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Feature Article

Self-Assembled Block Copolymers: Bulk to Thin Film

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Abstract: Block copolymers that two or more polymer chains are covalently linked have drawn much attention due to self-assembly into nanometer-sized morphology such as lamellae, cylinders, spheres, and gyroids. In this article, we first summarize the phase behavior of block copolymers in bulk and thin films and some applications for new functional nanomaterials. Then, future perspectives on block copolymers are described.

Keywords: block copolymer, self-assembly, functional nanomaterials, soft templates.

Introduction

Since block copolymers have been successfully synthesized by living anionic polymerization,^{1,2} they have been widely used in the thermoplastic elastomer industry due to their unique physical properties not attainable with the constituent homopolymers alone.³⁻¹⁴ Block copolymers have also gained considerable attention due to their self-assembly into nanometer-sized morphologies. The segregation of the block components arising from thermodynamic incompatibility and connectivity produces various microdomains such as, lamellar, cylindrical, spherical, and gyroid microdomains.³⁻¹⁶ At low temperatures, most block copolymers have microdomain structure depending upon the weight fraction (or volume fraction) of the constituent components.⁴ However, as the temperature is raised above a certain value, the microdomain structure disappears completely, giving rise to a disordered homogeneous phase. This tempera-

ture is referred to as the order-to-disorder transition temperature (T_{ODT}).¹⁵⁻²⁰ Some block copolymers exhibit the disorder-to-order transition (LDOT) with increasing temperature,²¹⁻²⁸ and a very few show the closed-loop (or immiscibility loop) phase behavior.²⁹⁻³⁷ Also, the order-to-order transition (OOT) has been reported for many block copolymers when temperature is changed.³⁸⁻⁶¹ This is due to the subtle change of the free energy with temperature to satisfy the packing constraints³⁹ and explained by self-consistent mean theories.^{62,63}

Since 1990, thin films of block copolymers have been extensively investigated because of their potential use as soft templates and scaffolds for the fabrication of functional nanostructured materials.⁶⁴⁻⁷⁴ According to SCI-finder source, the total number of papers published in SCI journals per year increased significantly after 1990. For instance, this already reached more than 6,000 per year in 2005.¹³ A large increase might be attributed to the fact that nanoscience and nanotechnology have greatly gained attention since 1990. Compared with bulk block copolymer where the final mor-

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phology has been well described in terms of volume fraction of one block, the Flory-Huggins interaction parameter between the blocks, and the total number of the segments (or the degree of polymerization), the film thickness and the surface tensions and the interfacial tensions of both blocks with the substrate should be considered to determine the phase behavior and final morphology of block copolymer thin films. Block copolymers could exhibit a micellar structure consisting of a corona and a core, when they are dissolved into a selective solvent (or homopolymer) for one of block copolymers or even inorganic precursors.⁷⁵⁻⁷⁹ These micellar structures could be used as drug delivery^{78,79} or templates for two- or three-dimensional array of metal, metal oxide, and semiconductor nanoparticles.⁸⁰⁻⁸⁵

In this paper, we first summarize the phase behavior of block copolymers in bulk and thin films and some applications for new functional nanomaterials. Then, future perspectives on block copolymers are described.

Block Copolymers in Bulk

The Order-to-Disorder Transition. Most block copolymers exhibit microdomains at lower temperature because of the incompatibility of the constituent components. However, with increasing temperature this incompatibility decreases, while the combinatorial entropy increases. Thus, at a critical temperature, the enthalpic repulsion is exactly compensated with favorable entropy; thus at temperatures higher than the critical temperature block copolymers become disordered state (or homogeneous state) where microdomains do not exist. This critical temperature is referred to as the T_{ODT} .¹⁵⁻²⁰ Numerous research groups have investigated theoretically or experimentally the phase behavior and T_{ODT} of various kinds of block copolymers.^{15-20,86-131} The T_{ODT} depends on the volume fraction of one block (f), total number of segments (or degree of polymerization index) (N), and the segmental interaction described by the Flory-Huggins interaction parameter (χ), and the conformational asymmetry of each block. Depending on the segregation power (χN), two cases are considered: strong segregation limit ($\chi N \gg 10$) and weak segregation limit ($\chi N \sim 10$). The T_{ODT} and the microdomain size (D) are easily obtained for these two limits. For the former, the free energy change (ΔG_m) between the ordered state and disordered state is simply given by enthalpic and entropic terms:^{16,86-89,129-131}

$$\Delta H_m = H_{int} - H_{homo} \quad (1a)$$

$$\Delta S_m = \Delta S_c + \Delta S_p \quad (1b)$$

Here, H_{int} is the increase of unfavorable interaction arising from the existence of two blocks in the interface, and it decreases with increasing the domain size (D). H_{homo} is the enthalpic penalty in the homogeneous state. On the other hand, ΔS_c is the constraint entropic loss arising from the

constraint that two blocks should be located at their own microdomain in the ordered state, and ΔS_p is the placement entropic loss attributed to the fact that the connection point should be located at the interface. Since ΔS_p is usually smaller than ΔS_c , eq. (1) can be written as:

$$\begin{aligned} \Delta G_m &= \Delta H_m - T\Delta S_m \\ &= C_1\chi^{1/2}(N/D) + C_2D^2/N - C_3 \end{aligned} \quad (2)$$

Here, C_1 , C_2 , and C_3 are the positive constants independent of χ , N , and D . When eq. (2) is differentiated with the respect to D , the D at the equilibrium (D_{eq}) is obtained:

$$D_{eq} \sim N^{2/3} \chi^{1/6} \quad (3)$$

Of course, when $\Delta G_m(D_{eq}) = 0$ at a certain temperature, this temperature becomes the T_{ODT} .

On the other hand, for WSL limit, the free energy is expressed by the power of the order parameter that is defined as the local concentration of block A minus the average volume fraction of A in the block copolymer. Leibler formulated the free energy difference between the ordered state and disordered state by using the density-density correlation function with the aid of random phase approximation (RPA).¹⁷ According to this theory, D is given by

$$D \sim N^{1/2} \chi^0 \quad (4)$$

However, both theories could not be used for intermediate segregation limit ($10 < \chi N < 100$). For this purpose, the self-consistent mean field theory (SCMF) has been developed. Phase behaviors of diblock copolymers predicted by SCMF⁶² and determined experimentally for polystyrene-*block*-polyisoprene copolymer (PS-*b*-PI) are given in Figure 1.⁴³

It is noted in Figure 1(a) that with increasing f , the microdomains change from closed packed spheres (CPS), passing through body-centered cubic spheres (Im3m), hexagonally packed cylinders (H) and bicontinuous gyroid (Ia3d), to lamellae (L) at lower values of χN . Although the bicontinuous gyroid phase is unstable compared with H or L at higher χN , an extended version of SCMF shows that the bicontinuous gyroid phase is stable even at higher χN .⁶³ These microdomains except CPS have been verified experimentally for many different block copolymers, as shown in Figure 1(b).³⁸⁻⁵³ On the other hand, the CPS phase (either face-centered cubic spheres or hexagonally packed cubic spheres), which is located between disordered state and Im3m, has not been found for neat diblock copolymer. However, the CPS phase was found for a diblock/solvent mixture⁵⁶⁻⁵⁹ and diblock/homopolymer mixture system.^{60,61} Very recently, a noncubic network structure in an orthorhombic unit cell belonging to Fddd space group was found for ABC triblock copolymer¹³² and SI diblock copolymer at very narrow range of f

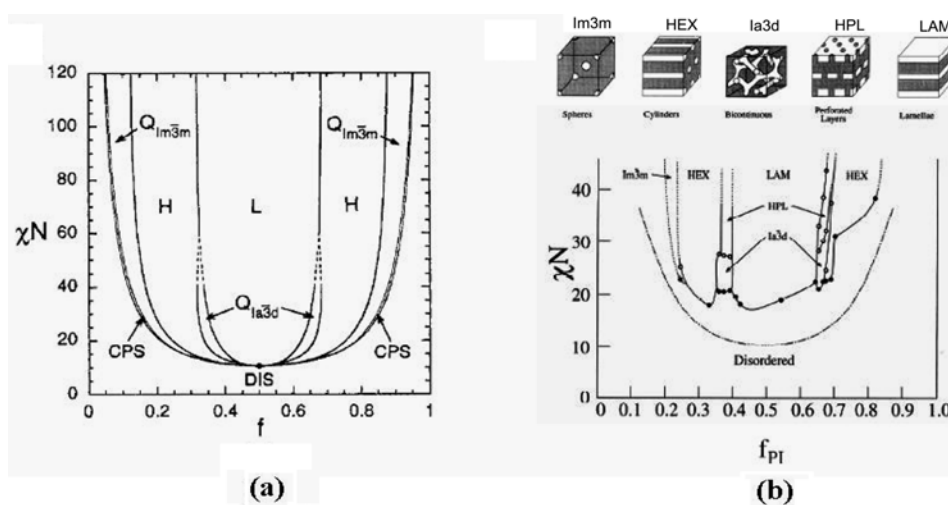


Figure 1. (a) The phase diagram of a diblock copolymer predicted by SCMF. (b) Experimentally determined phase diagram of PS-*b*-PI. Reproduced with permission from Ref. 62 and 43; Copyright 1996 and 1995, ACS publications.

between lamellar and gyroid phases.¹³³

It should be noted that the phase transition of highly asymmetric block copolymers is distinctly different from that of symmetric (or nearly symmetric) block copolymers.¹³⁴⁻¹³⁹ Namely, lamellar microdomains directly lose the long range ordering and become disordered state with thermally induced concentration fluctuation at the T_{ODT} , whereas the spherical microdomains lose long-range ordering at the lattice disordering transition and become disordered micelles with short-range ordering. With a further increase in temperature, disordered micelles are transformed into the micelle-free disordered phase with thermally induced compositional fluctuation at the critical micelle transition (or demicellization transition). The existence of the disordered micelles above the lattice disordering transition was verified experimentally¹³⁴⁻¹³⁸ and theoretically.¹³⁹

From Figure 1(b), the experimentally determined χN at $f = 0.5$ is ~ 17 , which is distinctly larger than the theoretically predicted value (10.495). Although this discrepancy could be resolved by the inclusion of the fluctuation concept (χN for symmetric block copolymer = $10.495 + 49.22 N^{-1/3}$; here $N = N(b^3/V_{o,ref})$ in which b and $V_{o,ref}$ are the Kuhn length, and the monomeric volume, respectively),¹⁴⁰⁻¹⁴² the fluctua-

tion concept could not be used for block copolymers with lower molecular weight block copolymers, for instance, most PS-*b*-PI or polystyrene-*block*-polybutadiene copolymer (PS-*b*-PB),¹⁴³ because of the breakdown of the Hartree assumption.¹⁴⁴ Thus, new theory or molecular simulation beyond the mean field concept should be developed to predict the T_{ODT} of block copolymers with finite molecular weight. Interestingly, an earlier version of SCFT theory developed by Helfand and coworkers^{16,86-89} predicts χN of ~ 17 for $f = 0.5$, close to the experimentally determined one. Thus, the predictions of the T_{ODT} for block copolymers by Helfand and coworkers are often close to the experimentally determined ones^{122,125,145} compared to the prediction based on the Leibler theory or SCMF theory without including the fluctuation concept.¹⁷

There exist numerous experimental methods to determine the T_{ODT} of block copolymers, which are summarized in Table I.^{99-128,146-151} Among them, small angle X-ray and neutron scatterings (SAXS and SANS) method⁹⁹⁻¹⁰⁷ and rheological method¹⁰⁸⁻¹²⁵ have been widely used. The scattering method could decide the exact microdomain structure but a relatively expensive and huge facilities providing X-ray (or neutron) source should be used to measure the scattering

Table I. Experimental Methods and the Related Theories to Determine T_{ODT}

Method	Plots	Related Theory
Scattering Method ⁹⁹⁻¹⁰⁷ (Small angle X-ray and neutron Scattering)	$1/I$ vs $1/\text{Temperature}$	Random Phase Approximation ¹⁷
Rheological Method ¹⁰⁸⁻¹²⁵	G' vs Temperature	Critical Phenomena ¹⁵²⁻¹⁵⁴
	$\log G'$ vs $\log G''$	Tube theory ^{155,156}
Depolarized Light Scattering (Birefringence) ¹²⁶⁻¹²⁸	Light intensity vs Temperature	
Differential Scanning Calorimetry ^{49,146-150}	Heat capacity (or Heat flow) vs Temperature	
Fourier Transformed Infra red Spectrum ¹⁵¹	Absorbance vs Temperature	

intensity ($I(q)$). On the other hand, the rheological method is easily accessible and rheological properties such as storage and loss moduli (G' and G'') and viscosity (η) are measured to determine the T_{ODT} and T_{OOT} of block copolymers. However, compared with scattering method, the microdomains in the equilibrium could not be measured because of the existence of shearing force.

