

Thermo-Solvent Annealing of Polystyrene-Polydimethylsiloxane Block Copolymer Thin Films

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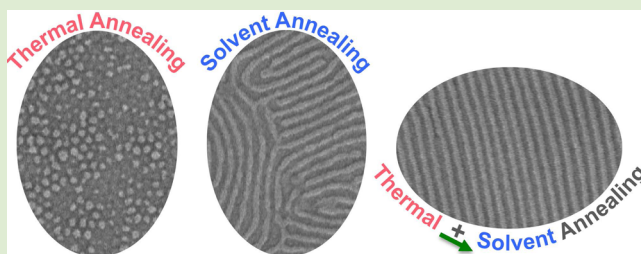
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S Supporting Information

ABSTRACT: A combined thermal and solvent vapor annealing process for block copolymer self-assembly is demonstrated. Films of cylinder-forming poly(styrene-*b*-dimethylsiloxane) (SD45, 45.5 kg/mol, $f_{\text{PDMS}} = 31\%$) were preheated for 2 min above the glass transition temperature of both blocks, followed by immediate introduction into a chamber containing room temperature saturated vapors of toluene and *n*-heptane. After quenching in air, microdomains had better order than those obtained from thermal or solvent annealing alone. The short time during which the film is both heated and exposed to solvent vapor played an important role in determining the final morphology.



Due to its simplicity, cost-effectiveness, and the tunability of size, shape, and periodicity, self-assembly of block copolymers (BCPs) is considered to be a candidate for a next-generation patterning technique that allows high-throughput fabrication of structures ranging from a few nm to ~ 100 nm.^{1–4} The block copolymer film is spin-coated from a solution, producing a kinetically trapped state consisting of disordered chains, micelles, or poorly microphase-separated microdomains. Thermal annealing, solvent annealing, or a combination of processes have been reported to achieve strongly segregated structures^{4–12} with improved ordering. The orientation of the microdomains has been controlled by various methods, including applying shear fields,¹³ a temperature gradient,¹⁴ graphoepitaxy,¹⁵ electric field alignment,¹⁶ magnetic field alignment,¹⁷ directional solidification,¹⁸ and solvent concentration gradient,¹⁹ and the patterns can be registered with topographical or chemical substrate features.^{5,20}

During thermal annealing, BCPs are typically heated above the glass transition temperature (T_g) but below the order-disorder transition temperature (ODT) to promote microphase separation. However, as the Flory–Huggins interaction parameter (χ) increases, the ODT is increased and the diffusion coefficient is reduced. High temperature annealing can lead to degradation or chain scission.²¹ Mobility can be enhanced at lower temperature by using solvent vapor annealing (SVA) in which solvent molecules are absorbed in the BCP, reducing the diffusive energy barrier and promoting chain rearrangements.⁷ By varying the selectivity of the solvent

vapor to the two blocks and, therefore, the effective volume fraction, a range of nonbulk morphologies can be produced in one BCP.^{22,23} The final morphology is also highly dependent on the solvent uptake and removal rate which affects the microdomain orientation and correlation length.^{19,22,24,25}

Combinations of SVA and thermal annealing offer a wide process parameter space within which the morphology can be modified. Heating a closed steel chamber containing a film of polystyrene-*b*-polydimethylsiloxane (PS–PDMS) and toluene vapor⁶ or heating a film of PS–PDMS that was placed within a vapor of toluene and heptane at ambient temperature⁷ both led to self-assembly within minutes. Heating has also been carried out using microwave excitation for polystyrene-*b*-poly(methyl methacrylate) and polystyrene-*b*-poly(2-vinylpyridine) annealed in tetrahydrofuran vapor²⁶ or for PS–PDMS in toluene vapor.²⁷ These techniques produced good ordering within short times, but the details of the processes are not well understood, because temperature affects the solvent vapor pressure, the solubility of solvent in the film, and the diffusivity of solvent and BCP molecules. Further, the temperature of the chamber, film, substrate and vapor may not be the same. In ref 7, the effects of heating the substrate and the chamber were separately identified by applying heat to a solvent-swollen BCP

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film without changing the temperature of the surrounding solvent vapor environment and by tracking the swelling ratio of thin films of PS–PDMS in situ as they were exposed to solvent vapor and subsequently to a thermal cycle. Well-ordered microdomains of PS–PDMS films annealed in toluene and *n*-heptane vapors for total process times of 30 s to 5 min were achieved on patterned substrates.⁷ The heating deswelled (or thermally quenched) the film, and the final morphology was very sensitive to the rates of both deswelling and heating, which occurred simultaneously.

