A Thermal and Manufacturable Approach to Stabilized Diblock Copolymer Templates

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ABSTRACT: Stabilization of the morphology in thin diblock copolymer films is critical for the generation of robust templates for subsequent device fabrication. Copolymers containing thermally cross-linkable groups, such as benzocyclobutene (BCB), can be annealed to induce an ordered microdomain morphology and then subsequently heated to cross-link the system, locking in the morphology and eliminating the need for multistep processing. Poly[(styrene-*r*-BCB)-*b*-lactic acid] (PSBCB-*b*-PLA) was synthesized by a combination of living free radical and ring-opening polymerizations. Thin films (∼30 nm) of PSBCB-*b*-PLA annealed at 170 °C, followed by cross-linking at 200 °C, showed that the ordered and oriented microdomain morphology was preserved. For PSBCB-*b*-PLA, with PLA volume fractions of 0.24 and 0.36, arrays of cylindrical microdomains of PLA oriented normal to the surface were produced in a cross-linked PS matrix. Washing these films with a weak base degraded and removed the PLA, producing a nanoporous cross-linked template.

Introduction

Diblock copolymers are of great interest as templates in nanofabrication due to their self-assembly into microphase-separated morphologies where the domain size is dictated by the size of the polymer chain and, therefore, is nanoscopic in size. The alignment of the microdomains of diblock copolymers using external fields such as shear, confinement, solvent annealing, electric fields, and neutral brushes has been studied in detail[1−8] and techniques such as UV, thermal, ozone, ion beam, and chemical etching processes[9−14] have been developed to generate nanoporous films by removal of the minor component. The resulting nanoporous films are finding applications as scaffolds and templates for the fabrication of nanostructured materials and advanced microelectronic devices.[15−19]

Removal of the minor component alone, however, is not sufficient. The surface area produced by the array of nanopores is quite large, and considering the surface energy, the energetic cost for producing the pores is significant such that, if the matrix were mobile, the pores would collapse. Consequently, the matrix must be immobilized to preserve the porosity. In the past, this has been accomplished by chemically cross-linking the matrix, crystallizing the matrix, or by keeping the matrix polymer below its glass transition temperature. The chemical cross-linking of PS-*b*-PLA thin films using RuO_4 has been explored with subsequent removal of the PLA to give a cross-linked nanoporous film.[13] Other studies have appeared on the use of dicumyl peroxide to cross-link polyisoprene-*b*-polydimethylsiloxane (PI-*b*-PDMS) with subsequent removal of the PDMS phase[11,12] and poly(α-methylstyrene)-*b*-poly(4-hydroxystyrene) (PαMS-*b*-PHOST) systems using a photoacid generator to promote cross-linking.[20] However, the addition of small molecules has limitations, including the incorporation of undesirable chemical functionality or metals associated with the cross-linking reaction. Selective degradation by ozone or reactive ion etching (RIE) has been used to produce nanoporous templates.[9,10] While being useful for nanolithographic templates, the resulting nanoporous polymer films may have unknown chemical functionalities, produced by the ozone or RIE process, that could limit subsequent chemical modification of the nanoporous polymer templates.

Diblock copolymers containing a high-T_g block can be used to increase the allowable processing temperature before collapse of the porous template. Poly(cyclohexylethylene) (PCHE) containing diblock copolymers yield nanoporous templates that resist collapse up to 136 °C, near the T_g of the PCHE block.[21] However, for temperatures above this, the pore structure collapses.

An attractive way to stabilize the matrix, while reducing the number of processing steps, is to incorporate thermally cross-linkable groups into the matrix block. This eliminates the need for small molecule cross-linking agents or the use of UV light. Additionally, the extent of cross-linking can be controlled by the number of cross-linkable groups incorporated into the chain during synthesis which permits the physical and mechanical properties of the template to be controlled. From a manufacturing viewpoint, a purely thermal process streamlines the fabrication of the template since cross-linking simply involves increasing the temperature following the standard thermal annealing used to orient and order the microdomain morphology. Thus, there is no additional handling of the film to produce a stable template.

In this article we report on a process where a diblock copolymer was synthesized in which the matrix component could be thermally cross-linked, and the minor component could be base-degraded to produce thin films with hydroxy-functionalized nanopores. Specifically, BCB units were statistically placed along a PS chain, the major component, while PLA constitutes the minor block. The thermal cross-linking of BCB has been shown to produce robust block copolymer templates when the minor component was PMMA.[22] Alternatively, with PSBCB-*b*-PLA, the PLA can be removed, leaving hydroxyl groups lining the pore walls (see Figure 1).

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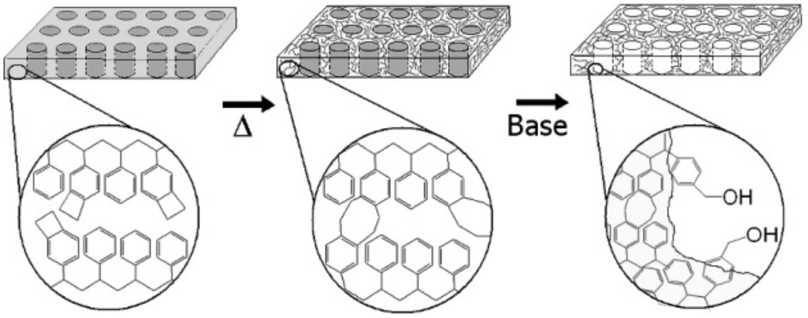

Figure 1. Creation of a nanoporous thin film with functionalized nanopores in a thermally stabilized matrix. Initial insets show changes in the PS matrix while the final inset details the proposed interfacial structure after hydrolysis.

