers spontaneously assemble into ordered morphologies such as lamellar, hexagonal-packed cylinder, body-centric cubic, close-packed spherical, and others with domain sizes from several to over a hundred

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nanometers on surfaces and in the bulk.[6,8,46−49] These polymers assemble into ordered arrays on this size scale because their blocks are linked through covalent bonds. The different blocks of these polymers cannot phase segregate on a macroscopic scale; rather, they must phase segregate on the size scale of an individual polymer. Thus, these polymers assemble on critical size scales for a variety of applications including pH selective filters, nanoreactors, scaffolds for the synthesis of inorganic materials, optical materials, and patterned surfaces for nanoelectronics.[2,8,16,21,22,27,46,50−55] It is a strength of this method that the morphologies and domain sizes can be controlled though the architecture of the block copolymer.

Despite the decades-long interest in block copolymers, their domain sizes after assembly are still mostly limited to less than 100 nm.[1,2,18,56−60] Some important exceptions to this size scale exist such as the assembly of ultrahigh molecular weight block copolymers (>500 000 g mol^{-1}). These polymers assemble into morphologies with domain sizes exceeding 100 nm, but they remain challenging to synthesize and assemble slowly. These limitations are typically overcome by assembling modest molecular weight linear block copolymers with low molecular weight homopolymers, plasticizers, or colloids to swell one or more blocks and increase the domain size. In another approach to assemble block copolymers into morphologies with domains exceeding 100 nm, Ikkala et al. synthesized polystyrene-*block*-poly(4-vinylpiridinium methanesulphonate) and assembled it in the presence of 3-*n*-pentadecylephenol.[1,2] In this example, 3-*n*-pentadecylephenol hydrogen bonded to the polymer to swell one phase of the morphology and acted as a plasticizer to speed assembly. This material yielded domain sizes exceeding 100 nm and appeared green. An important limitation of these solutions is that the additives used to swell the assembled polymers introduce defects in the final arrays due to macroscopic phase segregation. For instance, homopolymers will segregate from the block copolymers to form regions with defects rich in homopolymers. These defects are unavoidable and limit their applications where precise materials are required. This gap exposes an opportunity to assemble block copolymers without additives to study whether their arrays may be well ordered for precise optical applications and fabrication of patterned soft materials.

This challenge in assembling block copolymers into morphologies with domain sizes exceeding 100 nm is critical because they have exciting applications as optical materials.[57,58,60−64] The alternating bands of materials with different dielectric constants on this size scale forms materials that are optically colored. The reason for this color has been assigned to iridescence or, within parts of the polymer community, the formation of a partial photonic band gap.[2,58,60,64−66] For both descriptions, it is necessary that alternating bands of the block copolymers be on the size scale of approximately one hundred nanometers to cause these materials to appeared colored. Importantly, these materials do not contain dyes and can be fabricated from organic polymers. This field is exciting because assembled block copolymers offer an attractive solution to form optical materials because their structures can be modified in a rational manner to tune the optical properties of their arrays. The potential for these optical applications is one driving force for the field of block copolymers to find new methods to assemble arrays with domain sizes exceeding 100 nm.

In this Article, we will report the synthesis and assembly of high molecular weight comb block copolymers in the solid state with domain sizes exceeding 100 nm without the need for additives (Figure 1). Comb polymers are a relatively new architecture of polymer that consist of a polymeric backbone with regularly and densely spaced arms.[58,63,65,67−84] The dimen-

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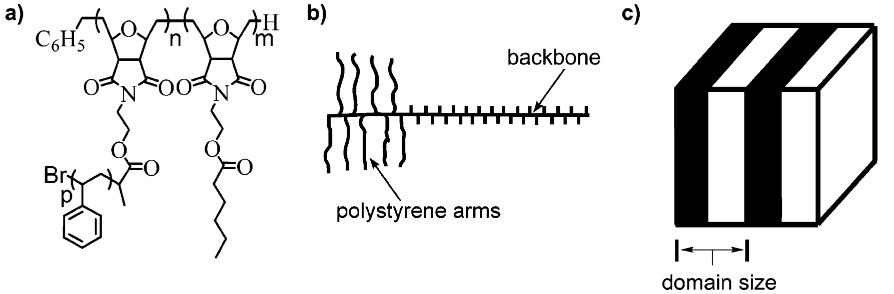

Figure 1. (a) An example of a comb block copolymer that we report in this Article and (b) a schematic of its structure showing long polystyrene arms, backbone, and ester arms along one block of the backbone. (c) An example of a lamellar morphology where the alternating black and white bands correspond to different blocks of the polymer. The domain size is the repeat unit of the morphology.

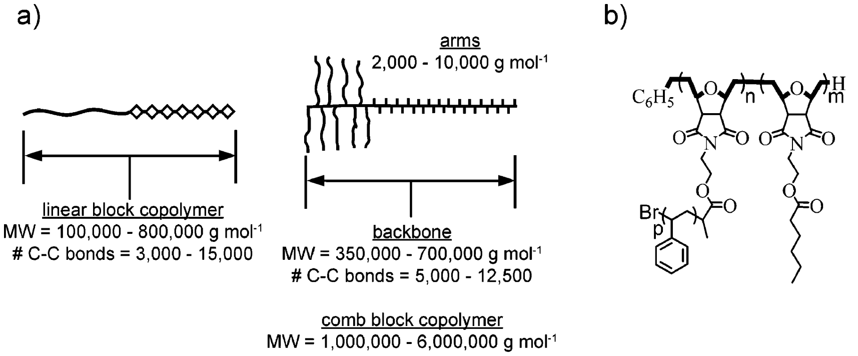

Figure 2. (a) A comparison of the molecular weights and number of carbon−carbon bonds along the backbones of linear block copolymers and comb block copolymers. By these two methods of measurement, the backbone polymers of our comb block copolymers have similar molecular weights and lengths as linear block copolymers. The much higher molecular weights of comb block copolymers as compared to linear block copolymers is due to the number of low molecular weight polystyrene arms. (b) The bonds in bold are the ones we counted to measure the number of carbon−carbon and carbon−oxygen bonds along the backbone of our polymers.

sions and molecular weights of comb polymers can differ remarkably from linear polymers because the arms are also polymers. The architecture of these polymers is critical for their assembly in two ways. First, steric crowding between the polymeric arms may cause the backbone to elongate; consequently, comb polymers may appear as rigid rods depending on the density and size of the arms. This term means that some comb polymers are shaped as rods with occasional bends and kinks along the backbone that vary in number according to the architecture of the polymer. Second, comb polymers have ultrahigh molecular weights; they often exceed 1 000 000 g mol^{-1} and can exceed 10 000 000 g mol^{-1}.

