Interfacial Energy Effects on the Electric Field Alignment of Symmetric Diblock Copolymers

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ABSTRACT: The alignment of diblock copolymer microdomains by an electric field depends on the segmental interaction between two blocks and the difference in the interfacial energies of each block with the substrate. Morphologies having mixed orientations are predicted when the difference in the interfacial energies of the two blocks is large. By modifying a surface with random copolymer brushes, interfacial energies were controlled and the influence of interfacial energy on the orientation of the copolymer microdomains by an electric field was examined. Complete alignment of the lamellar microdomains was achieved only when the interfacial interactions were balanced. In all other cases, lamellae adjacent to the substrate were oriented parallel to the substrate surface, whereas in the center of the sample the lamellae oriented in the direction of the applied field. These results can be ascribed to a pathway-dependent alignment and a high energetic barrier to achieve complete reorientation of the lamellae adjacent to the surface.

Introduction

Thin films of block copolymers have attracted significant attention due to their potential uses as templates, masks, and scaffolds for nanostructured materials.[1−3] However, a crucial element for the success of such strategies is the complete alignment of the copolymer microdomains. The interfacial energies of the blocks of the copolymer play a key role in achieving full alignment of the copolymer microdomains. The preferential segregation of one block to the substrate will orient the microdomains parallel to the substrate surface.[4] To overcome such surface-directed orientation, external fields have been used.[5−8] For example, lamellar and cylindrical microdomains in thin films of poly(styrene-*b*-methyl methacrylate) (P(S-*b*-MMA)) can be oriented normal to the substrate with an electric field, achieving complete orientation in the direction of the applied field.[9−11]

Several theoretical studies have appeared addressing the alignment of symmetrical diblock copolymers in thin films by an electric field.[12−15] The roles of the applied electric field strength, interfacial energies, film thickness, dielectric constant difference between the two blocks, and commensurability of the film thickness and the natural period of the copolymer have been investigated. From these, however, the interfacial energies of the blocks emerge as the critical parameter or impediment in achieving complete alignment of the domains. A parallel orientation of the microdomains is favored when there is a difference in the interfacial energies, whereas a normal orientation of the microdomains is favored by the applied electric field. Under certain conditions, a mixed orientation of the microdomains is predicted. Here, parallel orientation of the microdomains at the surface occurs, whereas away from the surface, the influence of the applied electric field dominates and the microdomains orient in the direction of the applied electric field. With such mixed orientations, “T” junctions form when the lamellae oriented in orthogonal direction meet. These defects represent a significant energetic penalty. A dimensionless parameter δ can be defined as $\delta = |(\gamma_{AS} - \gamma_{BS})|/\gamma_T$, where γ_{AS} and γ_{BS} are the interfacial energies of block A and B with the substrate, respectively, and γ_T is the interfacial energy between block A and block B. Theoretical calculation done by Pereira et al. predict that in the strong segregation limit, for $\delta = 1$, only normal orientation is favored, whereas for $\delta > 1$, a mixed orientation is predicted.[12] It should be noted that Tsori and Andelmann, using the identical variables, predict normal orientations when $\delta < 2$ and a mixed orientation when $\delta > 2$.[13]

Here, an experimental study on the influence of the interfacial energies on the alignment of symmetric diblock copolymers, of poly(styrene-*b*-methyl methacrylate), P(S-*b*-MMA), is shown as a function of δ. Complete alignment of the lamellar microdomains normal to the surface, i.e. in the direction of the applied field, is found only when the interactions of the blocks with the substrate are balanced ($\delta = 0$). In all other cases, a mixed orientation of the microdomains was found. This very narrow window in δ contradicts theoretical predictions but can be ascribed to a kinetic trapping of the microdomain orientation and a high activation energy associated with reorienting the microdomains.