Similar work using un-cross-linked PS-*b*-PLA nanoporous monoliths demonstrated that the alcohol groups lining the pore walls could be easily functionalized at conditions below the T_g of the matrix.[14] In our approach, using PSBCB-*b*-PLA, the nanoporous templates are cross-linked and base-degraded, giving primary alcohol groups within the pores, potentially opening facile routes to postfunctionalization, even at elevated temperatures.

Experimental Section

Materials. 3-Bromobenzocyclobutene was provided by the Dow Chemical Co. The hydroxy-functionalized alkoxyamine initiator and 3-vinylbenzocyclobutene were synthesized according to established procedures.[23] Styrene, tetra-*n*-butylammonium fluoride (Aldrich), and triethylaluminum (Aldrich, 1.0 M in hexanes) were used as received. DL-Lactide (Aldrich) was recrystallized from ethyl acetate and benzene was distilled over sodium and benzophenone. Gold-coated silicon substrates (35 nm Au, on 2 nm Cr) were prepared in-house on precleaned Si wafers. Chlorobenzene (Aldrich) was used as received.

Instrumentation. Size exclusion chromatography (SEC), using polystyrene standards, was used to determine molecular weights and molecular weight distributions, M_w/M_n, of the polymers. SEC measurements were done in THF at a flow rate of 1.0 mL/min, using two polymer laboratories PLGel 5 μm Mixed-D and one PLGel 5 μm 50Å columns, a Knauer K-501 HPLC pump, a Knauer K-2301 RI detector, and a Knauer D-2600 dual wavelength UV detector.

Small-angle X-ray scattering (SAXS) was used to determine the bulk morphology by drop-casting films from chlorobenzene solutions onto a Kapton film and drying overnight in vacuo. In situ temperature-dependent SAXS measurements were performed under vacuum using an Osmic MaxFlux X-ray (Cu Kα, 0.154 nm) source with a Molecular Metrology, Inc. camera consisting of a three-pinhole collimation system, a 150 cm sample-to-detector distance (calibrated using silver behenate), and a 2-dimensional, multiwire proportional detector (Molecular Metrology, Inc.).

Scanning force microscopy (SFM), in both height and phase contrast modes, was used to characterize the thin film morphology with a Dimension TM3000 scanning force microscope. TEM images were obtained using a JEOL 2000KX transmission electron microscope at 200 kV. TEM thin film sample preparation is described below. Film thickness measurements for the swelling experiments were done using a Filmetrics interferometer model F20 with FILMeasure v.2.4.3 software.

Polarization-modulation infrared reflection−absorption spectroscopy (PM-IRRAS)[24] was used to characterize the removal of the PLA in cross-linked films on gold substrates. PM-IRRAS was performed on a Thermo Nicolet Nexus 670 FT-IR spectrometer equipped with a PEM module including a Hinds Instruments PEM-90 photoelastic modulator system and a liquid nitrogen cooled MCT-A detector. The difference reflectance measurements at 83° angle of incidence were collected for total of 1024 scans in the range of 4000−750 cm^{-1} at a resolution of 4 cm^{-1}. The ratio taken between the spectra and those of previously scanned metal substrates was used to obtain the desired signal from the thin films.

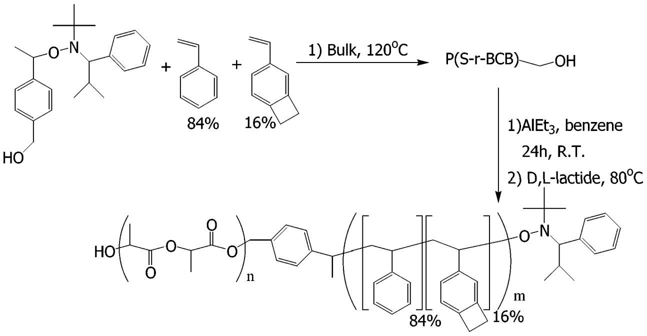

Figure 2. Synthesis of poly[(styrene-*r*-benzocyclobutene)-*b*-DL-lactic acid].

Synthesis. Poly(styrene-*r*-benzocyclobutene) (PSBCB) was made using established procedures.[23] Two different homopolymers were used in this study. The 18 kg/mol diblock copolymer (PDI = 1.05) was made using PSBCB homopolymer, 13 kg/mol (PDI = 1.06), containing 26 mol % BCB units. PSBCB homopolymer, 11.3 kg/mol (PDI = 1.09), containing 16 mol % BCB units was used to make the 19 kg/mol diblock copolymer (PDI = 1.08). For the 18 kg/mol diblock copolymer, the *tert*-butyldimethylsilyl (TBDMS) protecting group was removed using 1.0 M tetra-*n*-butylammonium fluoride (TBAF) in THF. The TBAF solution (0.5 mL) was added to a solution containing the protected polymer (1.0 g) in THF (4.0 mL) and stirred at room temperature for 24 h. Acidic methanol was added to quench the reaction and the polymer was precipitated into methanol and filtered. The synthesis of the diblock copolymer does not require protecting the hydroxyl group, so preparation of the 19 kg/mol diblock copolymer was done without the protection/deprotection step (see Figure 2). The PLA block was grown using DL-lactide and AlEt$_3$ in benzene, adapted from a previous procedure.[14] For a typical reaction, a polymerization tube with a Teflon stopcock was charged with PSBCB-OH (0.3 g) and backfilled with nitrogen. Benzene (5.0 mL) and AlEt$_3$ (25 μL of 1.0 M) were added via syringe and allowed to react overnight. DL-Lactide (0.625 g) was added in a glovebag under a nitrogen atmosphere. The tube was sealed and heated at 80 °C for 7 h. The polymers were isolated by precipitation into acidic methanol and washed with cyclohexane to remove any unreacted PSBCB homopolymer. The final diblock copolymers were 18 kg/mol (PDI = 1.05), 0.24 v/v PLA, and 19 kg/mol (PDI = 1.08), 0.36 v/v PLA. PSBCB-*b*-PLA diblock copolymer ^{1}H NMR (300 MHz, CDCl$_3$): δ = 6.2−7.3 (m, 5H from styrene, 3H from BCB units, Ar−H), 1.2−2.2 (m, 3H, C**H**−C**H**$_2$ from PSBCB), 3.1 (br s, 4H, C**H**$_2$ from the cyclobutene ring), 5.2 (m, 1H, C**H** from PLA), 1.6 (m, 3H, C**H**$_3$ from PLA).

