Morphology evolution of PS-b-PDMS block copolymer and its hierarchical directed self-assembly on block copolymer templates

Rasappa, Sozaraj; Schulte, Lars; Borah, Dipu; Hulkkonen, Hanna; Ndoni, Sokol; Salminen, Turkka; Senthamaraikanan, Ramsankar; Morris, Michael A.; Niemi, Tapio

Published in:
Microelectronic Engineering

Link to article, DOI:
[10.1016/j.mee.2018.02.002](https://doi.org/10.1016/j.mee.2018.02.002)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Rasappa, S., Schulte, L., Borah, D., Hulkkonen, H., Ndoni, S., Salminen, T., Senthamaraikanan, R., Morris, M. A., & Niemi, T. (2018). Morphology evolution of PS-b-PDMS block copolymer and its hierarchical directed self-assembly on block copolymer templates. *Microelectronic Engineering*, 192, 1-7.
<https://doi.org/10.1016/j.mee.2018.02.002>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Accepted Manuscript

Morphology evolution of PS-b-PDMS block copolymer and its hierarchical directed self-assembly on block copolymer templates

Sozaraj Rasappa, Lars Schulte, Dipu Borah, Hanna Hulkkonen, Sokol Ndoni, Turkka Salminen, Ramsankar Senthamaraiakanan, Michael A. Morris, Tapio Niemi

PII: S0167-9317(18)30062-5
DOI: <https://doi.org/10.1016/j.mee.2018.02.002>
Reference: MEE 10729
To appear in: *Microelectronic Engineering*
Received date: 3 October 2017
Revised date: 2 February 2018
Accepted date: 3 February 2018

Please cite this article as: Sozaraj Rasappa, Lars Schulte, Dipu Borah, Hanna Hulkkonen, Sokol Ndoni, Turkka Salminen, Ramsankar Senthamaraiakanan, Michael A. Morris, Tapio Niemi , Morphology evolution of PS-b-PDMS block copolymer and its hierarchical directed self-assembly on block copolymer templates. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Mee(2017), <https://doi.org/10.1016/j.mee.2018.02.002>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Morphology evolution of PS-*b*-PDMS block copolymer and its hierarchical directed self-assembly on block copolymer templates

Sozaraj Rasappa^{1*}, Lars Schulte^{2,3}, Dipu Borah⁴, Hanna Hulkkonen¹, Sokol Ndoni^{2,3}, Turkka Salminen¹, Ramsankar Senthamaraikanan⁴, Michael A Morris⁴ and Tapio Niemi^{1*}

¹Laboratory of Photonics, Tampere University of Technology, P. O. Box 692, FI-33101, Finland.

²Department of Micro and Nanotechnology, Technical University of Denmark, DK-2800 Kgs, Lyngby, Denmark.

³Center for Nanostructured Graphene CNG, Technical University of Denmark, DK-2800 Kgs, Lyngby, Denmark.

⁴AMBER Centre and CRANN, Trinity College Dublin, Dublin 2, Ireland.

*Corresponding Authors: sozaraj.rasappa@tut.fi (SR), tapio.k.niemi@tut.fi (TN)

Abstract:

Cylinder-forming polystyrene-*block*-polydimethylsiloxane (PS-*b*-PDMS, 27.2k-*b*-11.7k, SD39) block copolymer having a total molecular weight of 39 kg mol⁻¹ was exploited to achieve in-plane morphologies of lines, dots and antidots. Brush-free self-assembly of the SD39 on silicon substrates was investigated using solvents that were PS or PDMS selective, neutral and non-solvents based on their Hansen solubility parameters. The different morphologies were achieved with annealing times ranging from 10 min to 1 h at room temperature. The SD39 patterns were used as an etch mask for transferring the pattern into the underlying substrate. Directed self-assembly and hierarchical directed self-assembly on block copolymer templates for confinement of dots was successfully demonstrated. The strategy for achieving multiple morphologies using one BCP by mere choice of the annealing

solvents on unmodified substrates provides a simplified method for surface nanopatterning, templated growth of nanomaterials and nanofabrication.