Experimental Section

P(S-*b*-MMA) was prepared by anionic synthetic routes and contained 50 vol % styrene. The number-average molecular weight M_n is 7.19×10^4 with a polydispersity of 1.08 as measured by size exclusion chromatography using polystyrene standards and refractive index detector. Silicon wafers were modified by anchoring hydroxyl-terminated random copolymers of styrene and methyl methacrylate, prepared by living free radical procedures, to the substrate.[16] Four random copolymers with styrene fractions of 0.58 (58/42), 0.7 (70/30), 0.8 (80/20), and 0.9 (90/10) were anchored to the surface, as described previously, to give a covalently attached random copolymer brush with thicknesses of approximately 6 nm. Using $\gamma_T = 0.8$ erg/cm^2, the respective values of δ are 0, 0.62, 0.73, and 0.94, respectively.[17] Films of P(S-*b*-MMA), ∼900 nm

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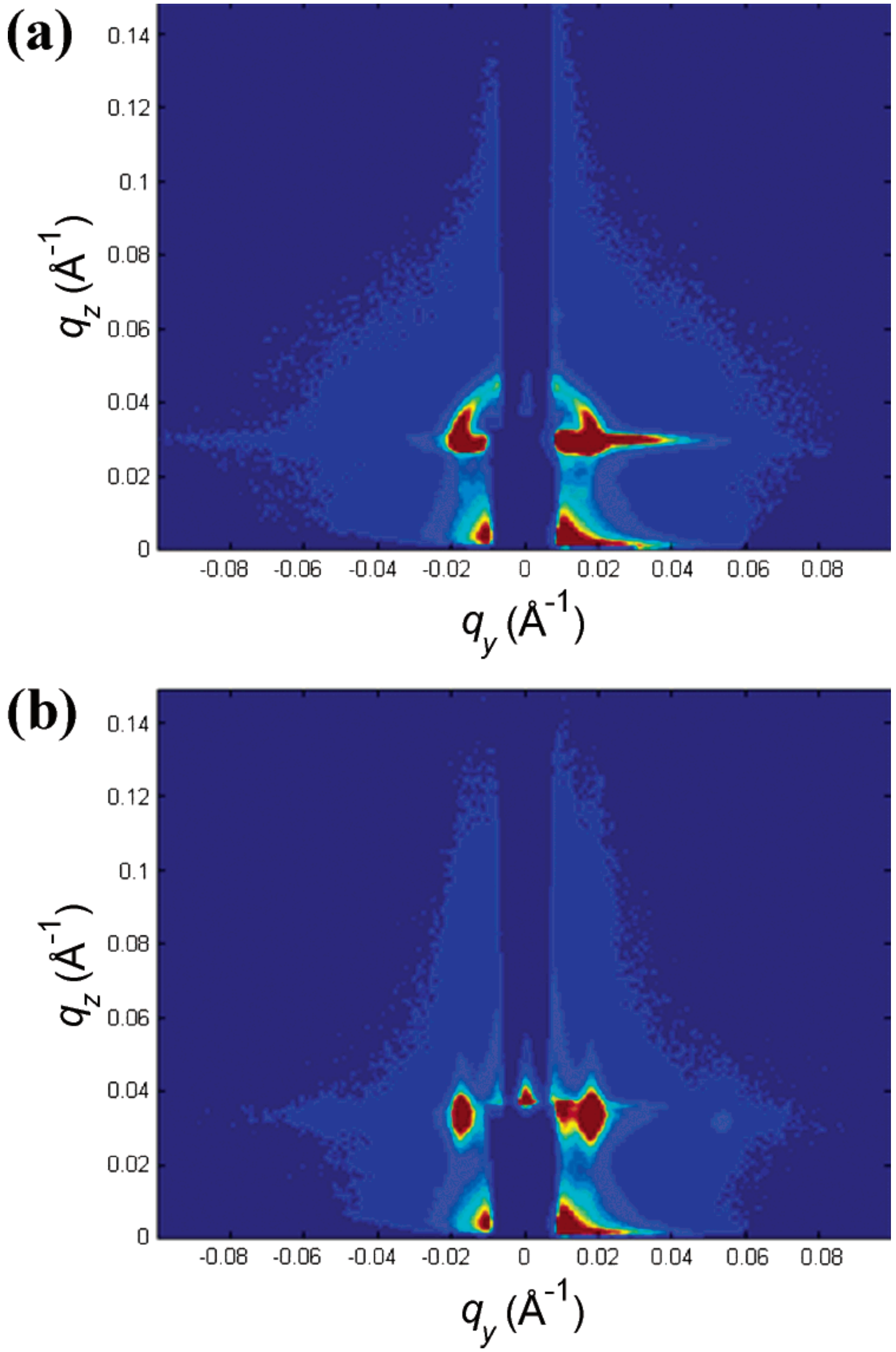

Figure 1. Grazing angle small-angle X-ray scattering patterns of P(S-*b*-MMA) (~900 nm) films on silicon substrate with native oxide layer (a) after annealing under vacuum and (b) after annealing under ~40 V/μm electric field.