Thin Film Sample Preparation. Films were spin-coated from 1% chlorobenzene solutions onto a 35 nm gold surface. Gold substrates gave consistent perpendicular orientation of the microdomains, and the polymer remained adhered to the gold substrate upon base degradation. Preliminary studies indicate that films >80 nm thick on the gold substrate resulted in the parallel orientation of the morphology upon heating as

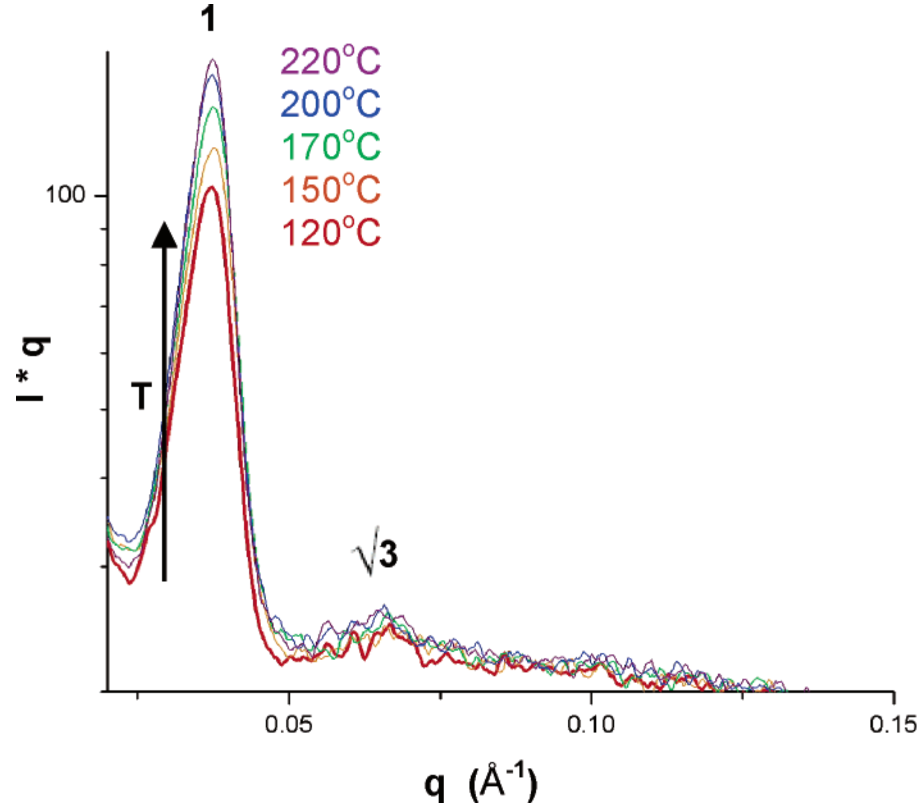

Figure 3. SAXS peaks from a bulk sample cast from chlorobenzene onto Kapton indicate a cylindrical morphology. Multiple temperatures were examined in situ from 120 to 220 °C.

measured by SFM. The films used in this study were ~30 nm thick. Cross-linked samples were prepared by annealing under nitrogen at 170 °C for 2 h and then heating to 200 °C for 5 h. Base degradation was performed by submerging the films into a 0.5 M sodium hydroxide solution in 50:50 water:methanol, at room temperature, for 7 h (unless otherwise noted). The films were then washed with methanol:water to remove any residual base. The PLA block can also be degraded using MF-319 (Rohm and Haas) a commercially available developer containing aqueous trimethylammonium hydroxide and surfactants. However, all the studies reported in this article on the thermal and solvent stability of the nanoporous cross-linked films were done using the sodium hydroxide degraded films. Thin film samples used for TEM studies were removed from the gold surface by floating the film into an aqueous solution of potassium iodide and iodine and picked up using copper grids.

Samples were also embedded in epoxy for SFM studies on the underside of the film. For embedding, films still on the substrate were coated with a few nanometers of evaporated carbon and then embedded into epoxy and cured at 60 °C overnight. The embedded films were removed from the substrates using liquid nitrogen, exposing the underside of the films.

Swelling Studies. PSBCB homopolymer thin films (~140 nm) were cast from 5% chlorobenzene (3000 rpm) onto silicon wafers. Films using both PSBCB homopolymers (containing 16 and 26 mol % BCB units) were studied under different thermal histories: unheated, heated to 170 °C for 2 h, heated to 170 °C for 2 h + 200 °C for 30 min, heated to 170 °C for 2 h + 200 °C for 1 h, heated to 170 °C for 2 h + 200 °C for 3 h, and heated to 170 °C for 2 h + 200 °C for 5 h. After thermal treatment, each film was introduced into a glass container with a quartz window. Nitrogen was bubbled through THF at a flow rate of 23 mL/min and passed over the thin film sample in the container. Measurements of film thicknesses were taken in situ, prior to THF introduction and after reaching equilibrium, using an interferometer. The heated samples reached an equilibrium swelling thickness after ~7 min, whereas the unheated films dewetted from the substrate after ~7 min. Unheated film measurements reported are prior to dewetting, and all swelling measurements were done at 21 °C.