In this Letter, a different approach is taken to achieve combined thermal and solvent annealing by first heating the film and then rapidly introducing it into a solvent vapor at ambient temperature. Films of bulk-cylindrical morphology 45.5 kg/mol PS–PDMS (SD45, $f_{\text{PDMS}} = 31\%$) on smooth oxidized Si substrates with PDMS brush were preheated for 2 min at a temperature above the T_g of PS, inserted into a chamber containing a toluene and heptane vapor at room temperature for up to 50 min, then air quenched. Well ordered in-plane cylindrical microdomains were produced with a few defects per square μm and with much better order than was obtained by thermal or solvent annealing alone.

The temperature of the sample holder during the preheating step is shown in Figure 1a. The heating and cooling of the film takes about 1 min. The increase in film thickness due to thermal expansion was less than 4%, Figure 1b, followed by a sharp drop when the heater was turned off. The expansion of films of PDMS homopolymer and PS homopolymer was also measured during preheating using spectral reflectometry. A higher swelling ratio was observed in the PDMS compared to the PS homopolymer, due to the higher thermal expansion coefficient (α) of the former ($\alpha_{\text{PS}} \sim 70 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{\text{PDMS}} \sim 310 \times 10^{-6} \text{ K}^{-1}$), Figure 1b). The expansion of the SD45 was intermediate between that of the homopolymers. The thermal expansion overcame structural relaxation leading to the swelling of films rather than collapsing or densification.^{28–30} As a result, the SD45 films were already thermally expanded by $\sim 4\%$ before introduction into the solvent annealing chamber, and their χ and diffusivity were characteristic of the preheating temperature.

As the preheated film was introduced into the chamber, it simultaneously swelled by solvent uptake and cooled. It experienced a slower initial swelling rate compared with the unheated film, because the high temperature of the preheated film reduced the solubility of solvent, as shown in the inset of Figure 1c. The unheated film (green data in Figure 1c) showed a small drop in swelling ratio corresponding to about 3% of the dry thickness within 5 min of annealing which is in agreement with previous findings.^{7,25,31} This was attributed⁷ to a relaxation of free volume of the as-cast film, which occurred once its mobility was sufficiently increased by solvent uptake, analogous to Case 2 diffusion for glassy polymeric films. For the preheated samples, the drop in thickness was not observed suggesting the preheating had partly relaxed the film. After about 20 min annealing the preheated film reached a slightly larger swelling ratio than the unheated film, which was maintained through the remainder of the anneal.

SEM revealed that the as-spun film consisted of micelles, Figure 2a. The preheating alone appeared to make the micelles less regular, Figure 2b. In contrast, 50 min solvent annealing alone transformed the micelles into poorly ordered in-plane cylindrical microdomains, Figure 2c. However, when 2 min preheating was combined with 50 min solvent annealing, the

