THREE-DIMENSIONAL SELF-ASSEMBLY OF BRUSH BLOCK COPOLYMERS TO PHOTONIC CRYSTALS

Thesis by

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In Partial Fulfillment of the Requirements
For the Degree of
Bachelor of Science in Chemical Engineering

California Institute of Technology
Pasadena, California
2013

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Acknowledgments

My Caltech experience has been filled with highs and lows but one constant throughout has been incredible people that have supported me.

I would like to first acknowledge my research advisor Professor Bob Grubbs. He has given a chemical engineer with almost no synthetic experience the incredible opportunity to explore chemistry. His guidance on this work has been invaluable. In addition, his stories about his pursuits inside and outside the laboratory have granted me perspective as I go forward with my career. His words have helped to transform me into a much more independent researcher.

It would have been impossible for me to have completed this work without the help of my graduate student advisor, Benjamin Sveinbjörnsson. He has allowed me to take over his hood for the past year and has taught me almost everything I know about polymer synthesis. On top of that, his guidance has helped to push me towards self-sufficiency, while still researching efficiently. I have truly enjoyed working with him and I know that he is on a path to a successful career. The rest of the Grubbs group has been incredible at teaching me laboratory skills as well as just being fantastic people to be around. The upbeat spirit of the second floor of Church has made long hours extremely enjoyable.

Outside of the Caltech community, I must thank Bradley D. Olsen for his mentoring in my previous research experiences at MIT. He took someone who had no idea how to use a pippette and taught her how to conduct experiments thoughtfully and properly. I know that my excitement to learn about polymers and self-assembly stems from those summers. I must also thank the entire Olsen group for their support year after year, even after I was no longer conducting research in the group. The guidance, especially from Matthew Glassman, Mitchell

Wang, and Christopher Lam, has helped me to decide on a direction for life after Caltech and to enjoy my time here even more.

Obviously, my parents' love and support through my entire journey through Caltech has been invaluable. From paying my tuition to being on the other end of the phone whenever I needed to talk, my mom and dad have gone light-years beyond their duties as parents. I look forward to being closer to home and seeing them more often in the coming years. My friends at Caltech have helped me tremendously to become the person I am today. I came to Caltech naïve and excited; I leave much more mature and focused and I know that I am a better person through this process. These changes are largely due to the relationships and friendships I made while a student here. I do not think there are any words to adequately express the gratitude to my parents and friends as those who have shaped my life so well. Thank you for everything.

Abstract

The development of Ring Opening Metathesis Polymerization has allowed the world of block copolymers to expand into brush block copolymers. Brush block copolymers consist of a polymer backbone with polymeric side chains, forcing the backbone to hold a stretched conformation and giving it a worm-like shape. These brush block copolymers have a number of advantages over tradition block copolymers, including faster self-assembly behavior, larger domain sizes, and much less entanglement. This makes them an ideal candidate in the development of a bottom-up approach to forming photonic crystals. Photonic crystals are periodic nanostructures that transmit and reflect only certain wavelengths of light, forming a band gap. These are used in a number of coatings and other optical uses. One and two dimensional photonic crystals are commercially available, though are often expensive and difficult to manufacture. Previous work has focused on the creation of one dimensional photonic crystals from brush block copolymers. In this thesis, I will focus on the synthesis and characterization of asymmetric brush block copolymers for self-assembly into two and three dimensional photonic crystals. Three series of brush block copolymers were made and characterized by Gel Permeation Chromatography and Nuclear Magnetic Resonance spectroscopy. They were then made into films through compressive thermal annealing and characterized by UV-Vis Spectroscopy and Scanning Electron Microscopy. Evidence of non-lamellar structures were seen, indicating the first reported creation of two or three dimensional photonic crystals from brush block copolymers.

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Introduction

Brush Polymers

Brush polymers consist of a linear polymer backbone with densely spaced, polymeric side chains. Due to these side chains, the high molecular weight macromolecule is forced to hold a cylindrical or worm-like shape. This shape and brush block copolymer's length of up to several hundred nanometers give a number of possible applications in the growing field of nanoscience, including as molecular actuator[1], precursors for nanocapsules[2] and nanotubes[3], and templates for inorganic particles.[4] However, in order to effectively use brush polymers, it is necessary to be able to control their shape, size, and functionality. Using traditional methods of polymer synthesis has proved difficult to form brush polymers.

There are three main methods used to make brush polymers: grafting from, grafting onto, and grafting through. In the grafting from approach, a backbone with initiator sites is synthesized. Monomers are then added and polymerized at each of these sites. However, there are some major limitations; on the backbone, if the initiator sites are too dense, not all will successfully initiate, making the grafting density hard to predict and not giving the density of side chains that is desired with brush polymers. Beyond that, it is difficult to control the side chains' length. In the grafting onto approach, a polymer backbone and polymer side chains are pre-made and then are chemically attached. Due to the kinetics of these reactions and steric hindrance, this approach leads again to low grafting density. It does provide the benefit of full control of the backbone and side chain lengths.[5] Finally, in the grafting through approach, macromonomers, consisting of the side chain and a polymerizable backbone unit, are synthesized and then polymerized together. Unlike the other two methods, grafting through guarantees 100% grafting density and control of side chain length. However, due to steric hindrances and the low density in solution of polymerizable groups, it is difficult to make brush polymers with low polydispersity index (PDI) and high molecular weight.[6] However, recent work from Grubbs et al. has shown that Ring Opening Metathesis Polymerization (ROMP) is a suitable method for facilitating the grafting through approach, making it possible to reach ultra-high molecular weight brush polymers while maintaining low PDIs.[7] Thus, the grafting through approach coupled with ROMP will be used in this project.

Photonic Crystals

Photonic crystals occur through a periodic optical nanostructure; this structure causes some wavelengths of light to be reflected while others are transmitted, causing the crystals to be colored. They are made of periodic dielectric nanostructures that change how electromagnetic waves propagate through the material. Repeating regions of materials with high and low dielectric constants are used to create the photonic crystals. Wavelengths that are allowed to propagate through the material are known as bands and those that are stopped are known as band gaps. To create a band gap, the periodicity of the photonic crystal must be about half the wavelength of the diffracted wavelength.[8] Photonic crystals can occur in one, two, and three dimensions depending on their fabrication and each will interact with light slightly differently. The one-dimensional case is known as a Bragg reflector or dielectric mirror, where alternating layers are simply stacked on top of one another.

