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Kinetically constrained block copolymer self-assembly a simple method to control domain size

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ABSTRACT

In this work asymmetric polystyrene-block-polyethylene oxide (PS-PEO) diblock copolymers were blended with high and low molecular polystyrene (PS) homopolymer and spin cast, resulting in the rapid self-assembly of vertically oriented PEO cylinders in a matrix of PS. Due to the kinetically constrained phase separation of the system, increasing addition of homopolymer is shown to reduce the diameter of the PEO domains, even when the homopolymer was of significantly higher molecular weight than the PS block in the PS-PEO diblock copolymer and would be predicted to macro-phase separate from the copolymer. The outcomes of this study provide a novel method that requires the adjustment of a single variable to tune the size of vertically oriented PEO domains between 10 and 100 nm, with potential applications in a number of areas including membrane technologies.

1. Introduction

Block copolymers self-assemble into periodic morphologies with nanometer size domains, providing the ability to position high densities of nano-elements with significant potential for use in data storage, microelectronics and separation technologies [1–6].

Diblock copolymers are two homopolymer segments (A and B) covalently bonded together at one end. Self-assembly occurs to minimize free energy, by minimizing the number of enthalpically unfavourable contacts between the A and B blocks [7]. The size of the domains and the inter-domain spacing are controlled by the molecular weight of the polymers. Self-assembly can result in various morphologies from lamellar to cylindrical to spherical as well as other more complex morphologies and is determined by the asymmetry between segments in the copolymer as well as processing parameters [7–9].

The utilization of block copolymer self-assembly to template or position items on the nanometer length scale within a two-dimensional film is currently the focus of considerable research [4,9–13]. However, many of the techniques used to generate films with well-defined domains and high degrees of long range ordering; (a) require lengthy processing (such as annealing) [14–16] or alignment steps (shear, electric field, epitaxial) [10,17–22], (b) are only possible for specific film thicknesses (layer quantization) [23–25], or (c) require defined substrates (surface energy driven arrangement) [26,27].

In this study, we extend a previously described method of rapid assembly of asymmetric PS-PEO into vertically oriented cylinders, which relies upon spin casting from a non-selective solvent [1,8,9]. This method does not suffer from the aforementioned limitations due to assembly occurring very rapidly. No further alignment is thus required, it is applicable across a wide range of film thicknesses, and it occurs independently of the substrate. We demonstrate that the addition of increasing quantities of the majority component homopolymer (PS), irrespective of molecular weight, is a simple and reproducible method for controlling the domain size of the self-assembled PEO cylinders. This finding is also of fundamental interest to the field of block copolymer assembly, as theory would predict macro-phase separation of the higher molecular weight homopolymer from the lower molecular weight copolymer under equilibrium

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conditions [28]. This study therefore provides an example of how desirable, but non-equilibrium morphologies, can be obtained by applying kinetic constraints on the polymer system through processing parameters.

It is important to note that this study reports a finding that is different to previously published papers [1,24,28–40] that have utilized the addition of homopolymer to alter block copolymer domain size. In previous studies, the addition of low molecular weight homopolymer, typically of the minority component of the block copolymer, to the copolymer system results in domain swelling due to the solubilisation of the homopolymer within the corresponding domain of the self-assembled copolymer. Here, in contrast, we utilize the addition of both high and low molecular weight homopolymer, in combination with kinetically constrained processing parameters, to demonstrate a unique method of controlling the domain size of vertically oriented PEO cylinders in a PS matrix.

It is hypothesized that since this system is rapidly assembled the structure is kinetically constrained and the addition of the homopolymer simply acts to dilute the copolymer, thus resulting in smaller domain sizes. Ultimately we show that a single and very easily controllable variable can be used to alter the PEO domain size. Finally, as expected, we demonstrate that upon annealing, the cylindrical domain structure is destroyed.

2. Materials and methods

2.1. Materials

Polystyrene-block-polyethylene oxide (PS-PEO) and polystyrene (PS) polymers were purchased from Polymer Source Pty. Ltd. (Montreal, PQ, Canada) (properties listed in Table 1). HPLC grade toluene was purchased from Aldrich and used as supplied. Silicon wafers (100 orientation, Boron doped) were purchased from Micro Materials and Research Consumables Pty. Ltd.

2.2. Dynamic light scattering

Dynamic light scattering experiments were conducted on a Malvern Instruments Zeta Sizer Nano, solvents were filtered through 0.2 μm Teflon filters prior to use.

2.3. Substrate preparation and spin casting

Silicon wafers were cut into 2 cm squares before being rinsed thoroughly in acetone, followed by isopropanol and dried under a stream of nitrogen. The wafers were then exposed to UV/ozone for 10 min to remove any remaining organics and to generate a uniform silicon oxide (SiO_2) surface layer. Thin films were generated by spin casting at 2000 rpm from polymer solutions containing 1% (wt/vol) total polymer concentration in toluene.

