Effect of Composition of Substrate-Modifying Random Copolymers on the Orientation of Symmetric and Asymmetric Diblock Copolymer Domains

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ABSTRACT: The ability of random copolymer brushes and cross-linked mats to induce the vertical orientation of domains in overlying films of lamellae- and cylinder-forming block copolymers was investigated as a function of the composition. The substrate-modifying layers consisted of styrene and methyl methacrylate random copolymers and contained either a terminal hydroxyl group or a third polar comonomer of 2-hydroxyethyl methacrylate (HEMA) for grafting brushes to silicon oxide surfaces or glycidyl methacrylate (GMA) for cross-linking the random copolymer into a mat. Polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) lamellae- and cylinder-forming block copolymers (both PS and PMMA minority block copolymers) were deposited and annealed on the modified surfaces. In all cases the vertical orientation of domains was observed for a range of random copolymer composition, but the ranges of composition were different for each combination of surface layer and block copolymer. The cylindrical domains of PS exhibited vertical structures for a very narrow range of compositions compared to cylindrical domains of PMMA or lamellae. As expected, the incorporation of polar HEMA or GMA monomers in the surface layers shifted the composition range for the perpendicular orientation of domains to higher fractions of styrene. The results are discussed in terms of the equilibration of the films in the presence of the chemically modified surfaces.

Introduction

Block copolymer thin films have shown excellent promise as templates for nanomanufacturing as they can self-assemble into structures with sub-30 nm length scales and can be integrated into existing manufacturing processes.[1] Dense arrays of lines or spots can be fabricated using lamella-forming or cylinder-forming block copolymers, respectively, with their domains oriented perpendicular to the substrate. Lamellae and cylinders that are oriented perpendicular to the underlying substrate may have advantages in pattern transfer over spheres or parallel cylinders because of the higher aspect ratio of the resulting template and the vertical side walls.[2] The perpendicular alignment of block copolymer domains in thin films can be accomplished by several methods such as solvent annealing,[3] the application of an electric field,[4] the blending of homopolymers or multiple block copolymers,[5−7] and chemical modification of the substrate.[8−19] Random copolymer brushes or mats are widely used for chemical modification of the substrate to control the interfacial interactions or wetting behavior of the blocks of the copolymer and the substrate. Brushes are thin polymer layers in which each chain is chemically grafted to a surface and mats are thin cross-linked networks that may or may not be covalently attached to a surface. Both brushes and mats, when of sufficient thickness, have the effect of modifying the chemical composition of a surface and controlling the interactions between an overlying material and the substrate.

Brushes with hydroxyl groups that attach to silicon oxide surfaces through condensation reactions are an important class of surface-modifying layers. In a seminal work, Mansky et al.[8] showed that hydroxyl-terminated random copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) could form brushes for controlling polymer−surface interactions. We previously reported a new molecule with a third monomer in the random copolymer backbone to improve the ease of synthesis and reduce the time required to form a brush.[16] We produced a random copolymer consisting of styrene, methyl methacrylate, and a small percentage of 2-hydroxyethyl methacrylate (HEMA). The hydroxyl groups in the HEMA monomer that are distributed along the polymer backbone react with the oxide surface to create the anchoring sites for the brush. Both controlled living radical polymerization and classical free radical polymerization with an AIBN initiator were used to synthesize the random copolymer, and it was confirmed that both resulting polymers were equally effective in inducing the perpendicular orientation of block copolymer domains.

Because of the condensation reaction that can occur between two hydroxyl groups, brushes containing hydroxyl groups are useful for modifying hydroxyl-rich surfaces. For some applications, however, it is desirable to modify substrates such as metals or polymers that do not have a sufficient density of surface hydroxyl groups to form brushes from hydroxyl condensation. Ryu et al. developed one solution: a polymer that would form a cross-linked mat on a variety of surfaces (including Al, Si_3N_4, Kapton, and PET).[13] In the work by Ryu et al., random copolymers containing the cross-linking agent benzocyclobutene (BCB) were thermally cross-linked at 200 or 250 °C to obtain an insoluble thin film mat. Because of the desire to create cross-linked mats of other monomer units that are temperature-sensitive, there is a need to develop materials with cross-linking groups that can cross-link at lower temperatures.

Investigations have been performed by both us[16] and others[15] to create substrate-independent photo-cross-linkable surface layers. Polymers containing acryloyl, epoxide, or azide groups cross-link upon photoexposure to modify surfaces independent of the surface material. These materials have the benefit of being

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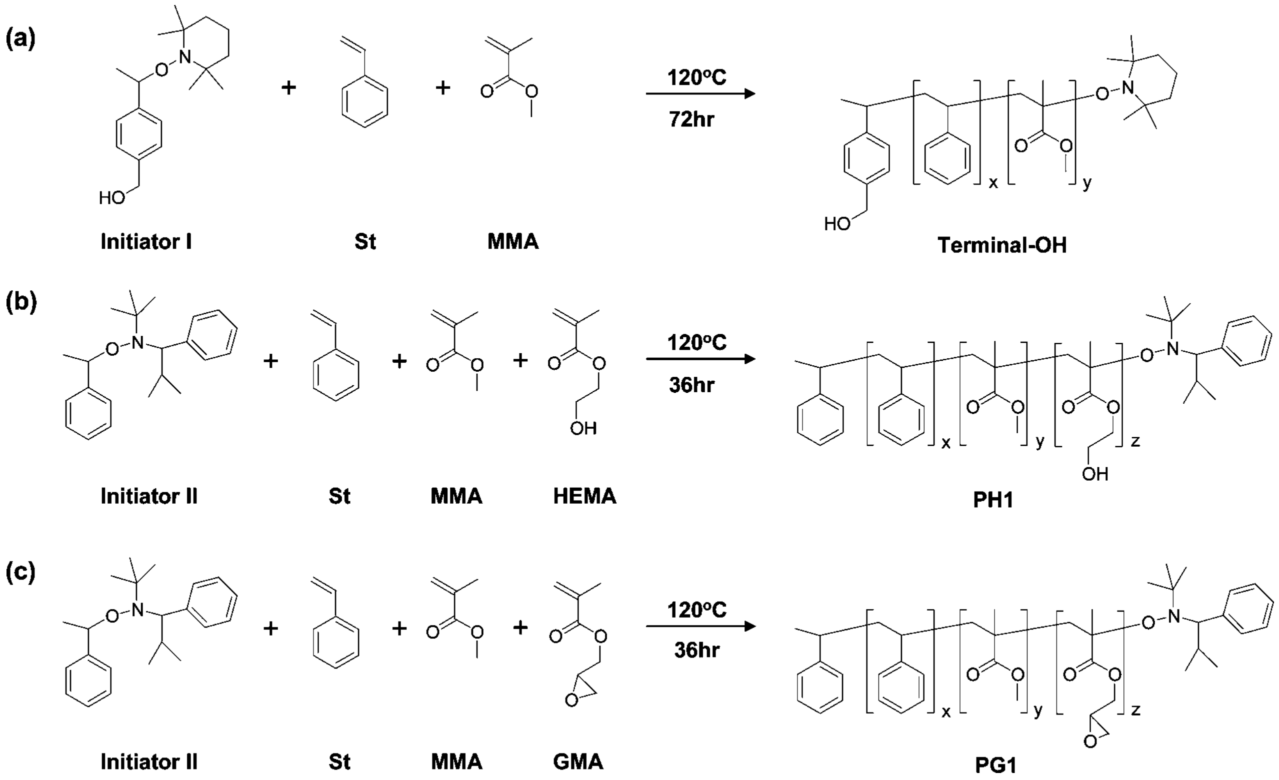