in thickness, were prepared by spin-coating (~10^3 rpm) a 7% (w/v) toluene solution of the copolymer onto the substrate. Films ~3 μm in thickness were prepared by spin-coating (~500 rpm) a 10% (w/v) toluene solution of the copolymer on the substrate. An aluminized Kapton film comprised the top electrode, where a thin layer (20−25 μm) of cross-linked PDMS (Sylgard) was used as a buffer layer between the Kapton electrode and the copolymer thin film.[18] The PDMS layer conforms to the electrode surface, eliminates air gaps between the top electrode and the copolymer film, and maintains a smooth surface of the copolymer film. The copolymer films were heated to 170 °C under N_2 with an applied electric field of ~40 V/μm for 16 h and then quenched to room temperature before removing the electric field. The samples were embedded in epoxy,[19] microtomed with a diamond knife at room temperature, and transferred to a copper grid. The thin sections were exposed to ruthenium tetraoxide for 35 min to enhance the contrast. Electron microscopy experiments were performed on a JEOL 100CX TEM at the accelerating voltage of 100 kV. Grazing angle small-angle X-ray scattering (GASAXS) was performed at the National Synchrotron Light Source (Brookhaven National Laboratory), using X-rays with a wavelength of 0.1567 nm. Typical exposure times were 90 s per sample.

Results and Discussion

Shown in Figure 1 are the GASAXS patterns for a ~900 nm thick P(S-*b*-MMA) film on a silicon substrate

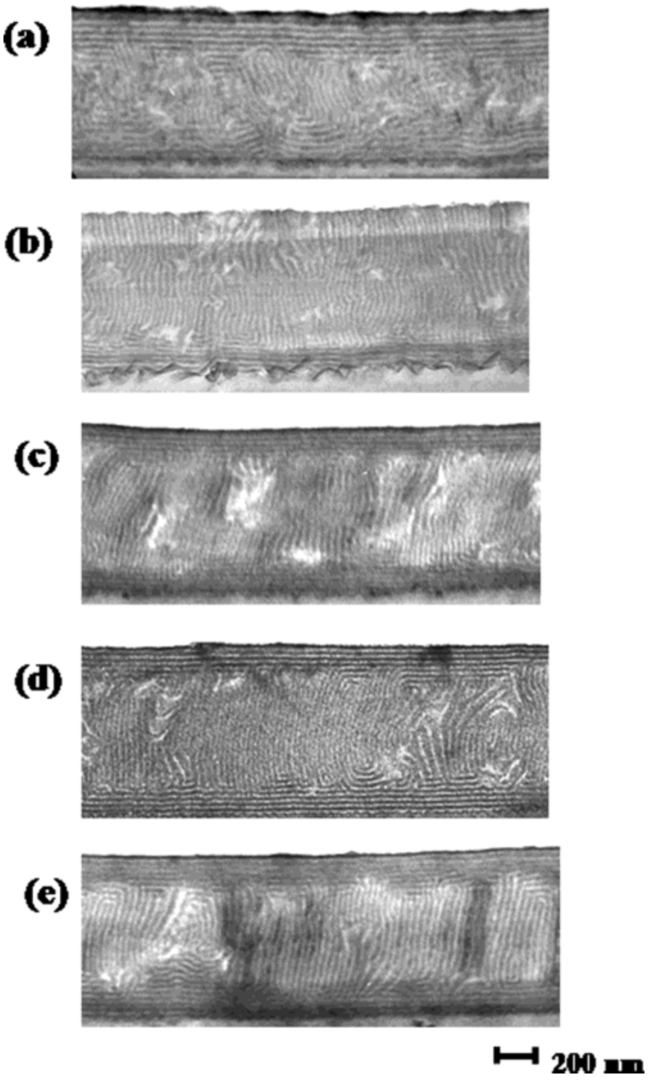

Figure 2. Transmission electron microscopy cross-section images of P(S-*b*-MMA) thin films after (a) annealed under vacuum for 48 h on the substrate modified with 90/10 random copolymers, annealing under ∼40 V/μm electric field on the substrates modified with different random copolymers, (b) 58/42, $\delta = 0$, (c) 70/30, $\delta = 0.62$, (d) 80/20, $\delta = 0.73$, (e) 90/10, $\delta = 0.94$, after spin-coating.

with a native oxide layer, obtained at a ∼0.2° incidence angle. Figure 1a is for the sample annealed at 170 °C under vacuum for 48 h with no applied field. The arclike pattern indicates that the lamellar microdomains are randomly oriented in the film. The scattering from a similar sample annealed under an applied electric field (∼40 V/μm) is shown in Figure 1b. The two equatorial spots show that the lamellae orient normal to the surface, in the direction of the applied field. However, with GASAXS, it is not possible to discern whether the alignment of the microdomains extends completely to the interfaces, only that the average degree of alignment is high.