(**Keywords:** block copolymer; hierarchical self-assembly; Hansen solubility; selective solvent)

Introduction:

In recent years, block copolymers (BCPs) have been extensively studied as a cost effective patterning platform for the fabrication of ultra-small device structures [1-4]. BCPs are covalently coupled molecules that can self-organize and form periodic patterns [5]. The size and shape of the final morphology of the BCP can be precisely tuned by its molecular weight and volume fraction of the blocks [6, 7]. The size of the structures formed by the micro-phase separation of the BCPs are typically in the range of 5 nm to 100 nm [8] enabling the production of sub-10 nm feature sizes [9]. The spin coated BCP film is disordered but it can be organized by thermal annealing, solvent annealing or solvo-thermal annealing [10-13]. However, controlling the orientation of the BCP blocks in thin films, long-range ordering and point defects are still a challenge [14, 15]. Ordered BCP thin films can act as a template for the fabrication of metal/metal-oxide nanostructures and as an etch mask for pattern transfer [16-19].

Among other BCPs, PS-*b*-PDMS has a high Flory-Huggins value ($\chi=0.29$), which enables the formation of ultra-small feature sizes and sharply defined patterns due to the strong segregation force between the polymer blocks [20]. Furthermore, the PDMS block contains inorganic moieties (silicon) resulting in a good *in-situ* etch contrast for nanolithography [21]. Recent reports show a variety of morphologies such as spheres, cylinders, lamellae and perforated lamellae that were achieved by tuning the volume fractions of the blocks and by tailoring the surface chemistry of the substrate [22, 23]. To direct the BCP towards the desired morphology and orientation, polymer brush layers or self-assembled monolayers are

typically applied on the surface of the substrate [24, 25]. Asymmetric PS-rich PS-*b*-PDMS primarily produces in-plane and out-of-plane cylinders. Hexagonally perforated lamellae or antidots are more difficult to acquire using PS-rich BCPs and thus PDMS-rich BCPs are utilized to achieve the antidot structures [14, 15].

The present study highlights the means to control the morphology of the (PS-*b*-PDMS, 27.2k-*b*-11.7k, SD39) thin film through solvent annealing in selected solvents without any surface pretreatment or complex top-coat processes which considerably increase the overall processing time. The solvents and solvent mixtures were selected to be either neutral or non-solvents for both blocks or selective for one of the blocks based on their Hansen solubility parameters (HSP). The optimization of the BCP annealing conditions was conducted using BCP thin films on silicon (Si) substrates. The line, dot and antidot morphologies were then used as etch masks to transfer the nanopattern into the substrate. Directed self-assembly (DSA) and hierarchical directed self-assembly on SD39 templates shows regular alignment without any brush layer. This hierarchical directed self-assembly will help in developing quantum and nanoplasmonic structures.

Experimental

Solvents / Polymer synthesis

All chemicals and solvents used in the present investigation were purchased from Sigma-Aldrich and utilized as received without further purification. The tested solvents were: Cyclopentanone (Reagent plus, $\geq 99.9\%$), N,N Dimethylformamide or dimethylformamide (anhydrous, 99.8%), 1,4 Dioxane or dioxane (anhydrous, 99.8%), Tetrahydrofuran (inhibitor-free, CHROMASOLV Plus, for HPLC, $\geq 99.9\%$), Toluene (CHROMASOLV, for HPLC, 99.9%), Hexane (for HPLC, $\geq 95\%$), and Heptane (for HPLC, $\geq 99\%$). Buffered Oxide Etchant or Buffered HF (BOE 7:1) was purchased from Microchemicals and used as received. The SD39 was synthesized by living anionic polymerization following a reported procedure [26,

27]. The average molecular weights per block and the polydispersity index (PDI) were determined using size exclusion chromatography and a total molecular weight of 38.9 kg mol⁻¹ (M_{PS} : 27.2 kg mol⁻¹ and M_{PDMS} : 11.7 kg mol⁻¹) and PDI of 1.03 were estimated.