Figure 1. PS/PMMA random copolymers: (a) hydroxyl-terminated random copolymer (**terminal-OH**), (b) side-chain hydroxy-containing random copolymer (**PH1**), (c) side-chain epoxy-containing random copolymer (**PG1**).

patternable, at least at the micron scale, to direct the surface layers to specific locations.

The composition of any surface-modifying molecule is critical for controlling the interfacial energy of the substrate with the block copolymer for directing the orientation of block copolymer domains. Creating a surface capable of orienting block copolymer domains perpendicular to the substrate requires that the random copolymer surface layer falls within a certain composition range. This range is referred to as the perpendicular window throughout the text. Mansky et al. previously reported[20] that P(S-*r*-MMA) brushes having $0.50 < f_{St} < 0.65$ exhibited perpendicular orientation for symmetric P(S-*b*-MMA) (where f_{St} is the fraction of styrene in the molecule). They reported using films $2.5L_0$ to $3.5L_0$ thick of a symmetric block copolymer. Because these films were thick, they showed mixed domain orientations, with vertical orientation at the substrate interface and parallel orientation at the free surface. For thinner films on brushes near $f_{St} = 0.6$, the perpendicular structures persisted throughout the thickness of the film.[21] Such thin assembled block copolymer films are necessary in applications such as advanced lithography and nanotemplate formation, in which the domains in thicker films have a tendency to collapse (lamellae) or etch unevenly (dots). Ham et al. recently reported the effect of block copolymer thicknesses and hydroxyl-terminated random copolymer brush composition on the orientation of lamellar and cylindrical (PMMA minority) domains.[22] It is of interest, however, to understand how the perpendicular window shifts for both lamellar and cylinder forming block copolymer with the incorporation of a third polar comonomer in the random copolymer. In this work we present the perpendicular windows for brushes and mats using both symmetric and asymmetric block copolymers and consider the thermodynamics that lead to the morphologies produced by each block copolymer/surface layer combination.

Experimental Section

Materials. Styrene (St), methyl methacrylate (MMA), glycidyl methacrylate (GMA), and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich and distilled under reduced pressure. Initiator I[23] and initiator II[24] were synthesized according to the literature. Three block copolymers were purchased from Polymer Source Incorporated (Dorval, Quebec, Canada) and used without further purification: symmetric P(S-*b*-MMA) (PS 52 kg/mol, PMMA 52 kg/mol, polydispersity index (PDI), 1.09, lamellar period $L_0 = 49$ nm), asymmetric PMMA cylinder forming P(S-*b*-MMA) (PS 50.5 kg/mol, PMMA 20.9 kg/mol, PDI, 1.06, lattice spacing $L_0 = 43$ nm), and asymmetric PS cylinder forming P(S-*b*-MMA) (PS 20.2 kg/mol, PMMA 50.5 kg/mol, PDI, 1.07, $L_0 = 40$ nm). These three block copolymers are referred to throughout as **L5252**, **PMMA-C5020**, and **PS-C2050**, respectively.

Random Copolymer Synthesis. In the following discussion, **PH1** refers to a PS and PMMA random copolymer with 1% HEMA in the main chain, and **PG1** refers to a PS and PMMA random copolymer with 1% GMA in the main chain. **Terminal-OH** refers to the hydroxyl-terminated P(S-*r*-MMA). Our previous work has shown that 0.01−0.03 mole fraction HEMA with 0.58 mole fraction of styrene produced perpendicularly oriented lamellae.[16] For this study, we fixed the amount of third monomer (HEMA or GMA) at 0.01 mole fraction and varied the styrene fraction from 0.45 to 0.80.

All random copolymer samples were synthesized by nitoxide-mediated living free radical polymerization (NMP) following similar procedures. The synthesis scheme is shown in Figure 1. A representative procedure is detailed here: For one sample of **PH1**, a mixture of initiator II (0.02 g, 0.061 mmol), St (2.46 g, 23.6 mmol), MMA (1.29 g, 12.9 mmol), and HEMA (0.0479 g, 0.369 mmol) was degassed by three freeze/thaw cycles and sealed under nitrogen. The polymerization mixture was reacted at 120 °C for 36 h. (For **terminal-OH** synthesis, the polymerization lasted 72 h). The resulting viscous mixture was diluted with THF and precipitated into methanol. The precipitated solid was filtered and dried under reduced pressure to yield the random copolymer **PH1** as a white solid.

Table 1. Feed and Actual Ratios of Styrene for PH1 and PG1 Random Copolymers[a]

PH1	f_{St}	0.45	0.50	0.53	0.56	0.60	0.62	0.64	0.66	0.68	0.70	0.72	0.74	0.76
	F_{St}	0.48	0.53	0.56	0.59	0.62	0.64	0.65	0.69	0.70	0.72	0.74	0.75	0.76
PG1	f_{St}	0.45	0.50	0.53	0.56	0.58	0.60	0.64	0.66	0.68	0.70	0.72	0.74	0.78
	F_{St}	0.48	0.53	0.56	0.55	0.58	0.59	0.63	0.65	0.66	0.69	0.74	0.77	0.80

[a] f_{St} is the mole fraction of styrene in the feed, and F_{St} is the mole fraction of styrene in the resulting random copolymer as measured by ^{1}H NMR.

Materials Characterization. For each synthesized random copolymer, a ^{1}H NMR spectrum was recorded in solution ($CDCl_3$) with a Bruker AC+ 300 (300-MHz) spectrometer, with the tetramethylsilane (TMS) proton signal as an internal standard. GPC was performed with a Viscotek GPCmax VE-2001 chromatograph using two columns (VARIAN 5M-POLY-008-27 and VARIAN 5M-POLY-008-32) and Viscotek Model 302 TDA detectors. THF was used as an eluent with 1 mL/min flow rate at 30 °C. Monodisperse polystyrene standards were used for calibration. Molecular weights were determined as polystyrene equivalents using the refractive index detector. The film thicknesses of the brush and block copolymer layers were measured by ellipsometry (Rudolph Research Auto EL). Static contact angles of sessile drops were measured to characterize the hydrophilicity of the surface layers with a Dataphysics OCA 15 Plus goniometer. Top-down scanning electron microscope (SEM) images of the block copolymer microdomains were acquired with a LEO-1550 VP field-emission instrument using an accelerating voltage of 1 kV and a 30 μm aperture.