2.4. Hydrophobic substrate preparation

Silicon wafers were prepared as above. Post ozone treatment the wafers were boiled under reflux in benzyl alcohol (BnOH). The wafers were then rinsed thoroughly in isopropanol and dried under a stream of nitrogen. Thin films were spin cast on these BnOH treated substrates as described above.

2.5. Solvent vapour annealing

Films were placed inside a glass chamber that was filled with saturated chloroform vapour for a period of 3 h. The saturated chloroform atmosphere was then removed and the films were left in the chamber for 24 h.

2.6. Contact angle measurements

The water contact angle of surfaces was measured on an optical contact angle machine (OCA20, Dataphysics Inc., GmbH, Germany). Surfaces had at least three contact angle measurements taken, their contact angles were computed using Laplace–Young fitting and the values averaged.

2.7. Atomic force and scanning electron microscopy

Non-contact atomic force microscopy (AFM) was performed using an Asylum Research Molecular Force Probe (MFP-3D); cantilevers, Budget Sensors 300 No Al backside, with a nominal spring constant of 42 N/m were utilized. Scanning electron microscopy (SEM) was performed on a Jeol6300F field emission microscope. Prior to SEM analysis samples were coated with a 2 nm layer of platinum.

3. Results and discussion

3.1. Solution properties

Due to the amphiphilic nature of PS-PEO, dynamic light scattering was performed to investigate the structure of the polymer in toluene (Table 2). The results indicate that no pre-existing micellar structures are present in solution. From the results it can be inferred that any nano-patterned structure observed in the manufactured films is generated via micro-phase separation during the spin casting process.

Table 1
Polymer properties.

Polymer	Mn (kDa)			Polydispersity index
	A	B	Total	
LMW PS	–	–	10	1.09
HMW PS	–	–	202	1.05
LMW PS-PEO	51	11.5	62.5	1.05
HMW PS-PEO	190	48	238	1.07

Table 2
Radius of gyration of block copolymer solutions as predicted (freely jointed chain model) and measured (dynamic light scattering).

Polymer (dissolved in toluene)	Calculated radius of gyration (nm)	Measured radius of gyration (nm)
1% HMW PS-PEO	18.1	20.9 ± 0.21
1% LMW PS-PEO	9.2	11.1 ± 0.15

3.2. Assessment of pure diblock copolymer films

Fig. 1 shows the AFM topography and phase image of pure LMW and HMW PS-PEO micro-phase separated thin films. The phase image highlights differences in surface elasticity; the bright regions in the image correspond to soft PEO (Young's modulus 0.2 GPa) [41]. The dark regions to the stiff PS (Young's modulus 5.2 GPa) [41]. Analysis of the atomic force microscopy data indicates that the block copolymer has self-organised into cylindrical domains perpendicular to the surface. This alignment of the micro-phase separated domains normal to the surface is in agreement with previous investigations that have used asymmetric PS-PEO spin cast from a non-selective solvent [42,43].

Ho et al. [44] and Kim et al. [45] have demonstrated that a perpendicular orientation, although metastable in comparison to parallel orientation of polymer domains, is generated due to the rapid evaporation of solvent during film casting. As toluene is a good solvent for both the PS and PEO blocks [46] it serves to mediate the non-favourable interactions between component polymers resulting in a disordered system. During the spin casting process the solvent begins to evaporate, generating a gradient of solvent concentration through the film perpendicular to the substrate. The solvent concentration is lowest at the free surface of the nascent film, and as the concentration falls below a critical value (the order–disorder transition (ODT)) micro-phase separation occurs. Due to the polymers asymmetric architecture a cylindrical conformation is favoured, which is then propagated by the solvent ordering front, vertically through the film from the free surface towards the substrate. This ordering front continues until the PS glass transition is reached, freezing into position the metastable structure of vertically oriented cylinders.

The conclusion that the vertically oriented cylinder structure is initiated at the free surface of the film is supported by the fact that the same cylindrical morphology is developed on both hydrophilic silicon wafers (SiO_2–water contact angle: <5°) and wafers treated to be more hydrophobic (BnOH–water contact angle: 42°) (Fig. 2).

The PEO domains of the HMW PS-PEO film shown in Fig. 1 are larger by ~3× than those observed for the LMW PS-PEO (Table 4). This is likely due to the increased PEO chain length. They also have a wider size distribution, which can be attributed to the reduced mobility of the HMW PS-PEO during the spin casting process, preventing the perfect ordering of the cylinders as the solvent evaporation front moves through the film.

