Enhancement of Diblock Copolymer Ordering Kinetics by Supercritical Carbon Dioxide Annealing

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The morphology and periodicity of microphase-separated diblock copolymers can be precisely controlled by manipulating the chemical composition and molecular weights of the segments, respectively.[1,2] Numerous applications that exploit copolymer morphology as scaffolds and templates for nanostructures with periodicities from 1 to 50 nm are emerging that make use of the unique chemical structure of each block and the ability to carry out chemistry within one domain selectively. For example, Park et al. have used copolymer morphologies as templates for pattern transfer to a substrate to generate nanodots.[3] Thurn-Albrecht et al. have produced terabit arrays of nanowires in thin films using block copolymer templates.[4] Stucky and co-workers have synthesized porous silica by the cooperative assembly and condensation of tetraethyl orthosilicate with nonionic block copolymer surfactants.[5] Hillmyer and co-workers selectively incorporated and cross-linked an epoxy resin within the poly(ethylene oxide) (PEO) domains of a PEO-*b*-poly(ethylethylene) copolymer.[6] Templated metal nanoclusters have been prepared by Cohen and co-workers by in situ reaction within thin block copolymer microdomains with selectively bound organometallic compounds.[7−9] Recently, using supercritical carbon dioxide, Brown et al. have selectively deposited metals and semiconductors within one domain of a block copolymer template.[10]

Since the domain spacing in block copolymers (*D*) scales with the number-average degree of polymerization (*N*) in a known manner ($D \sim N^{\nu}$ where ν is $^2/_3$ for lamellar morphologies in the strong segregation limit), it is easy, in principle, to design copolymer systems that exhibit microdomain spacings at any desired length scale. Xu et al. have used this approach to generate nanoporous films where the pore size was dictated by the copolymer molecular weight.[11] Of particular interest are periods on the order of $\lambda/4n$, where λ is the wavelength of light and *n* is the index of refraction of the material. At this length scale, block copolymers can serve as templates for photonic devices.[12,13]

The simplest structure for photonic applications is an alternating two-component multilayer film. For low molecular weight copolymers, well-ordered lamellar structures can be obtained by simply annealing symmetric diblock copolymer films above the glass transition temperatures of both blocks. For thin films, Russell

and co-workers have shown that the interactions of the blocks with the air and substrate interfaces induce near perfect orientation of the microdomains parallel to the substrate surface.[14] Templates for photonic devices require periods on the order of ~100 nm, which, in the case of a diblock copolymer of polystyrene and poly-(methyl methacrylate) [P(S-*b*-MMA)], requires molecular weights in excess of 3×10^5 g/mol.

Unfortunately, attempts have not been successful in preparing well-ordered and oriented structures from copolymers with high molecular weights by thermal annealing. The high degree of entanglement coupled with the thermodynamic barrier of diffusing one polymer block through a domain of second poses severe kinetic barriers to ordering.[15−17] Consequently, alternative strategies must be used to achieve large *D* spacings. One route is to increase the domain size by the addition of low molecular weight homopolymers that swell each domain and enhance mobility. However, this approach has the unintended consequence of exacerbating defects by the accumulation of the homopolymer at these sites.[18]

Alternatively, a transient plasticizing agent can be used that enhances the mobility to allow ordering but can subsequently be removed easily. Supercritical CO_2 is ideal for this purpose.[19,20] It is a poor solvent for most polymers: equilibrium sorption is modest and can be controlled by pressure-mediated adjustments in fluid density.[21] For example, sorption of CO_2 in PS ranges from 1.3 wt % at 5 bar to 10.2 wt % at 72 bar at 35 °C[21] and ranges from 0.9 wt % at 25 bar to 6.5 wt % at 174 bar at 180 °C.[22] Moreover, CO_2 diffusion in most systems is rapid, so the diluent reaches an equilibrium distribution rapidly in thin polymer films. Finally, upon controlled depressurization that prevents foaming, the solvent completely desorbs from the film without damaging the block copolymer morphology. Here, we show the preparation of ordered, high molecular weight copolymer thin films using CO_2 as the diluent at elevated pressure. Identical films could not be ordered by thermal means alone, regardless of the temperature or length of the annealing period up to 240 h.