Photonic crystals have a variety of interesting applications. There are a few natural photonic crystals, such as in butterfly wings and opals. However, many other photonic crystals are man-made. One-dimensional crystals are often used in thin-film optics for coatings. In addition, they are used for color changing paints and inks. Two-dimensional photonic crystals do not have widespread commercial usage yet, but photonic crystal fibers, which use their microstructure to confine light, are beginning to gain some commercial appeal as they are better for nonlinear devices and exotic wavelengths. Three-dimensional photonic crystals have not been used in any commercial applications yet, but it is speculated that they will be necessary for optical transistors needed for optical computers.

Traditionally, to form one-dimensional photonic crystals, layers of alternating materials with different dielectric constants are deposited sequentially to form the desired photonic band gaps in one dimension. This is known as top-down fabrication, where the materials are premade and then processed to form the desired structures. Other top down fabrication techniques include layer-by-layer stacking[9], electrochemical etching[10], multibeam holography[11], and phase mask lithography.[12] While these methods are typically extremely precise, there is also a large amount of processing required and very specialized equipment needed; these fabrication methods are very expensive and difficult to bring to mass production. There has been some work with bottom-up fabrication, particularly with colloidal assembly. However, these approaches are typically limited to face-centered cubic geometries. These techniques are significantly less expensive and quicker than the top-down ones, but typically, in order to reach a full photonic band gap, inorganic materials with a high refractive index must be added.[13,14] Thus, currently, there is no commercial method to produce photonic crystals in an inexpensive way.

In particular, one suggested application for photonic crystals is in coatings. However, coatings require a significant amount of material, so current methods of fabrication are not at all sufficient for these applications. In particular, photonic crystals that reflect infrared and near infrared light are of great interest. Due to increased urbanization, there are a number of negative effects on the environment; in particular, there are higher temperatures in cities than their surrounding rural areas due to the Urban Heat Island (UHI) effect.[15] UHI is caused by having more asphalt and concrete, which absorb infrared radiation, than grass and dirt, which absorb less infrared energy. These higher temperatures often require more energy to cool the city spaces, causing increased pollution and worse living conditions. While it is not possible to get rid of the surfaces that absorb infrared radiation, there have been suggestions that having coatings that reflect infrared radiation on these surfaces could help to mitigate the UHI effects. Photonic crystals with band gaps in the infrared are the ideal candidate for such a coating.

Block Copolymers for Photonic Crystals

Block copolymers are the ideal material for these low-cost and large scale uses.[16] Block copolymers self-assemble into ordered nanostructures quickly and with minimal processing. Block copolymer self-assembly is a bottom-up approach; as discussed earlier, these are less expensive and easier to use on a large scale. However, block copolymers are difficult to make at molecular weights that will correspond to visible or infrared wavelengths. The chains begin to entangle rather than segregate, making the self-assembly slower and inhibiting ordered morphology on a long length scale.[17] Work has been done to make block copolymers self-assemble better at higher molecular weights through the use of additives like solvent[18] and homopolymers[19], but these require more complicated processing techniques, which minimizes the initial benefit of the bottom-up fabrication.

Block copolymers can self-assemble into periodic structures with domain spacing on the order of 10 to 100 nm.[20] Due to the incompatibilities between the two blocks, there are a number of specific morphologies that can be reached such as spheres, cylinders, lamellae, or gyroid, which can be used for various technological applications as described above. The morphology that a diblock copolymer will hold is based on three main parameters: the Flory Huggins parameter, χ, the total degree of polymerization, N, and the volume fraction of each block.[21] χN, which scales as the inverse of the temperature, has three main regimes. These are the weak, intermediate, and strong segregation limits. In strong segregation, the two blocks are strongly segregated and the blocks are stretched to form sharp interfaces between the microdomains. Significant work has been done to construct the phase diagrams of many types of block copolymers relating the morphologies observed to the volume fractions and values of χN. Diblock copolymers with equal sized blocks will assemble into lamaellar morphologies; however as one block becomes progressively larger than the other, it will shift to gyroidal, then cylindrical, and spherical. It is in these regimes that we are interested in investigating for potential two and three dimensional photonic crystals.

Recent work has shown that brush block copolymers can self-assemble into longer wavelength reflecting photonic crystals without the use of swelling agents. The grafting through approach with ROMP ensures uniform brush block copolymers, while the side chains are large enough to prevent entanglement that causes loss of morphology in typical block copolymers. It was found that with equal volume fractions of poly-styrene and poly-lactic acid, one-dimensional stacked lamellae were formed. Wavelengths of up to 540 nm were reached with solvent annealing; with a different sample, wavelengths of up to 1311 nm were reached with thermal annealing.[7] Other systems of macromonomers have been tested, including polyisocyanates, which are more rigid, to eliminate the need for thermal annealing.[22] However, these studies have all been done with equal or close-to-equal volume fractions. As predicted by Bates' block copolymer phase diagrams, two and three dimensional morphologies will begin to appear at more uneven volume fractions; these can include gyroidal, cylindrical, and spherical as opposed to the lamellar morphologies that have been seen with brush block copolymers in the past. By controlling the volume fractions of each macromonomer in the brush block copolymer, it is predicted that we will see these previously unseen morphologies in photonic crystals made from brush block copolymers.

Results

Accessing Morphologies by Changing Volume Fractions of Macromonomers

The first main step to see if self-assembly of three dimensional photonic crystals from brush block copolymers was a possibility was to increase the volume fraction of one of the macromonomers. The two macromonomers were first synthesized; both the lactide (L) and styrene (S) macromonomers (MM) were synthesized in a series of steps using an *exo*-norbornene functionalized initiator. The norbornene allows for the ROMP step, creating the backbone of the brush block copolymer. The **L-MM** was synthesized using ring opening polymerization of 3,6-dimethyl-1,4-dioxane-2,5-dione, while the **S-MM** used atom transfer radical polymerization (ATRP). Once these were made and characterized by Nuclear Magnetic Resonance and Gel Permeation Chromatography, they were used to create various samples of brush block copolymers. Due to the ease of synthesis, **L-MM**, the polylactic acid macromonomer, was chosen to be the larger block. These reactions were run such that each macromonomer was added in the equivalency desired in the final copolymer. For example, for a brush block copolymer with total degree of polymerization of 100 and a 85:15 ratio of **L-MM**:**S-MM** respectively, 85 equivalents of **L-MM** and 15 equivalents of **S-MM** would be used with 1 equivalent of catalyst. Five experiments were done aiming at 350 total degree of polymerization with volume fractions ranging from 65 to 85% **L-MM**. The samples are shown below in Table 1.