While most block copolymers exhibit phase-mixing behavior upon heating due to the increase in the translational (or combinatorial) entropy as well as the decrease in the segmental interactions, some block copolymers such as polystyrene-*block*-poly(*n*-butylmethacrylate) copolymer (PS-*b*-PnBMA), 1,2 polybutadiene-*block*-1,4 polyisoprene copolymer have been shown to undergo a transition from the phase-mixed to phase-separated state upon heating. This transition is referred to as the lower disorder-to-order transition (LDOT).²¹⁻²⁶ This behavior is explained either by the equation-of-state arguments that incorporate differences in the thermal expansion coefficients or by the directional enthalpy (or entropy).^{157,158}

Closed-Loop Phase Behavior. Closed-loop phase behavior is known in systems with specific intermolecular interactions such as water/nicotine mixture and water/poly(ethylene oxide).¹⁵⁹⁻¹⁶¹ In weakly interacting systems, this phase behavior was for the first time observed for polystyrene-*block*-poly(*n*-pentylmethacrylate) copolymer (PS-*b*-PnPMA).²⁹ To demonstrate the closed-loop phase behavior, symmetric PS-*b*-PnPMA with different molecular weights (the values of the number average molecular weights are 46,470 for B-I, 49,900 for B-IV and 51,250 for B-V) are synthesized by the sequential, anionic polymerization of styrene and *n*-pentylmethacrylate in tetrahydrofuran at -78 °C under purified argon by using *s*-butyl lithium as the initiator.

Figure 2(a) shows SAXS profiles for B-IV as a function of the scattering vector q ($q=(4\pi/\lambda)\sin\theta$ where 2θ is the scattering angle, and λ is the wavelength) taken at 2.5 °C intervals from 112 to 246 °C at a heating rate of 0.5 °C min^{-1} . At lower temperatures, a broad maximum in the scattering is observed, which arises from the correlation hole scattering of a block copolymer in the disordered state.¹⁷ With increasing temperature, the maximum in the scattering profile sharpens and intensifies. This is typical behavior of block copolymers undergoing a transition from the disordered to the ordered state. With further increasing temperature, the scattered intensity reaches a maximum and begins to decrease. The peak broadens, and a diffuse and weak scattering maximum, characteristic of a disordered copolymer, is observed. TEM images of samples rapidly quenched after heating to 120 , 180 and 240 °C are also shown. At 120 °C the TEM image (Figure 2(b)) shows the mottled texture of concentration fluctuations of a disordered copolymer.^{162,163} At 180 °C (Figure 2(c)) the symmetric block copolymer microphase-separates into a lamellar morphology. At 240 °C (Figure 2(d)), only concentration fluctua-

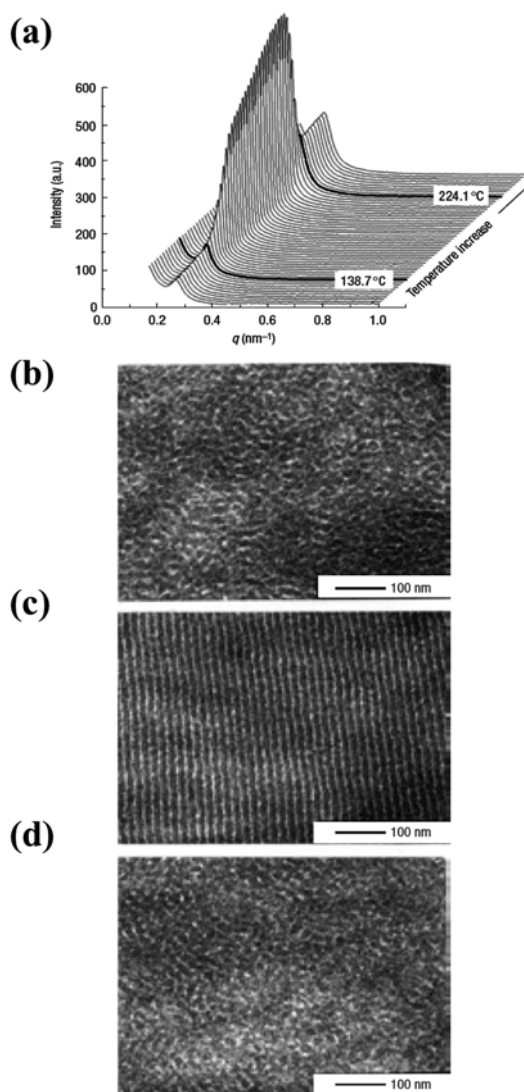


Figure 2. (a) Small-angle X-ray scattering (SAXS) profiles for PS-*b*-PnPMA as a function of q at various temperatures. Also shown are TEM images of B-IV annealed for 24 h at (b) 120 °C, (c) 180 °C, and (d) 240 °C. Reproduced with permission from Ref. 29; Copyright 2002, Nature Publishing Group.

tions are evident. The block copolymer therefore orders, then disorders with increasing temperature.

Figure 3 gives temperature dependence of shear modulus, G' for various symmetric PS-*b*-PnPMAs. For B-I, G' is seen to continuously decrease with increasing temperature, which is typical for a homogeneous, molten polymer. However, for B-BL, B-BH and B-IV, sharp increases in G' are seen, which is characteristic of the microphase separation of block copolymers. Subsequently, G' gradually decreases, as would be expected. However, at higher temperatures, G' decreases sharply, which would be expected for a block copolymer transitioning into the disordered state.^{108,112,125} For B-V, G' is high and gradually decreases with increasing temperature,

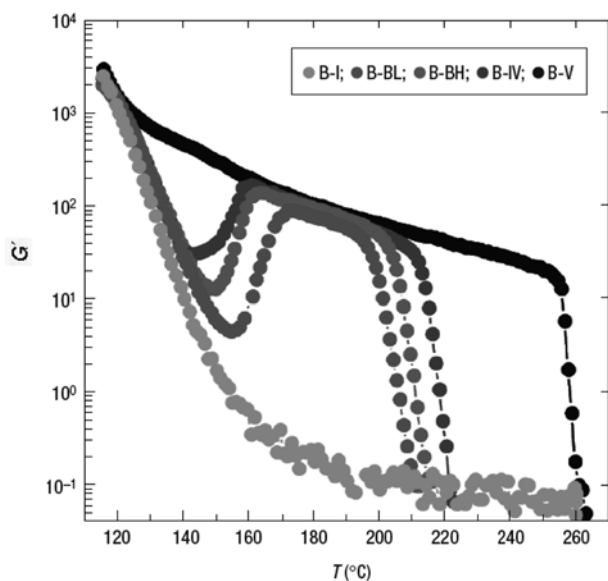


Figure 3. The temperature dependence of the shear modulus (G') for PS-*b*-PnPMA. Reproduced with permission from Ref. 29; Copyright 2002, Nature Publishing Group.

indicating that the block copolymer remains ordered up to about 255 °C, then drops sharply as it disorders.

The closed-loop phase behavior of PS-*b*-PnPMA can be explained by the effective Flory-Huggins interaction parameter χ_F expressed by two terms (χ_{app} and χ_{comp} , where χ_{app} is the conventional exchange energy including favorable interaction and χ_{comp} represents the compressibility difference between constituent blocks).^{27,164} Figure 4 gives the temperature dependence of these two terms predicted from a compressible random phase approximation.²⁷ It is seen that χ_{app} increases first and becomes a maximum, and finally decreases with increasing temperature. At low temperatures, the

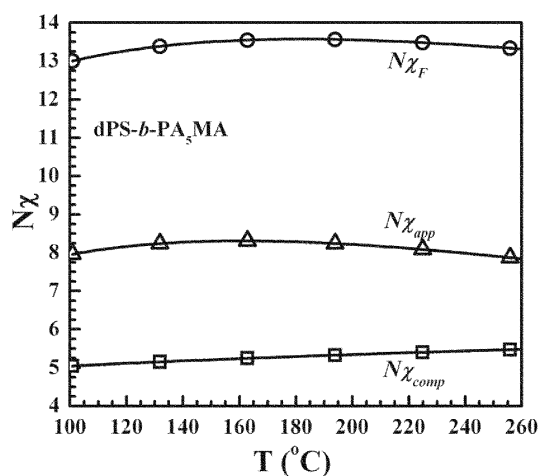


Figure 4. $N\chi_F$ along with $N\chi_{app}$ and $N\chi_{comp}$ for dPS-*b*-PnPMA. Reproduced with permission from Ref. 27; Copyright 2007, ACS Publications.

favorable interaction, although small, can exist arising from the dipole in the phenyl ring of PS and the induced dipole of PnPMA resulting from the formation of a cluster with a size of 1-2 nm.^{151,165} However, with increasing temperature, this directional energy should be decreased. At a higher temperature, a reduction in the repulsion interaction decreases, causing the decrease in χ_{app} . On the other hand, the free volume term always increases with increasing temperature. But, the magnitude of χ_{comp} is about half of χ_{app} . Combining these two effects, χ_F becomes a maximum; therefore a closed-loop phase behavior could be predicted.

To understand the exact mechanism of the closed-loop type phase behavior in a molecular level of each chain, we investigated, via two-dimensional heterospectral correlation analysis of wide angle X-ray scattering (WAXS) and Fourier transform infrared (FTIR), the specific chemical interactions existing for PS-*b*-PnPMA. Figure 5(a-c) shows the synchronous 2D heterospectral correlation analysis between WAXS and FTIR spectra for PS-*b*-PnPMA at three temperature regimes (disordered state at lower temperatures, ordered state at intermediate temperatures, and disordered state at higher temperatures).¹⁶⁵ It is seen in Figure 5 that the synchronous 2D heterospectral correlation spectrum in the ordered state is completely different from that in the two disordered states. Specifically, the cluster peak at $\sim 6 \text{ nm}^{-1}$ in the ordered state is strongly correlated with all the functional groups (or bands) corresponding to 1000-1800 cm^{-1} .

This is because of the microdomain structures of PnPMA block in the ordered state. It is also seen that the band for the C=C stretching mode of the phenyl ring ($\sim 1602 \text{ cm}^{-1}$) in the PS block becomes a positive correlation with WAXS profiles for all three temperature regimes. Very interestingly, a disordered state at higher temperatures, a band at 1274 cm^{-1} corresponding to the C-C-O stretching mode, and a band at 1452 and 1492 cm^{-1} corresponding to the phenyl ring stretching mode as well as the C=C stretching mode in the PS block become positive correlations with the cluster peak, whereas these two peaks except for C=C stretching modes (~ 1550 and 1602 cm^{-1}) in the PS block in another disordered state did not have any correlation with the cluster peak. Another interesting thing in Figure 5(c) is that the change in the cluster peak for C-C-O groups (~ 1275 and $\sim 1450 \text{ cm}^{-1}$) with temperature in the disordered state at higher temperature showed tiny maxima at two values of q at ~ 4.0 and 7.5 nm^{-1} rather than $\sim 6 \text{ nm}^{-1}$. Since these two q values (~ 4.0 and 7.5 nm^{-1}) are close to the peak positions for PnPMA and PS homopolymers, we consider that the probability that PS (or PnPMA) chains are located at their own neighboring PS (or PnPMA) chains in the disordered state at higher temperature is larger than that in another disordered state at lower temperature. Therefore, we consider that the side chains of PS and PnPMA in a lower disordered state are more randomly distributed than those in another disordered state at high temperatures. Since a favorable specific inter-

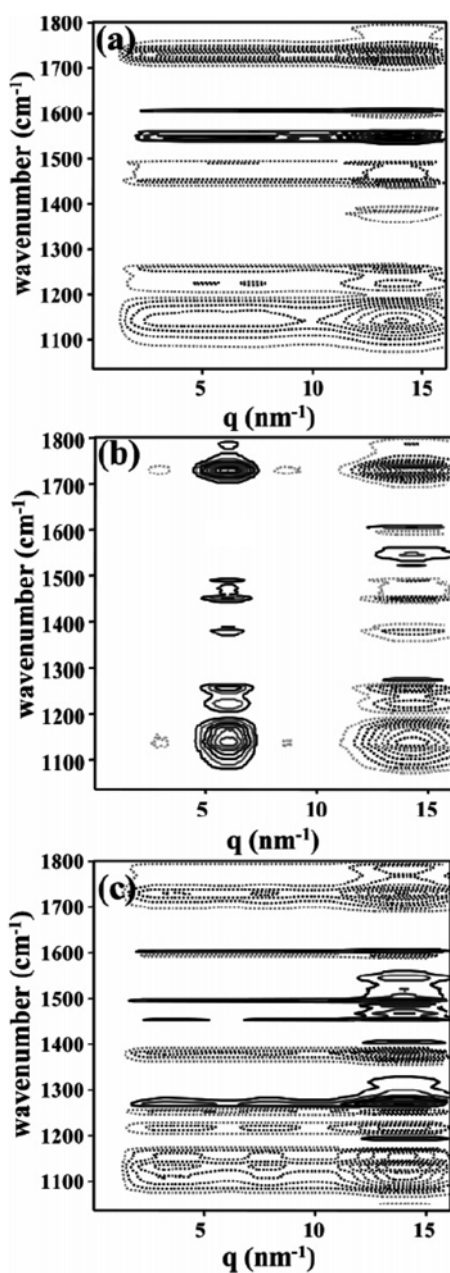


Figure 5. Synchronous 2D heterospectral correlation analysis between WAXS and FTIR spectra in 1000–1800 cm^{-1} focusing on the side groups for PS-*b*-P*n*PMA at three different temperature regimes: (a) a disordered state below the LDOT (120–140 °C), (b) an ordered state (150–200 °C), and (c) another disordered state above the UODT (220–260 °C). Solid and dashed lines in the spectra represent positive and negative cross-peaks, respectively. Reproduced with permission from Ref. 165; Copyright 2006, ACS Publications.

action mainly arises between the C-C-O and the phenyl ring, the degree of the specific interaction at a lower disordered state would be larger than that at a higher disordered state.