Discussion

Synthesis and Bulk Characterization. Two PS-BCB-*b*-PLA polymers were studied in detail. One had a molecular weight of 18 kg/mol with a PLA volume fraction of 0.24 (28% w/w) and 26 mol % of BCB per mole of styrene. The other had a molecular weight of 19 kg/mol with a PLA volume fraction of 0.36 (43% w/w) PLA and 16 mol % of BCB per mole of styrene. Both diblock copolymers microphase separated into cylindrical microdomains of PLA, despite the difference in volume fractions. This is consistent with the observations of Hillmyer and co-workers[14] for the non-BCB containing analogues. The average center-to-center distances of the PLA cylindrical microdomains were 21.4 nm (*d* spacing = 18.5 nm) and 21.8 nm (*d* spacing = 18.9 nm) for the 0.24 and 0.36 PLA volume fraction polymers, respectively, as measured by SAXS. The domain sizes, calculated using the *d* spacing and volume fractions of PLA, are 11 and 14 nm, respectively. This is in agreement with the cylinder diameters as measured by SFM of ~10 and ~14 nm.

The PSBCB-*b*-PLA copolymers studied were found to self-assemble into a cylindrical microdomain morphology in the bulk, as determined by SAXS, where the first- and second-order scattering peaks were found at scattering vectors, relative to the first-order reflection, of 1:$\sqrt{3}$ (see Figure 3). The 2D SAXS pattern shows a diffuse ring, indicating the presence of many small grains of hexagonally packed cylindrical microdomains with no long-range order. SFM and TEM studies on thin films support these conclusions. The microphase-separated morphology was found to persist up to 220 °C (the limit of the SAXS heating stage), which is above

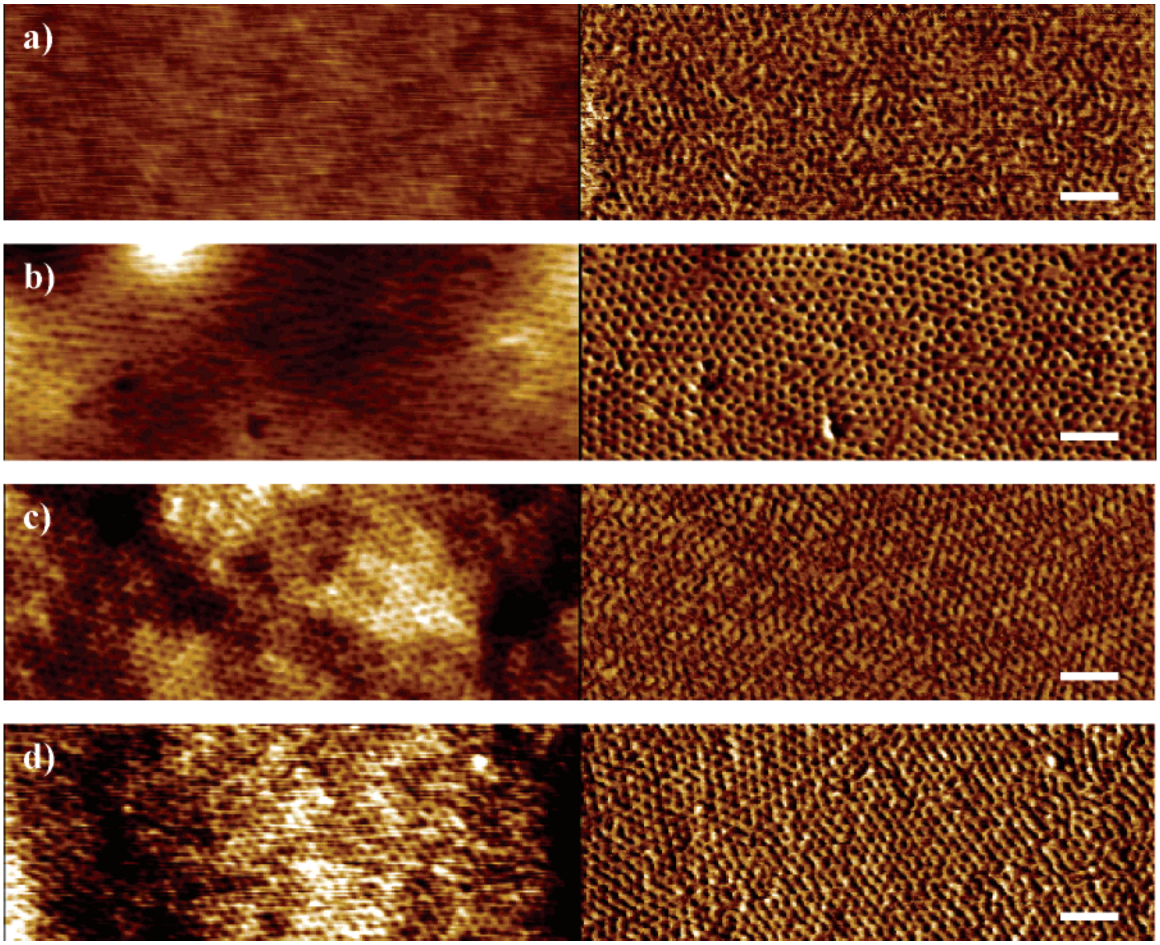

Figure 4. SFM images of PSBCB-*b*-PLA (19 kg/mol) (a) as cast and (b) annealed at 170 °C for 2 h and then base-degraded for 30 min. Annealed at 170 °C for 2 h, cross-linked at 200 °C for 5 h, and then base-degraded for (c) 90 min and (d) 11 h. Scale bar = 100 nm. Left images are height, scale = 5 nm, and right images are phase, scale = 20° (for a and b) and 30° (for c and d).

the temperature where the BCB groups undergo cross-linking (~170 °C).