BCP template and nanopattern fabrication

All Si substrates were polished single-crystal silicon with <100> orientation, p-type doped and used without any surface pretreatment. The SD39 solution of 1 wt% in toluene was made and 20 μ l of the solution was directly spin coated at a spin speed of 2000 rpm for 40 s resulting in a film thickness of 18 nm. The BCP film thickness was measured by a laser ellipsometer (Rudolph Research AutoEL III) with a HeNe laser at a 70° incident angle. The film thickness measurement was carried out in at least five different locations on each substrate and averaged. SD39 thin films were solvent annealed at room temperature (21°) between 10 min and 1 h in a tightly closed glass jar using solvents and solvent mixtures selected based on their Hansen solubility values. The glass jar for solvent annealing has a volume of 50 cm³ and was filled with 1-5 ml of monosolvent or solvent volumetric mixtures under saturated atmosphere. The annealed films were etched with SF₆ plasma (7 sccm) with 30 W RIE and 50 W ICP at 2.0 Pa (15 mTorr) pressure for 3 s to remove the PDMS wetting layer. Then the PS was selectively etched using O₂ plasma for 10 s with 1200 W ICP and 50 W RIE powers at 2.0 Pa (15 mTorr) pressure (Oxford Plasmalab System 100, ICP). The application of O₂ plasma will simultaneously oxidize the PDMS block. The oxidized PDMS was then used to etch Si using SF₆ (15 sccm) and O₂ (5 sccm) plasma with 20 W RIE and 300 W ICP powers at 0.66 Pa (5 mTorr) for 18 s. Finally all of the samples were rinsed with BOE to remove any residual oxidized PDMS.

Substrates for DSA

The substrates have a low pressure chemical vapor deposited silicon nitride (Si₃N₄) coating (resistivity, $\rho = 1 \times 10^{14}$ to 1×10^{16} Ω cm) on p-type silicon <100> with a native surface

oxide layer of 2 nm. The topographically patterned Si_3N_4 films with pitches in the range of 75–500 nm, variable mesa widths of 30–700 nm, and depth of 60 nm were fabricated via 193 nm UV-lithography and processed by means of conventional mask and etch techniques.

Scanning Electron Microscopy (SEM)

Top-down and tilted SEM images were obtained by using a field emission scanning electron microscope (Zeiss Ultra 55) with 3 kV acceleration voltage. Unless otherwise stated, all SEM images are after PS removal and oxidation of the PDMS block. The dimensions were analyzed from the SEM images the dots and the antidots using Image J software.

Results and discussion

Scheme 1. The process flow of SD39 thin film deposition, solvent annealing, etch and pattern transfer.

Scheme 1 illustrates the process flow of fabrication of nanostructures by SD39 including film deposition, solvent annealing and etch procedures. As outlined in Scheme 1, after annealing, the PDMS was observed to form a thin wetting layer on top at the air-polymer interface. This is attributed to the surface tension of PDMS ($\gamma_C = 24 \text{ mNm}^{-1}$) being lower than that of PS ($\gamma_C = 32.8 \text{ mNm}^{-1}$) [11]. Thereafter, a brief PDMS etch was applied to remove the top layer before the complete removal of PS by O_2 plasma. The Hansen solubility parameters (HSP) for the solvents and solvent mixtures used here are listed in Table 1 and supporting information (SI).

Table 1. HSP of the solvents and Ra for PS and PDMS relative to the used solvents and solvent mixtures. Subscripts denote the volume ratio of the mixtures. Ra values below 4 indicates selective solvent and below 2 highly selective solvent.

Selectivity	Solvent/Solvent mixture/polymer	δ_D	δ_P	δ_H	Ra	
		[MPa ^{1/2}]	[MPa ^{1/2}]	[MPa ^{1/2}]	PS	PDMS
Neutral	toluene	18.0	1.4	2.0	5.2	5.0
	dioxane	17.5	1.8	9.0	6.5	6.1
PS	cyclopentanone	17.9	11.9	5.2	5.9	12.6
	tetrahydrofuran	16.8	5.7	8.0	4.2	7.1
	cyclopentanone ₁ :toluene ₁	17.9	6.6	3.6	1.0	7.8
	tetrahydrofuran ₁ :toluene ₁	17.4	3.5	5	2.7	4.7
	dimethylformamide ₁ :toluene ₁	17.7	7.5	6.6	2.7	8.5
	hexane	14.9	0.0	0.0	9.1	4.6
PDMS	heptane	15.3	0.0	0.0	8.7	4.2
	hexane ₁ :toluene ₁	16.5	0.7	1.0	6.6	3.3
	hexane ₁ :toluene ₂	16.7	0.9	1.3	6.1	3.4
	hexane ₁ :toluene ₃	17.2	1.05	1.5	5.7	3.8
	PS	17.6	6.1	4.1	-	-
	PDMS	15.9	0.0	4.1	-	-