On the basis of the above results, we conclude that a disordered state at lower temperatures is different from that at higher temperatures. Namely, the main chain might be randomly distributed at both of the two disordered states, whereas the side chains of PS (and P*n*PMA) in a disordered state at higher temperatures are located at their own neighboring PS (and P*n*PMA) chains compared with those at a lower disordered state. This indicates that the specific interaction at a lower disordered state might be stronger than that at another disordered state at higher temperatures. Therefore, we consider that the disordered state at lower temperatures mainly arises from the relatively strong favorable interaction between the C-C-O group and the phenyl ring via induced dipole-dipole interaction, whereas the disordered state at higher temperatures is mainly due to the strong increase in the combinatorial entropy, although a small interaction still exists.

Recently, it was found that even though neat PS-*b*-P*n*BMA shows only LDOT at an experimentally accessible temperature region, the addition of the mixture of two solvents³⁴ or simply dioctyl phthalate alone³⁷ to PS-*b*-P*n*BMA reduces the upper order-to-disorder transition (UODT) dramatically, whereas the LDOT is not much changed. Thus, a closed loop phase behavior is even observed within an experimentally accessible temperature range. This is because the χ_F of PS-*b*-P*n*BMA becomes a rather plateau at higher temperatures, which is easily modified by mixed solvents.³⁷

Baroplasticity. The pressure dependence of the phase transitions of block copolymers has been a subject of intense research both experimentally^{23,24,166–174} and theoretically.^{157,158,175–182} It has been found that the ODT is only weakly dependent on pressure, while the LDOT are strongly dependent on pressure.^{23,24} Since the LDOT are related to

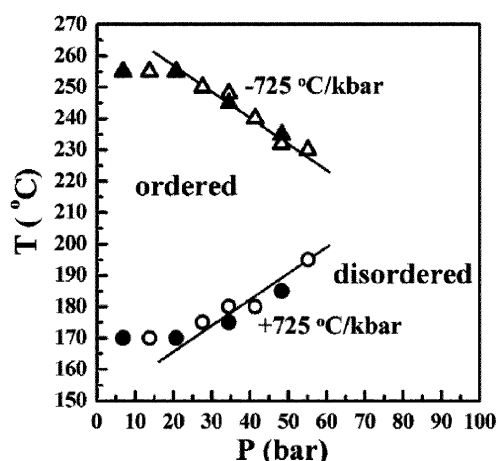


Figure 6. The change of T_{LDOT} (circle) and T_{UODT} (triangle) for dPS-*b*-P*n*BMA with hydrostatic pressure measured by SANS (solid symbols) and optical birefringence (open symbols). Reproduced with permission from Ref. 31; Copyright 2003, The American Physical Society.

differences in thermal expansion coefficients of the components, arguments based on equation-of-state theories have been developed to predict the pressure dependence of these transitions.^{157,158}

On the other hand, the closed-loop phase behavior has an entropic origin; thus the two transitions consisting of the loop should depend strongly on pressure. Figure 6 gives the changes in the T_{LDO} and T_{UOD} with pressure measured by small angle neutron scattering (SANS) and birefringence measurements.³¹ Interestingly, dT/dP for both transitions is very large: for LDOT it is 725 °C/kbar and for UODT it is -725 °C/kbar at pressures above 20.7 bar.

Large pressure coefficients allow one to use PS-*b*-PnPMA as a “baroplastic” material, which can be processed at a low temperature under medium pressure.^{171,183-186} To demonstrate the processability of PS-*b*-PnPMA at a lower temperature and pressure, we performed compression molding at 90 °C and 50 bar, from which PS-*b*-PnPMA was indeed well-shaped into the desired form, as shown in Figure 7(a).¹⁸⁷ On the other hand, even when much larger pressure of 1,000 bar and higher temperature of 120 °C were employed for the compression molding of PS-*block*-poly(ethylene-*co*-butylene)-*block*-PS (Kraton G 1652; Shell Chem. Co.), the powders were clearly seen; thus we could not shape SEBS into the desired form at this processing condition (Figure 7(b)).¹⁸⁷ The molecular weight of Kraton G 1652 was 54,000, very close to that of PS-*b*-PnPMA, but the glass transition of PEB block in Kraton G 1652 was -40 °C, which is ~70 °C lower than that of PnPMA block.

We expect that the baroplasticity due to the very large pressure coefficients of the transition temperatures could be further utilized to generate nanopatterns at lower temperatures (even at room temperature). This would be more effective in fabrication of the nanosized pattern compared with nanoimprinting lithography that needs high temperatures (at least larger than 100 °C) or an additional crosslinking step.

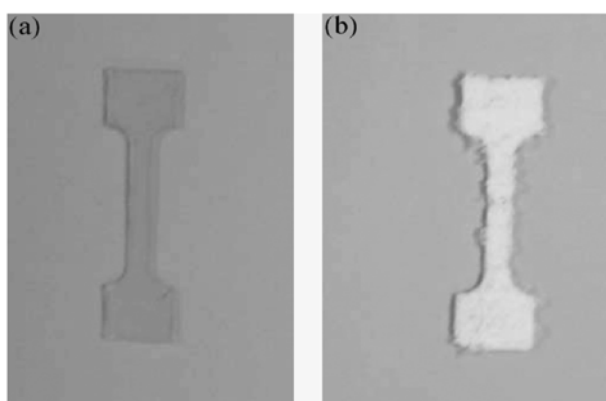


Figure 7. Compression-molded articles prepared by (a) dPS-*b*-PnPMA at 90 °C and 50 bar, and (b) Kraton G 1652 at 120 °C and 1,000 bar. Reproduced with permission from Ref. 187; Copyright 2006, WILEY-VCH Verlag GmbH & Co. KGaA.

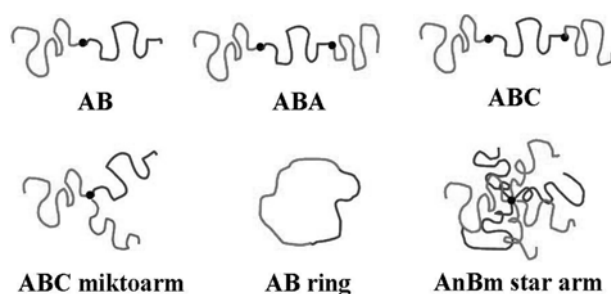


Figure 8. Various molecular architectures of block copolymers.

Phase Behavior of Various Architectures of Block Copolymers. Besides the A-B diblock or A-B-A triblock, block copolymers having different molecular architectures are synthesized by anionic polymerization, as shown in Figure 8, and the phase behavior of these block copolymers has been extensively investigated.¹⁸⁸⁻²⁰²

Among them, the linear triblock copolymer having three different blocks (ABC) has widely investigated for phase behavior and microdomains structures. Matsushita and coworkers were the first to investigate microdomain structures for polystyrene-*block*-polyisoprene-*block*-poly(2-vinyl pyridine) copolymer (PS-*b*-PI-*b*-P2VP) by SAXS and SANS.¹⁸⁸⁻¹⁹¹ Then, PS-*block*-PB-*block*-poly(methylmethacrylate) copolymer (PS-*b*-PB-*b*-PMMA),¹⁹²⁻¹⁹⁵ PS-*block*-PI-*block*-poly(ethylene oxide) copolymer (PS-*b*-PI-*b*-PEO) and PI-*b*-PS-*b*-PEO^{132,198-201} were synthesized and their morphologies were investigated. Due to three different blocks in ABC, the phase behavior of ABC linear triblock copolymers depends on three different Flory interaction parameters (χ_{AB} , χ_{BC} , and χ_{CA}), volume fractions of three block segments ($f_A + f_B + f_C = 1$), the total degree of polymerization (N), and the sequences of three block segments (ABC, BCA, and CAB). According to the SCMF theory, 30 different morphologies are predicted,¹⁹⁶ and some of the interesting microdomain

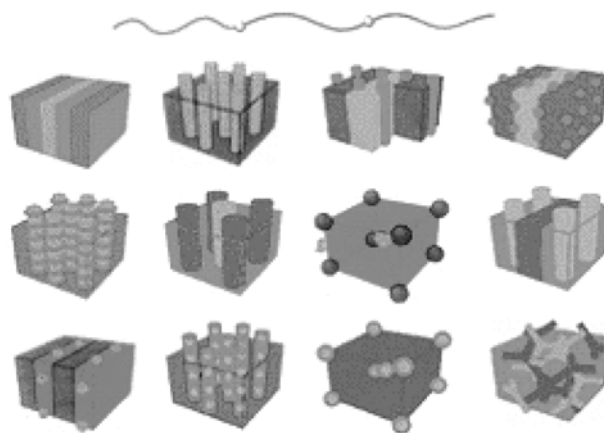


Figure 9. Various morphologies for linear ABC triblock copolymer. Reproduced with permission from Ref. 197; Copyright 1999, American Institute of Physics.

structures are shown in Figure 9.¹⁹⁷

An ABC linear block copolymer exhibits more complicated structures that are not observed for AB diblock (or even ABA triblock) copolymer, for instance, bicontinuous cubic structure belonging to “Plumber Nightmare”.²⁰¹ Although the synthetic effort for ABC block copolymer is much in demand compared with AB block copolymer, the former can be used for functional nanomaterials. For example, when ABC exhibits three lamellar microdomains, these can be used for polymer battery. Namely, two microdomains corresponding to the end blocks could be used for anode and cathode, respectively, while the middle can be used as an electrolyte layer.^{203,204} When ABC triblock copolymer exhibits three lamellar microdomains, the sequence of the lamellar microdomains becomes symmetric as expressed by ABCBAABC. However, when ac diblock copolymer is mixed with ABC triblock, the lamellar sequence becomes either symmetric (ABCcaacBAABC), or non-centrosymmetric (ABCcaABCcaABC). The latter could exhibit piezoelectricity, and the second order non-linear optical properties due to the anisotropic nanostructures.²⁰⁵ Matsushita and coworkers showed that the non-centrosymmetry is also obtained by linear tetrablock of ABCA.²⁰⁶ Finally, ABC triblock copolymer exhibiting core-shell gyroids can be used as nano-membrane.²⁰⁷

Bates and coworkers synthesized linear CECEC penta block copolymer (Here, C is the poly(cyclohexyl ethylene) made by the hydrogenation of polystyrene, and E is the polyethylene made by the hydrogenation of 1,4 polybutadiene). It showed very unique mechanical strength which cannot be obtained by CEC triblock copolymer, because CEC triblock copolymer should inevitably have loop structures that cannot play a role in the trans-domain coupling. On the other hand, CECEC penta block copolymer has fully trans-domain coupling; thus it exhibits much stronger resistance to external mechanical forces.²⁰⁸⁻²¹⁰

The mikto-arm type ABC triblock copolymers (or 3-arm star block copolymer) were synthesized and their morphologies have been investigated. This has different architecture from linear ABC linear triblock copolymer (see Figure 8). It is rather similar to AB diblock copolymer in that a C block is grafted at the junction of AB blocks. Matsushita and coworkers synthesized PI-*b*-PS-*b*-P2VP star block copolymer and investigated extensively how each of the microdomains is packed in the space.²¹¹⁻²¹⁶ They found that ABC star block copolymers tend to form cylinder-based structures whose cross-sections are represented with two-dimensional Archimedean tiling patterns consisting of triangles and squares.²¹⁶ Although most microdomain structures of these block copolymers show periodic Archimedean tiling, they found, by using mixture of ABC star block and A homopolymer, a very interesting morphology of a nonperiodic tiling pattern covered with equilateral triangles and squares, and their triangle/square number ratio of 2.3, as

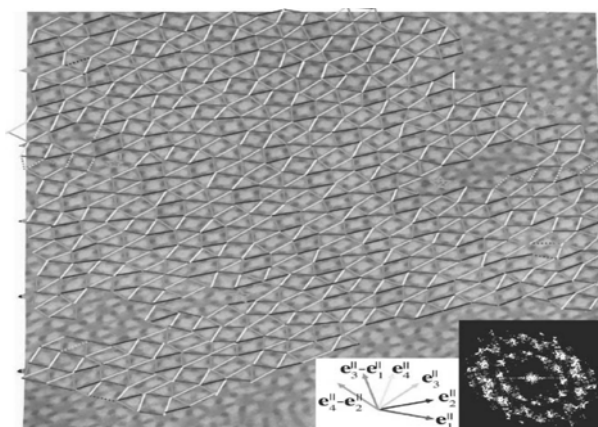


Figure 10. Non-periodic tiling pattern for PI-*b*-PS-*b*-P2VP/PS homopolymer mixture. Reproduced with permission from Ref. 216; Copyright 2007, The American Physical Society.

shown in Figure 10.²¹⁶ This dodecagonal quasicrystalline structure was first observed for polymers with size of ~ 50 nm, while the same structure has been found for metal alloys with a size of ~ 0.5 nm, chalcogenides with a size of ~ 2 nm, and liquid crystals with a size of ~ 10 nm.