Thin Film Phase Separation and Characterization. Thin films of PSBCB-*b*-PLA were spin-coated onto gold substrates from chlorobenzene solutions. SFM of the thin films showed that the cylindrical morphology was oriented normal to the surface. Degradation of the PLA using a sodium hydroxide solution produced a nanoporous film (Figure 4) where the majority of the PLA could be removed by soaking the film (still on the substrate) in the basic solution for 30 min. Complete removal of the PLA requires 7 h of base degradation, as indicated by the SEC in Figure 5.

While the SEC results show that PLA can be removed from un-cross-linked PSBCB-*b*-PLA films, it cannot be used for the cross-linked insoluble films. Spectroscopic studies on the cross-linked films indicate that, after base degradation for 7 h, ~87% of the PLA is removed (see Figure 6). Degradation of the PLA block can also be achieved using MF-319, a commercially available chemical developer used in lithography. A similar base degradation study was done using this developer, and it was found to completely degrade the PLA block, in a 30 nm thick film, after 5 h as monitored by SEC (not shown). Further studies using the nanoporous cross-linked films reported in this article, however, used the sodium hydroxide solution for the PLA degradation.

The thermal cross-linking of the matrix is, as would be expected, critical. With PS-*b*-PLA the porous film, produced by removal of the PLA, is not stable upon heating. Pore collapse is seen when the films are heated to 200 °C. Even with PSBCB-*b*-PLA, where there are BCB groups present for cross-linking, the cross-linking must be performed before removal of the PLA to prevent collapse of the pores (see Supporting Information).

Films of PSBCB-*b*-PLA were annealed at 170 °C for 2 h to promote ordering of the microdomains. After this initial heating, SEC indicates that the films are slightly cross-linked, even at these low temperatures. This is evidenced by the appearance of a higher molecular weight tail in the SEC and a decrease in signal corresponding to the molecular weight of the original diblock copolymer (Figure 7). When the films are placed into a vial of THF at room temperature, the “as cast” material dissolves instantly, while the film heated to 170 °C does not completely dissolve after dissolution for 30 min.

To sufficiently cross-link the thin films for solvent and thermal resistance, the films were annealed at 170 °C for 2 h and then cross-linked at 200 °C for 5 h under a nitrogen atmosphere. Although SEC indicates that the sol fraction is minimal after heating the films for 1 h at 200 °C, the film is not sufficiently cross-linked after this time. SFM studies of the stability of the porous films after cross-linking for 1 h, vs cross-linking for 5 h, indicate the collapse of the porous morphology if the films were cross-linked for only 1 h (see Supporting Information). Swelling measurements using thin films of the PSBCB homopolymers support the SEC data and indicate that heating the thin films at 170 °C for 2 h and then at 200 °C for 5 h is sufficient to cross-link the

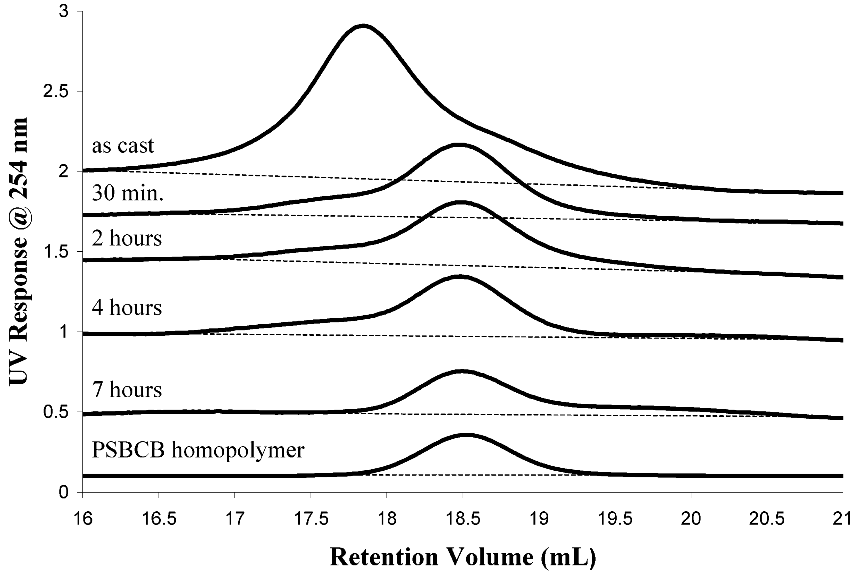

Figure 5. SEC traces (UV detector at 254 nm) of substrate-supported non-cross-linked films after base degradation for different lengths of time, as specified, followed by dissolution in THF. The weak signal and baseline drift of the base-degraded samples are due to the low concentration used for the SEC injection, since the films (1 cm × 1 cm × 30 nm) were dissolved directly off of the gold substrate using 0.4 mL of THF. PSBCB homopolymer RI trace of bulk sample (4 mg/mL sample concentration) is shown for comparison (intensity of this peak was adjusted to facilitate comparison). Dashed lines are added for clarity.

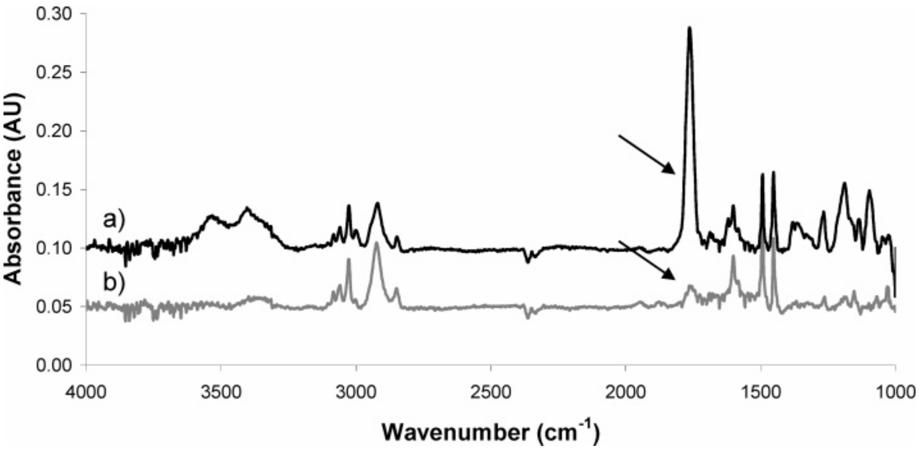

Figure 6. PM-IRRAS spectra of (a) cross-linked sample and (b) cross-linked sample after base degradation. The fraction of PLA degraded was determined from the disappearance of the carbonyl peak at 1763 cm^{-1}.