Based on the HSP values, we calculated the Hansen distance (R_a) of PS and PDMS relative to the used solvents and solvent mixtures. The Hansen distance is defined as, $R_a = [4(\delta_{D,\text{Polymer}} - \delta_{D,\text{Solvent}})^2 + (\delta_{P,\text{Polymer}} - \delta_{P,\text{Solvent}})^2 + (\delta_{H,\text{Polymer}} - \delta_{H,\text{Solvent}})^2]^{1/2}$ [28] where δ_D is the dispersive force factor, δ_P is the dipole force factor and δ_H is the hydrogen-bonding factor and calculated as described elsewhere [29, 30]. A small R_a value indicates that the polymer is more soluble in the solvent [30]. The solvents and solvent mixtures were classified by comparing the calculated R_a values for PS and PDMS as selective (small R_a for one polymer), neutral (similar R_a) or non-solvents (large R_a for both polymers) as shown in Table 1. We observed

Figure 1. Top-down SEM images of the oxidized PDMS on the Si substrate. The line and the dot samples were annealed between 10 min and 18 min. The antidot samples were annealed for 1h.

that the annealing solvents which are PS selective and neutral lead to the formation of lines or dots whereas PDMS selective solvents formed antidots as depicted in Scheme 1. Figure 1 shows SEM images of the PDMS templates from the SD39 thin films annealed under PS selective, neutral and PDMS selective solvents. From Figures 1A & 1D it is evident that annealing under PS selective solvents such as cyclopentanone and tetrahydrofuran produced densely packed regular dots and irregular line structures with dislocation and disclination defects. SD39 switches between lines and dots for PS selective solvents since PS swells more than PDMS and the change in the effective volume fraction of PS shifts the polymer system from the cylinder phase towards the dot phase [31, 32]. Neutral solvents such as dioxane and toluene forms dots and well aligned line patterns. Annealing with toluene produced well-defined PDMS lines with fewer defects than annealing with tetrahydrofuran. This is attributed to the mobility of PDMS chains which is limited under PS selective solvents and leads to better organization when switched to neutral solvent (Table 1) [7]. The line width, $\langle d \rangle$, of the PDMS lines after annealed under toluene and tetrahydrofuran were the same 21 ± 1 nm. However, domain spacing $\langle L_0 \rangle$ for toluene is 36 ± 1 nm but for tetrahydrofuran it is not uniform. Annealing under the PDMS selective solvents, such as hexane and heptane, produces an inverted dot morphology (antidots) although the ordering of the patterns is poor as observed from Figures 1C & 1F. Annealing under PDMS selective solvent makes rubbery natured PDMS to flow more easily and enforcing the glassy PS chains to migrate. The intrinsically PS-rich SD39 behaves like a PDMS-rich under PDMS selective solvents but due to the limited mobility only poorly organized antidots were observed. Annealing in dimethylformamide which is a non-solvent for both blocks, resulted in a mixture of lines and dots as shown in Figure S1. This proves that a non-solvent can also be used to favor self-assembly and this could be due to its stronger δ_H [33]. The inclusion of toluene as the second solvent in a dual solvent vapor annealing markedly improved the microphase separation in

comparison to the mono solvents as shown in Figure 2. The irregular cylindrical pattern shown in Figure 1D obtained under PS selective tetrahydrofuran evolved into a conventional ‘fingerprint’ line morphology under volumetric mixture of tetrahydrofuran₁:toluene₁ (**Figure 2A**). This shows that the addition of toluene makes the tetrahydrofuran₁:toluene₁ solvent mixture highly selective to PS ($R_{\text{PS}}=2.7$) which brought a uniform $\langle L_0 \rangle$ of 36 ± 1 nm as with toluene (**Figure 1E**). Interestingly, the mixed morphology of cylinders and dots under dimethylformamide (**Figure S1**) changed to well-ordered and shaped dots under dimethylformamide₁:toluene₁ vapors (**Figure 2B**) as the solvent changes from a non-solvent to highly PS selective ($R_{\text{PS}}=2.7$). The size of the PDMS dots under dimethylformamide₁:toluene₁ vapors increased by about 3 ± 2 nm compared to other solvents with a periodicity of 46 ± 2 nm. A similar variation in periodicity for PDMS structures was observed for cylinder forming PS-rich PS-*b*-PDMS and was documented elsewhere [7].