Finally, PS-*block*-poly(dimethyl siloxane) and PS-*b*-P2VP ring type block copolymers were synthesized and the phase behavior was investigated.^{217,218} The formation of the microdomains for AB ring block copolymer is completely different from the AB diblock copolymer. For AB linear diblock copolymer, two chains of each block contribute to the size of each microdomain. However, due to the loop formation in the ring polymer, one chain of each block contributes to the size of each microdomain. Thus, AB ring block copolymer is similar to the loop formation of ABA triblock copolymer, even though ABA triblock contains a single loop of the middle B block whereas AB ring block copolymer contains double loops for A and B blocks. Based on the mean field theory, the value of (χN) at spinodal for symmetric ($f=0.5$) AB ring block copolymer is 17.8,²¹⁹⁻²²¹ which is similar but slightly smaller than that (17.995) for ABA triblock copolymer.²²²

Block Copolymer Micelles. When amphiphilic block copolymers are dissolved into a selective solvent, a micellar structure consisting of a soluble corona and an insoluble core is formed. The most widely used block component in the micelles is PEO, poly(acrylic acid) (PAA), P2VP, and poly(4-vinylpyridine) (P4VP). The other blocks consisting of the amphiphilic block copolymers are PS, poly(propylene oxide) (PPO), polyethylene (PE), poly(ethyl ethylene) (PEE).^{75-77,223-229} When the hydrophilic block becomes a major composition in the block copolymer, the micelle formed is usually spherical micelles (or hairy micelles). Here, we assume that the solvent is selective to hydrophilic block. With a decrease in the volume fraction of the hydrophobic block, the micelles become cylindrical (or worm-like). Crew-cut

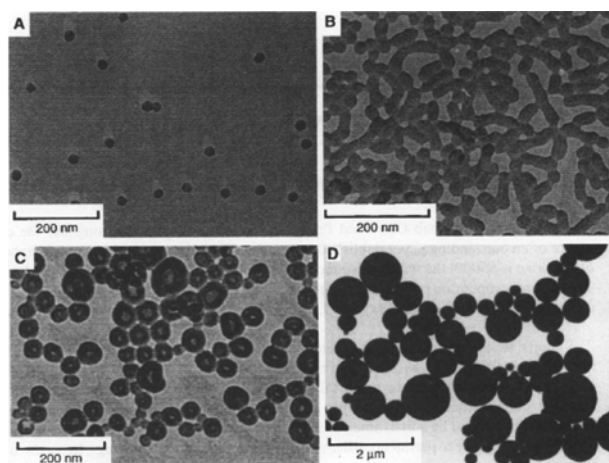


Figure 11. Various morphologies of the crew-cut aggregated from PS-PAA in water. (a) PS(200)-PAA(21), (b) PS(200)-PAA(15), (c) PS(200)-PAA(8), and (d) PS(200)-PAA(4). The numbers in the parentheses are styrene and acrylic acid units per chain. Reproduced with permission from Ref. 76; Copyright 1995, American Association for the Advancement of Science.

type micelles are formed at smaller volume fraction of the hydrophilic block. In this situation, an interesting morphology of vesicles could form. The micelle morphology in the solution is investigated by cryo-transmission electron microscopy.²³⁰

Various morphologies of the crew-cut micelles prepared by PS-*b*-PAA in water are given in Figure 11.⁷⁶ The micelles morphology is also changed by the ionic strength in solution.

When PAA-*block*-poly(methylacrylate)-*block*-PS linear triblock copolymer is dissolved into water/tetrahydrofuran mixture in the presence of 2,2'-(ethylenedioxy)diethylamine, interesting morphologies of toroid²³¹ or disk-shape²³² micelles are formed. The morphology of mikto-arm ABC triblock copolymer micelles was also studied. Polyethylene-*block*-PEO-*block*-polyperfluoropropylene oxide (EOF) mikto-arm type block copolymer in water shows disk-like fluorocarbon (F) domains sandwiched by two layers of hydrocarbon (E), while the hydrophilic blocks (O) emanate from the disk/disk interface to stabilize the whole micellar core in water.²³³⁻²³⁵ This system belongs to the superstrong segregation limit in which the interfacial energies overwhelm the entropic penalties for stretching the shorter block.^{233,234}

Once spherical micelles are formed, these can be used for drug delivery.^{78,79,236-238} Namely, the core part of the micelles can be compatible with many useful drugs, and the shell part is miscible with water. Also, block copolymers containing a biodegradable block, for instance, poly(lactic acid), have been widely used due to easy degradability inside the human body.²³⁹

Block Copolymers Containing Crystalline (or Liquid Crystalline) and Rigid Rod Block Components. Most block copolymers employed for phase behavior or the T_{ODT}

(or T_{OOT}) are amorphous. However, when one or both block can crystallize, the phase behavior of this kind of block copolymer becomes more complicated. Widely used crystalline block copolymers are 1) HPB-*block*-poly(ethylene-*ran*-propylene), HPB-*block*-PS, HPB-*block*-PEO, HPB-*block*-poly(vinyl cyclohexane), HPB-*block*-poly(head-to-head propylene);²⁴⁰⁻²⁵² 2) PEO-*block*-poly(propylene oxide), PEO-*block*-poly(butylene oxide), PEO-*block*-PS;²⁵³⁻²⁵⁶ and 3) PCL-*block*-PEG, PCL-*b*-PB, PCL-*block*-poly(*l*-lactide).²⁵⁷⁻²⁶⁰ Here, HPB means the hydrogenated 1,4 polybutadiene, and 2~3 ethyl branch exists per hundreds of carbons; thus T_m of HPB becomes 100~110 °C, which is lower than that (~140 °C) of high density polyethylene. There exist two different chain foldings: “perpendicular folding” where chain folding is perpendicular to the lamellar layer, and “parallel folding” where chain folding is parallel to the lamellar layer.⁹ Also, depending on the crystallization temperature compared with the T_{ODT} , the microdomains could be maintained even after the crystallization, or spherulite formation breaks down the pre-existing microdomains. Kornfield and coworkers showed that a liquid crystal gel was prepared by ABA triblock copolymer with the liquid crystalline moiety and the orientation of the liquid crystal phase is easily controlled by an electrical field.²⁶¹

Also, the phase behavior of block copolymers having liquid crystalline block are investigated. Even though PS-*b*-PI exhibits disordered state in the entire temperature range, the addition of the liquid crystalline group increased the T_{ODT} significantly.²⁶² Iyoda and coworkers²⁶³⁻²⁶⁷ prepared an interesting liquid crystalline block copolymer, PEO-*b*-PMA(Az) where liquid crystal moiety of azobenzene (Az) is attached to PMA block. Here, two different domains are generated: microdomains due to the chain segregation between PEO and PMA(Az) blocks, and nanodomains arising from the liquid crystal smectic phase of Az. When they prepared the film of this block copolymer, the nanodomain orientation of Az smectic phase became parallel to the film, which induces the microdomains aligned perpendicular to the substrate. They also generated perpendicularly oriented cylindrical nanodomains in a wide area by continuous gravure-type coating method. This block copolymer was employed as effective templates for preparing ordered arrays of nanodots or nanowires of various metal or metal oxide nanowires, because PEO blocks could have a strong interaction with metal cations. Ho and coworkers prepared PS-*block*-poly(*l*-lactic acid) copolymer (PS-*b*-PLLA). Because of the chirality of PLLA and the immiscibility of constituent blocks, the hexagonally packed helical microdomains of PLLA in the PS matrix were generated. Furthermore, these helical microdomains in bulk were transformed into cylinders by crystallization and shear. Interestingly, core-shell cylindrical microdomains were formed for another PS-*b*-PLLA with PLLA rich phase. As the degradable PLLA blocks were hydrolyzed in the core-shell cylindrical microdomains,

tubular nanostructures were fabricated. They also achieved the perpendicular orientation of cylindrical microdomains of PLLA in PS-*b*-PLLA thin film on ITO substrate by spin-coating with an appropriate solvent. They also fabricate Ni nanodots by electrodeposition inside cylindrical nano channels, which could be used as a catalyst for the growth of carbon nanotubes.²⁶⁸⁻²⁷²

Finally, block copolymers having a rigid rod block are synthesized.²⁷³⁻²⁸¹ These block copolymers exhibit unique electric (or photoelectric) properties and can be used as organic (or plastic) solar cells.^{273,274} Typical rigid blocks are poly(*p*-phenylene vinylene) (PPV), poly(3-hexyl thiophene), and poly(hexyl isocyanate), while the counterpart blocks are PS, PMMA, PI, and P2VP. While most block copolymers containing rigid rod show very strong segregation, which limits the investigation of phase behavior or T_{ODT} , poly(isoprene)-*block*-poly(2,5-di (2'-ethylhexyloxy)-1,4-phenylenevinylene) (PI-*b*-DEH-PPV) shows a weak-segregation limit.²⁷⁵⁻²⁷⁷ Lamellar structures were observed even at large volume fraction (~0.85) of DEH-PPV. This block copolymer at higher volume fraction of DEH-PPV showed two phase transitions upon heating: lamellar to nematic phase, and nematic phase to isotropic phases. Recently, the phase behavior of P3HT-*b*-P2VP synthesized anionic polymerization was investigated. This shows nanofiber structure at low volume fraction of P2VP, but with increasing volume fraction of P2VP, lamellar and cylindrical microdomains are observed.²⁷⁸ Lee and coworkers²⁷⁹⁻²⁸¹ showed that rodlike poly(*n*-hexylisocyanate) (PHIC) chains in PHIC-*b*-poly(2-vinylpyridine) (P2VP) was highly oriented and anisotropic organized as a self-assembled monolayer through lyotropic liquid crystalline ordering on a substrate surface.

Application of Block Copolymers in Bulk. Recently, materials exhibiting photonic band gap properties have gained a great attention because of future applications for new kinds of semiconductors controlled by light instead of conventionally used electrons.²⁸² Since these materials should respond to visible wavelength (400~700 nm), the domain spacing should be at least 100 nm. For this purpose, the block copolymer microdomains having sizes of 10~50 nm are not efficient compared with the array of polymer (or inorganic) spherical beads having sizes of 100~500 nm. It is known that double diamond microdomains are very useful for high photonic band gap.^{282,284} Recently, Thomas and coworkers prepared a photonic band gap gel whose domains are greatly changed by PH and temperature.²⁸⁵ To increase the microdomain size greater than ~100 nm, Thomas and coworkers added two homopolymers (PS and PI) to PS-*b*-PI.²⁸⁶ Depending on the amount of homopolymer, the lamellar domain size increases accordingly. The reflection changes from blue to red color range. It is noted that the molecular weight of homopolymers should be judiciously controlled so that macrophase separation should not occur. Generally, when the molecular weight of homopolymers is

less than that of the corresponding block, no macrophase separation occurs. The phase behavior of mixtures of block copolymer and homopolymer has been extensively studied experimentally and theoretically.²⁸⁷⁻³⁰⁸

A large domain size can be also obtained by using the microemulsion concept.^{309,310} When the amount of added homopolymers to block copolymers becomes too large, macrophase separation occurs. However, just before the macrophase separation, microemulsion made of the coexistence of AB block copolymer and A and B homopolymers is formed at a very narrow region of total volume fractions of the homopolymers. Since microemulsion morphology shows cocontinuous structure, it is very useful for fuel-cell applications.^{311,312} Recently, Park and Balsara³¹³ prepared poly(styrene-*co*-sulfonated styrene)-*block*-polymethyl butylenes. This block copolymer can show microdomains even when the total molecular weight is as small as 3,200. Due to the very small molecular weight, the size of hydrophilic phase becomes 2~4 nm, which is a very useful range for polymer electrolyte membranes to enhance significantly the proton conductivity.

Block copolymers have also been utilized as a template for inorganic materials.³¹⁴⁻³²⁰ Wiesner and coworkers used PI-*b*-PEO as structure-directing agents for organically modified ceramic precursors, 3-glycidylpropyl trimethoxysilane (GLYMO) and aluminum sec-butoxide (Al(O⁺Bu)₃).^{314,315} Depending upon the amount of GLYMO-Al(O⁺Bu)₃ precursors which are compatible with PEO block, morphologies covering spheres, cylinders, bicontinuous cubic structures are found similar to those observed in A-B diblock copolymers. Interestingly, the bicontinuous cubic morphology is the Plumber's nightmare morphology,³¹⁷ which is in contrast to the double gyroid morphology observed for diblock copolymers. Very recently, high crystalline mesoporous transition-metal oxides with large and uniform pores were fabricated by *in-situ* formed carbon as a rigid support.³¹⁸ These mesopores retain the original mesoporous structure even after heat treatment to temperatures as high as 1,000 °C.