The relationship between PEO domain size and spin casting solution concentration was investigated by spin casting films of both HMW and LMW PS-PEO from 1%,

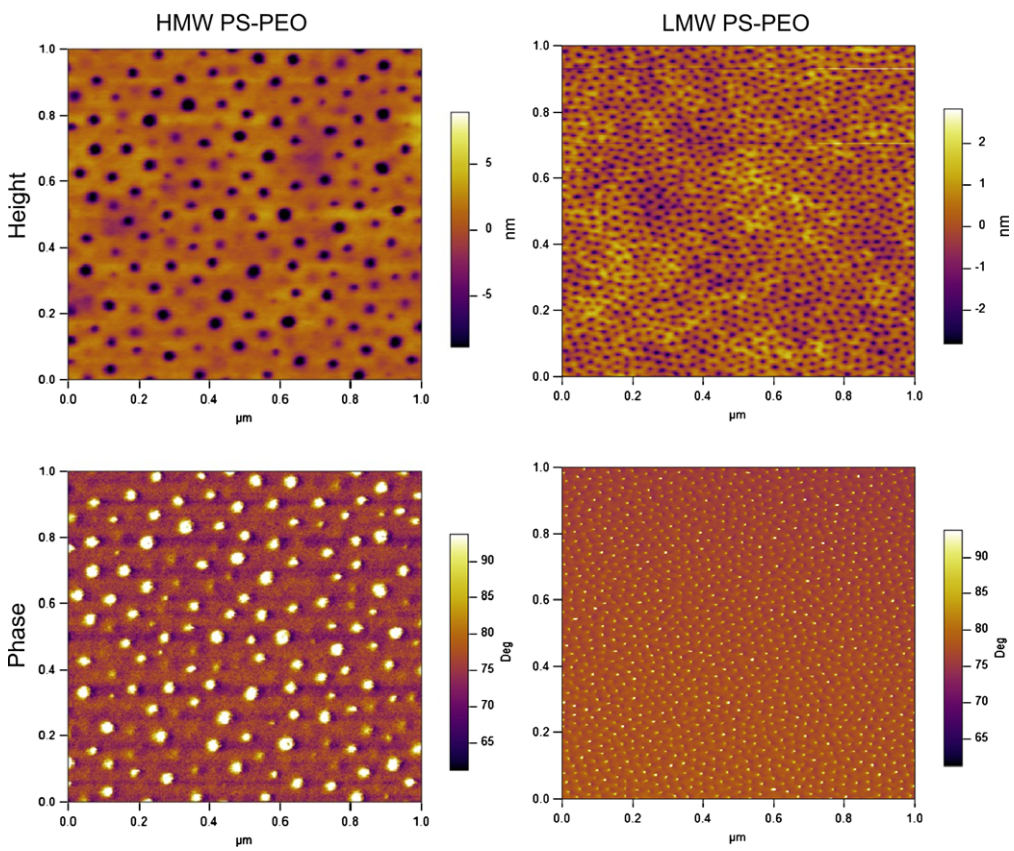

Fig. 1. AFM height (top) and phase (bottom) image of a HMW PS-PEO thin film (left) and a LMW PS-PEO thin film (right) spin cast from a solution 1% (wt/vol) solution in toluene.

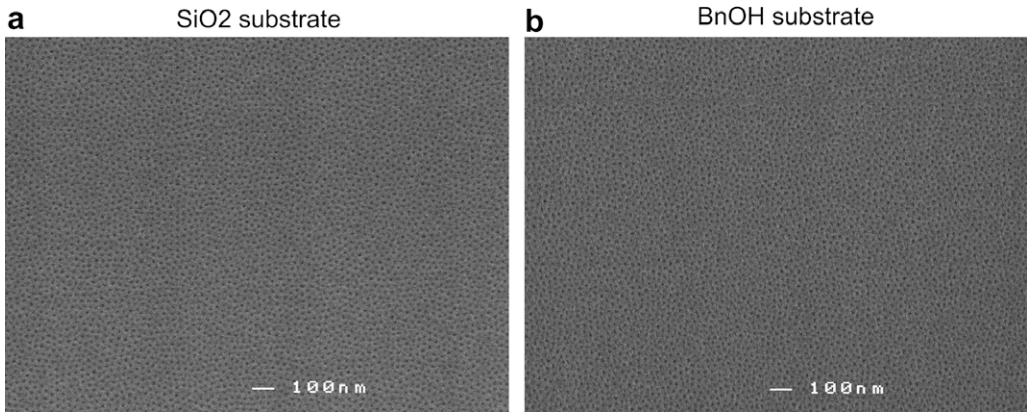

Fig. 2. Comparison of the morphology of LMW PS-PEO thin films spin cast on (a) hydrophilic SiO_2 substrate and (b) hydrophobic BnOH substrate.