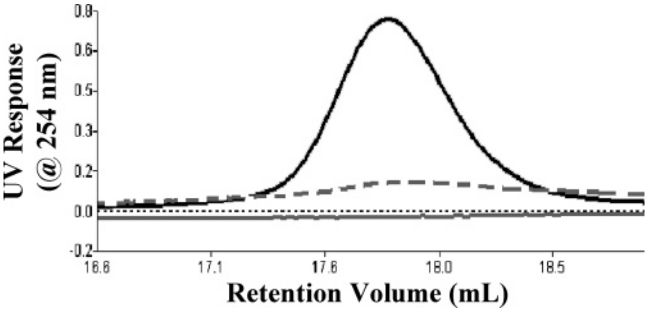

Figure 7. SEC traces (UV detector at 254 nm) for the sol fraction of the thin films extracted using THF at room temperature. Unheated sample (solid black line) dissolves completely. Sample heated at 170 °C for 1 h, cooled, and extracted with THF for 30 min (dotted gray line) does not completely dissolve. Heating at 200 °C for 1 h (solid gray line) causes further cross-linking, and no soluble polymer is extracted. The variation in intensity between the curves corresponds to the amount of polymer extracted. Curves shown are for 1 cm × 1 cm × 30 nm films, each extracted in 1.0 mL of THF.

matrix (see Figure 8). As would be expected, the homopolymer containing 26% BCB units swelled less after cross-linking than did the homopolymer containing 16% BCB units. In both cases, heating at 170 °C for 2 h plus 200 °C for 3−5 h yields the highest cross-link density for the number of BCB units in the polymer chain. After applying this thermal treatment to the diblock copolymer thin films, base degradation produced a cross-linked nanoporous films with the same morphology as the un-cross-linked films.

The molecular weight between cross-links, M_c, can be calculated[25] from this swelling data using

$$N_c = \frac{(L_e/L_0)^3}{\phi(^1/_2 - \chi)} \tag{1}$$

This equation is used for the unidirectional swelling behavior of surface-attached polymer networks, where N_c is the number of segments between cross-links, ϕ is the volume fraction of polymer in the swollen network, χ is the polymer−solvent interaction parameter, L_e is the average swollen thickness, and L_0 is the thickness of the dry film.[25] For our system, χ is ~0.006, using the solubility parameters from the literature.[26] The average M_c can be calculated using N_c (see Table 1).

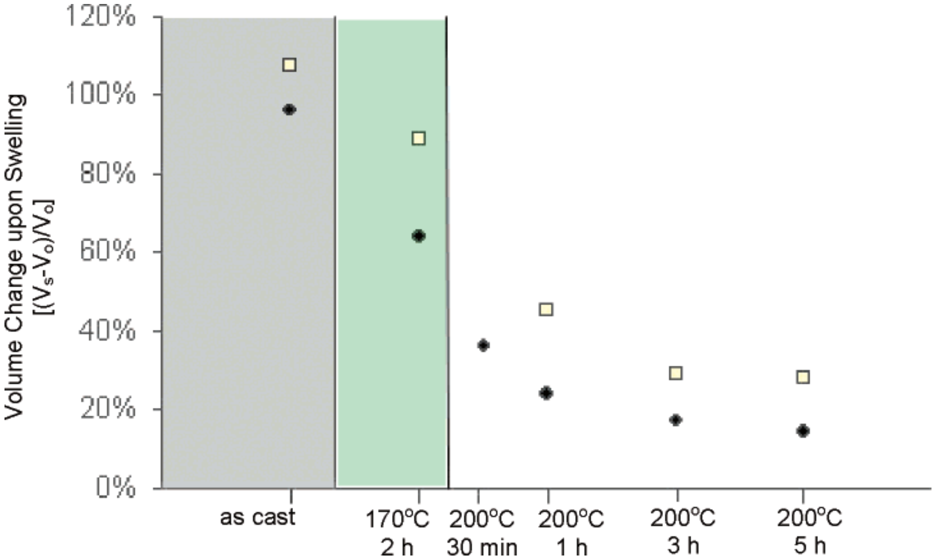

Figure 8. Swelling experiments in THF vapor using PSBCB homopolymer thin films (~140 nm) at various stages of thermal treatment. PSBCB homopolymer, 13 kg/mol containing 26% BCB units (dark circles); PSBCB homopolymer, 11.3 kg/mol containing 16% BCB units (open squares). Films that were heated at 200 °C for the times below had undergone a prebake at 170 °C for 2 h.