Block Copolymers in Thin Films

Control of Nanodomain Orientation. Thin films of block copolymers have gained intensive attention due to their potential use as templates and scaffolds for the fabrication of nanostructures.^{64-74,321-327} To apply the block copolymer thin film to nanotechnology, the orientation of the microdomains becomes very important. Especially, when the anisotropic microdomains, such as lamellar and cylinders, are aligned to one direction, it can be used for nanopatterns with a specific orientation. For lamellar forming block copolymer thin film, the lamellar microdomains are usually oriented parallel to the substrate. Namely, one block with the lower surface energy tends to migrate to the surface (air side), whereas the other block having a preference with a

substrate is located at the substrate.³²⁸⁻³³⁰ For an A-*b*-B diblock copolymer having lamellar microdomain, the orientation of microdomains also depends on the film thickness (*t*). When the A block is located on both the air surface as well as the substrate, a parallel orientation without having islands (or holes) morphologies is achieved for $t = nL_o$ (in which *n* is the integer and L_o is the lamellar domain spacing). This is referred to as the commensurability condition for the symmetric wetting, as found for PS-*b*-PI or PS-*b*-P*n*BMA.³²⁸ On the other hand, when the A block prefers to locate on the air side, but the B block is located on the substrate, the commensurability condition is met for $t = (n + 1/2)L_o$. This is referred to as the commensurability condition for the asymmetric wetting, as found for PS-*b*-PMMA.³²⁹ When the film thickness does not satisfy the commensurability condition, islands (or holes) with thickness of L_o form.

Although the parallel orientation of cylindrical microdomains can be used to prepare nanowires connecting to two different electrodes, the vertical orientation (or alignment) of nanodomains in block copolymer thin film would be very important since it can be used as pattern mask or nanoporous membrane. For this purpose, a widely used block copolymer is PS-*b*-PMMA having lamellar or cylindrical microdomains.³³¹⁻³³⁵ When PS-*b*-PMMA is spin-coated onto a silicon surface, PMMA block has a preference with silicon surface due to the hydrophilic property, and PS block is placed on the top of the film due to lower surface energy. These two effects induce PMMA microdomains with lamellar or cylinders parallel to the silicon substrate. In order to overcome these two effects enough to generate perpendicular orientations, the interaction between each block and substrate should be similar and there should be the judicious thickness control. For PS-*b*-PMMA with lamellar microdomains, a parallel orientation becomes most unstable when *t* is close to nL_o .

To provide a similar interaction between each block and a substrate, the surface should be modified. For instance, when a random copolymer brush made of polystyrene-*ran*-poly(methyl methacrylate) (PS-*r*-PMMA) is attached to the silicon substrate, the PMMA cylinders (or lamellae) in PS-*b*-PMMA are oriented perpendicular to the silicon substrate when $t \sim L_o$.³³¹⁻³³³ PS-*r*-PMMA should have an end-functional group of OH that can react with native silicone oxide; thus the random copolymer chains are anchored to the substrate. However, this random polymer cannot be used when a substrate does not have any functional group to react with hydroxyl group.

To overcome the limit of a hydroxyl terminated PS-*r*-PMMA, Russell and Hawker and coworkers^{334,335} employed a new random copolymer consisting of styrene and methyl methacrylate and benzocyclobutene (BCB). Since BCB is thermally crosslinked by itself, this random copolymer brush is very effective to generate a vertical orientation of cylindrical nanodomains of PMMA in PS-*b*-PMMA on various

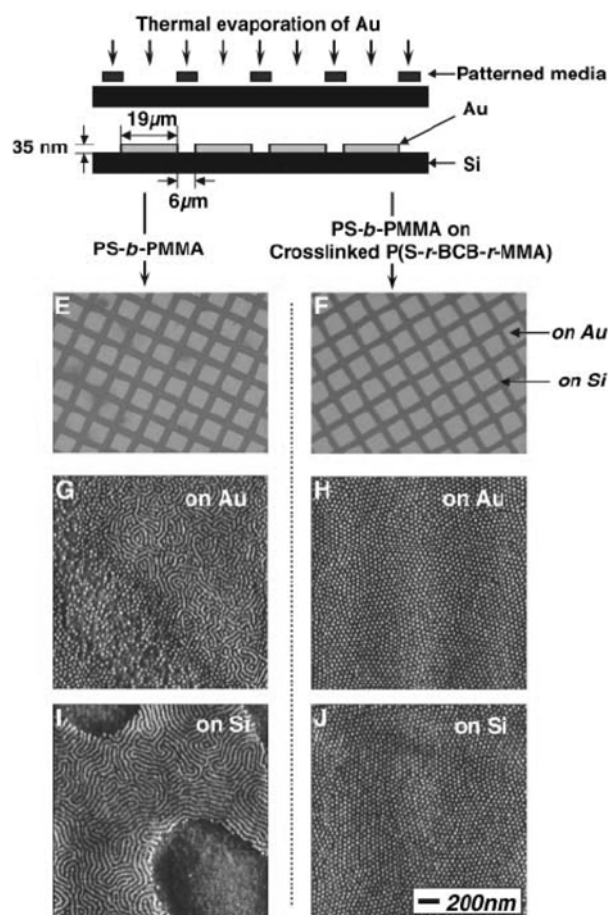


Figure 12. (a) Diagram of the evaporation process used to generate gold squares in a grid of silicon oxide, a chemically heterogeneous surface. Left panels are obtained by directly spin-coating onto this heterogeneous surface. Right panels are obtained on a surface where a cross-linked random copolymer film is used. Reproduced with permission from Ref. 334; Copyright 2005, American Association for the Advancement of Science.

substrates including metals, semiconductors and even polymers, as shown in Figure 12. However, the random copolymer brush approach for the vertical orientation is only valid for a relatively small thickness ($t \sim L_o$), since the neutral condition near the substrate becomes faded with increasing *t*. Very recently, Kim *et al.*³³⁶ achieved a perpendicular orientation of a relatively thick film by repeat spin-coating followed by the crosslinking by using a block copolymer with thermo-crosslinkable block. However, the BCB monomer is hard to synthesize, and a significant amount of heat (> 200 °C) is required to effectively crosslink the thin film and the neutralization layer cannot be photochemically patterned. To overcome these disadvantages, Bang *et al.*³³⁷ synthesized a new type of crosslinkable random copolymer with azide functional group that can be selectively crosslinked by either heat or UV light.

Other methods to obtain a vertical orientation of the

microdomains are to use an electric field (E-field)³³⁸⁻³⁴⁵ and a magnetic field,³⁴⁶ although the latter is not efficient compared with the former. When the dielectric constant between the constituent blocks is different, the E-field aligns the microdomains toward the E-field direction; thus vertically oriented cylindrical microdomains are obtained for a relative thick film up to several microns. Hashimoto and coworkers showed that lamellar microdomains of PS-*b*-PMMA thin film having a thickness of ~ 500 nm were aligned vertically on a rough substrate.^{347,348} This is because lamellar microdomains should be bent to accommodate into the rough surface to be oriented parallel to the substrate. This increases the enthalpic penalty for the bending of the block; thus perpendicular orientation is more preferred, as suggested by the theory.^{349,350}

Although most methods are based on the equilibrium condition, the vertical orientation of lamellar or cylindrical microdomains can be achieved by utilizing the non-equilibrium condition.³⁵¹⁻³⁵⁴ For instance, the solvent evaporation rate affects significantly the orientation of the cylindrical microdomains of PS in the PS-*b*-PB-*b*-PS thin films. When the solvent (toluene) evaporation is too slow, a parallel orientation is observed. However, when the rate is rather fast (5 *ml/s*), a perpendicular orientation is generated.³⁵¹ Although the reason for the vertical orientation by the solvent is still unclear, it might be explained as follows. When PS cylinders are aligned parallel to the substrate, a rigid block (here PS) could prevent the solvent pass-way; thus vertical cylinders are more preferred to remove the solvent very fast. If the evaporation is too fast, there is not enough time for the alignment for PS cylinders perpendicular to the substrate. However, since the obtained morphology based on the solvent evaporation method is not at equilibrium, further annealing could change the pre-existing alignment. For instance, when a film having vertically orientated PS cylinders is annealed at temperatures higher than the glass transition of PS block, parallel oriented PS cylinders are formed. Russell and coworkers also found that PEO cylindrical microdomains in PS-*b*-PEO thin film are oriented vertically to the substrate when PS-PEO is spin-coated onto a silicon substrate.³⁵⁵⁻³⁵⁷ Later, they found that the lithium salt, which was introduced during the anionic polymerization of PS-*b*-PEO, helps the vertical orientation of PEO in the thin film through the complexation of lithium salt and PEO block.^{358,359} The solvent evaporation process is a fast and simple route for fabrication of vertically oriented nanostructures, although it does not utilize the equilibrium condition.

Kramer and coworkers found that lamellar and cylindrical microdomains of polyethylene in polycyclohexylethylene-*block*-polyethylene-*block*-polycyclohexyl ethylene triblock copolymer are oriented normal to the film thickness ($t \sim 600$ nm).³⁶⁰ This was explained by the SCMF theory that for a small difference in the surface energy between two blocks, the entropy penalty associated with the midblock looping in

the surface wetting layer for the parallel orientation is larger than the enthalpic penalty arising between two blocks.³⁶¹

Once the microdomains are aligned vertically to the substrate, the microdomain size can be easily controlled by either using different molecular weights or adding homopolymers.³⁶²⁻³⁶⁶ Jeong *et al.*³⁶³⁻³⁶⁶ demonstrated that the domain size of PMMA microdomains in PS-*b*-PMMA thin film was tuned by the addition of homopolymers of PMMA or PEO. When the added homopolymer is much smaller than that of the block copolymer, it becomes uniformly mixed with the microdomains. In this situation, the microdomain size does not increase. With increasing amount and molecular weight of added homopolymer, the lattice spacing and microdomain sizes are gradually increased, as shown in Figure 13.³⁶⁵ To increase the microdomain size effectively, the homopolymer must be located in the middle of the microdomain. The vertically oriented PMMA cylindrical microdomains in PS-*b*-PMMA thin film are easily removed; thus vertically aligned nanoholes are generated.

However, it is not easy to reduce the microdomain domain size (or hole size) to less than ~ 10 nm. Because the hole size (or microdomain size) is proportional to two-thirds power to molecular weight (see eq.(3)), the molecular weight of PS-*b*-PMMA becomes very small to have a microdomain size with less than ~ 10 nm. Unfortunately, such a small molecular weight block copolymer could not microphase-separate because $\chi N < 10.5$. Therefore, to achieve small sized holes, two different methods have been employed. One is to extract only PMMA homopolymer

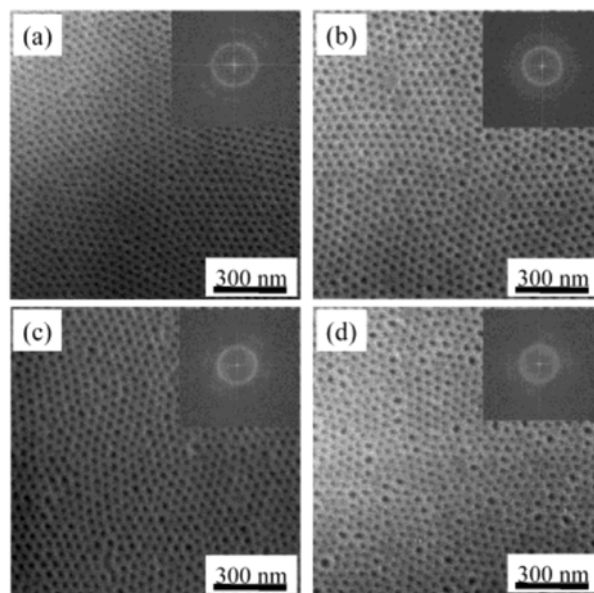


Figure 13. SEM images of PS-*b*-PMMA/PMMA mixture films after removal of all PMMA in the film. The amounts of PMMA homopolymer in the total PMMA phases are: (a) 0.0, (b) 0.03, (c) 0.09, and (d) 0.13. Reproduced with permission from Ref. 365; Copyright 2003, ACS Publications.

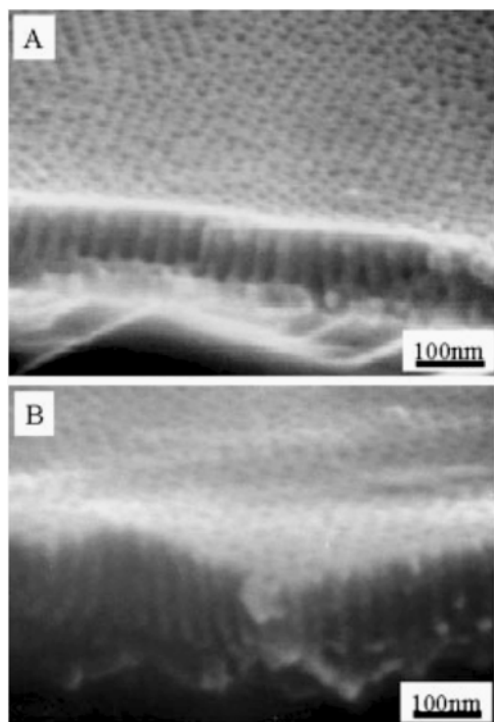


Figure 14. Cross-sectional SEM images of mixture of PS-*b*-PMMA/PMMA homopolymer film with high aspect ratio cylinders oriented vertically to silicon substrate. Thicknesses of the films are (a) 92 nm and (b) 329 nm. Reproduced with permission from Ref. 370; Copyright 2004, WILEY-VCH Verlag GmbH & Co. KGaA.

located at the middle of PMMA cylindrical microdomain in PS-*b*-PMMA/PMMA mixture film.³⁶³ The other is to use crosslinking of PS matrix by ozone treatment of the PS-*b*-PMMA film.³⁶⁶

It is not easy to have vertical orientation of PMMA cylindrical microdomains in PS-*b*-PMMA film with a very large thickness unless an external field as E-field is used, even though simulation results suggest the possibility.³⁶⁷⁻³⁶⁹ Jeong *et al.*³⁷⁰ showed that vertically oriented PMMA cylinders were obtained even for a film thickness up to 330 nm, which is more than ten times larger than the domain spacing, as shown in Figure 14. This was achieved by using PS-*b*-PMMA/PMMA mixture film spin-coated on a random brush modified silicon substrate. It is noted that PS-*b*-PMMA was synthesized by atomic transfer radical polymerization (ATRP), not anionic polymerization. The large persistence of cylindrical microdomains toward the thickness direction is the combined effect of high localization of PMMA homopolymer at the center of PMMA microdomain and the tacticity of PMMA blocks of PS-*b*-PMMA synthesized by ATRP giving lower glass transition compared with PS-*b*-PMMA prepared by anionic polymerization. The vertically aligned cylindrical microdomains in relatively large film thickness could be very useful for preparing metal or

conductive polymer nanowires having high aspect ratio and filtration membrane.