When switching from dioxane to solvent mixtures of dioxane₁:toluene₁, the morphology evolved from dots to a mixture of lines and dots (**Figures 1B & S2**) as R_a of dioxane₁:toluene₁ is smaller than that of dioxane. This concludes that when the annealing solvent or solvent mixture is neutral or highly PS selective then the morphology evolves to lines, dots or mixture of lines and dots. The addition of a neutral solvent to a PDMS selective solvent enhances the chain mobility of both of the blocks in SD39 and resulted in antidot structures [34]. This is attributed to their asymmetric swelling behavior and changes in the effective volume fraction, which is due to the difference in affinities of the two blocks.

Mixing heptane or hexane with toluene improved antidot formation (heptane₁:toluene₂, heptane₁:toluene₃, hexane₁:toluene₂, hexane₁:toluene₃) and both solvents produced identical morphologies, possibly because of their nearly similar R_a values (3.5 and 3.4) and their average antidot sizes were 32 ± 2 nm and 31 ± 2 nm. As shown in figures 2E & S2, solvent mixtures of hexane₁:toluene₂ and heptane₁:toluene₂ are highly selective to PDMS block

favoring the formation of uniform antidot patterns. When the volume fraction of heptane and hexane increased in the mixtures, disordered structures or multilayers occurred (not shown here). On the other hand when the volume fraction of toluene was increased, mixed lines and disordered antidots were observed as shown in **Figure 2F & S2**. This is because the increase of toluene made the mixture less selective to PDMS. Furthermore, **Figure 2E** indicates that there is an optimum solvent ratio, where PS-rich SD39 produced uniform antidots. Other tested solvent ratios lead to mixed morphologies (Figure 2D & 2F).

Figure 2: Top-down SEM images of the oxidized PDMS on the Si substrate. The lines and dots samples were annealed between 10 min and 18 min whereas the antidot samples were annealed for 1h.

Results of the pattern transfer into Si substrate from oxidized PDMS are compiled in **Figure 3**. A plasma of SF_6 and O_2 was applied to etch the nanopatterns into the Si substrates with an etch depth of $21 \pm 2 \text{ nm}$. This demonstrates that there is a good etch contrast between the oxidized PDMS mask and Si under the employed etching conditions. Figures 3A, 3C & 3E represents the large area top-down SEM images of Si lines, dots and antidots. Figures 3B, 3D & 3F shows the corresponding cross-sectional SEM images of lines, dots and antidots. This

Figure 3: Top down and cross-sectional SEM images of the Si nanostructures. (A, C & E) Top down SEM images of the lines, the dots and the antidots. (B, D & F) Cross-sectional SEM images of the lines, the dots and the antidots.

represents a significant breakthrough in the area of block copolymer lithography of achieving multiple morphologies by simply choosing annealing solvent based on its HSP.

Hierarchical directed self-assembly on SD39 templates

Directed self-assembly (DSA) on nanostructured templates supports the self-assembly of BCPs into longer range ordering. DSA has been extensively explored related to applications in microelectronics over the past few years [20, 35]. Nanostructured templates can be made by conventional nanolithography techniques such as immersion photolithography, electron-beam lithography or nanoimprint lithography. However, down scaling their resolution below sub-20 nm is hard and alignment of individual nanofeatures of sub-10 nm is even more difficult. To advance the applications of the self-assembly of BCPs we made two experiments with DSA of SD39. First, we utilized the DSA substrates having 250-350 nm wide trenches

Figure 4: Directed and hierarchical directed self-assembly. (A&B) SD39 lines and antidots aligned on graphoepitaxial trench substrate. (C&D) Hierarchical directed self-assembly of dots in between lines and antidots of SD39 block copolymer templates.

in Si_3N_4 film to direct the lines and the antidots. The results of annealing either under the PS selective or the PDMS selective solvent mixtures are shown in Figures 4A & 4B. Well-ordered alignment in the guiding trenches and morphology similar to the planar substrates can be observed. This demonstrates the long range lateral ordering on the templates made by conventional lithography. Second, we used the self-assembled lines and antidots of the oxidized PDMS as templates for hierarchical DSA of SD39. The hierarchical DSA results in self-alignment of the individual PDMS dots as shown in Figures 4C & 4D. This approach supports the future applications in positioning nanostructures for semiconductor quantum technology and nanoplasmonics [36].