Sample Name	Molecular Weight	Total Degree of Polymerization	Percent **L-MM** expected	Percent **S-MM** expected	Percent **L-MM** obtained	Percent **S-MM** obtained	Max UV-Vis (nm)
A	1033000	499	65	35	70	30	399
B	883200	418	70	30	63	37	UV
C	868200	420	75	25	70	30	UV
D	786800	393	80	20	79	21	UV
F	661500	336	85	15	85	15	UV

Table 1. *Series of Brush Block Copolymers Examining Increasing Percentages of* ***L-MM***. A series of samples with increasing percentages of **L-MM** were created and tested by UV-Vis Spectrometry and Scanning Electron microscopy for their band gap wavelength and morphology.

Clearly this series did not proceed as expected. As the volume fraction of **L-MM** goes up, it is more difficult to reach a high degree of polymerization, leading to lower molecular weight polymers. Nonetheless, there is a variety of volume fractions ranging from 63% **L-MM** to 85% **L-MM**. It is also notable that only **A** has a peak on the UV-Vis spectrum outside the UV part of the spectrum. All the samples were tinted blue, but given the spectrum, these visible colors were due to the shoulders on the UV peaks rather than a peak in the visible spectrum. This is an indication that good order is not being reached in the samples. More processing techniques will need to be tested to improve these. In addition, in Figure 1, it is interesting to see that with an additional solvent evaporation annealing step, where the sample is placed in a jar with THF in a beaker for about ten minutes, the peak shifts slightly further to the right, implying longer domains.

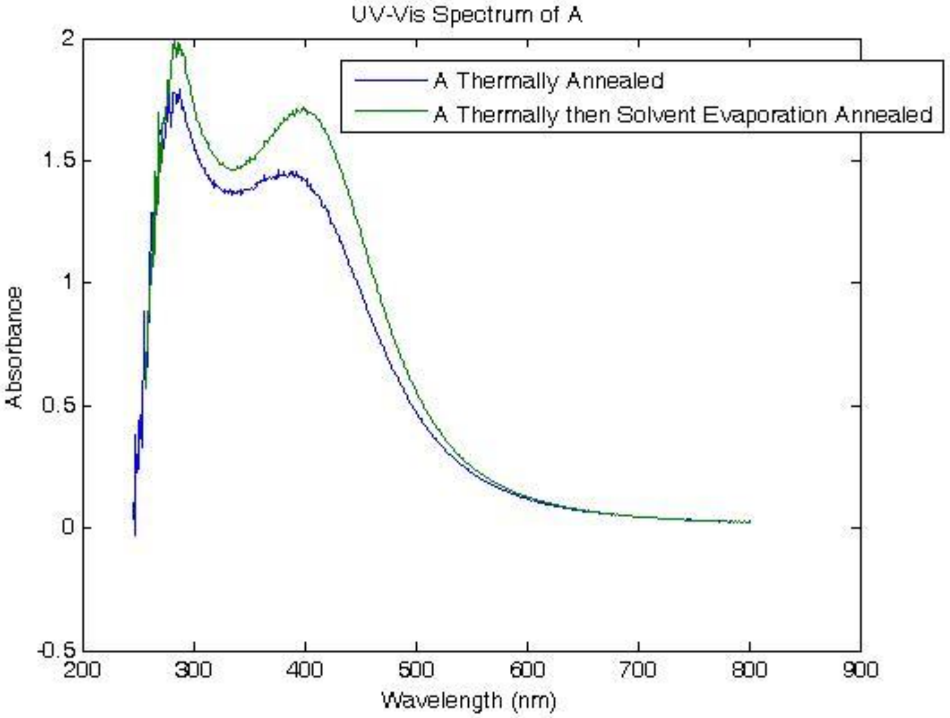


Figure 1. *UV-Vis Spectroscopy of **A***. The UV-Vis spectrum shows a strong peak in the UV part of the spectrum as is seen in all the samples, but also a secondary peak in the visible, indicative of the well-ordered films. This secondary peak becomes stronger after solvent evaporation annealing.

It is expected that as volume fractions increase, there will be a morphology shift from lamellae to cylinders to spheres. Morphology was examined with scanning electron microscopy (SEM) and is shown in Figure 2.