To examine the orientation of the microdomains at the interfaces, TEM was used. Figure 2a shows a cross-sectional TEM image of P(S-*b*-MMA) thin film after annealing under vacuum for 48 h with no applied field. The film is on a substrate modified with random copolymer with a styrene fraction of 0.9. The lamellar microdomains are parallel to the substrate at both interfaces due to the preferential wetting of the PS block. In the center of the film, the effect of the interface dissipates, and the microdomains assume random orientation. Figure 2b,c,d,e shows the cross-section TEM images of P(S-*b*-MMA) thin films after annealing under a ∼40 V/μm electric field on four different substrates to which random copolymers with styrene fractions of 0.58, 0.7, 0.8, and 0.9, respectively, were anchored. From the TEM sample preparation,[19] the top of each image corresponds to the copolymer/substrate interface. An orientation of the lamellar microdomains in the direction of the applied field is seen in the middle of the films. Complete alignment of the lamellae extending to the interfaces was achieved only when $\delta = 0$, i.e., when the interactions between the surface and the blocks were balanced. Mixed orientations were seen in all other cases, even when the difference in the interactions between the blocks and the substrate was much smaller than the interfacial energy between the two blocks. In comparison with the theoretical calculations, the observed range in δ to achieve complete orientation of the microdomains is much narrower.

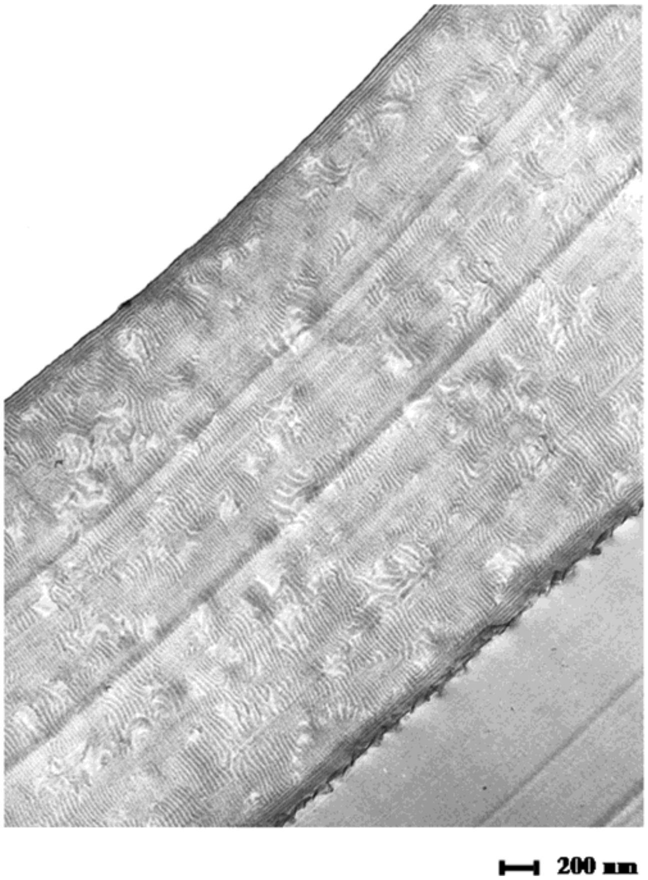

Figure 3. Transmission electron microscopy cross-section image of P(S-*b*-MMA) thin films (∼3 μm) after annealing under ∼40 V/μm electric field on the substrates modified with 90/10 random copolymers.