Experimental Section. P(d-S-*b*-MMA), with a total molecular weight of 301 000 g/mol (denoted 301K) with a polydispersity of 1.08 and P(S-*b*-MMA) with molecular weight of 34 500 g/mol (34.5K) with volume fractions of PS close to 0.5, was purchased from Polymer Laboratories. These copolymers exhibit a lamellar morphology in the ordered state. Polymer thin films were spin-coated from 4 wt % solutions in toluene onto polished silicon substrates to yield a film thickness of approximately 0.3 μm. Samples were either annealed in a vacuum oven at 175 °C or in the presence of CO_2 (at a density of around 0.5 g/cm³) at 175 °C and 346 bar in a high-pressure vessel.[23] CO_2 was supplied using a computer-controlled ISCO high-pressure pump. Samples were analyzed using an Olympus BX60 optical reflection microscope (ORM), atomic force microscopy (AFM) was performed using a Digital Instruments Dimension 3000 scanning probe microscope, and X-ray photoelectron spectroscopy (XPS) was performed using a Perkin-Elmer Physical Electronics 5100 spectrometer with a Mg Kα source.

Results and Discussion. Ordering of thin diblock copolymer films at ambient pressure is enhanced by

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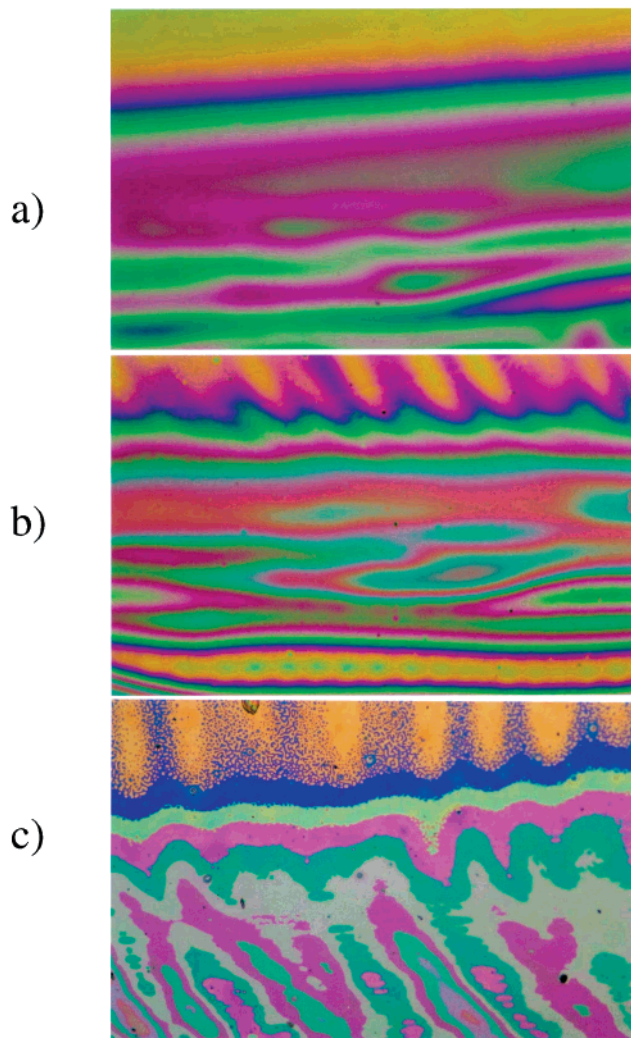
Figure 1. Optical reflection micrographs of (a) 301K P(d-S-*b*-MMA) film edge (as cast) on silicon substrate. (b) A similar film annealed in a vacuum oven at 175 °C for 240 h. The interfaces remain diffuse. (c) A similar film annealed in a high-pressure vessel at 175 °C in the presence of 346 bar of CO_2 for 48 h. The sharp interfaces between the color bands indicate terracing near the edge of the film. All images were acquired at the same magnification.