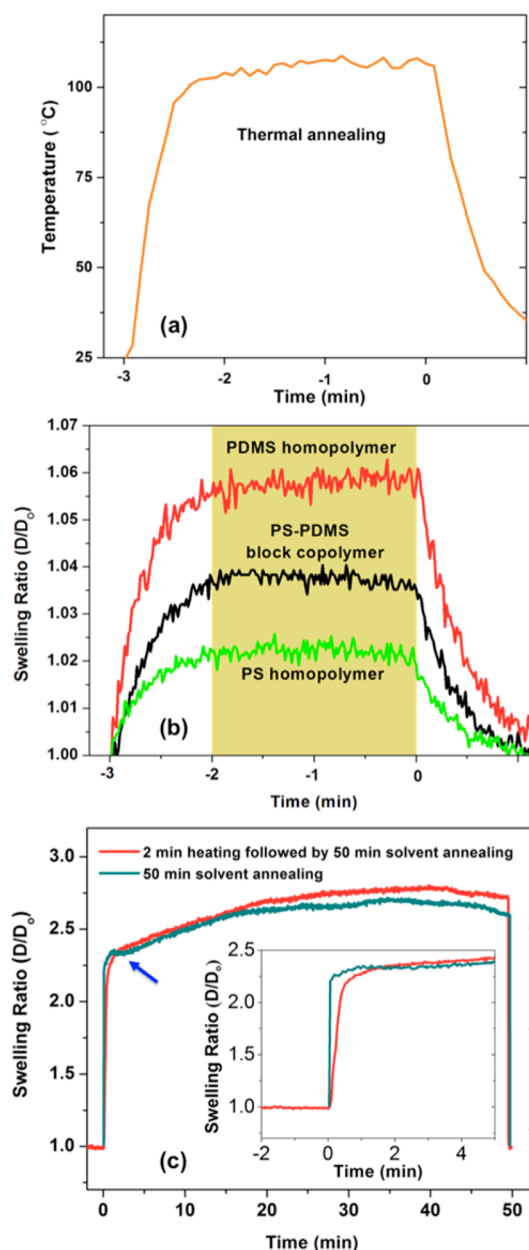


Figure 1. (a) Temperature cycle and (b) expansion of PS, PDMS homopolymer, and SD45 block copolymer during the preheating step. (c) Swelling ratio of 32 \pm 2 nm thick SD45 films after insertion into solvent vapor. Red: sample initially preheated; green: no preheating. The inset shows the initial solvent swelling which occurred faster for the unheated film. The drop in swelling in the unheated film is shown with an arrow.

long-range ordering of the microdomains was significantly improved, with only a few defects (junctions and terminations) within an image area of 1.5 $\mu\text{m} \times 1.5 \mu\text{m}$ on a smooth substrate, Figure 2d.

The dramatic enhancement in ordering due to the thermosolvent process could be related to the relaxation and preanneal of the film during the preheating (indicated by the absence of the drop in swelling ratio after a few minutes of solvent anneal); the slower initial swelling of the preheated film in the solvent; the somewhat larger swelling ratio of the preheated film in the second half of the solvent anneal; or the high mobility during the time the film is both swelled and