We hypothesized that comb block copolymers would assemble in the solid state into morphologies with domain sizes exceeding 100 nm based on analogy to linear block copolymers. The domain size of linear block copolymers is related to the molecular weight of the polymer: the domain size becomes larger as the molecular weight increases. Two practical limits in the field of linear block polymers that limit the domain sizes are the challenge of synthesizing block copolymers with molecular weights exceeding 500 000 g mol^{-1} and the time required to assemble high molecular weight block copolymers.[6,48,64] As the molecular weight increases, the time required to assemble a linear block copolymer increases due to the time necessary for reptation into ordered arrays. These limits have been overcome to some degree by others who synthesized linear block copolymers with molecular weights up to approximately 800 000 g mol^{-1} and assembled them into ordered arrays without the presence of additives to swell the domain sizes.[64] Still, this work required special polymerization methods and represents an upper limit to what has been reported using this method.

The comb block copolymers that we report in this Article will have much higher molecular weights than linear block copolymers that have been assembled in the solid state, but the molecular weights of the backbone polymer will be more modest (Figure 2). The largest linear block copolymers that have been assembled in the solids state have approximately 3000 to over 15 000 carbon−carbon bonds along the backbone (Figure 2b).[64] This number is an important consideration because it is related to the distance the polymer must reptate in the solid state to move the entire polymer by its length. In contrast, we report comb polymers in this Article with molecular weights exceeding 1 000 000 and up to 6 000 000 g mol^{-1}. The backbones of these comb polymers have molecular weights from 350 000 to 700 000 g mol^{-1} and from 5000 to 12 500 carbon−carbon (or carbon−oxygen) bonds along the backbone. Both the molecular weights and the number of bonds along the backbone are similar for our comb block copolymers and linear block copolymers that have been assembled by others. It is due to the polystyrene arms with molecular weights from 2000 to over 10 000 g/mol that cause the overall molecular weights of our comb polymers to be so large.

Our hypothesis that comb block copolymers possessing much higher molecular weights than linear block copolymers will

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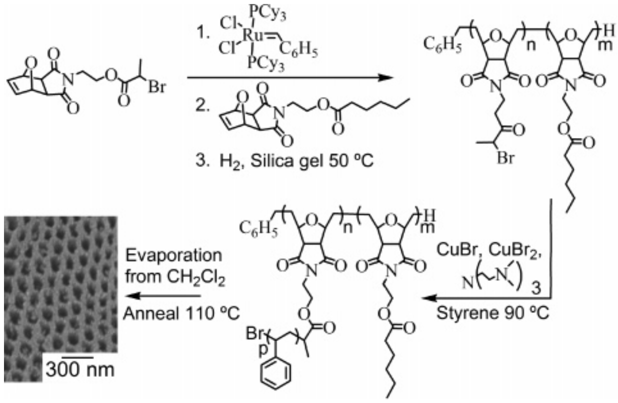

Figure 3. An outline of the synthesis and assembly of comb block copolymers with molecular weights exceeding 1 000 000 g mol^{-1}.

assemble on reasonable time scales is based on the molecular weights and number of carbon−carbon bonds along the backbone polymer. Because our comb polymers have backbones with sizes similar to those of linear block copolymers, they will reptate similar distances to assemble in the solid state. Thus, the time scales for assembly may be favorable for comb block copolymers. Of course, comb polymers possess long arms as compared to linear block copolymers, but others have shown using rheology and theory that comb polymers can reptate in the solid state and provide some basis for understanding how the polymeric arms affect this process.[68,69,71,73,75,76,85]

In this Article, we address one of the beliefs in the field of assembling block copolymers that polymers with molecular weights exceeding 1 000 000 g mol^{-1} will assemble only on long time scales. This belief is very reasonable for linear block copolymers, but we believe that it fails for newer architectures of comb block copolymers with backbones decorated with low molecular weight arms. We will describe the synthesis of comb block copolymers and how they assemble into ordered morphologies in the solid state with the largest domain sizes that have been reported.

Results and Discussion

Our method to synthesize comb block copolymers is shown in Figure 3. This work is based on our prior results to grow comb polymers using both ring opening metathesis polymerization (ROMP) catalyzed by the Grubbs' first generation catalyst and Cu-mediated atom transfer radical polymerizations (ATRP).[78,86] These two polymerization methods have been combined by a variety of scientists, and their combination increases the complexity of polymer architectures and monomers that can be synthesized.[87−99] Our prior method to synthesis comb block copolymers required four steps; in this Article, we will build on this method to synthesize comb block copolymers in two simple steps.

Synthesis of Backbone Polymers by ROMP. We choose to synthesize comb block copolymers by first block copolymerizing two oxonorbornene imides with the Grubbs' first generation catalyst. These monomers were chosen for the backbone polymer because their polymerizations can be described as "living" and they possess fast rates of reaction with Grubbs' first generation catalyst, which enable high degrees of polymerization.[78,100,101] The fast polymerization rates are critical because they prevent broadening of the polydispersity by allowing the polymerization to be complete within the lifetime of the catalyst and before cross metathesis becomes a noticeable problem.

We choose to use ROMP for the synthesis of the backbone based on our prior work where we showed several critical features of this polymerization relevant to this Article.[78] First, we showed that this catalyst could be used to synthesize homo or block polymers with degrees of polymerization over 2000 in less than 5 h. This result is significant because it provides a route to synthesize polymers with large molecular weights displaying diverse functional groups. On the basis of our prior work, we synthesized the block backbone polymers shown in Table 1 with degrees of polymerization from 1100 to 2450. Second, we showed that the backbone could be hydrogenated in the same pot as the polymerization. Hydrogenation was accomplished by adding Si gel, H_2, and excess Grubbs' catalyst after polymerization and heating to 50 °C for 12 h. We believe that the Grubbs' catalysts decompose on Si gel to form a metal surface that acts as a hydrogenation catalyst.[78,99,102] Thus, in one reaction vessel we were able to synthesize high molecular weight linear block copolymers via ROMP that did not possess olefins along the backbone. Third, we showed that monomers displaying ATRP initiators could be polymerized by Grubbs' catalyst. This functional group did not interfere with the polymerization or the hydrogenation.