Surface Modification and Block Copolymer Deposition. (i) **Terminal-OH** brush: Solutions of **terminal-OH** in toluene (1% w/w) were spin-coated at 2000 rpm onto silicon wafers and then annealed under vacuum at 160 °C for 2 days. The substrates were sonicated in hot toluene to remove ungrafted random copolymer and rinsed with fresh toluene.

(ii) **PH1** brush: Solutions of **PH1** in toluene (1% w/w) were spin-coated at 4000 rpm onto silicon wafers and then annealed under vacuum at 160 °C for 2 days. The substrates were sonicated in hot toluene to remove ungrafted random copolymer and rinsed with fresh toluene.

(iii) **PG1** mat: Solutions of **PG1** in toluene (0.5% w/w) were spin-coated at 4000 rpm onto silicon wafers and then annealed under vacuum at 160 °C for 2 days. The substrates were sonicated in hot toluene to remove random copolymer that was not cross-linked and rinsed with fresh toluene.

On these random copolymer modified wafers, solutions of lamellae-forming **L5252** in toluene (1.5% w/w), PMMA-cylinder-forming **PMMA-C5020** in toluene (1% w/w), or PS-cylinder-forming **PS-C2050** in cyclopentanone (1% w/w) were spin-coated at 4000 rpm to produce films with thicknesses of 45, 32, and 22 nm, respectively. The choice of these thicknesses is discussed in both the Results and Discussion sections. Since the quality of perpendicular structures is dependent on the block copolymer film thickness and annealing temperature as well as the random copolymer composition, we held the block copolymer film thickness and annealing temperature constant to isolate the brush effects. All block copolymer films were annealed at 190 °C for 72 h under vacuum to attain the equilibrium morphology prior to imaging.

Results

Polymer Characteristics. We synthesized three different random copolymers with varying compositions: **terminal-OH**, **PH1**, and **PG1**. The M_n of the **terminal-OH** copolymers was in the range of 2000−7500 g/mol, with PDI values of 1.2−1.4, whereas the M_n of **PH1** and **PG1** were in the range of 60 000−70 000 g/mol, with PDI values of ~1.2. Table 1 shows the feed ratios of the styrene monomers and the actual styrene fraction in the resulting **PH1** and **PG1** copolymers, as measured by ^{1}H NMR. (See Supporting Information for the characteristics of the synthesized **terminal-OH** random copolymers.) A small difference between the feed ratio (f_{St}) and actual styrene fraction (F_{St}) was observed in most cases, which was probably caused by slight variations in the batch size during polymerization or by slightly less than complete conversion of reactants. For the remaining discussion we refer to the composition of each copolymer by its F_{St} value, and not f_{St}, as F_{St} reflects the composition of the final material.

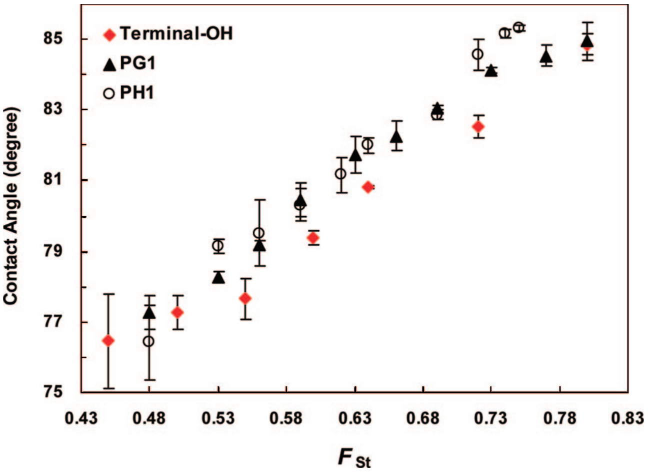
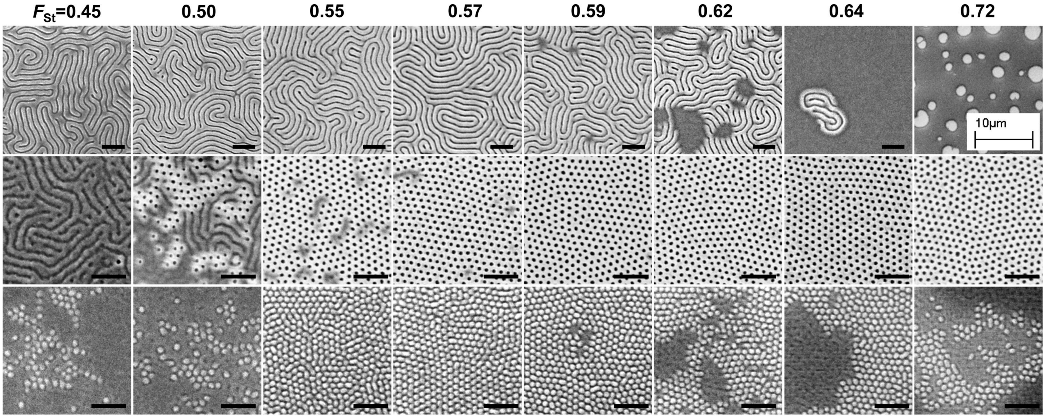
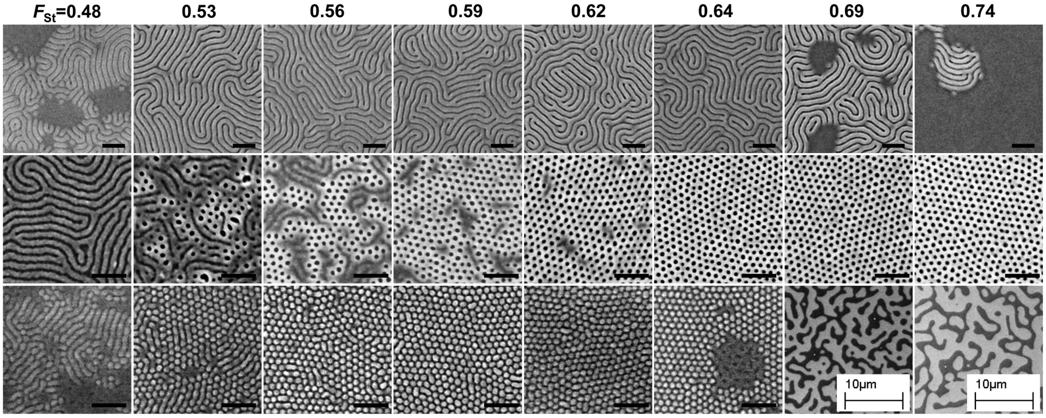


Figure 2. Contact angles for water on the **terminal-OH**, **PH1**, and **PG1** modified surfaces as a function of F_{St}. Error bars show the standard deviation of each measurement.