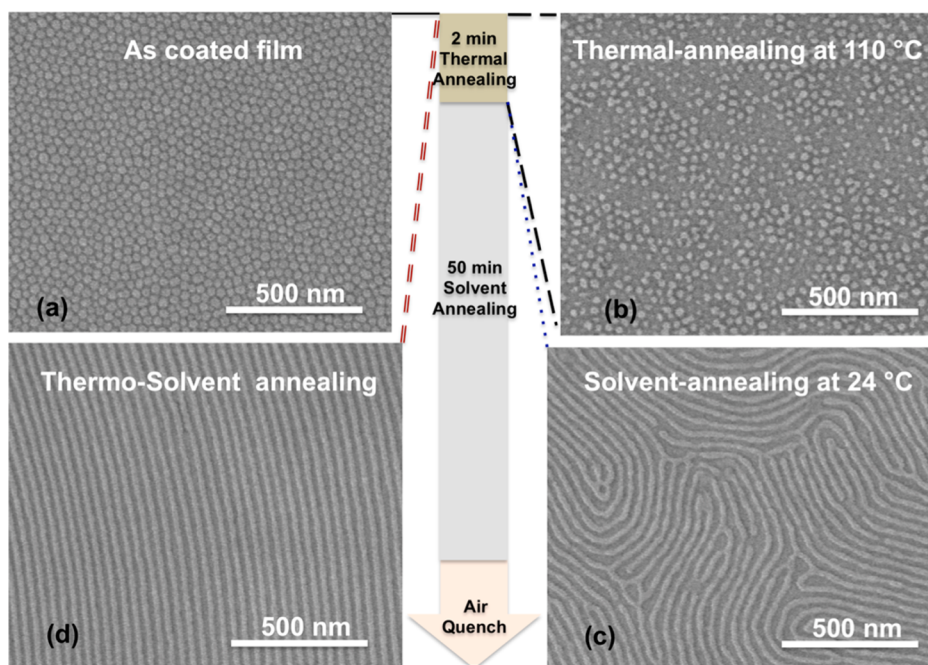


Figure 2. Process flow and SEM images of the thermal, solvent, and thermo-solvent annealing processes. (a) As-spun SD45 film with micellar structures from PGMEA solution. (b) SEM image of a SD45 film after 2 min thermal annealing at 110 °C. (c) SEM image showing surface morphology of a SD45 film after 50 min solvent annealing at 24 °C followed by air quenching. (d) SEM image of a PS–PDMS thin film that was annealed thermally for 2 min at 110 °C, then immediately solvent annealed at 24 °C for 50 min, then air quenched. The schematic at the center shows the sequence of processes, and the dotted and dashed lines indicate which processes were applied to each sample.

heated. From experiments on other PS-*b*-PDMS block copolymers,³² we do not believe the small difference in swelling ratio at longer times is responsible for the large difference in ordering.

To establish the importance of an elevated film temperature at the beginning of the solvent anneal, another film was preheated then allowed to cool for 30 min before insertion into the solvent vapor (Figure 3a). A total of 30 min is long enough

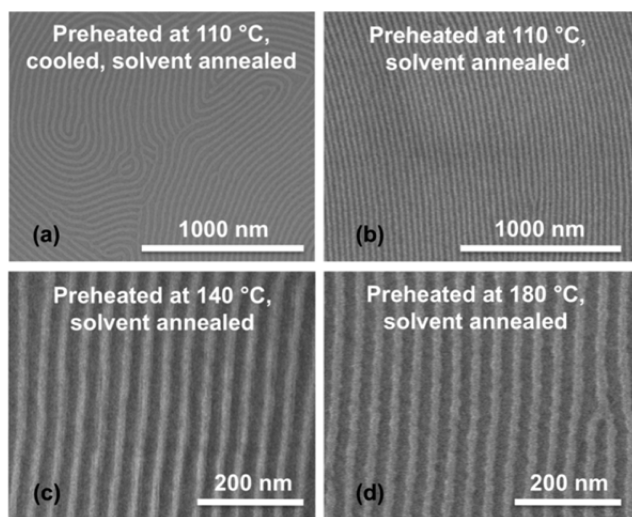


Figure 3. SEM images of (a) a SD45 film that was preheated, cooled for 30 min, and then solvent annealed. This morphology resembles Figure 2c; (b–d) SD45 films after thermo-solvent annealing at (b) 110 °C (same process as Figure 2d), (c) 140 °C, and (d) 180 °C. Ripples in (d) are due to vibration in the SEM; (c) and (d) are at higher magnification than (a) and (b), but show similar defect levels.

to allow the preheated film to cool back to room temperature. This can be compared with Figures 3b and 2d, which were preheated and immediately solvent-annealed. The morphology of Figure 3a was less well ordered than Figures 2d and 3b and similar to that of Figure 2c, which underwent solvent annealing alone. This suggests that the short heating cycle itself did not lead to large changes in morphology. We believe instead that the time period over which the film simultaneously experienced both elevated temperature and solvent swelling plays an important role in the thermo-solvent annealing process.

Preheating at temperatures of 140 and 180 °C (Figure 3c,d) did not improve the ordering of the microdomains significantly as compared with preheating at ~110 °C (Figure 3b). This may be because the higher temperatures prevented solvent uptake, which does not occur until the sample has partly cooled. However, at the higher temperatures, more dewetting was observed.

To further illustrate the effects of 110 °C preheating on the first few minutes of solvent annealing, the surface morphology of the unheated sample was examined after 5 min solvent annealing. The as-cast film consisted of densely packed micelles (Figure 2a), whereas as Figure 4a shows, after 5 min solvent annealing, the quenched film contained clusters or islands of micelles. AFM revealed that the micellar islands had heights exceeding 15 nm (Figure 4c), which is a large fraction of the initial thickness of the film, ~32 nm. On the contrary, in a preheated sample, the micelles became less regular after 5 min solvent annealing and quenching (Figure 4b), but there were no islands at that time and no drop in swelling ratio. Instead, micellar islands were observed after about 10 min of annealing (Figure 4d). The role of the islands in the morphological evolution of the film is not known, nor whether they were present in the swelled film or formed on drying. However, this result does illustrate that the preheating, which delayed the