We fully characterized the backbone polymers described in Table 1 using NMR spectroscopy, size exclusion chromatography, and light scattering. After polymerization and hydrogenation, ^{1}H NMR spectroscopy was used to verify the composition of the polymer and that the backbone was completely hydrogenated. In Figure 4, we show a ^{1}H NMR spectrum of a block copolymer synthesized by ROMP and hydrogenated to show that no olefinic protons were present. Size exclusion chromatography coupled with refractive index and light scattering detectors provided the true molecular weights of these polymers. The predicted and measured molecular weights of the backbone polymers matched each other well, and the polydispersities were low.

Synthesis of Polystyrene Arms by ATRP and Characterization of Comb Block Copolymers. In the next step of our

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Table 1. Characterization of Comb Block Copolymers As Synthesized in Figure 3

		backbone polymer			comb block copolymer					polystyrene arms	
entry	M_1/C:M_2/C[a]	predicted[b] $M_n \times 10^{-3}$ (g mol^{-1})	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	predicted[c] $M_n \times 10^{-3}$ (g mol^{-1})	measured $M_n \times 10^{-3}$ (g mol^{-1})	PDI	R_z[d] (nm)	R_h[e] (nm)	measured[f] M_n (g mol^{-1})	PDI
1	150:1016	366	346	1.03	996	730	1.25	160	88	4200	1.03
2	200:1016	383	370	1.04	1263	1000	1.23	116	61	4400	1.05
3	250:1016	401	390	1.04	1451	1150	1.22	73	54	4200	1.02
4	100:1016	349	300	1.03	1349	1500	1.28	40	31	10 000	1.03
5	100:1524	506	500	1.04	1126	980	1.32	74	73	6200	1.02
6	150:1524	523	496	1.02	1153	1050	1.44	52	44	4200	1.06
7	100:2033	663	730	1.04	1103	860	1.43	221	122	4400	1.02
8	200:2033	698	725	1.16	1418	1040	1.17	46	44	3600	1.27
9	250:2033	715	750	1.20	1665	1260	1.15	47	35	3800	1.04
10	300:2033	732	775	1.20	1992	1760	1.14	40	31	4200	1.04
11	450:2033	784	791	1.06	2584	2030	1.24	44	35	4000	1.08
12	500:508	330	385	1.07	5330	6400	1.43	70	61	10 000	1.01

[a] The ratio of the first monomer, M_1, to catalyst and the ratio of the second monomer, M_2, to catalyst. [b] The predicted molecular weight from the composition of the backbone. [c] The predicted molecular weight of the comb block copolymer from the composition of the backbone and the measured molecular weights of the polystyrene arms after cleavage from the backbone. [d] The root-mean-square radius of the comb block copolymer. [e] The hydrodynamic radius of the comb block copolymer. [f] The polystyrene arms were cleaved from the backbone according to Figure 5, and their molecular weights were measured by size exclusion chromatography.

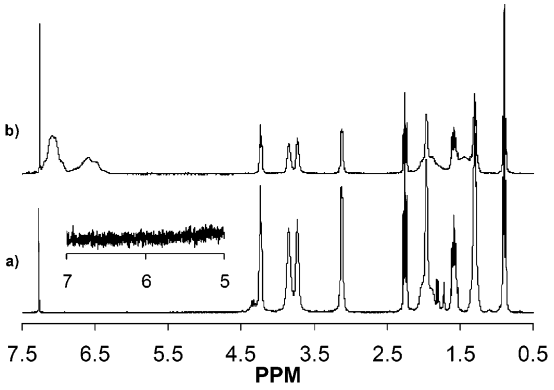

Figure 4. ^{1}H NMR analysis of comb block copolymer of entry 8 in Table 1. (a) We show the backbone copolymer after hydrogenation with the olefinic region blown up to show the absence of any olefinic peaks. (b) After the synthesis of polystyrene arms, the ^{1}H NMR spectrum shows the presence of polystyrene on the comb block copolymer.

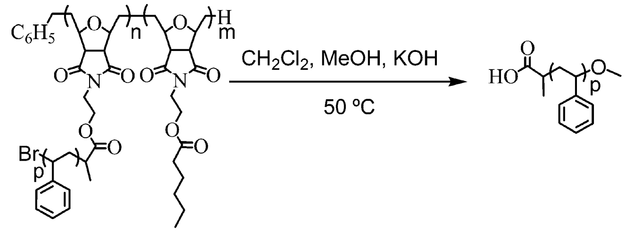

Figure 5. The polystyrene arms were cleaved from the backbone under basic conditions.

synthesis, we grafted polystyrene arms from the backbone polymers using ATRP. These arms were grown using Cu(I)/Cu(II) catalyzed ATRP at very low dilutions to ensure that the comb polymers did not cross-link. A high concentration of radicals in solution will lead to intercomb polymer cross-linking; thus, to synthesize a soluble polymer we kept the conversions of styrene to less than 5%. This method worked well and yielded a comb polymer that was soluble and characterized by ^{1}H NMR spectroscopy (Figure 4) and SEC with refractive index and light scattering detectors.

To fully characterize the comb polymers, we cleaved their polystyrene arms from the backbones by reaction with KOH in MeOH/H_2O (Figure 5). The arms were attached to the backbone through ester bonds that were readily cleaved under basic conditions. These polymers were then isolated and characterized by SEC to yield the molecular weights and polydispersities of the arms. We carried out this analysis because the ATRP of styrene was run at low conversions and high dilutions, conditions that are not typically used for ATRP.[103−105] Although uncommon, these conditions were successful as they yielded polystyrene arms with low polydispersities ($<$1.10). From the molecular weights of the arms and composition of the backbone, we calculated the molecular weights of the comb polymers. The calculated molecular weights closely matched the measured molecular weights of these polymers and provided further proof of their compositions.