0.75% and 0.5% (wt/vol) solutions (Fig. 3). Note that at concentrations below 0.5% (wt/vol) an incomplete film was observed. Analysis of the electron micrographs indicates that the mean PEO domain diameter is not strongly affected by the concentration of the spin casting solution (Table 3). The observation of a slight reduction in PEO domain size for only the 0.5% (wt/vol) HMW PS-PEO film is likely due to the following reasons: (1) a reduction in polymer concentration allows the solvent to diffuse more freely and thus evaporate faster, reducing the time available for the block copolymer to order, and (2) due to its increased size, HMW PS-PEO diffuses more slowly than the LMW PS-PEO and thus a shift in domain size is only observable in this system. These observations indicate that the ordering process is occurring extremely rapidly during the spin casting process.

Table 3
Image analysis results for PS-PEO films spin cast from various concentration solutions. Percentage polymer is weight per volume percentage of PS-PEO in toluene solution.

%Polymer	Mean domain diameter (nm) PS-PEO	
	HMW PS-PEO	LMW PS-PEO
1	51 ± 7.59	14.0 ± 0.11
0.75	49.5 ± 8.11	13.7 ± 0.52
0.50	42.6 ± 2.38	14.1 ± 0.59

3.3. Controlling domain size by blending with homopolymer

The effect of the addition of homopolymer on the domain size of rapidly assembled PEO cylinders was determined by spin casting both high and low molecular weight PS-PEO block copolymers blended with both high and low molecular weight homopolymers (it is important to note that in all films the total polymer concentration remains constant at 1% (wt/vol)). The electron micrographs in Fig. 4 indicate that there is a reduction in the PEO domain size with the increasing addition of homopolymer. This trend of decreasing domain size with increasing addition of homopolymer is observed in both the LMW PS-PEO

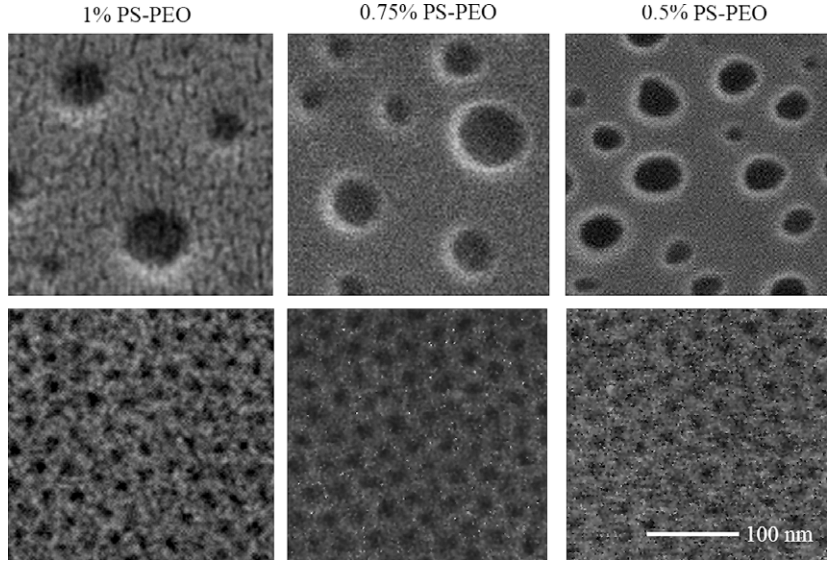

Fig. 3. SEM micrographs of HMW (top row) and LMW (bottom row) PS-PEO films spin cast from different concentration solutions.