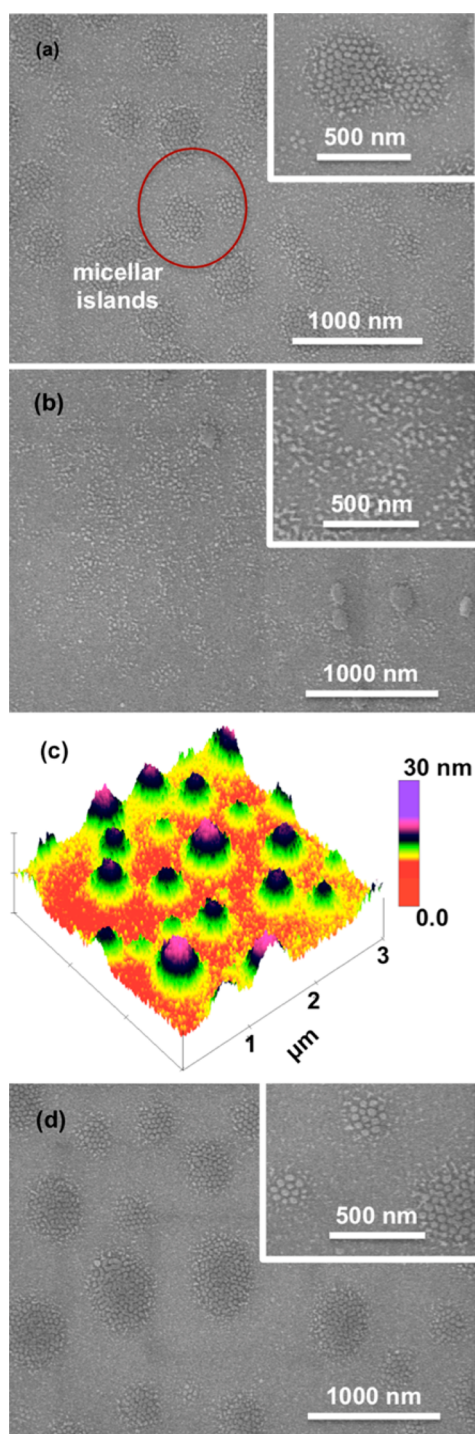


Figure 4. (a) SEM image of micellar islands in an unheated film after 5 min solvent annealing. (b) SEM image of a preheated film after 5 min solvent anneal without micellar island formation. (c) 3D AFM trace of an unheated film after 5 min solvent anneal showing island height of ~ 15 nm. (d) SEM image of a preheated film after 10 min solvent anneal showing micellar island formation. Insets show images at higher magnification.

initial uptake of solvent, as seen in Figure 1c, affected the kinetics of rearrangement of the polymer chains in the first 5–10 min of solvent annealing.

In summary, a thermo-solvent annealing process was introduced for self-assembly of block copolymer films consisting of a short thermal anneal at a moderate (110 °C)

temperature followed by insertion of the heated film into a solvent vapor at room temperature. The method enables independent control over both the thermal cycle and the solvent vapor. Sequential heating and solvent vapor anneal of the heated film led to the formation of microdomains in a PS–PDMS block copolymer with significantly improved order. Preheating at higher temperatures, 140 and 180 °C, did not improve the microphase separation and promoted dewetting.

The thermo-solvent annealing process makes use of a reversed sequence compared to the solvothermal process of ref 7 in which the film was swelled in a solvent vapor and then heated to drive out solvent. In both cases, the short time period lasting seconds to a minute during which the sample is both heated and exposed to solvent vapor appears to play a key role in determining the final morphology. It is likely that the postanneal morphology may be further manipulated by spin-coating from other solvents, which produce different initial arrangements of micelles or disordered polymer chains in the film. The combination of thermal and solvent vapor annealing facilitates self-assembly of block copolymers and could be useful in manufacturing processes requiring well-ordered block copolymer films.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, materials, and methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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