Lateral Long Range Ordering of Nanodomains. Although block copolymers provide various kinds of nanodomains, the lateral long range ordering of the nanodomains is very difficult to be achieved due to their self-assembly nature. However, when these nanodomains are applied for nanolithography, the defect (or grain boundary) should be minimized. To achieve this goal, numerous studies have been carried out. Various kinds of flow field (oscillatory and steady shear, elongational flow, and combined flows) have been applied to block copolymers.^{40,371-376} The shearing flow is easily generated by rotating rheometer. Although the lamellar microdomains could be aligned to three directions^{371,373} (flow direction (parallel orientation), velocity gradient direction (perpendicular orientation) and vorticity direction (normal orientation)), most lamellar microdomains are aligned to the shearing direction when the shearing force is small. A roll casting method was also used to generate the orientation in a large area.^{374,375}

Although the shearing on the thin film block copolymer with thickness of ~100 nm (or less) is not easily generated by a rheometer, Angelescu *et al.* successfully applied a shearing force to thin film block copolymer.^{377,378} They used a thick sacrificial layer of poly(dimethyl siloxane) to prevent rupture (or breakage) of the thin film during shearing, and obtained the long range ordering of cylindrical nanodomains aligned to the flow direction in the thin film. On the other hand, when the film consists of only a monolayer of spherical nanodomains, long range ordering could not be attained. However, when they used another thin film accommodating two layers of spherical nanodomains, the long range ordering was successfully achieved.³⁷⁸

Hashimoto and coworkers developed a temperature-gradient method to obtain long range ordering of PS-*b*-PI thick films.³⁷⁹⁻³⁸¹ This is similar to a zone-refining process which has been widely used to obtain a large grain size of single crystalline silicon. This apparatus has heating and cooling blocks and the temperature gradient direction is the thickness direction. When the sample moves very slowly, the originally disordered region of the block copolymer becomes the ordered state at the T_{ODT} . Due to the ordering very near the T_{ODT} of the block copolymer, the grain size becomes very large. After this part becomes the ordered state, the sample moves, and then the adjacent part becomes again the ordered state. However, this process is a too slow (2 mm/day) process to obtain the long range ordering of the block copolymer.

Thomas and coworkers utilized epitaxial crystalline growth to align polyethylene microdomains in polyethylene-*block*-poly(ethylene-*co*-propylene)-*block*-polyethylene.³⁸²⁻³⁸⁵ They used the crystalline substrate such as benzoic acid or anthracene. However, this method has some limitations. Namely, the film thickness should not be larger, because the

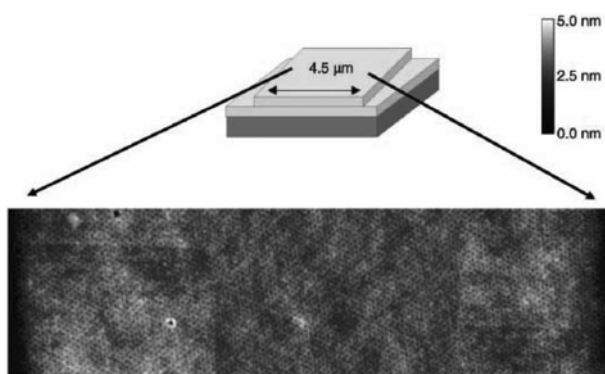


Figure 15. Scanning force microscopy image of PS-*b*-P2VP films with spherical microdomains of P2VP. The films are confined between solid walls. Reproduced with permission from Ref. 387; Copyright 2001, WILEY-VCH Verlag GmbH & Co. KGaA.

memory effect (epitaxial ability) fades away with increasing thickness. Also, the crystalline substrate and crystalline block copolymer are needed. To overcome these disadvantages, they used directional solvent crystallization which can be used to align the cylindrical microdomains parallel (or perpendicular) in PS-*b*-PI thin film to the substrate.^{385,386}

Kramer and coworkers^{387,388} developed a graphoepitaxy method to fabricate perfect lateral ordering of the spherical microdomains of P2VP in PS-*b*-P2VP copolymer, as shown in Figure 15. They first prepared a rectangular trough to make the geometric confinement by using conventional photolithography and chemical etching. The depth of the trough is the lattice spacing of PS-*b*-P2VP, where only a single layer of spherical microdomains is accommodated. This is a good example for the preparation of long range ordering of the microdomains by a combination of the top-down and bottom-up methods. The graphoepitaxy method was extended to generate the long range ordering of the cylindrical microdomains of P2VP in PS-*b*-P2VP.³⁸⁹

Later, Ross and Thomas and coworkers studied the packing of a multiple layer of poly(ferrocenyl dimethyl silane) (PFS) spherical microdomains in PS-*b*-PFS by varying the width of the trough (W).³⁹⁰⁻³⁹³ When $W = nd$ (in which n is the integer, and d is the distance between the rows of spherical domains in a closed-packed two dimensional array; thus $d = \sqrt{3}p/2$ in which p is the center-to-center spacing of spheres), the n layers of spherical microdomains with a diameter of D_o (in which D_o is the diameter of PFS in the bulk PS-*b*-PFS) are observed. However, for $(n - 1/2)d < W < nd$, the total layers of spherical microdomains are n , but the diameters of these spheres are smaller than D_o . On the other hand, for $nd < W < (n + 1/2)d$, the total layers of spherical microdomains are n , but the diameters of these spheres are larger than D_o . This is because the microdomains should be strictly confined to the rigid wall; thus there is no way to have island or hole structures with the maintenance of the

same D_o when $W \neq nd$. A similar behavior was also reported for the lamellar spacing change when the lamellar microdomains are confined between two flat rigid walls (one-dimensional confinement).³⁹⁴⁻³⁹⁸

When the rigid wall is not flat, for instance, cylindrical or spherical hard walls, spatial confinement due to curvature frustration induces many interesting microdomain structures that cannot be achieved by block copolymers without the confinement.³⁹⁹⁻⁴⁰³ For cylindrical (or two-dimensional) confinement, anodized alumina porous membranes with diameter (D) of 20-500 nm are widely used.³⁹⁹⁻⁴⁰² When D/L_o is larger than ~ 3 , the lamellar microdomains become concentric rings along the cylindrical axis of the pores. When D/L_o is not equal to n for symmetric wetting, the number of concentric rings becomes either $2n+1$ or $2n$ by changing the size of the microdomains. On the other hand, when D/L_o approached to 1, a very interesting morphology, such as torus and helical morphology, was obtained.³⁹⁹⁻⁴⁰² These morphologies are predicted theoretically.⁴⁰⁴⁻⁴⁰⁶ Three-dimensional confinement on microdomains was also investigated by using spherical nanoparticles.⁴⁰⁷ In this situation, lamellar microdomains become consecutive layers of lamellae on the spherical particles.

One of the easiest methods to fabricate long range ordering of microdomains is to use the solvent annealing introduced by Russell and coworkers.^{356,357} This is similar to the temperature gradient method, but solvent annealing is much more easily achieved. Figure 16 shows perfect long range ordering of PEO cylindrical microdomains in PS-*b*-PEO vertically aligned to the substrate.³⁵⁶ However, since it is not easy to remove PEO block, they introduced PS-*b*-PMMA-*b*-PEO triblock copolymer. In this case, both a long range lateral ordering and the easy removal of PMMA microdomains generate well-ordered cylindrical pores which can be used as excellent templates for future nanotechnology.⁴⁰⁸

Nealey and coworkers used a patterned surface prepared by soft X-ray technique,⁴⁰⁹⁻⁴¹⁴ which is similar to the method introduced by Russell and coworkers.^{415,416} Since the exposure area becomes hydrophilic, the hydrophilic part (here



Figure 16. Long range ordering of cylindrical microdomains of PEO in PS-*b*-PEO thin films annealed in a benzene vapor. Reproduced with permission from Ref. 356; Copyright 2004, WILEY-VCH Verlag GmbH & Co. KGaA.

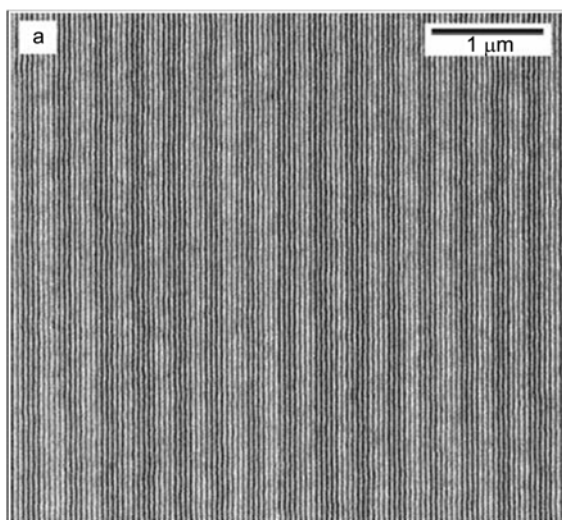


Figure 17. The perfect epitaxial ordering of PS-*b*-PMMA pattern extended over a $5 \times 5 \mu\text{m}$ area. Reproduced with permission from Ref. 409; Copyright 2003, Nature Publishing Group.

PMMA block) in the PS-*b*-PMMA is exactly placed onto the exposure area. In this way, they prepared perfect lateral ordering of the lamellar microdomains, as shown in Figure 17. It is very essential to control the width (W) of each pattern to obtain perfect lateral ordering.⁴¹⁰ Namely, without W being close to L_o of PS-*b*-PMMA, perfect lateral ordering could not be achieved. Recently, they extended this method to generate perfect lateral ordering of vertically oriented PMMA cylindrical domains in PS-*b*-PMMA.^{411,412} Also, various complex patterns having sharp angle and curvature that are encountered in commercially available chip architecture are also prepared by the addition of the homopolymer.^{413,414}

Application of Block Copolymer Thin Films. Block copolymer thin films can be widely used to generate a nanopattern. Register and coworkers prepared nanohole and nanodot arrays with a density up to $\sim 10^{12}/\text{in}^2$ by using PS-*b*-PB thin films.³²² For this purpose, a monolayer of spherical PB microdomains is first prepared by spin-coating of PS-*b*-PB in toluene solution. Then, ozone irradiation degrades PB spheres completely to generate nanoholes. Because of holes and a rigid PS matrix, the reactive ion etching rate becomes different; thus nanoholes are generated onto silicon nitride substrate. On the other hand, when PB is stained OsO_4 , the spheres have much resistance compared with PS matrix. In this case, the final structures after reactive ion etching (RIE) become a nanodots array. To avoid many steps required in the above method, Thomas and coworkers used PS-*b*-PFS.^{417,418} After the volume fraction of PFS block in PS-*b*-PFS is judiciously controlled, cylindrical microdomains of PFS are normally oriented to the substrate. In this situation, the etching rate of PS matrix is quite fast; thus a PFS nanodot array is one-step fabricated after spin-coating followed by RIE.

Russell and coworkers utilized PS-*b*-PMMA thin films having PMMA cylindrical microdomains aligned vertically to the substrate.^{70,331-334} Since PMMA is easily removed by ultra-violet irradiation followed by rinsing with acetic acid, PMMA cylinders become nanoholes that span through the entire film. Once nanoporous films with cylindrical pores are generated, these are widely used for various kinds of nanopattern masks, and functional nanomaterials. For instance, dense, ordered arrays of $\langle 100 \rangle$ -oriented Si nanorods were fabricated using PS-*b*-PMMA as etching resist and RIE. This approach combines control over diameter, orientation, and position of the nanorods and compatibility with complementary metal oxide semiconductor (CMOS) technology because no nonvolatile metals generating deep levels in silicon, such as gold or iron, are involved.⁴¹⁹ Also, by using PS-*b*-PMMA thin film, Toshiba prepared a high density array

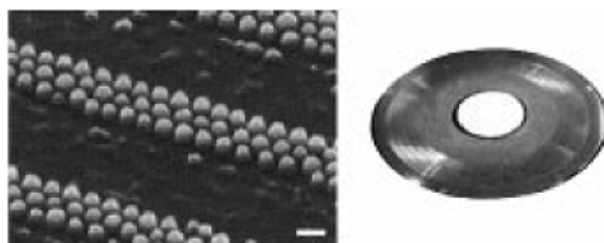


Figure 18. SEM image of the patterned magnetic medium ($\text{Co}_{74}\text{Cr}_6\text{Pt}_{20}$) with a 40 nm diameter. The scale bar indicates 100 nm. The right represents the whole image of the patterned media disk prepared on a 2.5 in HDD glass plate. Reproduced with permission from Ref. 420; Copyright 2002, IEEE.