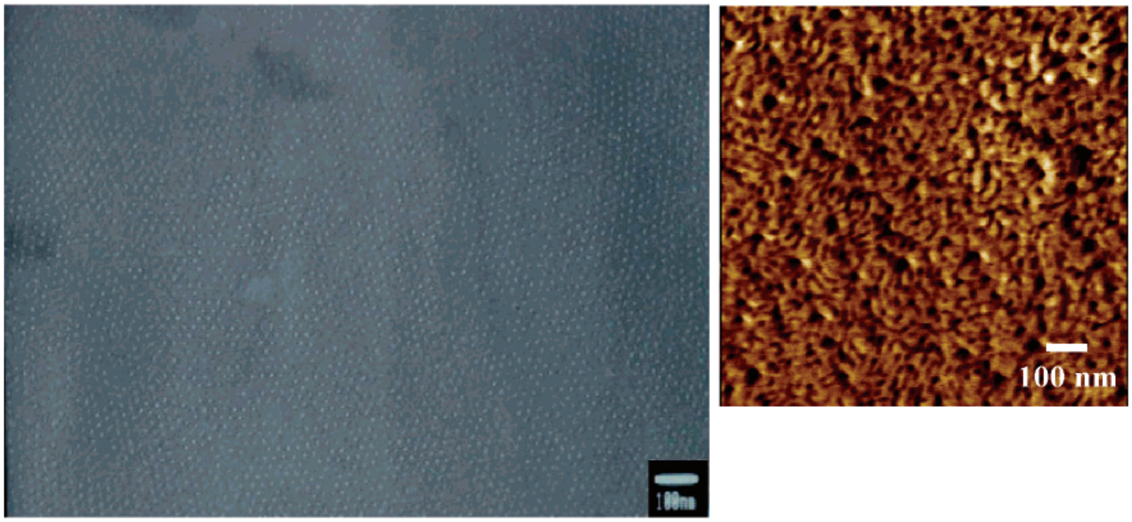

Figure 9. Characterization of the thin film porosity: TEM (left) looking down through a 30 nm cross-linked film with holes where the PLA was removed. SFM (right) of the bottom of a similar 30 nm film.

Table 1. Cross-Linking Values Calculated for Homopolymer PSBCB Thin Films after Different Thermal Treatments Using the Data from Figure 8 and Eq 1

	thermal treatment	% swelling	N_c[a]	M_c (g/mol)
26% BCB	170 °C, 2 h	64	23.5	2442
	170 °C, 2 h + 200 °C, 30 min	36	12.0	1251
	170 °C, 2 h + 200 °C, 1 h	24	8.6	894
	170 °C, 2 h + 200 °C, 3 h	17	7.1	739
	170 °C, 2 h + 200 °C, 5 h	14	6.5	673
			2.9−3.8[b]	300−400[b]
16% BCB	170 °C, 2 h	89	39.2	4079
	170 °C, 2 h + 200 °C, 1 h	45	15.2	1582
	170 °C, 2 h + 200 °C, 3 h	29	10.0	1041
	170 °C, 2 h + 200 °C, 5 h	28	9.7	1012
			5.8−6.7[b]	600−700[b]

[a] Number of segments between cross-links calculated using eq 1. [b] Number of segments calculated assuming 100% cross-linking and uniform distribution of BCB groups along chain.

The average M_c for the templates after cross-linking at 170 °C for 2 h and then at 200 °C for 5 h is ~670 and ~1000 g/mol for the 26% and 16% BCB containing polymers, respectively. This is higher than the theoretical molecular weight between cross-links calculated assuming complete BCB cross-linking and uniform placement of BCB groups. The higher M_c would indicate that the BCB groups are not fully cross-linked due to limited diffusion and availability of nearby BCB groups, since the BCB groups cross-link in pairs.

Persistence of the Morphology. TEM results of the film indicate that the cylindrical microdomains are oriented normal to the surface over large areas and penetrate through the film. Since the microdomain size of the PSBCB-*b*-PLA is ~1/2 of the film thickness, TEM provides strong evidence of the orientation of the pores (see Figure 9). Some of the pores in the image appear blocked, which may be due to the incomplete removal of the PLA in the cross-linked films (see Figure 6). A thin film was coated with carbon and embedded in epoxy to "flip" the sample, to allow SFM imaging of both the top and the bottom of the film. The SFM images indicate that the cylindrical microdomains span across the film, from the surface to the substrate. There is an added