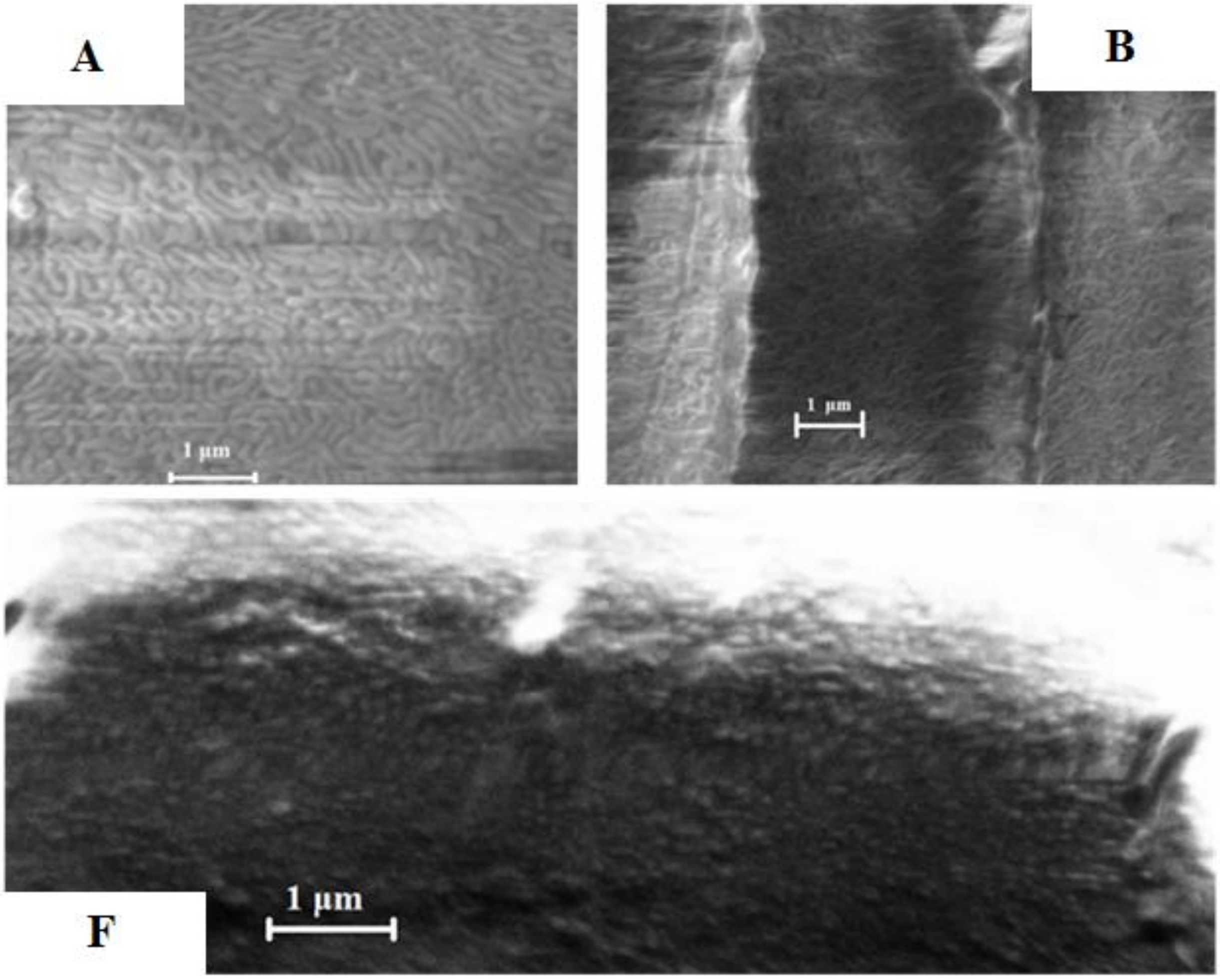


Figure 2. *Scanning Electron Microscopy of Brush Block Copolymers of Different Volume Fractions*. **A** and **B** assemble into lamellae as is clearly visible; these samples have between 63 and 70 percent **L-MM** in them. **F** has approximately 85% **L-MM** and shows some sort of rounded shape. This is likely either cylinders or spheres, though it is difficult to tell with SEM.

From the SEM images, it is apparent that there is a change between 63 and 85% **L-MM** volume fractions. In **A**, the long alternating light and dark patterns are indicative of lamellae. It is a very similar pattern to what is seen in Grubbs et al. for brush block copolymers with equal amounts of each macromonomer.[7] **B** shows similar patterns as well. However, **F** does not have this same morphology. Rather than long, skinny stripes, there are round bumps. This is indicative of one of the rounded geometries, either spheres or cylinders. Unfortunately, as SEM can only capture a two dimensional image, it is difficult to tell these phases apart. To confirm either morphology, further studies will need to be done; Transmission Electron Microscopy

(TEM), Small Angle X-Ray Scattering (SAXS), or Atomic Force Microscopy (AFM) could help to resolve the differences between spheres and cylinders. Nonetheless, this initial work suggests that three dimensional photonic crystals are possible; in addition, it has begun to help to construct the brush block copolymer phase diagram. However, it is clear that additional processing is needed to improve the quality of these films so that they show better assembly behavior.

Increasing Degree of Polymerization with 85:15 Volume Fractions

As discussed in the prior section, it is expected that at very uneven volume fractions of polymers, the morphology of the sample will be spheres. This appeared to be valid as shown in the series with increasing volume fractions. Thus, the next step that was taken was to develop a series of increasing molecular weight with constant volume fraction of 85% **L-MM**. We anticipate an increase in the maximum wavelength of the samples as the molecular weight increased as had been seen in the lamellar phase.

Brush block copolymers were synthesized in the same way as described in earlier sections. The samples are shown in Table 2.

Sample Name	Molecular Weight	Total Degree of Polymerization	Percent **L-MM** expected	Percent **S-MM** expected	Percent **L-MM**	Percent **S-MM**	Max UV-Vis (nm)
E	632500	323	85	15	86	14	UV
F	661500	336	85	15	85	15	UV
G	690900	351	85	15	85	15	UV
H	728400	367	85	15	82	18	UV
I	759500	387	85	15	86	14	UV
J	952600	486	85	15	86	14	UV
K	993100	503	85	15	84	16	443
L	1011000	515	85	15	85	15	UV
M	1064000	544	85	15	86	14	UV
N	1135000	578	85	15	85	15	UV
O	1146000	585	70	30	86	14	UV
P	1325000	670	85	15	83	17	UV
Q	1324000	673	85	15	85	15	UV

Table 2. *Series of Brush Block Copolymers with 85% of **L-MM**.* A variety of brush block copolymers with **L-MM** consisting of 82-86% of the total polymer were synthesized. They ranged in total degree of polymerization from 323 to 673. The maximum UV-Vis appears to have some, but minimal dependence on the molecular weight or the total degree of polymerization.

The molecular weights of these samples range from 661.5 kDa to 1325 kDa and have between 82% and 86% **L-MM** by weight. As in the first series, the UV-Vis data is inconclusive; to the naked eye, these films are all colored blue, but that is not reflected in the location of the peak. The color of the sample is likely due to the shoulder of this peak in the UV spectrum. There is one sample, **K**, which as a clear peak in the visible spectrum. This sample was allowed to thermally anneal for about 45 minutes, suggesting that processing is the limiting factor with these films.

A number of these samples were also tested by SEM to look at the morphology in the self-assembled films. As stated earlier, it is not possible to distinguish cylinders from spheres by SEM; however it is possible to see that self-assembly is occurring and that regular morphologies exist in the sample. These are shown in Figure 3.

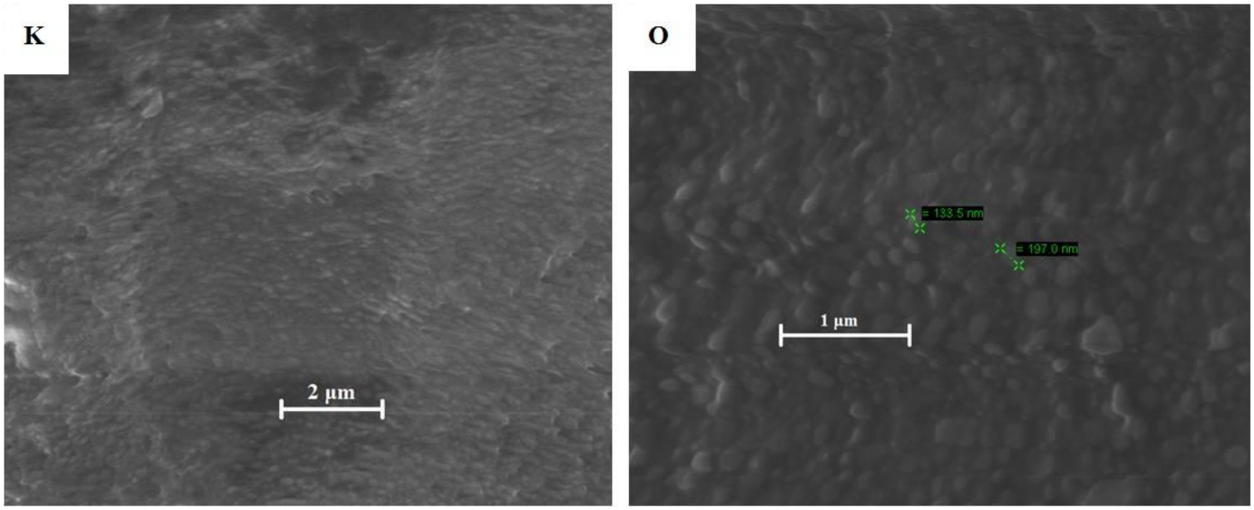


Figure 3. *Scanning Electron Microscopy of Brush Block Copolymers Consisting of 85%* ***L-MM***. From these images, it is clear that these are self-assembling into non-lamellar nanostructures. The round morphology is found to be about 133.5 nm across in the second sample, which has a total degree of polymerization of 583.