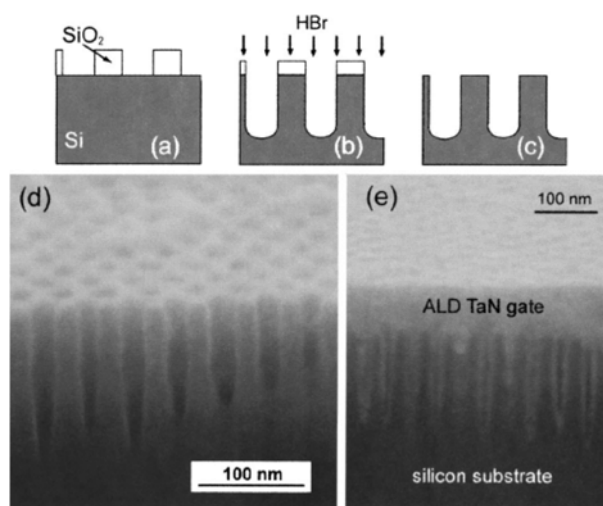


Figure 19. High aspect ratio silicon pore formation using a patterned oxide hard mask. Schematic diagrams of the process: (a) Patterned SiO_2 on silicon. (b) Silicon RIE using oxide hard mask. (c) Oxide removal. Titled SEM images of (d) Etched silicon pores after oxide removal, and (e) ALD TaN coating oxidized trench sidewalls. Reproduced with permission from Ref. 421; Copyright 2001, American Institute of Physics.

of magnetic particles in a 2.5 inch disk, as shown in Figure 18.⁴²⁰ To have long range ordering of microdomains, they used the graphoepitaxial method. They also prepared highly luminescent materials based on block copolymer thin film. Black and coworkers⁴²¹⁻⁴²³ fabricated porous silicon materials, as shown in Figure 19. These can be used as low dielectric materials. And, Russell and coworkers utilized nanoporous block copolymer thin film to fabricate a high density array of cobalt nanowires. Interestingly, the magnetic properties of nanowires are quite different from those of bulk cobalt.³⁴⁵

Also, nanoporous block copolymer thin film can be directly used for filtration membranes to separate many types of viruses.⁴²⁴ Figure 20 shows a schematic for the fabrication of asymmetric nanoporous membranes. The top separation layer (~80 nm thick) is made from a thin film of a mixture of PS-*b*-PMMA and PMMA homopolymer, with cylindrical microdomains of PMMA, on a ~100 nm thick sacrificial silicon oxide layer (Figure 20(a)). This thin film can be floated from the substrate by using a buffered HF solution to dissolve the oxide layer. Then, it is transferred onto the microfiltration polysulfone membrane, which acts as a support (Figure 20(b)). The adhesion between the block copolymer and the PSU membrane is sufficient to maintain the mechanical integrity of the system during the fabrication and filtration experiments. Porous thin films of the upper layer can be prepared by selectively removing the PMMA homopolymer from the cylindrical PMMA microdomains with acetic acid (Figure 20(c)). This produces a well-ordered array consisting of ~15 nm diameter pores with a narrow pore size distribution, which completely prevents the HRV14 virus (colored green) from penetrating into the pores, while proteins, such as bovine serum albumin (BSA)

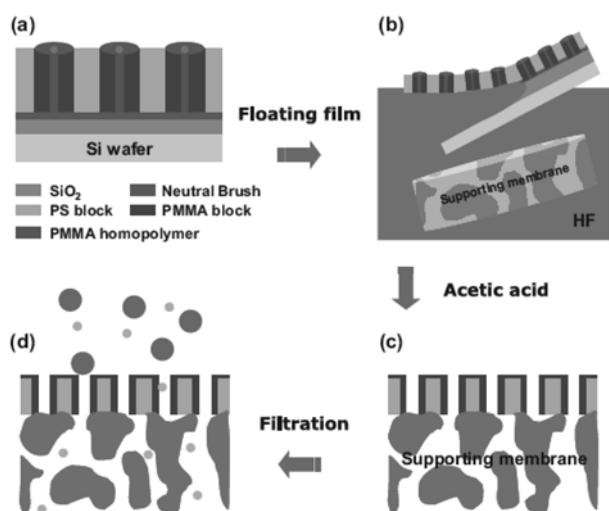


Figure 20. Schematic depiction of the procedure for the fabrication of asymmetric nanoporous membranes. Reproduced with permission from Ref. 424; Copyright 2006, WILEY-VCH Verlag GmbH & Co. KGaA.

(colored yellow) with a size of ~7.2 nm, can pass freely through the pores in the membrane (Figure 20(d)). Very recently, Kim and coworkers extended this filtration membrane for virus separation at high pressures. For this purpose, the nanoporous film thickness was increased to ~160 nm, where perpendicularly oriented nanopores are only observed at top and bottom surfaces, whereas a mixture of perpendicular and parallel cylindrical pores is formed.⁴²⁵

The analysis of these nanoporous structures is important to determine the shape of nanopores in the thin film. Kim *et al.*⁴²⁶⁻⁴²⁸ employed thin films of PS-*b*-PMMA having PMMA cylindrical microdomains oriented normal to a substrate as optical waveguide spectroscopy (OWS) in the Kretschmann configuration device, as shown in Figure 21. With this method, they characterized several nanofabrication processes, for instance, the pore generation by the removal of PMMA, the filling the nanopores by liquid media with different refractive indices, the reversible pore formation process by selective solvent swelling. They also predicted different optical properties of Au/block copolymer hybrid waveguide layers depending on the location of Au nanoparticles. The nanostructures in the thin films supported on substrates were also characterized by grazing incidence X-ray scattering. ⁴²⁹ 2D grazing incidence x-ray scattering (GIXS) measurements combined with a scattering theory were conducted for thin films of a mixture of PS-*b*-PMMA and PMMA homopolymer on a silicon substrate and porous structures prepared by UV irradiation and followed by acetic acid rinsing, and the results are shown in Figure 22. GIXS provides detailed structural information of nanostructure (i.e., shape, size and size distribution, orientation, and packing order).

Nanoporous block copolymer films can be used for excellent anti-reflection coating materials.⁴³⁰ For this purpose, nanoporous films were prepared by spin-coating of PS-*b*-PMMA on glass, followed by removing PMMA blocks by

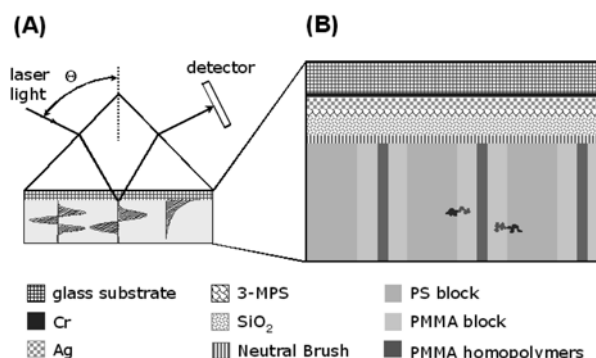


Figure 21. (a) Schematic depiction of the OWS setup based on the Kretschmann configuration, (b) schematic diagram of a thin film of PS-*b*-PMMA/PMMA mixture. Reproduced with permission from Ref. 427; Copyright 2005, WILEY-VCH Verlag GmbH & Co. KGaA.

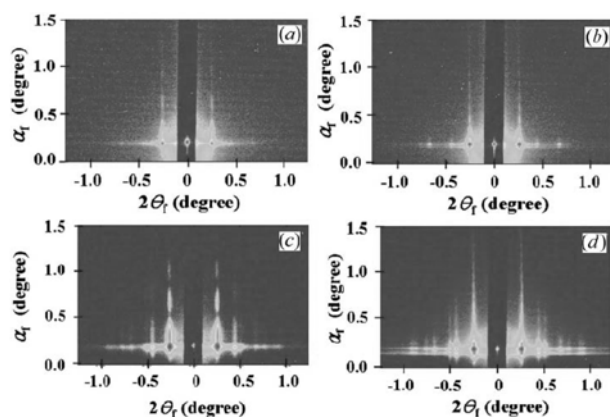


Figure 22. 2D GIXS patterns for thin films of a PS-*b*-PMMA/PMMA mixture deposited on silicon substrates before and after UV-etching: (a) unetched 28.5 nm thick film; (b) unetched 78.8 nm thick film; (c) etched 25.0 nm thick film; (d) etched 86.1 nm thick film. Reproduced with permission from Ref. 429; Copyright 2007, International Union of Crystallography.

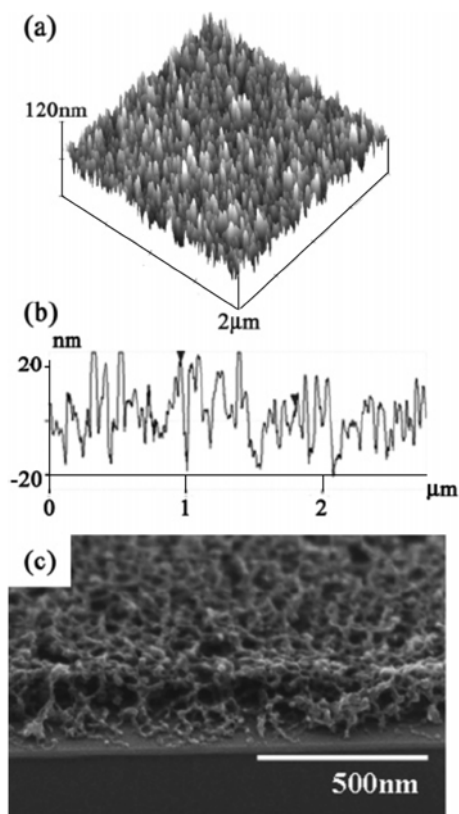


Figure 23. (a) Three-dimensional AFM height image, (b) height profile, and (c) cross-sectional FE-SEM image of PS-*b*-PMMA film after UV irradiation followed by rinsing with acetic acid. Reproduced with permission from Ref. 430; Copyright 2006, ACS Publications.

UV irradiation and rinsing with acetic acid, as shown in Figure 23. When spin-coated PS-*b*-PMMA was no longer annealed

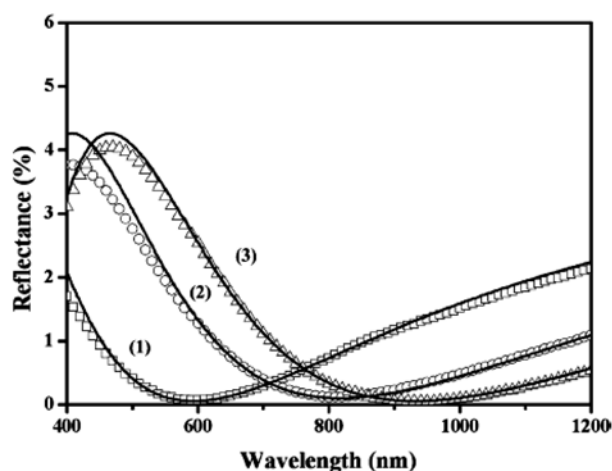


Figure 24. Reflectances of PS-*b*-PMMA film with three thicknesses (\square) 126 nm, (\circ) 169 nm, and (\triangle) 200 nm after UV irradiation followed by rinsing with acetic acid. The predicted reflectances by the theory were given as solid curves (1~3). Reproduced with permission from Ref. 430; Copyright 2006, ACS Publications.

at high temperatures, microphase separation between two blocks occurred only in the short-range scale. The porous films prepared from PS-*b*-PMMA with a volume fraction of PMMA block of 0.69 exhibited a sponge-like nanoporous structure over the entire film thickness and showed excellent antireflection with a minimum reflection less than 0.1% at visible and near-infrared wavelengths. The observed reflectances were in good agreement with the predictions based on the characteristic matrix theory, as shown in Figure 24.⁴³⁰

Finally, block copolymer micelles provide an excellent platform for fabricating highly ordered 2-D arrays of metal and semiconductor nanoparticles on various substrates. The size of the nanoparticle and the interspacing between the particles can be easily controlled by adjusting the length and volume fraction of each block.^{80-85,431-435} Three different approaches have been developed to fabricate 2-D arrays of nanoparticles by using the micellar templates. First, metal ions are selectively loaded to one of the blocks of block copolymer in solution and spin coated on solid substrates to obtain monolayer thin film. The utilization of high-energy irradiation such as plasma, electron beam or ion-beam removes the block copolymer template and generates nanoparticle arrays in a single step.^{436,437} The fabrication of Au, Pd and Pt nanoparticle arrays was successfully demonstrated by utilizing PS-*b*-PVP micellar template.^{438,439} Spatz *et al.* showed the tunable interspacing of Co and Co₃O₄ nanoparticle arrays by employing PS-*b*-PVP copolymer with different block lengths.⁴³⁸ 2-D arrays of optically active ZnO and TiO₂ nanoparticle have also been fabricated by using a micellar template.⁴⁴⁰ The TiO₂ nanoparticles are used as seeds for the growth of arrayed TiO₂ needle-like nanostruc-

tures. By varying the concentration of metal ion loading in PS-PVP micelles, Yun *et al.* showed the size tuning of iron oxide 2D nanoparticle arrays.⁴⁴¹⁻⁴⁴³ Recently, highly ordered arrays of Au nanoparticle in large areas were successfully fabricated from block copolymer micelles.⁴⁴⁴ Ethirajan *et al.* fabricated ordered 2-D arrays of magnetically attractive FePt nanoparticles on a silicon substrate by a micellar approach.⁴⁴⁵ Highly ordered arrays of silica dots, stripes and magnetic dots were also fabricated from block copolymer thin films.^{446,447}