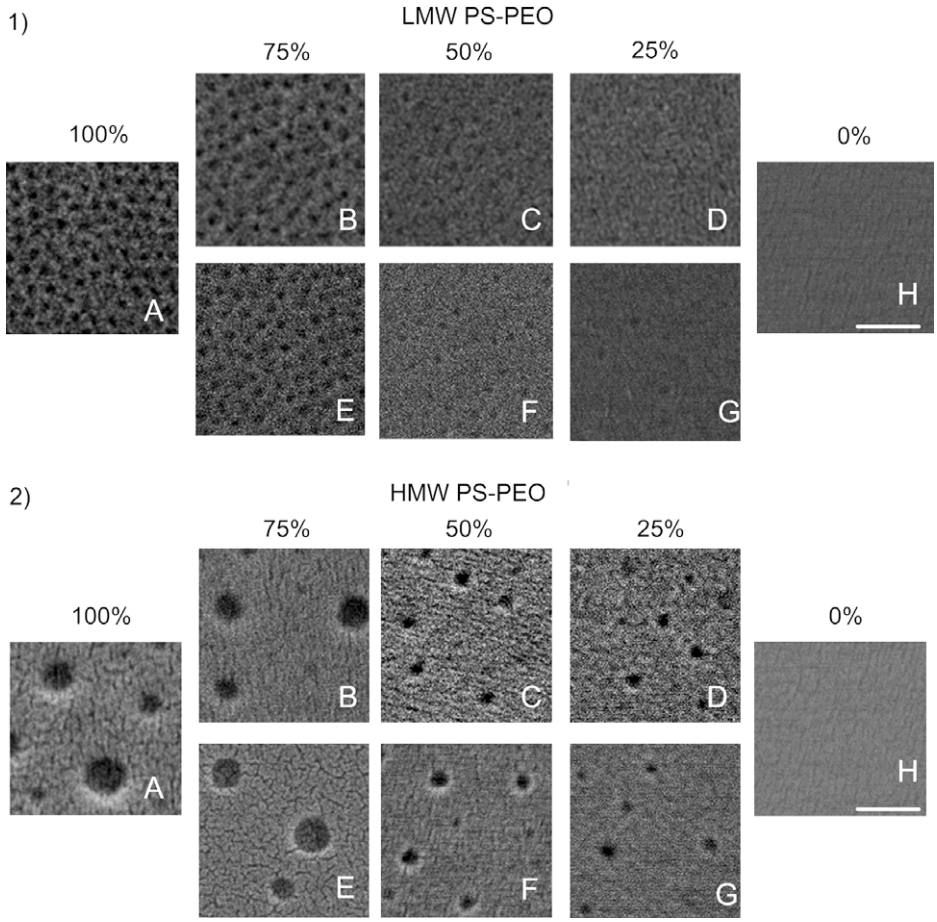

Fig. 4. SEM micrographs of (1) blends of LMW PS-PEO with both high and low molecular weight PS. (A) Pure LMW PS-PEO, (B)–(D) 75%, 50% and 25% LMW PS-PEO blended with LMW PS. (E)–(G) 75%, 50% and 25% LMW PS-PEO blended with HMW PS, (H) pure LMW PS. (Scale bar = 100 nm); (2) Blends of HMW PS-PEO with both high and low molecular weight PS. (A) Pure HMW PS-PEO, (B), (C) and (D) 75%, 50% and 25% HMW PS-PEO blended with LMW PS, (E), (F) and (G) 75%, 50% and 25% HMW PS-PEO blended with HMW PS, (H) pure HMW PS. (Scale bar = 100 nm).

Table 4
Summary of image analysis results for LMW PS-PEO system blended with HMW and LMW PS. %BCP is percentage of PS-PEO block copolymer to polystyrene (PS) homopolymer. Total polymer concentration of all solutions was 1% wt/vol in toluene.

%PCB	Mean domain diameter (nm) LMW PS-PEO	
	Blended with HMW PS	Blended with LMW PS
25	5.8 ± 0.03	5.6 ± 0.08
50	8.3 ± 0.08	8.5 ± 0.12
75	11.3 ± 0.18	11.2 ± 0.38
100	14.0 ± 0.11	14.0 ± 0.11

Table 5
Summary of image analysis results for HMW PS-PEO system blended with HMW and LMW PS.

%BCP	Mean domain diameter (nm) HMW PS-PEO	
	Blended with HMW PS	Blended with LMW PS
25	12.4 ± 1.31	11.4 ± 1.7
50	18.8 ± 1.62	18.3 ± 2.4
75	37.5 ± 7.01	42.1 ± 5.52
100	51.0 ± 7.59	51.0 ± 7.59

and HMW PS-PEO systems and is independent of the homopolymer molecular weight. Image analysis results summarised in Tables 4 and 5 and Fig. 5 indicate that there is a linear relationship between resulting domain size of the PEO component and the block copolymer concentration in the blend across all concentrations investigated in this study. This linear relationship between PEO domain size and copolymer concentration provides a powerfully simple method for controlling domain size.

Interestingly this linear trend of decreasing PEO domain size with decreasing concentration of block copolymer in blend films is not observed for pure block copolymer films spin cast from correspondingly lower concentration solutions (Table 3 and Fig. 3). There is no deviation in domain size for pure LMW PS-PEO films spin cast from 1%, 0.75% and 0.5% (wt/vol) solutions (domain size ~14 nm), whereas for blended films containing 100%, 75% and 50% block copolymer, with remaining percentage being comprised of PS, the resultant domain sizes are ~14, 11 and 8 nm respectively. A similar trend is observed for the HMW PS-PEO system. This result indicates that incorporation of PS into the films is critical for controlling domain