Surface-Layer Properties. After covalently grafting **PH1** or **terminal-OH** to the substrate, the resulting brush thickness was ~8 nm or in the range of 3−6 nm, respectively. In contrast with the **terminal-OH**, the thicknesses of the cross-linked mats like **PG1** were a function of the amount of material initially spin-coated onto the substrate. We produced **PG1** films that were measured to be ~8 nm thick after cross-linking and sonication in solvent. The **PG1** films were sufficiently thick to prevent any interactions between the block copolymer film and the substrate.[25] Water contact angles were measured for the films as a means to asses the uniformity and composition of each film. In all cases, the hydrophilicity of each random copolymer was a function of its molecular composition, as shown in Figure 2. While the contact angles of the **PH1** and **PG1** were very similar except at high F_{St}, the contact angles for the **terminal-OH**-coated substrates were consistently ~1° lower than for those substrates coated with **PH1** or **PG1** at a given F_{St}.

Dependence of Block Copolymer Domain Orientation on Surface Layer Composition. L5252, **PMMA-C5020**, and **PS-C2050** were spin-coated and annealed over the random copolymer-modified substrates. Each sample was imaged with SEM to determine the orientation of the domains. Figure 3 shows representative SEM images for the samples coated on the three surface layers. Perpendicular orientation of lamellae of **L5252** was achieved on **terminal-OH** brushes where $0.45 \leq F_{St} \leq 0.57$. For $0.59 \leq F_{St} < 0.64$, dark spots were observed on the **L5252** film, indicating regions of parallel orientation. The size of these regions increased as F_{St} increased. When $F_{St} \geq 0.72$, the surface was absent of perpendicular structures. In general, for substrate compositions that were between those compositions that yielded completely perpendicular or parallel domain orientation, a mixed morphology was observed, with some domains oriented perpendicular to the substrate and some parallel. For the mixed morphology, we refer to the parallel structures as "defects" since our goal was to produce uniformly


(a) Terminal-OH


(b) PH1

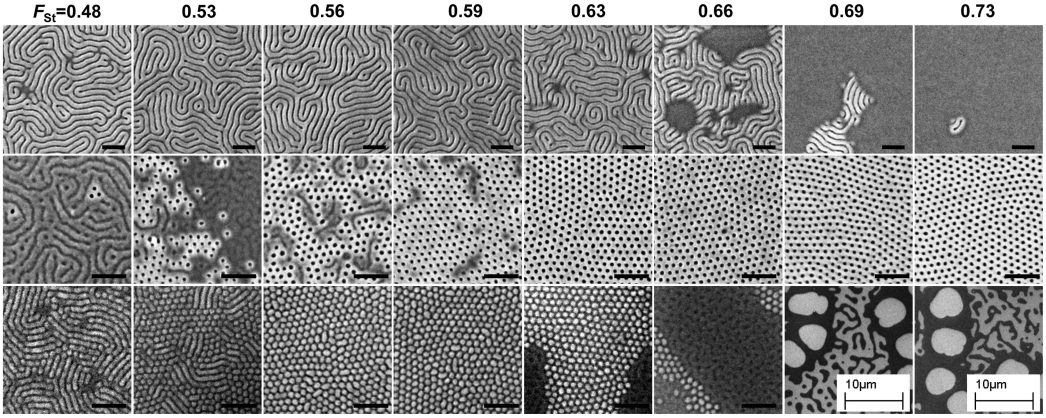

(c) PG1

Figure 3. SEM images of self-assembled block copolymer films on a (a) **terminal-OH**, (b) **PH1**, and (c) **PG1** modified surfaces containing different mole fractions of styrene in the random copolymer. **L5252**, 45 nm thick (first row), **PMMA-C5020**, 32 nm thick (second row), **PS-C2050**, 22 nm thick (third row.) Black scale bars represent 200 nm. For image clarity, only a subset of F_{st} is shown.

perpendicular structures. The appearance of defects delineates the lower and upper limits of surface composition to produce uniform perpendicular orientation of the block copolymer domains.

A different perpendicular window was observed for block copolymer cylinders than for lamellae on **terminal-OH**. Between $0.59 \leq F_{St} \leq 0.72$, **PMMA-C5020** assembled into vertically oriented structures. The vertical orientation was at significantly higher F_{St} than for the lamellae-forming **L5252**. At a composition of the brush outside of this range, defects were seen in the structure that could be either bridging between cylinders (loop structures) or cylinders parallel to the free surface. **PS-C2050** showed vertically oriented structures only between $0.55 \leq F_{St} \leq 0.57$, a significantly narrower window than for the other block copolymers. Even at this narrow range of compositions, the quality of vertical cylinders was not perfect and some bridging was observed. The three perpendicular windows for lamellae, PS cylinders, and PMMA cylinders did not overlap, as shown in Figure 4a. Similar analysis was repeated with both **PH1** and **PG1** modified substrates, and the perpendicular windows for each block copolymer/random copolymer combination are summarized in Figure 4b,c. We found that with **PH1** and **PG1**, the perpendicular windows for all three block copolymers were shifted toward higher F_{St} compared to the **terminal-OH** brushes.

The preceding results focused on brush and mat layer composition. The range of F_{St} that resulted in perpendicular structures also depended on film thickness. The morphologies shown in Figure 3a for **PS-C2050** were for 22 nm thick films. In contrast, Figure 5 shows the results for 31 nm thick **PS-**