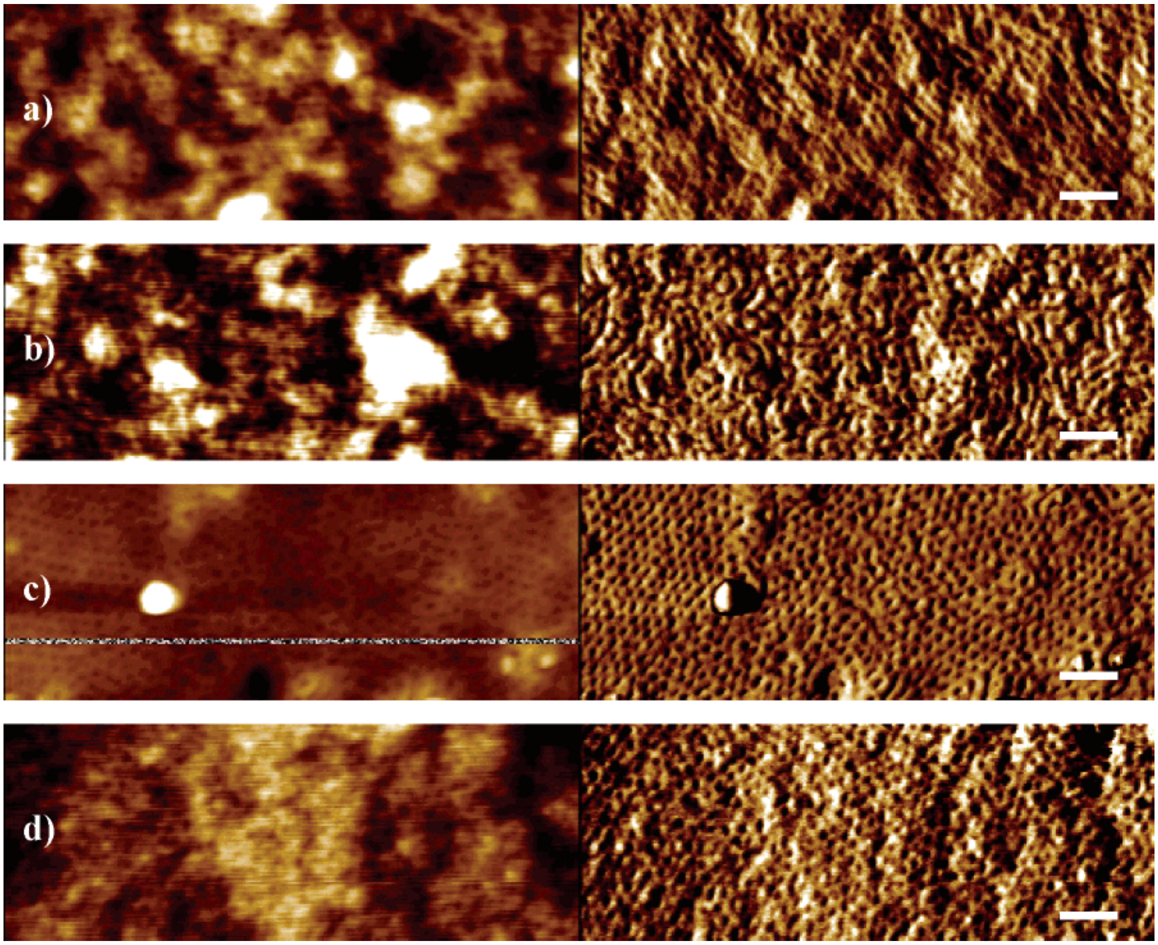

Figure 10. SFM images of porous films subjected to various thermal and solvent conditions: (a) base degraded for 11 h and then heated at 250 °C for 1 h; (b) base-degraded for 30 min and then heated at 200 °C for 11 h; (c) base-degraded for 30 min and then soaked in THF at room temperature for 3 days; (d) base-degraded for 11 h and then submerged in refluxing benzene for 3 h. Scale bars = 100 nm.

surface roughness due to the embedding of the films (see Figure 9).

Pore Stability in Cross-Linked Thin Films. After thermal treatment of the ~30 nm films, the PLA block was degraded using a weak base to produce the nanoporous film. These porous films are solvent resistant and do not dissolve or delaminate from the substrate upon soaking. Films soaked in THF at room temperature for 3 days, or treated more harshly by placing in refluxing benzene for 3 h, maintained the porous structure, as evidenced by SFM (see Figure 10). Heating studies done on the porous films show minimal collapse of the porous structure, in that the pores are maintained but show a slight rounding of the edges (see Figure 10).

To understand the effect of cross-linking, the modulus of the matrix required to maintain the nanoporous structure in the films can be estimated from the surface area produced by pore formation, the surface energy, and pore diameter, using the arguments of Muralidharan et al.[27] The modulus required to stabilize a nanopore with a given radius (r) can be estimated using the surface tension (γ) of the matrix, in our case, cross-linked polystyrene, assuming the matrix behaves as an infinite elastic solid and the polymer behaves as an incompressible solid, then

$$\frac{2Er}{3\gamma} > 1 \tag{2}$$

The modulus can then be used to determine the molecular weight between cross-links (M_c) needed to keep the porous morphology from collapsing by

$$E = \frac{3\rho RT}{M_c} \tag{3}$$

The density (ρ) and surface tension of PS at 473 K were calculated to be 0.9671 g/cm^3 and 27.7 mN/m using the bulk values for polystyrene at 200 °C.[28] This higher temperature was chosen because it is above the T_g of the un-cross-linked matrix and would promote collapse of the porous structure if the matrix was not sufficiently cross-linked. Using the above equations, the modulus required to support a 14 nm diameter pore in a PS matrix at 200 °C was calculated to be ~5.93 MPa. This modulus can be achieved by having an M_c of ≤ 2 kg/mol. The M_c for the PS matrix with 16 mol % BCB in the PS block is ~600−700 g/mol, assuming 100% cross-linking of the BCB along the chain and a uniform distribution of BCB groups. For comparison, pores with a diameter of 10 nm require an $M_c \sim 1.4$ kg/mol to support the porous structure, which is much greater than the $M_c \sim 300-400$ g/mol calculated for the PSBCB matrix used, assuming complete cross-linking of the 26 mol % BCB groups. In both cases, SFM and TEM observations confirm the retention of the pores in the films well above the T_g of PS when the films are cross-linked. The calculated M_c required for pore stability roughly corresponds to the actual M_c observed for pore stability (see Table 1). In comparing the theoretical and experimental values in Table 1, the porous morphology should be stable after heating for 200 °C for 1 h, but experimental observations suggest otherwise. Pore collapse is seen upon subsequent heating of the porous films (see Supporting Information).

Conclusions

In summary, a cross-linkable diblock copolymer was synthesized and used to create nanoporous thin films by a purely thermal process which has a number of advantages in terms of manufacturability over previous strategies. A cylindrical microdomain morphology with PLA as the minor component was produced with domains oriented perpendicular to the surface. By degrading the PLA, a nanoporous film was obtained where the pores penetrated through the film. Stability of the porous film was achieved by incorporating BCB into the matrix block to allow thermal cross-linking. The process presented here for the fabrication of nanoporous templates is simple, requiring minimal handling of the film and eliminating the need for UV irradiation, ion etching, or secondary chemical modification to remove the minor component. The hydroxy functionality within the cross-linked nanopores provides a versatile tool for incorporating and exploring chemical reactions in constrained geometries, and exploitation of this feature is currently under investigation.

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Supporting Information Available: Collapse of the porous morphology with insufficient cross-linking. This material is available free of charge via the Internet at http://pubs.acs.org.

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