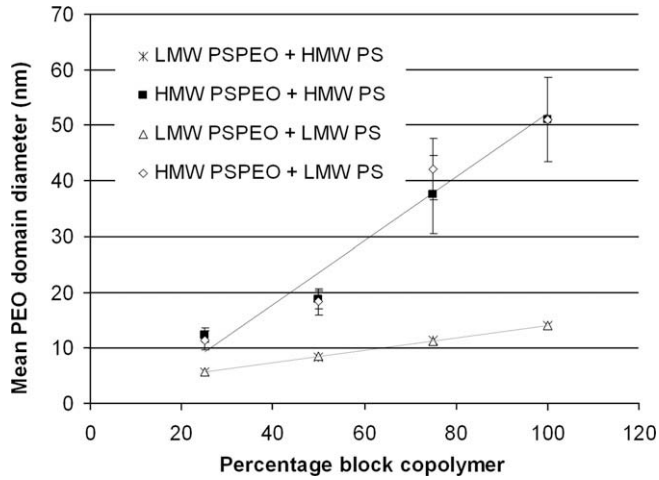

Fig. 5. Domain size vs. percentage block copolymer. Lines are linear regression. Error bars represent one standard deviation.

size. The mechanism at present is unknown. However, it is likely that the addition of PS mediates the assembly of PEO domains by reducing the effective diffusion coefficient of PS-PEO, inhibiting the formation of a quasi-equilibrium domain size for these rapidly assembled films (~14 nm for pure LMW PS-PEO). Such a mechanism would certainly account for the observed trend of decreasing PEO domain size with increasing PS content. By its very nature, this proposed mechanism is highly dependent upon the rapid kinetics of the system preventing macro-phase separation from occurring. Further experiments are underway to confirm this hypothesis.

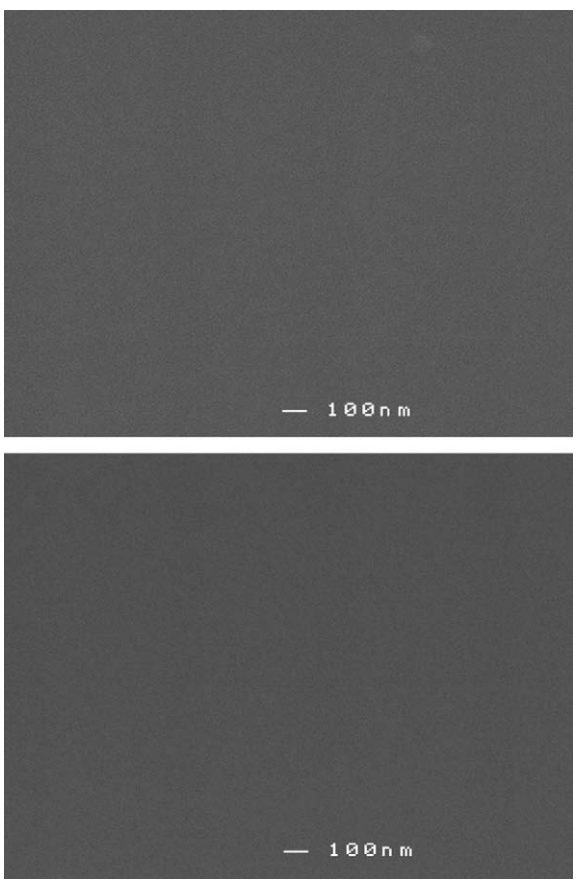

Fig. 6. HMW PS-PEO (top) and HMW PS-PEO + 50% HMW PS (bottom) annealed in chloroform vapour for 3 h. From the micrographs it is clear the vertically oriented cylindrical domains are no-longer present.

3.4. Annealing studies

Annealing thin polymer films via heat or solvent vapour treatment provides mobility to the polymer chains allowing relaxation or re-arrangement of their structure. During the solvent vapour annealing process the polymer film swells and the polymer chains gain significant mobility [20]. In this study annealing of the self-assembled PS-PEO block copolymer thin films, using chloroform vapour, was undertaken to investigate the stability of the developed morphology of vertically oriented cylinders of PEO. It is evident from Fig. 6 that the vertically oriented PEO domains are no-longer present after annealing. It is well reported that the vertically oriented cylinder morphology is metastable and this annealing study further corroborates this fact.

4. Conclusions

The results presented in the paper show that the addition of high or low molecular weight homopolymer is a simple method for tuning the domain size of vertically oriented cylinders of PS-PEO block copolymer. The application of this robust and simple methodology is expected to extend to other strongly interacting block copolymers that are rapidly cast from a neutral solvent. Briefly annealing the structure in chloroform vapour was shown to cause re-arrangement of the metastable structure, indicating that the processing conditions generate a non-equilibrium structure. Manufacturing block copolymer thin films in a non-equilibrium manner allows for the opportunity to access additional morphologies that would otherwise be

impossible if the system was driven to equilibrium, and is an area that will surely be the focus of much future investigation. The vertically oriented arrays of PEO cylinders presented in this study have significant potential for use in membrane filtration technologies, such as for water purification.