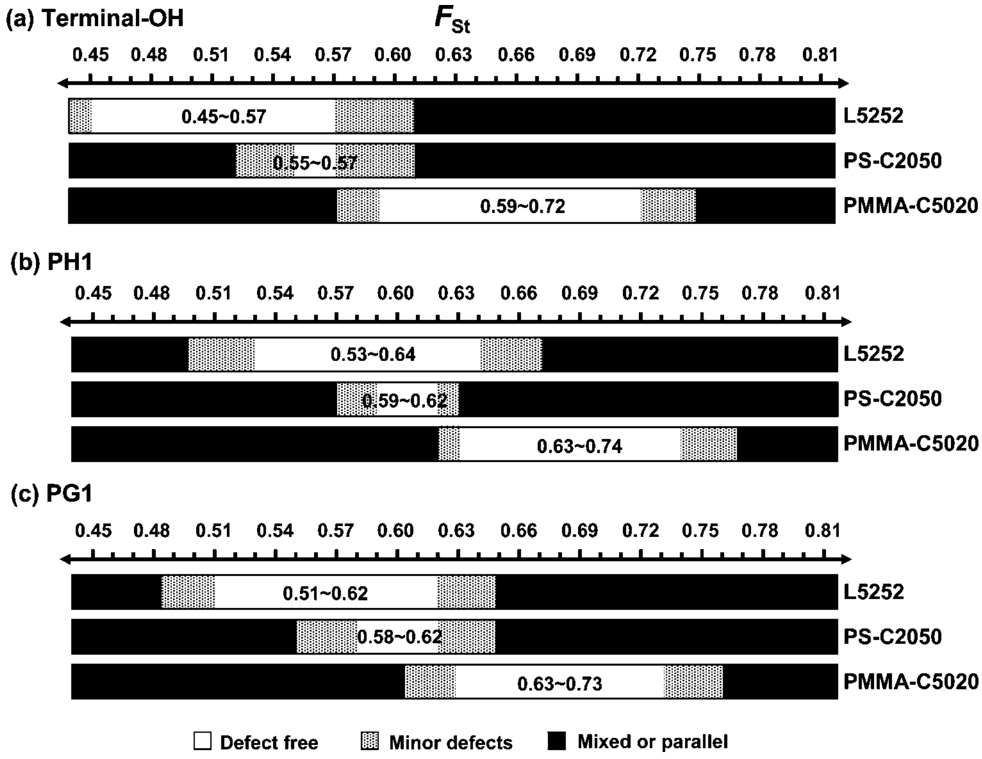


Figure 4. Perpendicular windows of **terminal-OH**, **PH1**, and **PG1** for symmetric and asymmetric block copolymers.

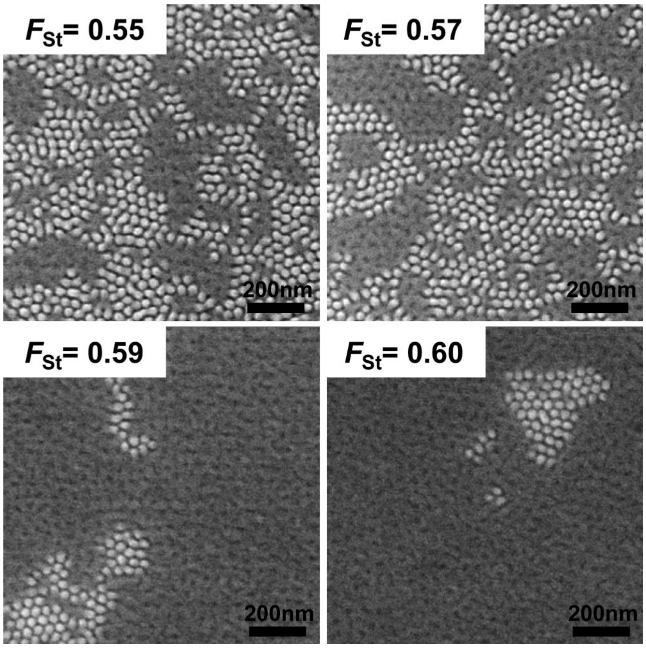


Figure 5. Terminal-OH modified surface with 31 nm thick **PS-C2050**.

C2050 on **terminal-OH** brushes. The slight increase in thickness from 22 to 31 nm caused the perpendicular cylinders to form only over small areas.

Discussion

Domain Orientation Influenced by Balance of Interfacial Energy and Polymer Entropy at Equilibrium. The differences in the composition ranges of the perpendicular windows for the different block copolymers, as shown in Figure 4, demonstrate that it is necessary to consider more than simply the interfacial energy of a random copolymer brush or mat with the respective homopolymers of the copolymer to determine whether the domains of the block copolymer will achieve a perpendicular orientation at equilibrium, even if γ_S for each homopolymer/brush combination is nearly equal. The perpendicular window for each block copolymer is a physical result of the minimization of the free energy of the film, but it does not indicate the actual free energy of the film. The free energy of the film as a function of F_{St} does not necessarily have a minimum at the center of the perpendicular window. For this reason, our analysis focuses on the overall size and position of the perpendicular window and not a single point.

Not only are the sizes of the windows different, but in some cases they do not overlap, even on the same surface coating. For example, in the case of **PH1**, it was impossible to define one particular random copolymer composition that would produce perpendicular domain orientation for all three block copolymers in the study. Similarly, the perpendicular windows for the two cylinder-forming block copolymers, **PMMA-C5020** and **PS-C2050**, were very different for all of the random copolymer-treated substrates, even though the only difference between the block copolymers was the reversal of the identity of the majority and minority blocks. **PMMA-C5020** and **PS-C2050** had the same overall molecular weight, majority volume fraction, and were annealed at the same temperature, and yet **PMMA-C5020** showed a wide perpendicular window at high F_{St}, whereas **PS-C2050** showed a narrower perpendicular window that was located at lower F_{St}. Results such as these lead us to conclude that it is necessary to consider the final assembled morphology in terms of the equilibration of the block copolymer film, including both its interface with the random copolymer-treated substrate and its free surface. Only by considering the overall equilibration process of the system can we understand the perpendicular window for any given combination of block copolymer film and substrate modifying random copolymer.

The equilibration of the system, comprising both the random copolymer and the overlying block copolymer, determines the equilibrium morphology and can be understood by considering the terms that contribute to the overall free energy of the system. Determining whether the domains of a block copolymer film will orient perpendicular, parallel, or with a mixed orientation relative to the interface requires determining which orientation has a lower free energy. As a rough estimate, the free energy of the block copolymer film can be expressed as the sum of four terms

$$F = F_{\mathrm{elastic}} + F_{\mathrm{S\text{-}MMA}} + F_{\mathrm{surface}} + F_{\mathrm{interface}} \qquad (1)$$

where F_{elastic} includes the entropic phenomena governing the chain conformations, $F_{\mathrm{S\text{-}MMA}}$ is the energy of interaction between blocks of the copolymer, F_{surface} is the surface energy at the free surface, and $F_{\mathrm{interface}}$ is the surface energy of the interaction of the block copolymer with the substrate.[26] The components of eq 1 have been defined analytically in some instances,[27] but to date, no analytical equations capture sufficient detail to predict the orientation of domains in films. Instead, simulations have been applied for such cases.[28−36] Here, we provide a phenomenological description of the components of eq 1 as they relate to the windows of perpendicular orientation that we have observed for the cylinder-forming block copolymers in our study.