interactions of the chain segments with both the substrate and free surfaces.[14,24] The block with the lower surface tension preferentially segregates to the air (free) interface whereas specific interfacial interactions will cause one block to segregate at the substrate. These interactions coupled with the connectivity of the blocks causes the film thickness, t, at any point on the sample to be given in terms of the period of the copolymer, L. If one of the blocks is at both interfaces (symmetric wetting), $t = nL$, where n is an integer. For asymmetric wetting, $t = (n + {}^1/_2)L$. If the film thickness is not commensurate with these conditions, a terraced topography with step heights of L is seen.[25] These terraces are readily seen by optical reflection microscopy and AFM and are a characteristic signature of parallel alignment of the microdomains.[26,27] Optical microscopic images of the edge of a P(d-S-*b*-MMA) film after spin-coating and after annealing for 240 h are shown in parts a and b of Figure 1, respectively. In both cases, the changes in the interference colors are continuous, indicating that the sample is not well aligned even after extensive annealing. Figure 1c shows an image of a film
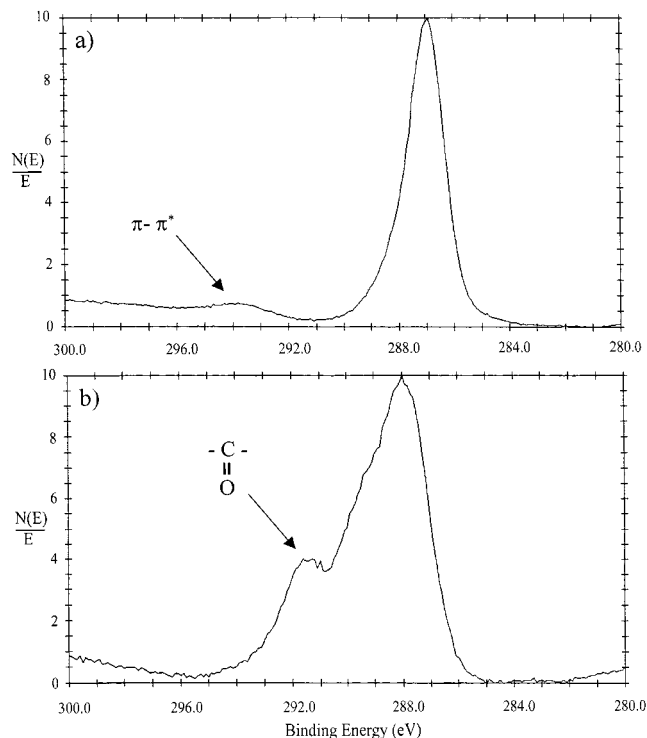
Figure 2. X-ray photoelectron spectroscopy using a 15° takeoff angle of the C 1s region of (a) thermally annealed 34.5K P(S-*b*-MMA) sample at 175 °C in a vacuum oven for 10 h and (b) 34.5K P(S-*b*-MMA) sample annealed at 170 °C in the presence of 346 bar of CO_2 for 10 h.

that was annealed in the presence of CO_2 (346 bar) at 175 °C for 48 h. Discrete changes in the interference colors, characteristic of a terraced topography, are evident. AFM measurements yield a step height for the terraces of 93 nm.

The enhanced ordering of the copolymer in these films can be ascribed primarily to an increase in chain mobility. At the conditions used for annealing, the copolymers absorb a significant amount of CO_2. For example, at 180 °C and 174 bar absorption of CO_2 in PS is approximately 6.4 wt %[22] and is expected to be higher in the case of PMMA. Moreover, it is well-known that CO_2 sorption significantly depresses the glass transition temperature of both PS and PMMA. For example, the glass transition temperature of PMMA and PS can be depressed by as much as 63 and 65 °C, respectively, upon CO_2 sorption at moderate pressures.[21,28] The influence of compressed CO_2 on the thermodynamics of the copolymer microphase separation during the preparation or processing of templates, however, should not be ignored. Previously, it was shown that CO_2 sorption can promote segment miscibility in systems that exhibit upper order−disorder transitions (UODT) but induces microphase segregation in systems such as polystyrene-*b*-poly(*n*-butyl methacrylate) [P(S-*b*-nBMA)] copolymers that display lower disorder−order transitions (LDOT).[29,30] The high molecular weights required to achieve the large periods discussed here virtually ensure the copolymers used will remain in the strong-segregation regime, but the interfacial width may be affected by the presence of solvent. P(S-*b*-nBMA) is a particularly interesting case as solvent sorption promotes both mobility and phase segregation. High-pressure neutron reflectivity studies are in progress to quantify these effects.[31]

Exposure to CO_2 may also change the wetting symmetry of the diblock copolymer. Upon annealing in a vacuum, P(S-*b*-MMA) films cast on the native oxide of silicon wafers exhibit asymmetric wetting with PMMA segregating to the polymer−substrate interface, while PS, the lower surface energy block, preferentially segregated to the surface.[14] CO_2 is selective for PMMA and could force the system into a symmetric wetting condition. P(S-*b*-MMA) of molecular weights 34.5K and 301K were used to study the wetting behavior of the diblock copolymer films in the presence of CO_2. Figure 2 shows XPS scans of the C 1s region of (i) 34.5K P(S-*b*-MMA) film thermally annealed at 175 °C for 10 h and (ii) an identical sample of 34.5K P(S-*b*-MMA) annealed in the presence of CO_2 at 346 bar at 170 °C for 10 h. The two spectra are markedly different. In the thermally annealed sample PS is at the air surface as would be expected. However, for the sample annealed in CO_2, the XPS profile is identical to that of pure PMMA with the higher binding energy shoulder on the C 1s peak attributed to the carbonyl group. Consequently, PMMA is at the surface. XPS analysis of 301K P(d-S-*b*-MMA) annealed at 170 °C in the presence of CO_2 also indicated that PMMA is located at the surface.

In conclusion, sorption of supercritical CO_2 is shown to be a simple means of enhancing the ordering kinetics of high molecular weight diblock copolymer in thin films. In addition, CO_2 can influence surface wetting, and in the case of P(S-*b*-MMA), the surface wetting is reversed. Solvent loading is easily manipulated using pressure-mediated adjustments in fluid density. Controlled decompression leads to facile desorption of carbon dioxide without damaging the ordered copolymer structure.