Because we used size exclusion chromatography with refractive index and light scattering detectors, we were able to measure the absolute molecular weights of the comb polymers and their polydispersities. In Figure 6, we show a light scattering micrograph of the comb polymer in entry 9 in Table 1 as the polymer exited the size exclusion columns. This micrograph shows curvature as a function of the scattering angle, which provides direct visual evidence of the high molecular weights of these comb polymers.

The size exclusion chromatographs of a backbone polymer and a comb polymer show conversion of one to the other (Figure 6). Although the separation between the high molecular weight backbone polymer from the comb polymer was not complete, the SEC traces in Figure 6 indicate that all of the backbone polymer reacted. Furthermore, the SEC trace of the comb polymer demonstrates that it was a narrow peak.

The combination of our analysis presented here and our previous work demonstrates that the comb polymers we synthesized in Table 1 had high molecular weights and well-defined compositions. Our method is important because we synthesized these comb polymers in two steps and were able to characterize them via a variety of techniques. Their synthesis was straightforward and amenable to varying the composition

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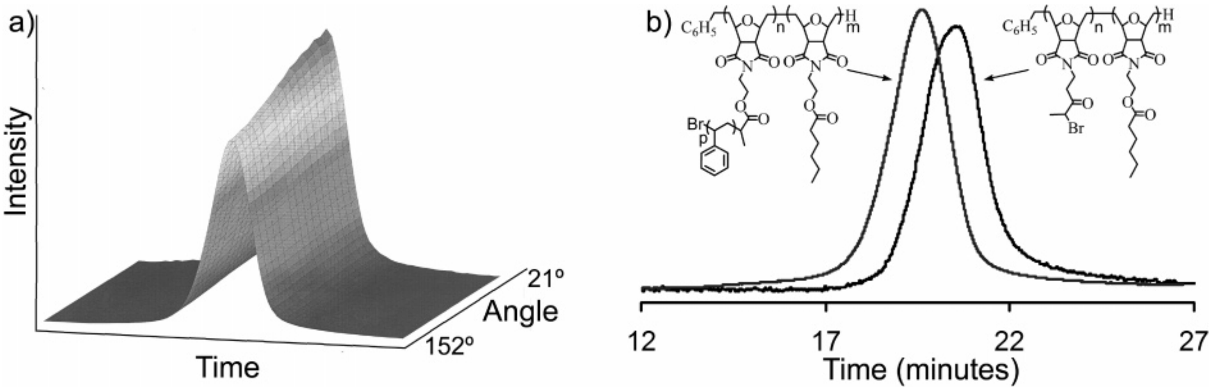

Figure 6. (a) The light scattering micrograph of entry 9 in Table 1 demonstrates that the comb polymer has an ultrahigh molecular weight. (b) SEC trace of a backbone block copolymer and its conversion to a comb block copolymer.

of the backbone and the molecular weights of the arms independent of one another. We used this method to synthesize a wide range of comb block copolymers as shown in Table 1.

Assembly of Comb Block Copolymers into Ordered Morphologies in the Solid State. The next step in this project was to study the assembly of these polymers into ordered arrays in the solid state. These polymers are new and have not been assembled before. Although we predicted that they would assemble into ordered morphologies with large domain sizes by analogy to linear block copolymers, the time and conditions necessary for their assembly were unknown.

To assemble these polymers, we first made dilute solutions in methylene chloride at concentrations from 5 to 100 mg mL^{-1}. These solutions were added to glass vials with small shards of Si wafers on the bottom to provide a surface on which they could be imaged. The solvent was allowed to evaporate at room temperature, and then the polymer film was annealed at 110 °C for 24 h. The assembly did not appear to be critically sensitive to the concentration of the polymer solution, and the thickness of the polymer film was limited by the solubility of the polymer in the solution. It was notable that the assembly was relatively straightforward and similar to that of linear block copolymers.

Characterization of Assembled Polymer Films. Polymer films were characterized by two techniques: scanning electron microscopy (SEM) and UV−vis spectroscopy. We first studied the types of morphologies that were present by SEM rather than TEM as we expected that the domain sizes would exceed 100 nm. The interior of the polymer film was viewed by either cutting with a microtome, freezing the film with liquid N_2 and fracturing it, or cutting it with a razor blade by hand. We stained each sample by exposure to RuO_4 vapor after cutting and prior to imaging by SEM.

These polymers assembled into lamellar, spherical, and cylindrical morphologies. To support these claims, we show SEM micrographs of each polymer. In Figure 7, we show SEM micrographs of entry 7 in Table 1 that clearly show it assembled into a lamellar morphology. The lamellar morphology was locally ordered but globally disordered. The SEM micrographs in Figure 8 show that entries 6 and 9 from Table 1 assembled into cylindrical morphologies. In particular, the micrographs in Figure 8a and b show an edge of the material revealing the long and short axes of the cylinders. Finally, in Figure 9, we show SEM micrographs of the spherical morphology for entries 11, 12, and 2 from Table 1. The spherical arrays appeared mostly disordered with little long-range order.

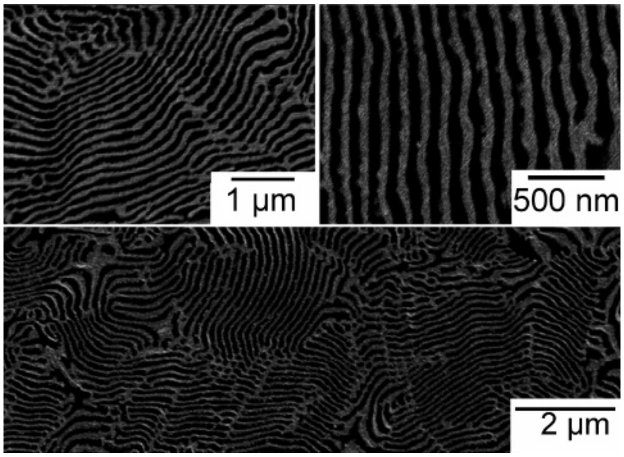

Figure 7. We show several SEM micrographs of entry 7 in Table 1 that show it assembled in the solid state into a lamellar morphology.

It is clear from these images that some areas are well ordered and others are poorly ordered. We showed numerous SEM micrographs to support our characterization of the arrays and to provide some evidence for the degree of long-range order. Although not well ordered over large distances, it is very interesting that these polymers assembled in the solid state under our conditions.