Both of these samples show clear circular patterns, indicating either cylinder or sphere morphology. In **K**, many small, rather regular circles are seen. In the more zoomed in **O**, it is possible to see the circles; some are similar in size, though others are slightly larger or smaller. One of the circular features is found to be about 133.5 nm across. As discussed earlier, it is not really possible to differentiate between spheres and cylinders through SEM as it is a two dimensional image. Further testing through SAXS, TEM, or AFM will be necessary to fully characterize these systems. However, this study has shown that a two or three dimensional morphology is possible in brush block copolymers. Furthermore, as these reflect visible light, brush block copolymers with this morphology can serve as two or three dimensional photonic crystals.

One problem that needs to be looked into in the future is better annealing techniques. These samples were thermally annealed under compression for about 15 minutes each, producing a vibrant color when removed from the oven. However, when SEM was performed, some sections were clearly not fully assembled and were therefore disorganized, producing messy pictures. Processing seems to be a key limiting factor in the creation of these. For example, see Figure 4 of sample **M**.

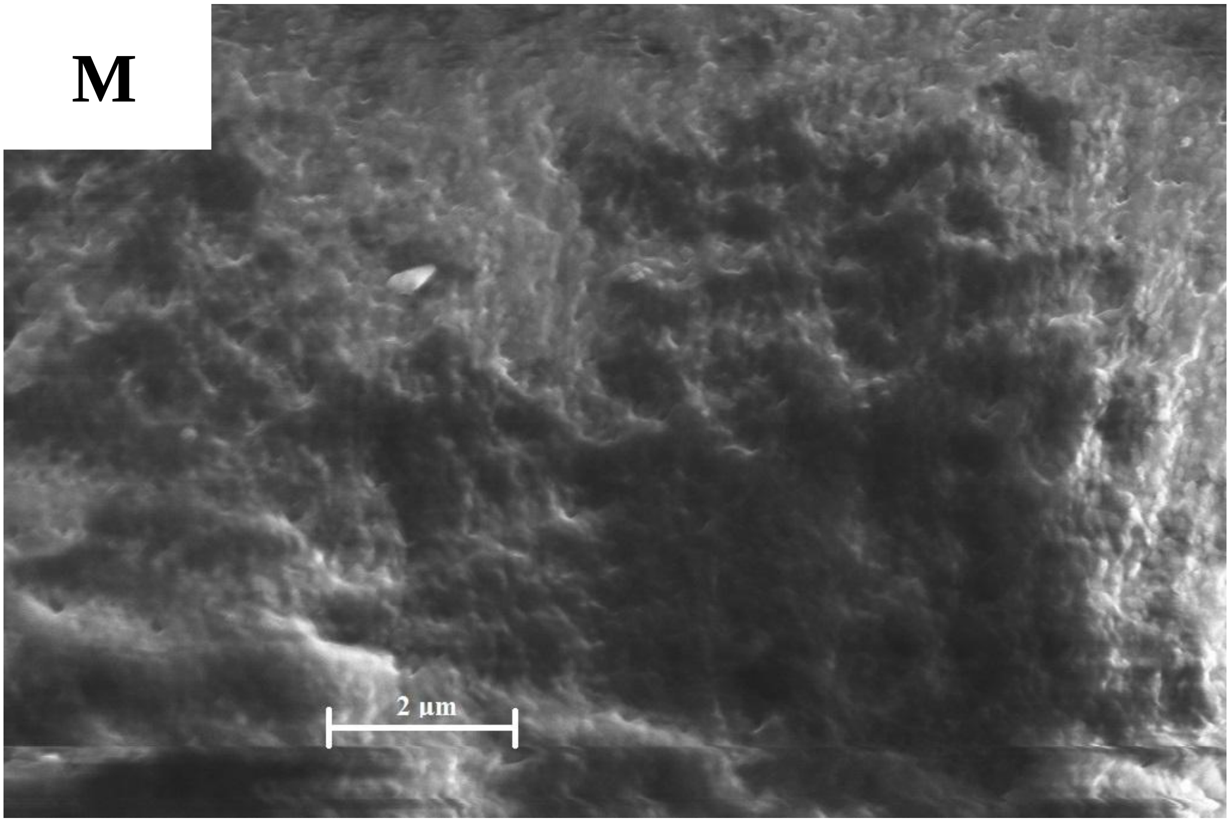


Figure 4. *Sample **M** Thermally Annealed for 10 Minutes*. It is clear that this sample did not fully form into an ordered morphology. It would be expected that it would form some sort of circular morphology as the samples with molecular weights slightly above and below it did.

It appears that there is some order in this sample with some portions showing circles, but it is much less conclusive than some of the samples shown earlier. Further testing must be done with other annealing conditions to produce better ordered samples. Solvent evaporation was briefly tested, producing mediocre results to the naked eye, but it may be worth retesting. Another possibility is longer heating times to allow the polymers more time to reach their self-assembled positions. After heating, it is also possible to expose the sample to vapor for an extended period of time. This would increase chain mobility, giving them more opportunity to assemble. Due to time restrictions, it was not possible to attempt these, allowing more room in this project for improvements.

Increasing Degree of Polymerization with 70:30 Volume Fractions

At volume fractions between where spherical and lamellar morphologies are seen, we expect to see mainly cylindrical morphologies. There is often a gyroidal phase as well, but it tends to be much smaller on the phase diagram, making it much harder to see. In block copolymer systems of polylactic acid and polystyrene, the cylindrical phase is very prevalent when one volume fraction composes about 70% of the total weight of the sample.[23] In the series where volume fractions were increased (**A-F**), the **A** and **C** samples both contained about 70% **L-MM** and appeared to assemble into lamellar nanostructures. However, as SEM only shows a two dimensional representation, it is possible that simply the wrong orientation was being captured and that these were indeed cylinders, just tipped on their side. It is anticipated as well that as the degree of polymerization and molecular weight increase that the wavelength reflected will also increase.