The free energy terms in eq 1 can be divided into additional components that arise from various physical interactions. The F_{elastic} term includes a component for chain ends preferring to be near a hard wall (favors parallel domains), a component for the stretching and alignment of the chains near a wall (favors perpendicular domains), and a component for the asymmetry of the block copolymer that favors the short blocks of asymmetric chains near a hard wall. The $F_{\mathrm{S\text{-}MMA}}$ term includes the surface-induced compatibilization of the A−B interface for chains near the surface, which decreases the free energy of the perpendicular orientation. Surface-induced compatibilization is a major reason why the perpendicular orientation forms.[31]

Because the free energy of the film is the sum of many terms, the perpendicular window for each system must be understood as the combined result of these factors. As we have seen experimentally, perpendicular domains are induced over a range of brush or mat compositions, not at a single point. At the point where the enthalpic interactions between both blocks and the substrate are balanced, it is the F_{elastic}, $F_{\mathrm{S\text{-}MMA}}$, and F_{surface} terms that are responsible for the perpendicular structure, since the $F_{\mathrm{interface}}$ should be nearly the same for both the perpendicular and parallel orientation. As the brush or mat composition moves away from the balance point, the free energy of the perpendicular structure increases, but as long as this is less than for the parallel case, the orientation of domains remains perpendicular. The range over which perpendicular structures are stable, the perpendicular window, is therefore determined as much by the F_{elastic}, $F_{\mathrm{S\text{-}MMA}}$, and F_{surface} terms as it is by the $F_{\mathrm{interface}}$ term. A complete understanding of why perpendicular structures form under a set of conditions requires full knowledge of all of the energetic contributions to the free energy of the system.

On the basis of simulation results, we can compare energetic quantities to estimate the expected width of the perpendicular windows. In the recent work by Meng and Wang,[31] the energy favoring a perpendicular structure for a lamellar block copolymer on a substrate with no preference for either block was between 0 and $\sim 0.02 k_{\mathrm{B}}T$ per chain, depending on the chain density near the surface. Even though this result was dependent upon the choice of the chain density profile near the interface and was calculated using $\chi N = 15$, it is the best estimate to date of the energetics of perpendicular orientation. The perpendicular structure for these lamellae is favored as long as the energy reduction of forming a wetting layer of block copolymer on the substrate is less than the energy favoring the perpendicular structures on a nonpreferential substrate. The energy that a fully preferential surface has for the blocks of the block copolymer chain is on the order of $-0.1 k_{\mathrm{B}}T$ per chain relative to a surface with no preference. Assuming a linear transition in surface energy with random copolymer composition, we can see that from Meng and Wang's result the width of the perpendicular window should be between approximately 0 and 0.2 F_{St}. The **L5252** windows shown in Figure 4 are about $0.1F_{\mathrm{St}}$ in width, giving a window width within the expected range.

Effect of Block Copolymer Composition. We can better understand the block copolymer wetting for each system by considering the energetics of each block copolymer film. In the case of **PMMA-C5020**, there are at least two free energy contributions that account for the perpendicular structures at high F_{St} that we do not observe for the other block copolymers. One of these contributions is in the enthalpic $F_{\mathrm{interface}}$ term. The total energy of interaction between the interface and the block copolymer is equal to the interaction of each block with the interface times the area fraction of that block at the interface. As described above, as F_{St} moves away from the point corresponding to balanced interactions for a given block copolymer/random copolymer combination, there is an increase in free energy for the perpendicular orientation relative to the parallel orientation. This increase differs for symmetric and asymmetric block copolymers.

Consider the case of **PMMA-C5020** on **terminal-OH**, where ~30% of the block copolymer is PMMA: as the fraction of PS in the brush increases above the point of balanced interactions, there is an increasing energetic penalty for the structure to remain perpendicular as opposed to parallel. This penalty, however, is only about 3/5 of what it would be in the symmetric block copolymer because the number of contacts between the brush and the PMMA domains is only 3/5 that with the symmetric block copolymer, due to the volume fraction of PMMA in the block copolymer. Thus, a higher F_{St} is achievable without producing the same energetic penalty and resulting shift in morphology. This argument can also account for why the perpendicular window does not extend to low F_{St}. Just as the perpendicular **PMMA-C5020** was stable to high F_{St} because of molecular asymmetry, the perpendicular structures would be destabilized by decreasing the PS content of the substrate layer to lower values of F_{St}.

Another contribution to the position of the perpendicular window for the asymmetric block copolymers is from the entropic term associated with the different block sizes in the block copolymer.[32] The smaller block preferentially adsorbs to the substrate interface because of the proximity of any segment along the smaller block to a chain end. Because of the fact that chain ends have a low entropic penalty near a hard wall, the short block to which the chain end belongs is energetically preferred near the wall. As this phenomenon causes the block copolymer minority component to wet the surface, for a perpendicular structure, the enthalpic interaction with the majority block must be made more favorable to compensate. This shifts the perpendicular window to a higher composition of majority component (higher PS for **PMMA-C5020** and higher PMMA for **PS-C2050**).

In contrast to **PMMA-C5020**, **PS-C2050** showed a very narrow perpendicular window. One explanation for the difference in window sizes is the preferential interaction of one of the blocks of the film with the free surface. At our annealing temperature, PS has a slightly lower surface energy than PMMA.[37] We would expect the perpendicular structures to be destabilized by this relative to parallel structures, where PS can be present across the entire free surface or form parallel half-cylinders, reducing the amount of PMMA present. Similar to the wetting of the cylinders at the substrate as described above, the energetic component of the free energy at the surface is a function of the block copolymer composition. **PS-C2050** is ~70% PMMA, and the high PMMA content imparts a free energy penalty to the **PS-C2050** perpendicular structure that is greater than for the other block copolymers. Even within the perpendicular window for very thin films we see some defects in the cylindrical structure of **PS-C2050**. These defect structures may be related to the high quantity of PMMA present at the free surface and the reduction in free energy that occurs when the PMMA is buried within the film. Indeed, it is possible that the domains at the interface alter their shapes somewhat from the basic cylindrical structure to minimize the free energy.[33,38]

The window for **L5252** extended to a fairly low F_{St} on all the surface coatings. In all cases it extended to a lower F_{St} than **PS-C2050**. It is difficult to explain the difference between **L5252** and the cylinder-forming block copolymers because the lack of asymmetry in **L5252** changes both the entropic and enthalpic contributions to the free energy in the film relative to the cylinder-forming block copolymer. On all of the surface coatings, **L5252** showed a perpendicular window of about $0.12F_{St}$ and the window for **PS-C2050** was a subset of this range. Film thickness is a critical parameter affecting the perpendicular window size and for **PS-C2050** it was seen that perpendicular structures only formed for thin films of ~22 nm. The small window size for **PS-C2050**, even at this thickness, may be due to $F_{surface}$, which favors parallel cylinders with PS at the surface or the hard-wall interaction with the asymmetric block copolymer chains. The differences in the thicknesses and asymmetry between **L252** and the cylinder-forming block copolymers makes a direct comparison between them challenging.