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References

[1] Jeong U, Kim HC, Rodriguez RL, Tsai IY, Stafford CM, Kim JK, et al. Asymmetric block copolymers with homopolymers: routes to multiple length scale nanostructures. Adv Mater 2002;14(4):274–6.
[2] Park M, Harrison C, Chaikin PM, Register RA, Adamson DH. Block copolymer lithography: periodic arrays of ~10^11 holes in 1 square centimeter. Science 1997;276:1401–4.
[3] Fasolka MJ, Mayes AM. Block copolymer thin films: physics and applications. Annu Rev Mater Res 2001;31(1):323–55.
[4] Manksy P, Harrison C, Chaikin P, Register RA, Yao N. Nanolithographic templates from diblock copolymer thin films. Appl Phys Lett 1996;68(18):2586–8.
[5] Hamley IW. Nanostructure fabrication using block copolymers. Nanotechnology 1993;14:R39–54.
[6] Krausch GRM. Nanostructured thin films via self-assembly of block copolymers. Adv Mater 2002;14(21):1579–83.
[7] Bates FS, Fredrickson GH. Block copolymer thermodynamics – theory and experiment. Annu Rev Phys Chem 1990;41:525–57.
[8] Kim SH, Misner MJ, Xu T, Kimura M, Russell TP. Highly oriented and ordered arrays from block copolymers via solvent evaporation. Adv Mater 2004;16(3):226–31.
[9] Park S, Wang J-Y, Kim B, Xu J, Russell TP. A simple route to highly oriented and ordered nanoporous block copolymer templates. ACS Nano 2008;2(4):766–72.
[10] Park C, Yoon J, Thomas EL. Enabling nanotechnology with self assembled block copolymer patterns. Polymer 2003;44(22):6725–60.
[11] Darling SB. Mechanism for hierarchical self-assembly of nanoparticles on scaffolds derived from block copolymers. Surf Sci 2007;601(13):2555–61.
[12] Cresce AV, Silverstein JS, Bentley WE, Kofinas P. Nanopatterning of recombinant proteins using block copolymer templates. Macromolecules 2006;39(17):5826–9.
[13] Bennett RD, Xiong GY, Ren ZF, Cohen RE. Using block copolymer micellar thin films as templates for the production of catalysts for carbon nanotube growth. Chem Mater 2004;16(26):5589–95.
[14] Peng J, Han Y, Knoll W, Kim DH. Development of nanodomain and fractal morphologies in solvent annealed block copolymer thin films. Macromol Rapid Comm 2007;28(13):1422–8.
[15] Bang J, Kim BJ, Stein GE, Russell TP, Li X, Wang J, et al. Effect of humidity on the ordering of PEO-based copolymer thin films. Macromolecules 2007;40(19):7019–25.
[16] Zhao J, Jiang S, Ji X, An L, Jiang B. Study of the time evolution of the surface morphology of thin asymmetric diblock copolymer films under solvent vapor. Polymer 2005;46(17):6513–21.
[17] Angelescu DE, Waller JH, Wu MW, Chaikin PM, Register RA. Method and apparatus for providing shear-induced alignment of nanostructure in thin films, 2006, US20060013956A1.
[18] Baker SM, Callahan A, Smith G, Toprakcioglu C, Vradis A. Shear effects on the geometry of polystyrene-polyethylene oxide copolymers at the solid-solvent interface. Physica B: Condens Matter 1997;241–243:1041–7.
[19] Wang H, Kesani PK, Balsara NP, Hammouda B. Undulations and disorder in block copolymer lamellae under shear flow. Macromolecules 1997;30(4):982–92.
[20] Knoll A, Lyakhova KS, Horvat A, Krausch G, Sevink GJA, Zvelindovsky AV, et al. Direct imaging and mesoscale modelling of phase transitions in a nanostructured fluid. Nat Mater 2004;3:886–90.
[21] De Rosa C, Park C, Lotz B, Wittmann JC, Fetters LJ, Thomas EL. Control of molecular and microdomain orientation in a semicrystalline block copolymer thin film by epitaxy. Macromolecules 2000;33(13):4871–6.
[22] Ouk Kim S, Solak HH, Stoykovich MP, Ferrier NJ, de Pablo JJ, Nealey PF. Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates. Nature 2003;424(6947):411.
[23] Green P, Limary R. Block copolymer thin films: pattern formation and phase behaviour. Adv Colloid Interfac 2001;94:53–81.
[24] Orso KA, Green PF. Phase behaviour of thin film blends of block copolymers and homopolymers: changes in domain dimensions. Macromolecules 1999;32(4):1087–92.