A series of brush block copolymers was synthesized with increasing molecular weight and a constant ratio of **L-MM** to **S-MM**. These samples are shown in Table 3.

Sample Name	Molecular Weight	Total Degree of Polymerization	Percent **L-MM** expected	Percent **S-MM** expected	Percent **L-MM**	Percent **S-MM**	Max UV-Vis (nm)
C	868200	420	75	25	70	30	UV
R	962200	465	70	30	70	30	UV
S	1024000	496	70	30	70	30	Thermal annealing: UV Solvent Evaporation annealing: 491
A	1033000	499	65	35	70	30	UV
T	1096000	539	70	30	75	25	UV
U	1142000	565	70	30	77	23	UV
V	1369000	665	70	30	72	28	UV
W	2000000	960	70	30	68	32	UV

Table 3. *Series of Brush Block Copolymers with 70% of **L-MM***. Samples of asymmetric brush block copolymers were synthesized and characterized. These ranged in total degree of polymerization between 420 and 960. There appears to be minimal correlation between the wavelength of light absorbed and the molecular weight.

The molecular weights of these samples are between 868 kDa and 1369 kDa and contain between 68 and 77% **L-MM**. Again, the processing on these films is inadequate to ensure complete assembly as reflected in the UV-Vis data. Interestingly, **S** gains a stronger peak after solvent evaporation annealing, indicating that this method does have an effect on the films. Once the samples were synthesized, their morphology was examined through SEM. From this, we expected to see that they were self-assembling and forming into some sort of circular (either spherical or cylindrical) morphology. Some of these images are shown in Figure 5.

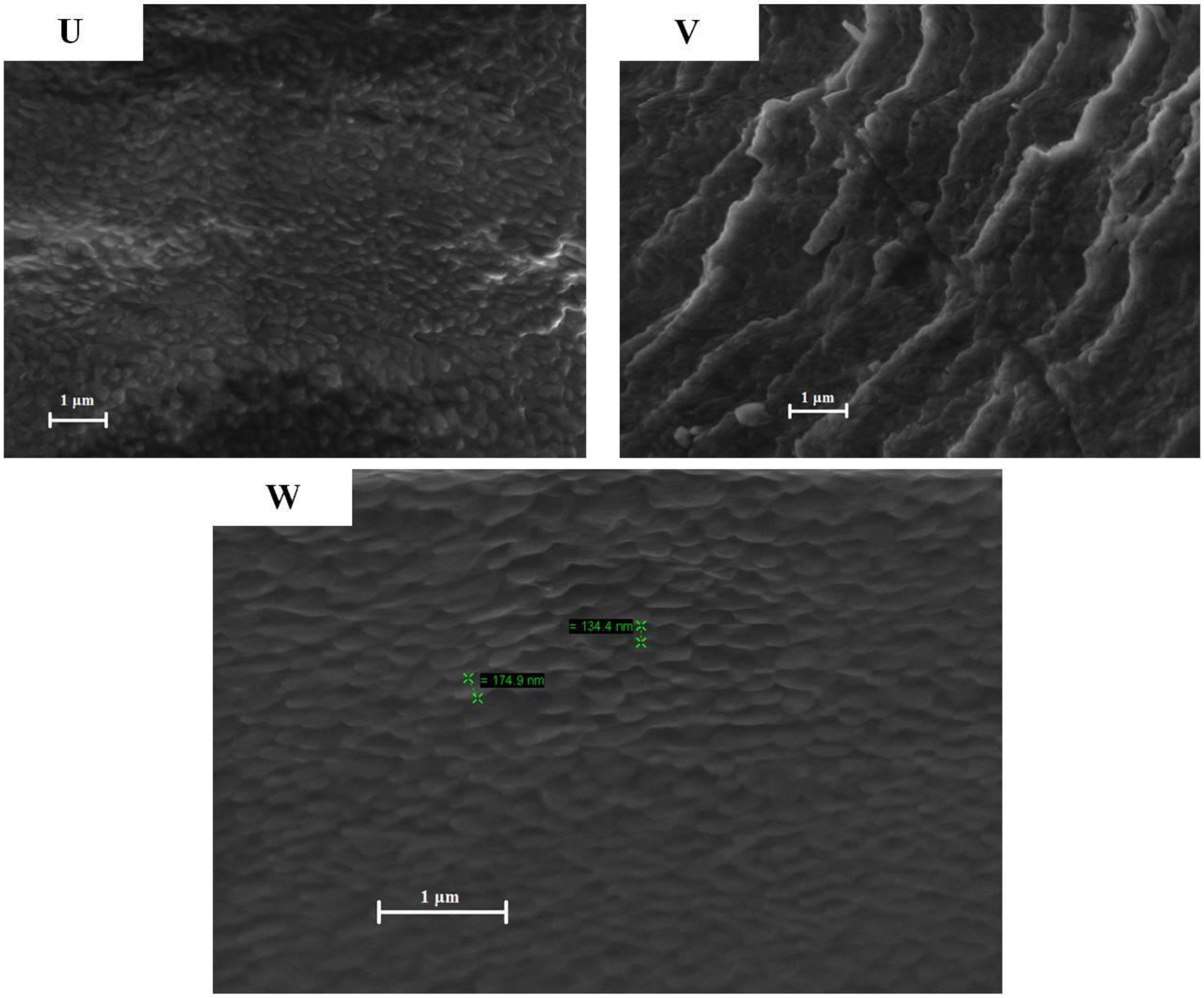


Figure 5. *Scanning Electron Microscopy of Brush Block Copolymers with 70%* ***L-MM***. Clear circular morphology is shown by SEM. In particular, circles of diameter of 134.6 nm and 174.9 nm were measured by SEM in **W**.

The expected circular shape is present in each of these samples. This indicates self-assembly into either cylindrical or spherical morphologies, which is indistinguishable in SEM. **W** had measurable circles of 134.6 nm and 174.9 nm. This indicates that the circular morphology is not fully regular. This could partially explain the rather broad UV-Vis peak seen in Figure 6.