Finally, the annealing temperature will affect the equilibration process by changing the terms in eq 1. We annealed the samples at 190 °C to match the temperature of annealing of previous experiments.[14,16] At higher annealing temperatures the difference in surface energy between PS and PMMA approaches zero,[37] such that there is less of a thermodynamic driving force for the domains to assemble parallel to the free surface. This suggests that higher temperatures may affect pattern quality and influence the perpendicular window size.

Inclusion of a Polar Monomer Shifts Perpendicular Window. In addition to the differences in the perpendicular windows observed for different block copolymers on the same random copolymer, differences were observed in the perpendicular windows of the same block copolymer on different random copolymer surface coatings. For example, for **PH1** and **PG1**, the perpendicular windows were shifted toward higher F_{St} values compared to the **terminal-OH** brushes. **PH1** and **PG1** differ from **terminal-OH** as they have a third polar comonomer in their chains. We believe the third comonomer shifts the perpendicular window because the reacted and unreacted hydroxyl or glycidyl groups within the layer will increase its polarity, requiring a higher styrene fraction to compensate.

To gain insight into the molecular differences between the three random copolymer coatings, we performed contact angle goniometry, yielding the results shown in Figure 2. Techniques such as NMR, FTIR, and XPS lack sufficient sensitivity to detect the low concentration of hydroxyl or epoxide groups in the random copolymer. The contact angle results for the random copolymer brushes reveal that the contact angle for a given F_{St} for either **PH1** or **PG1** was on average about one degree higher than for **terminal-OH**. To achieve the same contact angle with **PH1** or **PG1** as with the **terminal-OH**, the composition must be shifted to about 0.05 lower $F_{St.}$

Assuming the presence of unreacted hydroxyl or glycidyl groups in **PH1** and **PG1**, we might have initially expected the contact angles for **terminal-OH** to be higher than for **PH1** and **PG1**. The fact that the results are the opposite of this attests to the complexity of understanding the interfacial interactions with the brush or mat. One source of complexity to consider is the spatial reconfiguration of the polymer chains at the surface. We and others have shown that oxygen plasma-treated polystyrene can reconfigure its chains to reduce its surface energy, especially at high temperatures.[39−42] Polar groups initially on the free surface of a polymer film can move into the film and away from the free surface. In a similar way to oxygen plasma-treated polystyrene, the **PH1** and **PG1** molecules may significantly reorganize relative to the **terminal-OH** molecules during the grafting or cross-linking process to reduce the number of MMA, HEMA, or GMA units at the free surface.

The block copolymer perpendicular windows do not follow the trend given by the contact angle measurements. The appearance of block copolymer perpendicular windows for the **PH1** and **PG1** at higher F_{St} values suggests that **PH1** and **PG1** are more hydrophilic than **terminal-OH**, whereas the contact angle results suggest that the **PH1** and **PG1** brushes are less hydrophilic. This apparent discrepancy indicates that the substrate/block copolymer interaction is different from the interaction of the substrate with a drop of water. There are at least two mechanisms that could account for this. First, the surface layers may rearrange (in a manner similar to that discussed earlier) as they equilibrate in the presence of the block copolymer film. Second, the interpenetration of the random copolymer and the block copolymer may allow the block copolymer to effectively sense a different chemical composition than a droplet of water. A simplified view of the block copolymer/random copolymer interface might assume that both materials are in contact as atomically smooth, flat surfaces. Because the random copolymers and the block copolymers are long chain molecules in an amorphous state, however, they may interpenetrate during annealing and the degree of interpenetration may vary across the interfacial plane, significantly affecting the interaction.

Effect of Film Thickness. As noted in the Experimental Section on film preparation, we controlled the film thickness to permit the formation of perpendicularly oriented domains. In the case of the lamellar domains of **L5252** ($L_0 = 49$ nm), the film thickness was set to ~L_0, which has yielded perpendicular structures previously in our work,[2,26] and is well below the thickness limit for perpendicular structures found by other researchers.[21,43] In addition, this is near the optimal thickness reported by Ham et al.[22] The thickness of block copolymer films also has been shown to influence the equilibrium morphology of cylindrical domains.[33] For **PMMA-C5020,** 32 nm thick films were made, based on other results that the best film thickness for the formation of perpendicular cylinders is slightly below L_0 of the block copolymer.[5,22,44] For **PS-C2050**, we studied a range of film thicknesses and could only produce perpendicular structures with the thinnest film we tested, which was 22 nm thick. As shown in Figure 5, an increase in the film thickness of **PS-C2050** ($L_0 = 40$ nm) on **terminal-OH** from 22 to 31 nm effectively closed the perpendicular window for this block copolymer. Increasing the film thickness from 22 to 31 nm was a sufficient change in the block copolymer system to prohibit the formation of perpendicular domains throughout the film.

Conclusion

We found that the formation of perpendicular domains in thin films of block copolymers on a random copolymer brush needs to be viewed in terms of the equilibration of the block copolymer and the random copolymer brush in the presence of each other and not simply the interfacial energy of the blocks with the brush. All of the combinations of random copolymers and block copolymers showed unique perpendicular windows. The windows on **PH1** and **PG1** occurred at a higher F_{St} than for the

terminal-OH brush. The window for each block copolymer on a given brush was unique due to the individual energetic characteristics of each block copolymer. No single random copolymer composition could produce perpendicular structures in all of the block copolymers we tested, which would have been the case if only the interfacial energy of the random copolymer and block copolymer were necessary to determine the formation of perpendicular domains. In some cases, small changes in random copolymer chemistry led to very noticeable changes in the morphology of the overlying block copolymer. Through this investigation, the enhanced understanding of the formation of perpendicular domains on random copolymer-treated surfaces should prove useful in applications that require perpendicular domains, such as advanced lithography and templates for nanofabrication.