We measured the domain sizes of these morphologies from these and other SEM micrographs. Each domain size was the result of a minimum of 25 measurements, and we report the values and their standard deviations in Table 2. From these data, it is clear that these polymers assembled into morphologies with large domain sizes; in fact, these are the largest domain sizes observed for block copolymers assembled without additives. The domain sizes are clearly related to the total composition of each block rather than the molecular weight of individual polystyrene arms.

Our preliminary investigation of these morphologies indicates that the domain size may be predicted and tuned to the desired size. For instance, entries 6 and 9 both assembled into cylindrical arrays with domain sizes of 147 and 258 nm, respectively. These polymers had polystyrene arms of nearly the same molecular weights (4200 g mol^{-1} versus 3800 g mol^{-1}), but they differed in their backbones and total molecular weights. Entry 6 was the smaller comb block copolymer; it had a total molecular weight of 1 050 000 g mol^{-1}, a backbone with a degree of

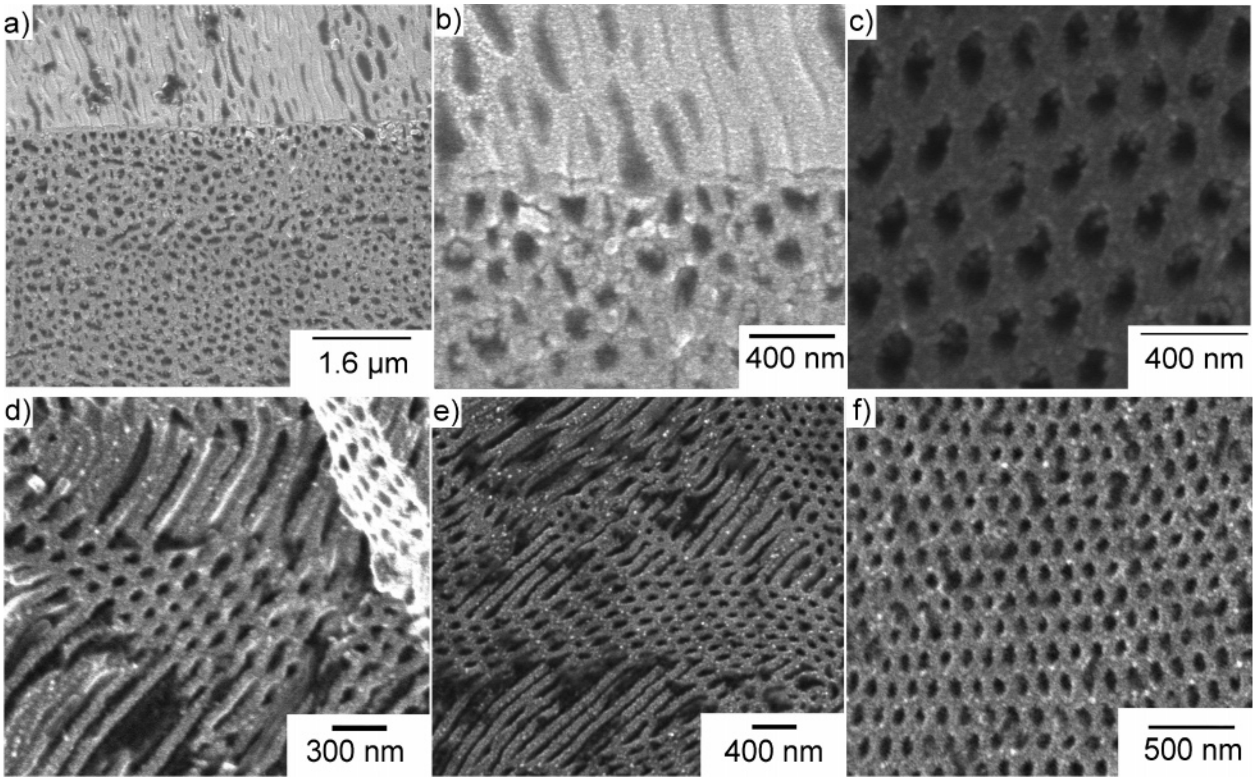

Figure 8. In (a), (b), and (c), we show SEM micrographs of entry 9 in Table 1 that show the polymers assembled into the cylindrical morphology. In (a) and (b), we show the edge of a polymer film that clearly shows the cylinders aligned in one direction. In (d), (e), and (f), we show SEM micrographs of entry 6 in Table 1 that show the polymers assembled into a well-ordered cylindrical morphology. Micrographs in (d) and (e) show both the long and the short axes of the cylinders; these images were shown to demonstrate that the morphologies were cylindrical. The micrograph in (f) shows an area with a high degree of order.