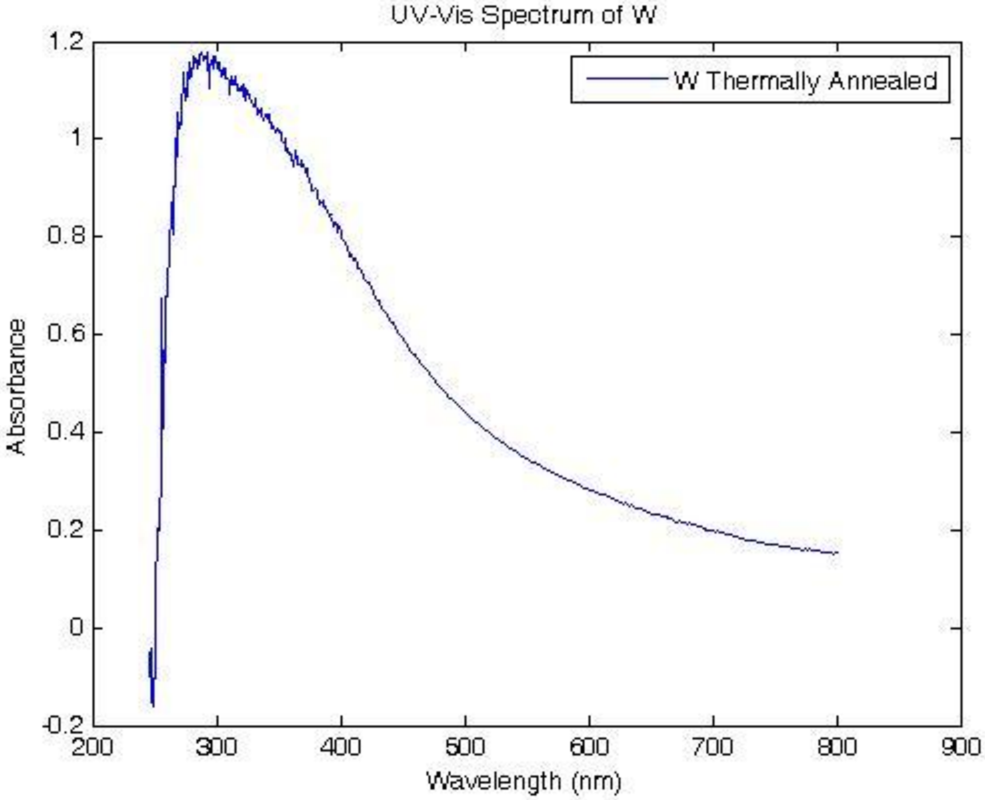


Figure 6. *UV-Visible Spectrometry on **W** Thermally Annealed Film.* This is a much broader peak than shown with previously produced lamellar films. This effect could be due to either the morphology or processing.

If different parts of the structure are restricting certain wavelengths, it will absorb more wavelengths but each wavelength's absorption will be weaker. Further testing on more processing techniques are needed to more fully determine the cause of these broad peaks.

Conclusions and Future Work

Three series of brush block copolymers were synthesized to test for the capability of self-assembly into two and three dimensional photonic crystals. The samples were characterized by Gel Permeation Chromatography and Nuclear Magnetic Resonance spectroscopy to determine molecular weight and relative percentages of each macromonomer. They were then made into film through compressive thermal annealing and characterized by Scanning Electron

Microscopy. This showed a few samples that assembled into lamellae, but many that had some sort of circular morphology. This could be either cylindrical or spherical, which cannot be concluded without some form of three dimensional imaging. Each sample was also characterized by Ultraviolet-Visible spectroscopy to suggest where the peaks of reflection in the sample would be.

In future work, a more advanced imaging or scattering technique such as Atomic Force Microscopy, Small Angle X-Ray Scattering, or Transmission Electron Microscopy will be used to show the actual morphology. Without this information, it is not possible to determine whether the circular morphologies that are being seen are spheres or cylinders. In addition, exploring other processing techniques, such as solvent annealing and longer thermal annealing times, possibly followed by exposure to solvent will be tested to look for more complete self-assembly behavior. These will give the chains more time to segregate, hopefully giving better final results and images. One additional idea is to etch out the **L-MM** blocks after it is assembled into a film and look into the leftover **S-MM** blocks as an imaging technique as these should have the spherical or cylindrical shape in the film.   These are extremely promising initial results for the demonstration of two and three dimensional photonic crystals made from brush block copolymers.

Materials and Methods

Materials

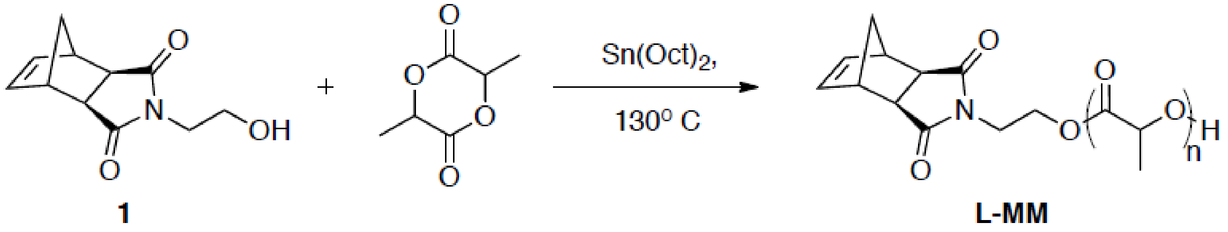
$(H_2IMes)(pyr)_2(Cl)_2RuCHPh$[24] and *N*-(hydroxyethanyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide[25] were prepared as described previously. Solvents were all purchased from VWR or Sigma-Alrich. Ruthenium-based metathesis catalyst was from Materia Inc. and stored in drybox. Other chemicals were purchased from Sigma-Aldrich. Dry solvents were purified with solvent purification columns. 3,6-dimehtyl-1,4-dioxane-2,5-dione was purified by sublimation under vacuum. All other solvents and chemicals were used without purification unless stated elsewhere.

General Information

NMR spectra were taken at room temperature on a Varian Inova 500 at 500 MHz. NMR spectra were analyzed with MestReNova software and reported relative to the deuterated chloroform peak (δ 7.26). NMR abbreviations: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad. Gel Permeation Chromatography (GPC) was done in THF on two Plgel 10 μm mixed-B LS columns (Polymer Laboratories) connected in series with a miniDAWN TREOS multiangle laser light scattering (MALLS) detector, a ViscoStar viscometer and Optilab rex differential refractometer (all from Wyatt Technology). The d*n*/dc values used for polylactide and polystyrene macromonomers were 0.050 and 0.180 respectively. dn/dc values for the brush block copolymers were done assuming 100% mass elusion from the columns. Scattering Electron Microscopy (SEM) was performed on a ZEISS 1550 VP Field Emission SEM. Reflection measurements were performed on a Cary 60 UV-Vis spectrophotometer.