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Supporting Information Available: Characteristics of terminal-OH brush. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Black, C. T. *ACS Nano* **2007**, *1* (3), 147–150.
(2) Stoykovich, M. P.; Nealey, P. F. *Mater. Today* **2006**, *9* (9), 20–29.
(3) Bang, J.; Kim, S. H.; Drockenmuller, E.; Misner, M. J.; Russell, T. P.; Hawker, C. J. *J. Am. Chem. Soc.* **2006**, *128* (23), 7622–7629.
(4) Morkved, T. L.; Lu, M.; Urbas, A. M.; Ehrichs, E. E.; Jaeger, H. M.; Mansky, P.; Russell, T. P. *Science* **1996**, *273* (5277), 931–933.
(5) Jeong, U.; Ryu, D. Y.; Kho, D. H.; Kim, J. K.; Goldbach, J. T.; Kim, D. H.; Russell, T. P. *Adv. Mater.* **2004**, *16* (6), 533–536.
(6) Chen, F.; Akasaka, S.; Inoue, T.; Takenaka, M.; Hasegawa, H.; Yoshida, H. *Macromol. Rapid Commun.* **2007**, *28* (22), 2137–2144.
(7) Kitano, H.; Akasaka, S.; Inoue, T.; Chen, F.; Takenaka, M.; Hasegawa, H.; Yoshida, H.; Nagano, H. *Langmuir* **2007**, *23* (11), 6404–6410.
(8) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. *Science* **1997**, *275* (5305), 1458–1460.
(9) Huang, E.; Rockford, L.; Russell, T. P.; Hawker, C. J. *Nature (London)* **1998**, *395* (6704), 757–758.
(10) Peters, R. D.; Yang, X. M.; Kim, T. K.; Nealey, P. F. *Langmuir* **2000**, *16* (24), 9620–9626.
(11) Peters, R. D.; Yang, X. M.; Kim, T. K.; Sohn, B. H.; Nealey, P. F. *Langmuir* **2000**, *16* (10), 4625–4631.
(12) Kim, S. O.; Solak, H. H.; Stoykovich, M. P.; Ferrier, N. J.; de Pablo, J. J.; Nealey, P. F. *Nature (London)* **2003**, *424* (6947), 411–414.
(13) Ryu, D. Y.; Shin, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P. *Science* **2005**, *308* (5719), 236–239.
(14) In, I.; La, Y. H.; Park, S. M.; Nealey, P. F.; Gopalan, P. *Langmuir* **2006**, *22* (18), 7855–7860.
(15) Bang, J.; Bae, J.; Lowenhielm, P.; Spiessberger, C.; Given-Beck, S. A.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2007**, *19* (24), 4552–4557.
(16) Han, E.; In, I.; Park, S. M.; La, Y. H.; Wang, Y.; Nealey, P. F.; Gopalan, P. *Adv. Mater.* **2007**, *19* (24), 4448–4452.
(17) Hawker, C. J.; Elce, E.; Dao, J. L.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29* (7), 2686–2688.
(18) Ludwigs, S.; Schmidt, K.; Stafford, C. M.; Amis, E. J.; Fasolka, M. J.; Karim, A.; Magerle, R.; Krausch, G. *Macromolecules* **2005**, *38* (5), 1850–1858.
(19) Cheng, J. Y.; Rettner, C. T.; Sanders, D. P.; Kim, H.-C.; Hinsberg, W. D. *Adv. Mater.* **2008**, published online: 7 July 2008.
(20) Mansky, P.; Russell, T. P.; Hawker, C. J.; Pitsikalis, M.; Mays, J. *Macromolecules* **1997**, *30* (22), 6810–6813.
(21) Liu, C. C.; Nealey, P. F.; Ting, Y. H.; Wendt, A. E. *J. Vac. Sci. Technol., B* **2007**, *25* (6), 1963–1968.
(22) Ham, S.; Shin, C.; Kim, E.; Ryu, D. Y.; Jeong, U.; Russell, T. P.; Hawker, C. J. *Macromolecules* **2008**, published on Web 08/06/2008.
(23) Ghani, M. A. A.; Abdallah, D.; Kazmaier, P. M.; Keoshkerian, B.; Buncel, E. *Can. J. Chem.* **2004**, *82* (9), 1403–1412.
(24) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121* (16), 3904–3920.
(25) Ryu, D. Y.; Wang, J. Y.; Lavery, K. A.; Drockenmuller, E.; Satija, S. K.; Hawker, C. J.; Russell, T. P. *Macromolecules* **2007**, *40* (12), 4296–4300.
(26) Edwards, E. W.; Montague, M. F.; Solak, H. H.; Hawker, C. J.; Nealey, P. F. *Adv. Mater.* **2004**, *16* (15), 1315–1319.
(27) Suh, K. Y.; Kim, Y. S.; Lee, H. H. *J. Chem. Phys.* **1998**, *108* (3), 1253–1256.
(28) Pickett, G. T.; Balazs, A. C. *Macromolecules* **1997**, *30* (10), 3097–3103.
(29) Huinink, H. P.; Brokken-Zijp, J. C. M.; van Dijk, M. A.; Sevink, G. J. A. *J. Chem. Phys.* **2000**, *112* (5), 2452–2462.
(30) Tang, W. H. *Macromolecules* **2000**, *33* (4), 1370–1384.
(31) Meng, D.; Wang, Q. *J. Chem. Phys.* **2007**, *126* (23), 234902.
(32) Wang, Q.; Nealey, P. F.; de Pablo, J. J. *Macromolecules* **2001**, *34* (10), 3458–3470.
(33) Knoll, A.; Horvat, A.; Lyakhova, K. S.; Krausch, G.; Sevink, G. J. A.; Zvelindovsky, A. V.; Magerle, R. *Phys. Rev. Lett.* **2002**, *89* (3), 035501.
(34) Wang, Q.; Nealey, P. F.; de Pablo, J. J. *Macromolecules* **2003**, *36* (5), 1731–1740.
(35) Yang, Y. Z.; Qiu, F.; Zhang, H. D.; Yang, Y. L. *Polymer* **2006**, *47* (6), 2205–2216.
(36) Yin, Y. H.; Sun, P. C.; Jiang, R.; Li, B. H.; Chen, T. H.; Jin, Q. H.; Ding, D. T.; Shi, C. *J. Chem. Phys.* **2006**, *124* (18), 184708.
(37) Mansky, P.; Russell, T. P.; Hawker, C. J.; Mays, J.; Cook, D. C.; Satija, S. K. *Phys. Rev. Lett.* **1997**, *79* (2), 237–240.
(38) Edwards, E. W.; Muller, M.; Stoykovich, M. P.; Solak, H. H.; de Pablo, J. J.; Nealey, P. F. *Macromolecules* **2007**, *40* (1), 90–96.
(39) Murakami, T.; Kuroda, S.; Osawa, Z. *J. Colloid Interface Sci.* **1998**, *202* (1), 37–44.
(40) Dupont-Gillain, C. C.; Nysten, B.; Hlady, V.; Rouxhet, P. G. *J. Colloid Interface Sci.* **1999**, *220* (1), 163–169.
(41) Li, J. W.; Oh, K. H.; Yu, H. *Chin. J. Polym. Sci.* **2005**, *23* (2), 187–196.
(42) Stuen, K. O.; In, I.; Han, E.; Streifer, J. A.; Hamers, R. J.; Nealey, P. F.; Gopalan, P. *J. Vac. Sci. Technol., B* **2007**, *25* (6), 1958–1962.
(43) Xu, T.; Hawker, C. J.; Russell, T. P. *Macromolecules* **2005**, *38* (7), 2802–2805.
(44) Guarini, K. W.; Black, C. T.; Yeuing, S. H. I. *Adv. Mater.* **2002**, *14* (18), 1290–1294.

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