[25] Morkved T, Jaeger H. Thickness-induced morphology changes in lamellar diblock copolymer ultrathin films. Europhys Lett 1997;40:643–8.
[26] Huang E, Russell TP, Harrison C, Chaikin PM, Register RA, Hawker CJ, et al. Using surface active random copolymers to control the domain orientation in diblock copolymer thin films. Macromolecules 1998;31(22):7641–50.
[27] Huang E, Pruzinsky S, Russell TP, Mays J, Hawker CJ. Neutrality conditions for block copolymer systems on random copolymer brush surfaces. Macromolecules 1999;32(16):5299–303.
[28] Koizumi S, Hasegawa H, Hashimoto T. Ordered structures of block copolymer/homopolymer mixtures 5. Interplay of macro- and microphase transitions. Macromolecules 1994;27:6532–40.
[29] Baek DM, Han CD, Kim JK. Phase equilibria in mixtures of block copolymer and homopolymer. Polymer 1992;33(22):4821–31.
[30] Budkowski A. Interfacial Phenomena in Thin Polymer Films: Phase Coexistence and Segregation 1999.
[31] Budkowski A, Klein J, Fetters LJ. Brush formation by symmetric and by highly asymmetric diblock copolymers at homopolymer interfaces. Macromolecules 1995;28:8571–8.
[32] Budkowski A, Klein J, Fetters LJ, Hashimoto T. Competitive adsorption at homopolymer interfaces from a binary mixture of diblock copolymers. Macromolecules 1995;28:8579–86.
[33] Jinnai H, Hasegawa H, Nishikawa Y, Sevink GJA, Braunfeld MB, Agard DA, et al. 3D Nanometer-scale study of coexisting bicontinuous morphologies in a block copolymer/homopolymer blend. Macromol Rapid Comm 2006;27(17):1424–9.
[34] Huang YY, Chen HL, Hashimoto T. Face-centered cubic lattice of spherical micelles in block copolymer/homopolymer blends. Macromolecules 2003;36(3):764–70.
[35] Jeong U, Ryu DY, Kho DH, Lee DH, Kim JK, Russell TP. Phase behaviour of mixtures of block copolymer and homopolymers in thin films and bulk. Macromolecules 2003;36(10):3626–34.
[36] Mayes AM, Russell TP, Satija S, Majkrzak CF. Homopolymer distributions in ordered block copolymers. Macromolecules 1992;25:6523–31.
[37] Shull K, Kramer EJ, Hadziioannou G, Tang W. Segragation of block copolymers to interfaces between immiscible homopolymers. Macromolecules 1990;23:4780–7.
[38] Shull K, Winey KI. Homopolymer distributions in lamellar copolymer/homopolymer blends. Macromolecules 1992:25.
[39] Tanaka H, Hasegawa H, Hashimoto T. Ordered structures in mixtures of a block copolymer and homopolymers. 1. Solubilization of low molecular weight homopolymers. Macromolecules 1991;24:240–51.
[40] Winey KI, Thomas EL, Fetters LJ. Swelling a lamellar diblock copolymer with homopolymer: Influences of homopolymer concentration and molecular weight. Macromolecules 1991;24:6182–8.
[41] Nie HY, Motomatsu M, Mizutani W, Tokumoto H. Local modification of elastic properties of polystyrene–polyethyleneoxide blend surfaces. The third international conference on nanometer-scale science and technology, Colorado (USA): Denver; 1995. p. 1163-6.
[42] Lin ZQ, Kim DH, Wu XD, Boosahda L, Stone D, LaRose L, et al. A rapid route to arrays of nanostructures in thin films. Adv Mater 2002;14(19):1373–6.
[43] Wang H, Djurisic AB, Chan WK, Xie MH. Factors affecting phase and height contrast of diblock copolymer PS-b-PEO thin films in dynamic force mode atomic force microscopy. Appl Surf Sci 2005;252(4):1092–100.
[44] Ho R-M, Tseng W-H, Fan H-W, Chiang Y-W, Lin C-C, Ko B-T, et al. Solvent-induced microdomain orientation in polystyrene-b-poly(l-lactide) diblock copolymer thin films for nanopatterning. Polymer 2005;46(22):9362–77.
[45] Kim G, Libera M. Morphological development in solvent-cast polystyrene-polybutadiene-polystyrene (SBS) triblock copolymer thin films. Macromolecules 1998;31(8):2569–77.
[46] Brandrup J, Immergut EH, Grulke EA, Abe A, Bloch DR, editors. Polymer Handbook. New York: Wiley; 1999.