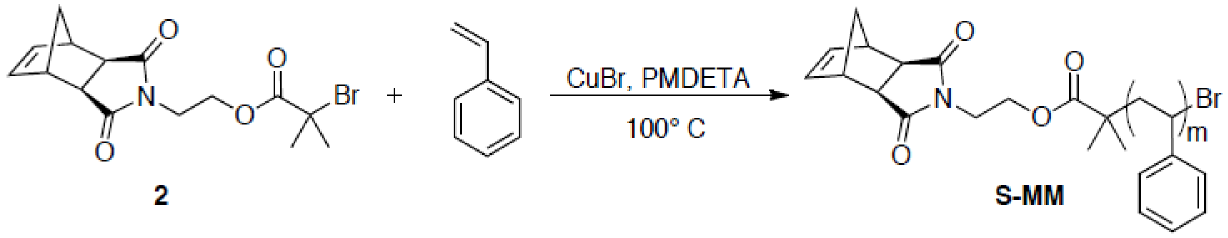
Synthesis

Norbornene-Polylactide (L-MM)



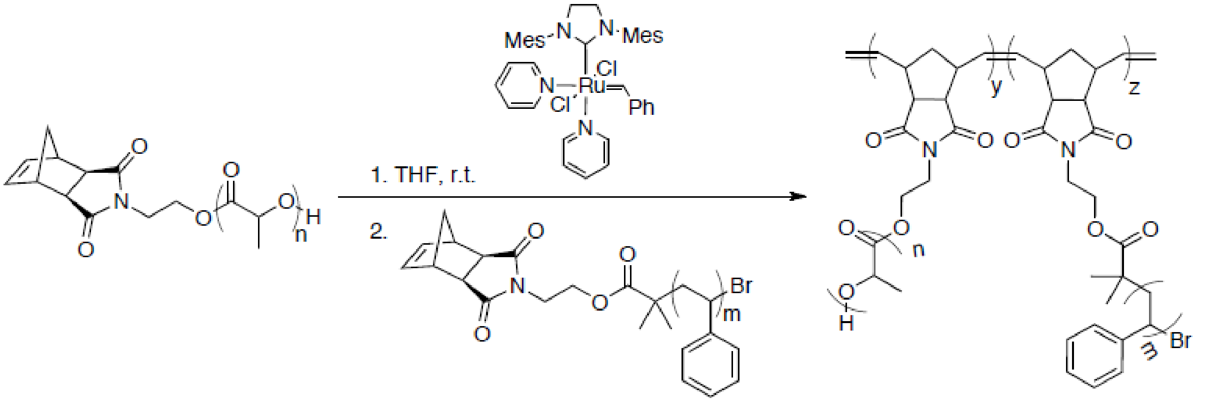
A Schlenck tube was first flame-dried and then charged with **1** (640.5 mg, 3.13 mmol), 3,6-dimethyl-1,4-dioxane-2,5-dione (8.9994 g, 62.5 mmol), and 2 drops of tin (II) 2-ethylhexanoate (about 2 mg, 5 μmol). The mixture was run through three vacuum-argon cycles and then added to an oil bath at 130° C to stir. After allowing the reaction to proceed for 2.5 hours, the solution was removed from the oil bath and allowed to cool to room temperature. The product was then dissolved in dichloromethane. It was filtered through celite to remove excess catalyst and precipitated into cold methanol. ^{1}H NMR (500 MHz, CDCl3): δ (ppm) 6.28 (br t, 2H), 5.31-5.00 (m, 46 H), 4.42-4.23 (m, 3H), 3.84-3.69 (m, 2H), 3.30-3.26 (s, 2H), 2.70 (m, 2H), 1.73-1.39 (m, 167 H), 1.24 (br d, *J* = 10 Hz, 1H).

Norbornene-Polystyrene (S-MM)



Styrene (52.2 mL, 0.454 mol) was passed through basic aluminum oxide and added into an oven-dried Schlenk tube with a septum. The styrene was then put through three freeze-pump-thaw cycles and was refrozen. CuBr (169.4 mg, 1.18 mmol) was added to the frozen styrene under argon. The mixture underwent three vacuum-argon cycles before allowing the styrene to melt under argon. PMDETA (238 µL, 4.14 mmol) was added to the Schlenck tube by syringe and the mixture was stirred for five minutes. The initiator **2** (1.4458 g, 4.054 mmol), prepared as in Grubbs et al., was then added to the Schlenk tube by syringe and the reaction mixture was stirred at 100° C.[7] After 4 hours, the reaction was stopped by cooling it with dry ice to cool it to room temperature and then adding THF to the mixture. The mixture was then passed through neutral aluminum oxide to remove catalyst and precipitated into methanol. Purification was carried out through repeated reprecipitations until no remaining styrene was observed by NMR. Further purification was done by silicia gel chromatography in dichloromethane until the macromonomer was able to undergo successful ROMP. ^{1}H NMR (500 MHz, CDCl3): δ (ppm) 7.25-6.29 (br m, 213 H), 6.28 (br s, 2H), 4.59-4.35 (m, 1H), 3.65-3.32 (m, 4H), 3.22 (br s, 2H), 2.62 (br d, *J* = 7.4 Hz, 2 H), 2.56-1.55 (br m, 36 H), 0.99-0.83 (m, 6H).

Block Copolymerization of Two Macromonomers via ROMP (A-L)



In a typical experiment, about 200 mg total of macromonomers were added to separate vials in the desired ratio. The desired amount of catalyst was added in a third vial. These vials were then brought into a dry box and the macromonomers were dissolved in THF to approximately 0.05 M concentration. The catalyst was dissolved in 1.00 mL of THF. The desired amount of catalyst solution was added to the **L-MM** macromonomer due to its fast kinetics at this concentration. **S-MM** was added after the polymerization of the first macromonomer was completed according to previously derived kinetics data. This solution was allowed to stir for an additional 1.5 to 2 hours. The reaction was taken out of the dry box, dichloromethane was added to lower the viscosity of the liquid, and the reaction was isolated by precipitation into methanol. To separate the product completely, it was centrifuged at approximately 20,000xg for 5-10 minutes and excess solvent was decanted. Conversion was 100% based on RI traces from GPC and isolated yields were typically over 85%.

Annealing by Slow Evaporation

Approximately 20 mg of solid polymer was put in a vial and dissolved in about 5 mL of dichloromethane. A glass substrate was subsequently added vertically and the solvent was allowed to evaporate at room temperature, depositing the polymer on the glass substrate.

Thermal Annealing between Two Glass Substrates

About 10 mg of solid polymer was sandwiched between two glass substrates and compressed with a clamp. The substrates with clamps were then put into an oven at 140° C for 15 minutes.

Secondary Solvent Evaporation Annealing

After compressive thermal annealing, the samples were placed into a jar containing a beaker filled with THF. They were allowed to sit on top of the beaker with the jar closed for about ten minutes.

SEM sample preparation

SEM samples were fractured on glass substrates and exposed to RuO_4 for ten minutes.

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