Mixed orientations were also found with thicker films. Figure 3 shows the cross-section TEM image of a P(S-*b*-MMA) film with a thickness of ∼3 μm, annealed in a ∼40 V/μm electric field. The substrate was modified with a 90/10 random copolymer. The lamellar microdomains are parallel to the substrate at the interfaces and are aligned with the electric field in the middle of the film. In comparison to Figure 2a (no field applied), Figure 2e (field applied, thinner film), and Figure 3 (field applied, thick film), no dramatic change in the number of parallel lamellar microdomains oriented parallel to the interface is seen. Thus, qualitatively the

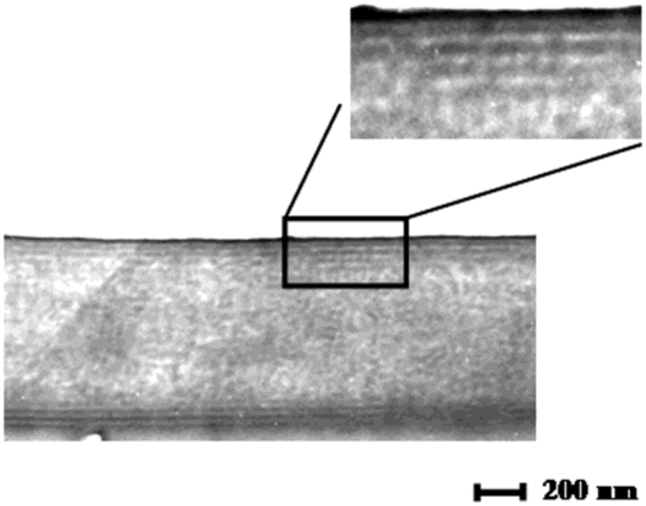

Figure 4. Transmission electron microscopy cross-section image of P(S-*b*-MMA) thin films after annealing under ~40 V/μm electric field for 1 h at 160 ± 5 °C on the substrates modified with 80/20 ($\delta = 0.73$) random copolymer.

number of the lamellar microdomains orientated parallel to the substrate interface is independent of the film thickness within the thickness range studied here (~700 nm−3 μm). This orientation depends primarily on the strength of the interfacial interaction. Quantitative arguments will be made on the relationship between the interfacial interaction and the number of the parallel lamellar microdomains in a forthcoming paper.[20] However, qualitatively, the trend is clear, as seen from the change in the microdomain orientation at the copolymer/substrate interface in Figure 2b−e, where, with increasing strength of the interactions, the distance over which parallel orientation penetrates into the film increases.

The theoretical arguments are based on a diblock copolymer in the strong segregation limit regime. For the diblock copolymer used here, PS-*b*-PMMA, $\chi N \sim 26$.[21] Though not in the very strong segregation limit, it is dearly not in the weak segregation limit. In addition, the interactions of blocks with the random copolymer modified substrates are smaller than the segmental interaction between the two blocks in all the cases shown here. Thus, one possible reason to account for the discrepancy between theory and experiment is a pathway dependence of the alignment process that is not considered theoretically.[22] Figure 4 shows the cross-section TEM image of the thin film after annealing at 160 ± 5 °C under an electric field of ~40 V/ μm for 1 h. A random copolymer was anchored to the surface such that $\delta = 0.73$. In this case, full alignment of the microdomains should occur. At the substrate interface, the lamellar microdomains are seen to orient parallel to the substrate initially, whereas in the center of the film, the copolymer, while microphase separated, is not aligned. Further annealing of the sample under an electric field produced the film shown in Figure 2d.

On the basis of these TEM images and others, it is evident that two kinetic processes are in competition, namely the alignment of the microdomains by the electric field and the surface-induced alignment of the microdomains. While an electric field can bias concentration fluctuations of a disordered copolymer,[9,21] it is apparent that the surface-induced orientation is a stronger field initially. This can be understood by the influence of a surface on the ordering of the copolymer. It has been shown that the order-to-disorder transition can be markedly increased in the vicinity of a surface.[23] Consequently, the copolymers near the interface microphase separate initially with an orientation that is strongly biased by the interface. The influence of the interface, of course, dissipates with increasing distance from the surface and, in the absence of other fields, the copolymer orders and orients under the influence of the applied field. Consequently, in the center of the film, the copolymer microdomains are oriented parallel to the applied field, i.e., normal to the substrate surface. This structure does not correspond to the equilibrium structure, since the formation of T-junctions is energetically costly. However, to fully orient the microdomains, the microdomains at the interface must be rotated 90°. A simple rotation of the micrdomains is not feasible, and an undulation of the microdomains is a more plausible route. This, however, increases the interfacial area between the microdomians and also necessitates the stretching and compression of the chains, since the substrate is flat. Thus, the energetic barrier to complete the transition to a fully aligned state is high, requiring a higher electric field than that predicted theoretically to achieve the perfectly aligned state.