References and Notes

(1) Hamley, I. W. *Block Copolymers*; Oxford University Press: Oxford, England, 1999.

(2) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501. (b) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32.

(3) Park, M.; Harrison, C.; Chikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.

(4) Thurn-Albrecht, T.; Schotter, J.; Kastle, C. A.; Emley, N.; Shibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.

(5) Melosh, N.; Lipic, P.; Bates, F.; Wudl, F.; Stucky, G.; Fredrickson, G.; Chmelka, B. *Macromolecules* **1999**, *32*, 4332.

(6) Hillmyer, M. A.; Lipic, P. M.; Hajduk, D. A.; Almdal, K.; Bates, F. S. *J. Am. Chem. Soc.* **1997**, *119*, 2749.

(7) Yue, J.; Cohen, R. E. *Supramol. Sci.* **1994**, *1*, 117.

(8) Clay, R. T.; Cohen, R. E. *Supramol. Sci.* **1995**, *2*, 183.

(9) Kane, R. S.; Cohen, R. E.; Silbey, R. J. *Chem. Mater.* **1996**, *8*, 1919.

(10) Brown, G. B.; Watkins, J. J. *Mater. Res. Soc. Symp. Proc.* **2000**, *584*, 169.

(11) Xu, T.; Kim, H.; DeRouchey, J.; Seney, C.; Levesque, C.; Martin, P.; Stafford, C. M.; Russell, T. P. The Influence of Molecular Weight on Nanoporous Polymer Films. Submitted to *Polymer*.

(12) Chen, J.; Thomas, E. L.; Ober, C. K.; Mao, G.-P. *Science* **1996**, *273*, 343.

(13) Fink, Y.; Urbas, A. M.; Bawendi, M. G.; Joannopolous, J. D.; Thomas, E. L. *J. Lightwave Technol.* **1999**, *17*, 1963.

(14) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.

(15) Green, P. F. *Macromolecules* **1995**, *28*, 2155.

(16) Helfand, E. *Macromolecules* **1992**, *25*, 492.

(17) Dalvi, M. C.; Eastman, C. E.; Lodge, T. P. *Phys. Rev. Lett.* **1993**, *71*, 2591.

(18) Urbas, A.; Sharp, R.; Fink, Y.; Thomas, E. L. Xenidou, M.; Fetters, L. J. *Adv. Mater.* **2000**, *12*, 812.

(19) Berens, A. R.; Huvard, G. S.; Korsmeyer, R. W.; Kunig, F. W. J. *Appl. Polym. Sci.* **1992**, *46*, 231.

(20) Chapman, B. R.; Gochanour, C. R.; Paulaitis, M. E. *Macromolecules* **1996**, *29*, 5635.

(21) Wissinger, R. G.; Paulaitis, M. E. *J. Polym. Sci., Phys. Ed.* **1987**, *25*, 2497.

(22) Sato, Y.; Yurugi, M.; Fujiwara, K.; Takishima, S.; Masuoka, H. *Fluid Phase Equilib.* **1996**, *125*, 129.

(23) For the preliminary experiments, PS−PMMA diblock copolymer films were spin-coated onto 0.5 in. × 0.5 in. silicon wafers and were annealed in CO_2 using a 25 mL Thar vessel (Thar Design, Inc.) rated to 690 bar. The vessel was heated using a tape heater controlled with a PID temperature controller.

(24) Menelle, A.; Russell, T. P.; Anastasiadis, S. H.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1992**, *68*, 67.

(25) Russell, T. P. *Physica B* **1996**, *221*, 267.

(26) Maaloum, M.; Ausserre, D.; Chatenay, D.; Coulon, G. *Phys. Rev. Lett.* **1992**, *68*, 1575.

(27) Mansky, P.; Tsui, O. K. C.; Russell, T. P.; Gallot, Y. *Macromolecules* **1999**, *32*, 4832.

(28) Condo, P. D.; Johnston, K. P. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 523.

(29) Vogt, B. D.; Brown, G. D.; RamachandraRao, V. S.; Watkins, J. J. *Macromolecules* **1999**, *32*, 7907.

(30) Watkins, J. J.; Brown, G. B.; RamachandraRao, V. S.; Pollard, M. A.; Russell, T. P. *Macromolecules* **1999**, *32*, 7737.

(31) RamachandraRao, V. S.; Gupta, R. R.; Russell, T. P.; Watkins, J. J. Interaction of Polymer Thin Films with Compressed/Supercritical Carbon Dioxide−In Situ High-Pressure Neutron Reflectivity. Manuscript in preparation.