Conclusions

We have demonstrated brushfree self-assembly of a cylinder-forming PS-*b*-PDMS (SD39) having a variety of densely packed morphologies of lines, dots and antidots. These were achieved by simply selecting the favorable annealing solvents and solvent mixtures based on HSP. The relation between the nature of the solvent and the final morphology was concluded as: neutral and PS selective/highly PS selective solvents produce lines, dots or mixture of lines and dots, whereas PDMS selective/highly PDMS selective solvents exhibit only antidots. Direct nanopatterning of Si using the produced morphologies shows a good etch contrast between the oxidized PDMS and Si producing well defined nanopatterns. Moreover, directed and hierarchical directed self-assembly on block copolymer templates was demonstrated. This hierarchical directed self-assembly could be potential for quantum technologies, metal nanodots isolation and nanogap tuning. Overall, the realization of all morphologies in one BCP (SD39) based on HSP of the annealing solvents demonstrates a simple nanopatterning method for future nanofabrication applications.

Acknowledgments:

Financial support for this work is provided by Tampere University of Technology- TUT Postdoc Grant, Center for Nano-structured Graphene sponsored by the Danish National Research Foundation (Project DNRF58, by the EU FP7 NMP project) and Science Foundation Ireland (SFI) AMBER Centre (grant 12/RC/2278).

References

1. D. Borah, M. T. Shaw, S. Rasappa, R. Farrell, C. A. O'Mahony, C. M. Faulkner, M. Bosea, P. Gleeson, J. D. Holmes, M. A. Morris, J. Phys. D: Appl. Phys. 44 (2011) 174012-174024.
2. H. W. Li, W. T. S. Huck, W. T. S, Nano Lett. 4 (2004)1633-1636.
3. C. T. Black, ACS Nano 1 (2007) 147-150.

4. D. J. C. Herr, *Journal of Materials Research* 26 (2011) 122-139.
5. S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. De Pablo, P. F. Nealey, *Nature* 424 (2003) 411-414.
6. Y. Someya, R. Mizuochi, H. Wakayama, S. Tadokoro, M. Kozawa, R. Sakamoto, *Proc. of SPIE*. 10146 (2017) 101461Y-1.
7. S. Jung, C. A. Ross, *Adv. Mater.* 21 (2009) 2540-2545.
8. X. M. Yang, S. Xiao, Y. Hsu, M. Feldbaum, K. Lee, D. Kuo, *Journal of Nanomaterials* 615896 (2013), Article ID 615896, 17 pp.
9. X. J. Zhang, K. D. Harns, N. L. Y. Wu, J. N. Murphy, J. M. Buriak, *ACS Nano* 4 (2010) 7021-7029.
10. S. S. Dinachali, W. Bai, K. H. Tu, H. K. Choi, J. Zhang, M. E. Kreider, L. C. Cheng, C. A. Ross, *ACS Macro Letters* 4 (2015) 500-504.
11. S. Rasappa, L. Schulte, D. Borah, M. A. Morris, S. Ndoni, *Colloids and Interface Science Communications* 2 (2014) 1-5.
12. S. B. Darling, *Prog. Polym. Sci.* 32 (2007) 1152–1204.
13. K. W. Gotrik, C. A. Ross, *Nano Letters* 13 (2013) 117-5122.
14. E. Kim, W. Kim, K. H. Lee, C. A. Ross, *Adv. Funct. Mater.* 24 (2014) 6981–6988.
15. J. Jeong, J. S. Ha, S. S. Lee, J. G. Son, *Macromol Rapid Commun.* 36 (2015) 1261-1266.
16. H. D. Koh, S. Park, T. P. Russell, *ACS Nano* 4 (2010) 1124-1130.
17. J. Chai, J. M. Buriak, *ACS Nano* 2 (2008) 489-501.
18. S. Rasappa, D. Borah, R. Senthamaraikannan, C. C. Faulkner, J. D. Holmes, M. A. Morris, *J Nanosci Nanotechnol.* 14 (2014) 5221-5228.
19. S. G. Jang, A. Khan, C. J. Hawker, E. J. Kramer, *Macromolecules* 45 (2012) 1553-1561.
20. S. Rasappa, J. M. Caridad, L. Schulte, A. Cagliani, D. Borah, M. A. Morris, P. Bøggliid, S. Ndoni, *Rsc Adv.* 5 (2015) 66711-66717.