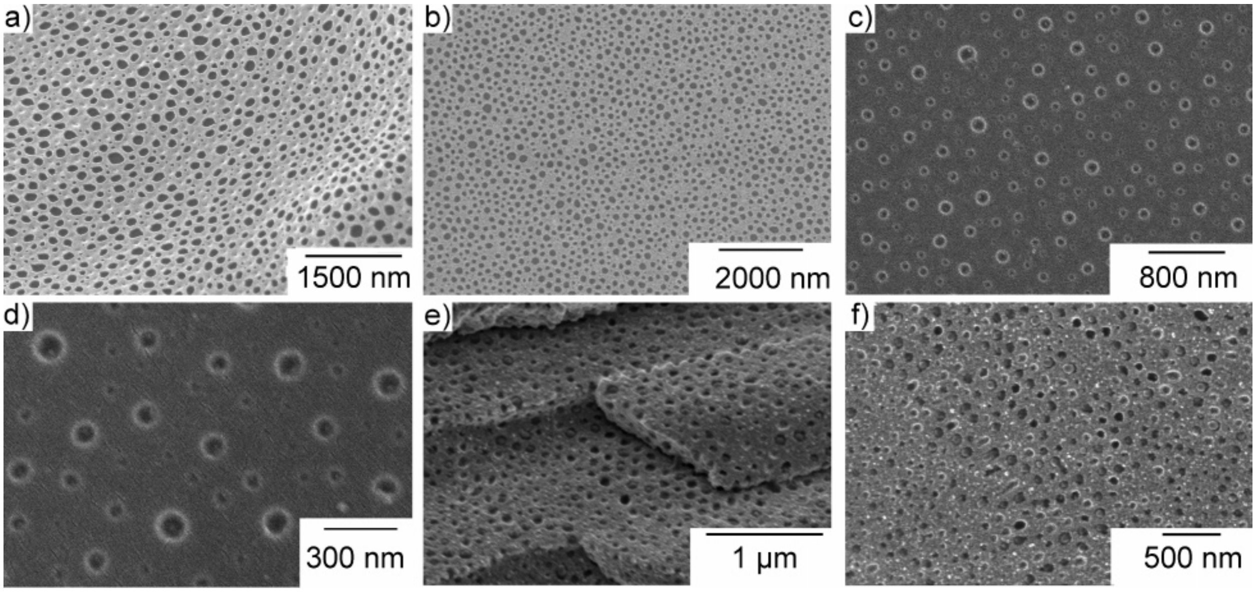

Figure 9. We show SEM micrographs of the surface or interior to show that entries 11 (a and b), 12 (c and d), and 2 (e and f) from Table 1 assembled into the spherical morphology.

polymerization of 1674, and 150 polystyrene arms per backbone polymer. Entry 9 was the larger polymer with a total molecular weight of 1 260 000 g mol^{-1}, a backbone with a degree of polymerization of 2283, and 250 polystyrene arms per backbone polymer. The domain size of entry 9 was clearly bigger than the domain size of entry 6 as predicted from their compositions. Similar analysis of the spherical morphologies of entries 2 and 11 showed the same dependence of domain size on composition. More work is necessary to fully understand how the molecular weight of the arms, the molecular weight of the backbone, the number of polystyrene arms along the backbone, and the overall molecular weight affect the domain sizes of these polymers.

We also examined a partial phase diagram of comb block copolymers to provide a basis for understanding their morphologies (Figure 10). Phase diagrams of linear block copolymers are based on their mole percent composition of block copolymer

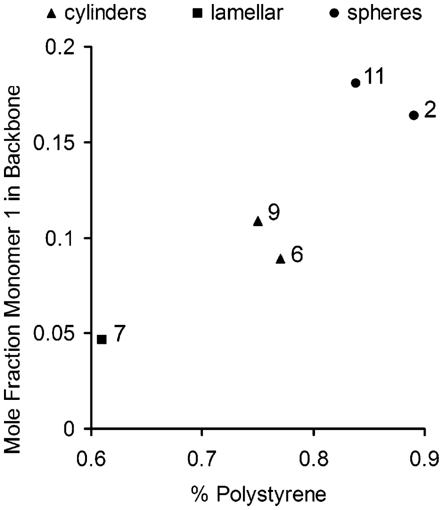

Figure 10. Preliminary phase diagram of assembled comb block copolymers. Here, the *y*-axis is changed from a traditional phase diagram because the comb polymers are in the high segregation limit, and this presentation emphasizes the importance of examining the composition of the backbone polymer. Because these are new polymers with several different parameters that may affect their assembly, several phase diagrams with different axes are possible.

Table 2. The Domain Sizes of Assembled Comb Block Copolymers

entry	assembly	M_1:M_2	polystyrene (mol %)	domain size (nm)
2	spheres	200:1016	89	132 ± 7
6	cylinders	150:1524	77	147 ± 18
7	lamellar	100:2033	61	145 ± 26
9	cylinders	250:2033	75	258 ± 27
11	spheres	450:2033	84	226 ± 13

and a segregation factor, χN, where χ is the Flory-interaction parameter between the two blocks and N is the degree of polymerization. To accommodate our specific asymmetric comb block copolymer architecture, we changed our preliminary phase diagram to look at two important parameters. On the *y*-axis, we plotted the mole fraction of our ATRP functionalized monomer in the backbone of the comb polymer. On the *x*-axis, we plotted the mole percent of polystyrene of the comb block copolymer. We choose to use a different *y*-axis than that found for linear block copolymers because our comb polymers have such high molecular weights that we expect they will be in the high segregation limit. In addition, the composition of the backbone is an important parameter in our polymers, and it may affect the morphologies even if it is not a critical variable for our current set of polymers.

The phase diagram of our comb block copolymers parallels what is seen for linear block copolymers when viewed at the high segregation limit and suggests that the overall composition of comb block copolymers determines their morphologies. This result is not unexpected as there are numerous similarities between our comb block copolymers and linear block copolymers. The phase diagram justifies our initial choice to synthesize backbone polymers with low amounts of the monomer that initiates the growth of polystyrene arms. We kept that block small so after the growth of polystyrene arms we could access a wide range of compositions including those with compositions of 60% to over 90% polystyrene.

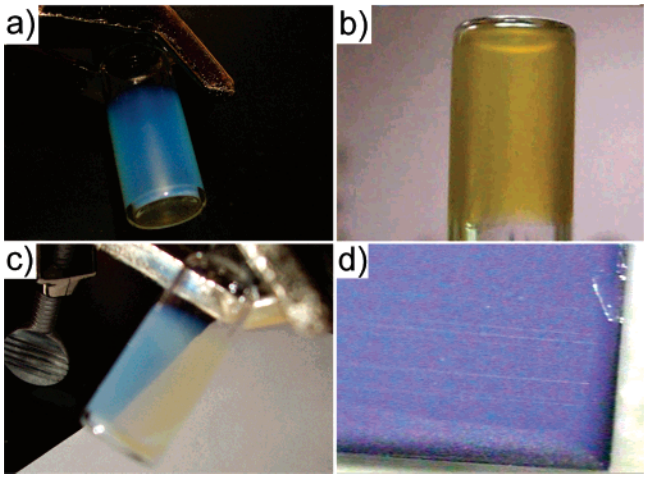

Figure 11. (a) An optical micrograph of entry 11 in Table 1 taken against black background to show blue light reflected from the polymer coating a glass vial. (b) An optical micrograph of the same polymer showing that it appears yellow when viewed through transmitted light. (c) We show an optical micrograph that simultaneously shows reflected (blue) and transmitted (yellow) light. (d) An optical micrograph of the polymer film assembled on a silica wafer, which blocks the transmission of any light through the film.