Conclusion

In conclusion, the interfacial energy was controlled precisely by anchoring random copolymers to the substrate, and the influence of interfacial energy on the electric field alignment of thin films of symmetric P(S-*b*-MMA) thin films was studied. Complete alignment of symmetric diblock copolymer thin films was found only when the interactions between the blocks of copolymer and substrate were balanced. Mixed orientations were found in all other cases, even when the difference in the block−substrate interactions were smaller than the interfacial energy between two blocks. Electron microscopy results suggest a pathway dependence of the alignment process to explain the discrepancy between the experimental results and the theoretical predictions.

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References and Notes

(1) Park, M.; Harrison, C. K.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.
(2) Huang, E.; Rockford, L.; Russell, T. P.; Hawker, C. J.; Mays, J. *Nature (London)* **1998**, *395*, 757.
(3) Thurn-Albrecht, T.; Steiner, R.; DeRouchey, J.; Stafford, C. M.; Huang, E.; Bal, M.; Tuominen, M.; Hawker, C. J.; Russell, T. P. *Adv. Mater.* **2001**, *12*, 787.
(4) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(5) Morkved, T.; Lu, M.; Urbas, A. M.; Ehrichs, E. E.; Jaeger, H. M.; Mansky, P.; Russell, T. P. *Science* **1996**, *273*, 931.
(6) Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.
(7) Mansky, P.; DeRouchey, J.; Mays, J.; Cook, D. C.; Morkved, T.; Jaeger, H.; Russell, T. P. *Macromolecules* **1998**, *31*, 4399.

(8) Boker, A.; Knoll, A.; Elbs, H.; Abetz, V.; Muller, A. H. E.; Krausch, G. *Macromolecules* **2002**, *35*, 1319.

(9) Amundson, K.; Helfand, E.; Davis, D. D.; Quan, X.; Patel, S. S.; Smith, S. D. *Macromolecules* **1991**, *24*, 6546.

(10) Amundson, K.; Helfand, E.; Quan, X.; Smith, S. D. *Macromolecules* **1993**, *26*, 2698.

(11) Amundson, K.; Helfand, E.; Quan, X.; Hudson, S. D.; Smith, S. D. *Macromolecules* **1994**, *27*, 6559.

(12) Pereira, G. G.; Williams, D. R. M. *Macromolecules* **1999**, *32*, 8115.

(13) Tsori, Y.; Andelmann, D. *Macromolecules* **2002**, *35*, 5161.

(14) Ashok, B.; Muthukumar, M.; Russell, T. P. *J. Chem. Phys.* **2001**, *115*, 1559.

(15) Onuki, A.; Fukuda, J. *Macromolecules* **1995**, *28*, 8788.

(16) Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.

(17) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. *Science* **1997**, *275*, 1458.

(18) Cross-link PDMS (Sylgard 184) was purchased from Dow Corning and used as is. The 10:1 mixture was mixed and spin-coated on top of the aluminized Kapton, cured for 24 h at 60 °C. Then the cross-linked PDMS-coated Kapton was annealed at 170 °C under vacuum for 12 h to remove the residue small molecules. The Si elemental concentration in the copolymer film after annealing with the electric field for 16 h is less than 1% measured by X-ray photoelectron spectroscopy with a probing depth of 4.5 nm.

(19) A thin layer of carbon (10−20 nm) was coated on the surface, and the film was embedded with epoxy and cured at 60 °C for 12 h. The film was peeled off from the substrate by dipping into liquid N_2. The substrate was checked with ellipsometry, and less than 5 nm film was left for all the samples shown here.

(20) Xu, T.; Hawker, C. J.; Russell, T. P. Manuscript in preparation.

(21) Russell, T. P.; Hjelm, R. P., Jr.; Seeger, P. A. *Macromolecules* **1990**, *23*, 890.

(22) Thurn-Albrecht, T.; DeRouchey, J.; Russell, T. P.; Kolb, R. *Macromolecules* **2002**, *35*, 8106.

(23) Mansky, P.; Russell, T. P.; Hawker, C. J.; Mays, J.; Cook, D. C.; Satija, S. K. *Phys. Rev. Lett.* **1997**, *79*, 237.

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