21. D. Borah, R. Senthamariakannan, S. Rasappa, B. Kosmala, J. D. Holmes, M. A. Morris, *ACS Nano* 7 (2013) 6583-6596.
22. W. Bai, A. F. Hannon, K. W. Gotrik, H. K. Choi, K. Aissou, G. Lontos, K. Ntetsikas, A. Alexander-Katz, A. Avgeropoulos, C. A. Ross, *Macromolecules* 47 (2014) 6000-6008.
23. W. Bai, K. G. Yager, C. A. Ross, *Polymer* 101 (2016) 176-183.
24. W. I. Park, K. Kim, H. I. Jang, J. W. Jeong, J. M. Kim, J. Choi, J. H. Park, Y. S. Jung, *Small* 8 (2012) 3762-3768.
25. J. H. Lee, Y. Kim, J. Y. Cho, S. R. Yang, J. M. Kim, S. Yim, H. Lee, Y. S. Jung, *Adv. Mater.* 27 (2015) 4814-4822.
26. S. Ndoni, P. Jannasch, N. B. Larsen, K. Almdal, *Langmuir* 15 (1999) 3859-3865.
27. S. Ndoni, C. M. Papadakis, F. S. Bates, K. Almdal, *Rev. Sci. Instrum.* 66 (1995) 1090-1095.
28. T. Li, Z. Wang, L. Schulte, S. Ndoni, *Nanoscale* 8 (2016) 136-140.
29. S. D. Bergin, Z. Sun, D. Rickard, P. V. Streich, J. V. Hamilton, J. N. Coleman, *ACS Nano* 3 (2009) 2340-2350.
30. P. Choi, T. A. Kavassalis, A. Rudin, *Industrial & Engineering Chemistry Research* 33 (1994) 3154-3159.
31. T. H. Andersen, S. Tougaard, N. B. Larsen, K. Almdal, I. Johannsen, *Journal of electron spectroscopy and related phenomena* 121 (2001) 93-110.
32. I. F. Hsieh, H. J. Sun, Q. Fu, B. Lotz, A. Kevin, K. A. Cavicchi, Z. D. Stephen, S. Z. Cheng, *Soft Matter* 8 (2012) 7937.
33. J. Bonnet, G. Suissa, M. Raynal, L. Bouteiller, *Soft Matter* 11 (2015) 2308-2312.
34. A. F. Hannon, W. Bai, A. A. Katz, C. A. Ross, *Soft Matter* 11 (2015) 3794-3805.
35. M. A. Morris, *microelectronic engineering* 132 (2015) 207-217.
36. D. O. Shin, J. H. Mun, G. T. Wang, J. M. Yoon, J. Y. Kim, J. M. Y, Y. B. Yang, Y. Oh, J. Y. Lee, J. Shin, K. J. Lee, S. Park, J. U. Kim, S. O. Kim, *ACS Nano* 7 (2013) 8899-8907.

Supporting Information:

Table SI. HSP of solvents used in all of the annealing experiments and Hansen solubility distances (www.hansensolubility.com) for PS and PDMS relative to the used solvents.

Selectivity	Solvent/Solvent mixture	δ_D [MPa ^{1/2}]	δ_P [MPa ^{1/2}]	δ_H [MPa ^{1/2}]	Ra	
					PS	PDMS
Non-solvent	dimethylformamide	17.4	13.7	11.3	10.5	15.8
Neutral	dioxane	17.5	1.8	9.0	6.5	6.1
PS	dioxane ₁ :toluene ₁	17.7	1.6	5.5	4.7	4.2
PDMS	hexane ₁ :toluene ₁	16.5	0.7	1.0	6.6	3.3

Non-solvent		Neutral solvent

	hexane ₁ :toluene ₂	16.7	0.9	1.3	6.1	3.5
	hexane ₁ :toluene ₃	17.2	1.05	1.5	5.7	3.8

Figure S1. Top-down SEM images of the oxidized PDMS mask template on the Si substrate annealed under non-solvent and neutral solvent mixture.

Figure S2: Top down SEM images of the oxidized PDMS mask template on the Si substrate under various annealing solvent mixtures of heptane:toluene.

Graphical abstract

Highlights:

1. Morphology evolution was achieved by mere choice of annealing solvent.
2. One BCP can produce different templates by choosing right solvent based on HSP
3. A high etch contrast to substrate produces different nanostructures.
4. Directed and hierarchical directed self-assembly was demonstrated.