Optical Properties of Morphologies of Comb Block Copolymers in the Solid State. Because of the large domain sizes and the ordered arrangement of blocks with different indexes of refraction, these polymers were colored in the visible spectrum of light (Figure 11). The final step in our synthesis of these polymers is the growth of the polystyrene arms by Cu-mediated ATRP. Because residual Cu would color these samples, the polymers are precipitated into methanol until they are white. These white polymers are then dissolved in methylene chloride, and the solvent is allowed to evaporate. When nearly all of the methylene chloride evaporated, we observed different colors including red and green due to swollen phases of the assemblies. After complete evaporation of solvent, most examples of our polymers were colored blue.

In Figure 11, we show examples of our polymers to demonstrate that they are colored blue by reflected light and yellow when viewed with light transmitted through the polymer sample. This difference in color is consistent because blue is the complementary color of yellow such that when light passes through the polymer film and blue light is selectively reflected, the light transmitted through the film should appear yellow.

We characterized these films by absorbance UV−vis spectroscopy so that the peak we observed is the maximum of the light that was reflected by the spectrometer (Figure 12). The polymers all appeared blue; in Figure 12 we show entry 11 from Table 1 that had a peak absorbance at 385 nm. During the assembly of these polymers, we observed different colors for the arrays when nearly all of the methylene chloride had evaporated. To access these colors and to demonstrate that the optical properties could be controlled, we exposed this polymer to methylene chloride vapor after the assembly was complete and it had been thermally annealed. We observed a green color and characterized it by UV−vis spectroscopy to have a peak at 445 nm. This red shift in the spectrum is consistent with the morphology being swelled by methylene chloride to increase the domain size.

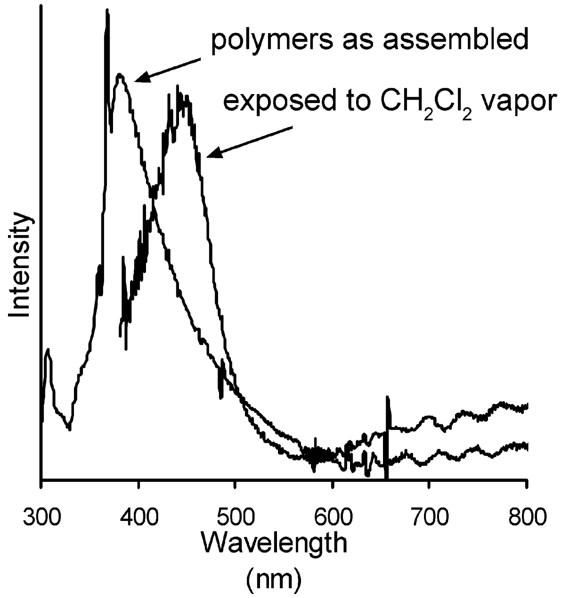

Figure 12. UV−vis absorption spectra of entry 11. The λ_{max} of the assembled polymer film is 385 nm, which shifts to 445 nm when exposed to CH_2Cl_2. The spike at 368 nm in the polymers as assembled spectrum is due to the instrument and not our polymers.

Summary and Conclusions

In this Article, we reported the simple two-step synthesis of high molecular weight comb block copolymers using ROMP and ATRP. The comb block copolymers, their backbones, and the arms were well characterized by light scattering and size exclusion chromatography to yield their true molecular weights. This method was robust, and we synthesized a range of comb block copolymers with molecular weights up to 6 000 000 g mol^{-1}.

The synthesis of these comb block copolymers is interesting, but their assembly in the solid state into ordered arrays is remarkable. These polymers yielded morphologies with domain sizes exceeding up to 258 nm, which is nearly twice as large as domain sizes from the largest linear block copolymers without additives. This work is not an upper limit to what is possible; rather it is a beginning of an effort to fully understand and study how this new architecture of polymers assembles in the solid state. Toward this end, we constructed a simple, preliminary phase diagram of these polymers to understand their morphologies. More work is necessary to fully explore the phase diagram and understand how varying the molecular weight of the backbone, the size of each block, and the molecular weights of the arms affects the morphologies and their domain sizes.

The importance of this work is in the assembly and properties of these polymers. We showed that high molecular weight comb block copolymers could assemble in the solid state into morphologies similar to those assembled from linear block copolymers. Certainly, the study of morphologies from the assembly of comb block copolymers will benefit from the large background of work on linear and lightly branched polymers. Our comb block copolymers provide access to materials patterned in three dimensions with domain sizes exceeding 200 nm. This result is interesting because of the challenges of fabricating complex three-dimensional materials on this size scale. Our method should be tunable based on the architecture of comb block copolymers to yield a variety of arrays with different domain sizes. The patterning of soft materials on this size scale is very interesting, yet is still a challenge. These polymers can act as optical materials by their selective reflection of visible light. Importantly, these materials are responsive to external stimuli; the color changed upon exposure to methylene chloride. In future work, we will fully explore the phase diagrams and optical properties of these polymers to investigate their limits and important parameters affecting assembly.

Experimental Section

Materials. 2-Bromopropionyl bromide, pyridine, styrene, copper(I) bromide, copper(II) bromide, benzylidene-bis(tricyclohexylphosphine)dichlororuthenium, and ruthenium tetroxide were purchased from Acros or Aldrich at their highest purity. We synthesized *N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethyltriethylenetetraamine and the pure exo isomer of *N*-(2-hydroxyethyl)-3,6-epoxy-1,2,3,6-tetrahydrophthalimide following literature procedures.[75] The GPC solvent was HPLC grade chloroform purchased from Acros Organics, and it was filtered through a glass frit before use. All other solvents were reagent grade and purchased from Acros Organics. Methylene chloride used for ROMP was degassed by freeze−pump−thawing three times before being taken into the glove box, poured over aluminum oxide, and stored.

Characterization. ^{1}H NMR and ^{13}C NMR were performed on a Bruker DPX 300 using $CDCl_3$ as the solvent and internal standard. Size exclusion chromatography (SEC) was performed using $CHCl_3$ as the mobile phase (1 mL min^{-1}) at 35 °C. A Waters 515 HPLC pump was used. Two Waters columns (styragel HMW7 & HMW7 or HR4 and HR5E) 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. Polymer films were imaged using the Hitachi S-4800 ultrahigh-resolution field emission scanning electron microscope at an acceleration voltage of 1 kV.

Monomer (M_1). *N*-(2-Hydroxyethyl)-3,6-epoxy-1,2,3,6-tetrahydrophthalimide (50 g, 0.239 mol) and pyridine (24.8 g, 0.31 mol) were added to 350 mL of THF and cooled to 0 °C before 2-bromopropionyl bromide (67 g, 0.31 mol) was added. The reaction was warmed to 25 °C and stirred for 6 h. The solvent was evaporated and the reaction was diluted with 300 mL of CH_2Cl_2, and both an aqueous and a basic workup were performed to remove impurities. The organic phase was dried over $MgSO_4$ and evaporated to give a yellow solid. The solid was recrystallized from methanol five times to yield colorless crystals. ^{1}H NMR ($CDCl_3$): δ 1.80 (d, 3H, $J = 6.9$ Hz), 2.89 (s, 2H), 3.78−3.82 (m, 2H), 4.29−4.37 (m, 3H), 5.27 (s, 2H), 6.53 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 21.42, 37.46, 39.82, 47.39, 61.93, 80.81, 136.46, 169.87, 175.85. HRMS calcd for $C_{13}H_{14}BrNO_5$: 343.0055. Found: 343.0035.

Monomer (M_2). *N*-(2-Hydroxyethyl)-3,6-epoxy-1,2,3,6-tetrahydrophthalimide (15.2 g, 73 mmol) and hexanoic anhydride (31.1 g, 145 mmol) were dissolved in 150 mL of CH_2Cl_2 and stirred for 10 min. Pyridine (11.5 g, 145 mmol) was added, and the reaction was stirred at 25 °C for 12 h. The reaction was diluted with 100 mL of CH_2Cl_2. The reaction was extracted with 3 × 100 mL of acidic water adjusting the final pH to 2, followed by a 3 × 100 mL of basic water adjusting the final pH to 10. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The solid was recrystallized from methanol five times to yield colorless crystals. ^{1}H NMR ($CDCl_3$): δ 0.86 (t, 3H, $J = 6.6$ Hz), 1.25−1.32 (m, 4H), 1.54−1.61 (m, 2H), 2.26 (t, 2H, $J = 7.5$ Hz), 2.87 (s, 2H), 3.75 (t, 2H, $J = 5.4$ Hz), 4.22 (t, 2H, $J = 5.4$ Hz), 5.27 (s, 2H), 6.52 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 13.88, 22.28, 24.29, 31.21, 33.94, 37.90, 47.42, 60.37, 80.86, 136.51, 173.54, 175.94. HRMS calcd for $C_{16}H_{21}NO_5$: 307.142. Found: 307.1415.

Synthesis of Polymer Backbone by ROMP. M_1 (248 mg, 0.72 mmol) was dissolved in 1.8 mL of CH_2Cl_2. Grubbs' first generation catalyst (77.3 mg, 94 μmol) was dissolved in 7.82 mL of CH_2Cl_2. 0.4

mL of the Grubbs' catalyst (3.95 mg, 4.8 μmol) solution was added to M_1 and allowed to stir for 10 min at 25 °C. M_2 (1.5 g, 4.8 mmol) was dissolved in 8.0 mL of CH_2Cl_2 and added to the polymerization. The reaction was stirred for an additional 60 min. 2 mL of the Grubbs' catalyst (20 mg, 24 μmol) solution and 300 mg of Si gel were added. The reaction was placed inside a Parr reactor, pressurized to 1000 psi H_2, and heated to 50 °C for 12 h. The reaction was then cooled, diluted with 10 mL of CH_2Cl_2, filtered through Si gel, and precipitated into methanol to yield a white solid. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J = 6.6$ Hz), 1.26−1.31 (m, 4.4H), 1.54−1.63 (m, 2.2H), 1.80 (d, 0.5H, $J = 7.2$ Hz), 1.90−2.05 (m, 4.7H), 2.25 (t, 2H, $J = 7.8$ Hz), 3.10−3.15 (m, 2.3H), 3.6−3.9 (m, 4.8H), 4.22−4.35 (m, 2.7H). GPC: $M_n = 346\,000$ g mol^{-1}, PDI = 1.03.

Grafting of Polystyrene Arms from Backbone. CuBr (36.9 mg, 0.3 mmol) and $CuBr_2$ (22.9 mg, 0.1 mmol) along with a stir bar were added to a Schlenk flask and placed under N_2. Styrene (103.1 g, 0.99 mol) was poured over aluminum oxide to remove inhibitor and added to the Schlenk flask. *N*,*N*,*N*′,*N*′,*N*″,*N*″-Hexamethyltriethylenetetraamine (91.3 mg, 0.4 mmol) was added, and the reaction was degassed by three freeze−pump−thaw cycles. The block copolymer backbone from entry 1 in Table 1 (0.626 g, 1.7 μmol) was dissolved in 5 mL of acetone and added to the flask. The reaction vessel was then placed in a 90 °C oil bath for 30 min, cooled in an ice bath for 30 min, and precipitated into methanol. The polymer was redissolved in minimal CH_2Cl_2 and precipitated into methanol to yield a pristine white polymeric powder. GPC: $M_n = 730\,000$ g mol^{-1}, PDI = 1.25.

Cleavage of Polystyrene Arms from Backbone. We followed the same procedure for all polymers and will report one representative example here. The comb polymer (0.2 g of entry 1 of Table 1) was dissolved in 40 mL of CH_2Cl_2. KOH (1 g, 18 mmol) was dissolved in 15 mL of methanol, added to the polymer solution, and heated at 60 °C for 24 h. The polymer was then precipitated into methanol. GPC: $M_n = 4200$ g mol^{-1}, PDI = 1.03.

Self-Assembly and Characterization of Comb Block Copolymer Films. Entry 2 of Table 1 was dissolved in CH_2Cl_2 at a concentration of 65 mg mL^{-1}. The solution was slowly evaporated at room temperature followed by annealing for 24 h at 110 °C. The polymer film was then partitioned by removing the surface of the film with a microtome. The film was preferentially stained with RuO_4 vapor for 15 min before imaging on a Hitachi S-4800 ultrahigh-resolution field emission scanning electron microscope with an accelerating voltage of 1 kV.

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