Second, the conversion of the loaded metal ions of the micelles core into nanoparticles in the solution itself provides another interesting method to fabricate 2-D nanoparticle arrays. Block copolymer micelles have been extensively used to prepare metal-sulfide nanoparticles with controlled size.⁴⁴⁸⁻⁴⁵⁰ However, only few reports were described the 2-D nanoparticle arrays.⁴⁵¹⁻⁴⁵³ The direct synthesis of metal-selenide nanoparticles in PS-*b*-PVP micelles leads to easy fabrication of 2-D nano-arrays on solid substrate, as shown in Figure 25.⁸⁵ Third, ordered micellar templates are obtained by spin coating the micelle solution (without metal ion loading) on a substrate and an exposure of this micellar template to a selective solvent favorable to the core of the micelles opens the core and corona partially, and generates ordered pores on the template surface.⁴⁵⁴ A porous template obtained by dipping the PS-*b*-P2VP micellar template in acetic acid was used for the growth of vertically oriented polyaniline nanowires.⁴⁵⁵ Metal and metal oxide nanoparticle arrays have also been fabricated by either exposing the PVP core opened PS-*b*-PVP micellar templates to metal ion precursor or immersing the templates in core favored solution containing metal ions.⁴⁵⁶⁻⁴⁵⁸ Surface functionalized CdSe nanoparticles are assembled in a highly ordered manner within

the PS-*b*-PVP films.⁴⁵⁹

Although inorganic materials replicated from block copolymer templates exhibit regular and periodic nanostructures, exquisite and chaos morphologies containing one-dimensional (1D) nanostructures have gain much attention. Recently, Kang *et al.* reported a sphere-to-string transition induced by the addition of a surfactant to or by the increase in ionic strength of an amphilic block copolymer micelle solution.⁴⁶⁰ Juan *et al.* showed a simple and facile process to fabricate two-dimensional strings of TiO₂ nanoparticles with donut-like structures based on block copolymer self-assembly coupled with a sol-gel process.⁴⁶¹

Summary and Outlook

In this paper, we have described in detail the phase behavior and some applications of block copolymers in bulk as well as thin films. The current research trends of the block copolymer areas are divided into two broad parts. The first part is to synthesize new kinds of block copolymers, for instance, block copolymers containing conducting polymers, based on anionic or atom transfer radical polymerization. The other is to utilize the block copolymer (especially thin film) as soft templates to prepare various functional nanomaterials. Block copolymers have shown good potential for nanopatterning with size less than 40 nm, nanotemplates for conducting polymer nanowires, and/or two dimensional arrays of many different nanoparticles. Also, amphiphilic block copolymers forming various kinds of micelles can be used for controlled drug release. And, nanoporous block copolymer thin film itself can be used for new filtration membranes.

On the other hand, there are still some unsolved problems in block copolymers. In particular, there is no comprehensive theory to predict the rheological properties such as shear moduli and/or viscosity of block copolymer in the homogeneous state as well as in the ordered state. Although the SCMF can predict successfully the phase behavior of block copolymers with various microdomains, the concept of the mean-field might not be in principle valid for the block copolymers. Even though the average force can be assumed not to change dramatically with position, the interaction (or repulsion) between two blocks should be position dependent. Because of the connectivity (or junction point) of the block copolymer, the interaction between two different molecules located near the connectivity point should be different from that of the average of the whole space. For this purpose, molecular dynamic approach (or computer simulation) should be done. We expect that this is utmost needed for block copolymers containing one (or both) rigid rod block.

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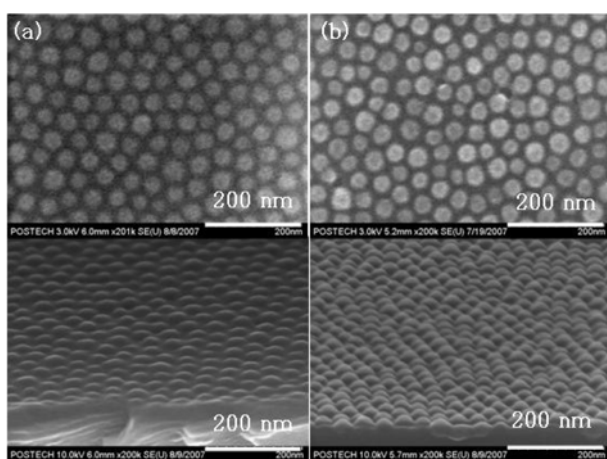


Figure 25. Top and 45° tilt view SEM images of two-dimensional array of pure CdSe nanoparticles prepared from (a) PS-*b*-P4VP-CdSe-1 and (b) PS-*b*-P4VP-CdSe-2 micellar solution. Reproduced with permission from Ref. 85; Copyright 2008, Royal Society of Chemistry.

References

- (1) M. Szwarc, *Nature*, **178**, 1168 (1956).
- (2) M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Process*, Interscience, New York, 1968.
- (3) G. Holden, E. T. Bishop, and N. R. Legge, *J. Polym. Sci.: Part C*, **26**, 37 (1969).
- (4) G. E. Molau, *Colloidal and Morphological Behavior of Block and Graft Copolymers*, Plenum Press, New York, 1971.
- (5) A. Noshay and J. E. McGrath, *Block Copolymers: Overview and Critical Survey*, Academic Press, New York, 1977.
- (6) R. B. Gallot, *Adv. Polym. Sci.*, **29**, 85 (1978).
- (7) G. Riess, G. Hurtrez, and P. Badadur, *Block Copolymers in Encyclopedia of Polymer Science and Technology*, J. I. Kroschwitz, Ed., 2nd Ed., Wiley Interscience, New York, 1985, Vol. 2.
- (8) N. R. Legge, G. Holden, and H. Schroeder, Eds., *Thermoplastic Elastomers*, Hanser, New York, 1987.
- (9) I. W. Hamley, *The Physics of Block Copolymers*, Oxford Univ. Press, New York, 1998.
- (10) I. W. Hamley, Ed., *Developments in Block Copolymer Science and Technology*, John Wiley & Sons Ltd., Chichester, England, 2004.
- (11) N. Hadjichristidis, S. Pispas, and G. Floudas, *Block Copolymer: Synthetic Strategies, Physical Properties and Application*, Wiley-Interscience, New Jersey, 2003.
- (12) T. P. Lodge, *Macromol. Chem. Phys.*, **204**, 265 (2003).
- (13) M. Lazzari, G. Liu, and S. Lecommandoux, Eds., *Block Copolymers in Nanoscience*, Wiley-VCH, Weinheim, 2005.
- (14) C. D. Han, *Rheology and Processing of Polymeric Materials*, Oxford Univ. Press, Oxford, 2007, Vol. 1.
- (15) T. Hashimoto, in *Thermoplastic Elastomers*, N. R. Legge, G. Holden, and H. Schroeder, Eds., Hanser, New York, 1996.
- (16) E. Helfand and Z. R. Wasserman, in *Developments in Block Copolymers*, I. Goodman, Ed., Applied Science, New York, 1982.
- (17) L. Leibler, *Macromolecules*, **13**, 1602 (1980).
- (18) F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.*, **41**, 525 (1990).
- (19) G. H. Fredrickson and F. S. Bates, *Ann. Rev. Mater. Sci.*, **26**, 501 (1996).
- (20) F. S. Bates, *Science*, **251**, 898 (1991).
- (21) T. P. Russell, T. E. Karis, Y. Gallot, and A. M. Mayes, *Nature*, **368**, 729 (1994).
- (22) T. Hashimoto, H. Hasegawa, H. Katayama, M. Kamigaito, M. Sawamoto, and M. Imai, *Macromolecules*, **30**, 6819 (1997).
- (23) M. Pollard, T. P. Russell, A. V. G. Ruzette, A. M. Mayes, and Y. Gallot, *Macromolecules*, **31**, 6493 (1998).
- (24) A. V. G. Ruzette, P. Banerjee, A. M. Mayes, M. Pollard, T. P. Russell, R. Jerome, T. Slaweki, R. Hjelm, and P. Thiyagarajan, *Macromolecules*, **31**, 8509 (1998).
- (25) R. Weidisch, M. Stamm, D. W. Schubert, M. Arnold, H. Budde, and S. Horing, *Macromolecules*, **32**, 3405 (1999).
- (26) H. Hasegawa, N. Sakamoto, H. Takeno, H. Jinnai, T. Hashimoto, D. Schwahn, H. Frielinghaus, S. Janben, M. Imai, and K. Mortensen, *J. Phys. Chem. Solids*, **60**, 1307 (1999).
- (27) D. Y. Ryu, C. Shin, J. Cho, D. H. Lee, J. K. Kim, K. A. Lavery, and T. P. Russell, *Macromolecules*, **40**, 7644 (2007).
- (28) J. Cho, K. Shin, K. S. Cho, Y.-S. Seo, S. K. Satija, D. Y. Ryu, and J. K. Kim, *Macromolecules*, **41**, 955 (2008).
- (29) D. Y. Ryu, U. Jeong, J. K. Kim, and T. P. Russell, *Nat. Mater.*, **1**, 114 (2002).
- (30) D. Y. Ryu, U. Jeong, D. H. Lee, J. Kim, H. S. Youn, and J. K. Kim, *Macromolecules*, **36**, 2894 (2003).
- (31) D. Y. Ryu, D. J. Lee, J. K. Kim, K. A. Lavery, T. P. Russell, Y. S. Han, B. S. Seong, C. H. Lee, and P. Thiyagarajan, *Phys. Rev. Lett.*, **90**, 235501 (2003).
- (32) D. Y. Ryu, D. H. Lee, U. Jeong, S.-H. Yun, S. Park, K. Kwon, B.-H. Sohn, T. Chang, and J. K. Kim, *Macromolecules*, **37**, 3717 (2004).
- (33) D. Y. Ryu, D. H. Lee, J. Jang, J. K. Kim, K. A. Lavery, and T. P. Russell, *Macromolecules*, **37**, 5851 (2004).
- (34) C. Li, D. H. Lee, J. K. Kim, D. Y. Ryu, and T. P. Russell, *Macromolecules*, **39**, 5926 (2006).
- (35) K. A. Lavery, J. D. Sievert, J. J. Watkins, T. P. Russell, D. Y. Ryu, and J. K. Kim, *Macromolecules*, **39**, 6580 (2006).
- (36) C. Li, G. H. Li, D. H. Lee, and J. K. Kim, *Polymer*, **48**, 4235 (2007).
- (37) C. Li, G. H. Li, H. C. Moon, D. H. Lee, J. K. Kim, and J. Cho, *Macromol. Res.*, **15**, 656 (2007).
- (38) K. Almdal, K. A. Koppi, F. S. Bates, and K. Mortensen, *Macromolecules*, **25**, 1743 (1992).
- (39) S. Sakurai, H. Kawada, T. Hashimoto, and L. J. Fetters, *Macromolecules*, **26**, 5796 (1993).
- (40) K. A. Koppi, M. Tirrell, and F. S. Bates, *Phys. Rev. Lett.*, **70**, 1449 (1993).
- (41) I. W. Hamley, K. A. Koppi, J. H. Rosadale, F. S. Bates, K. Almdal, and K. Mortensen, *Macromolecules*, **26**, 5959 (1993).
- (42) K. Almdal, K. A. Koppi, and F. S. Bates, *Macromolecules*, **26**, 4058 (1993).
- (43) A. K. Khandpur, S. Forster, F. B. Bates, I. W. Hamley, A. J. Ryan, W. Bras, K. Almdal, and K. Mortensen, *Macromolecules*, **28**, 8796 (1995).
- (44) N. Sakamoto, T. Hashimoto, C. D. Han, D. Kim, and N. Y. Vaidya, *Macromolecules*, **30**, 1621 (1997).
- (45) C. Y. Ryu, M. E. Vigild, and T. P. Lodge, *Phys. Rev. Lett.*, **81**, 5354 (1998).
- (46) C. Y. Ryu and T. P. Lodge, *Macromolecules*, **32**, 7190 (1999).
- (47) K. Kimishima, T. Koga, and T. Hashimoto, *Macromolecules*, **33**, 968 (2000).
- (48) J. K. Kim, H. H. Lee, M. Ree, K. B. Lee, and Y. Park, *Macromol. Chem. Phys.*, **199**, 641 (1998).
- (49) J. K. Kim, H. H. Lee, Q. J. Gu, T. Chang, and Y. H. Jeong, *Macromolecules*, **31**, 4045 (1998).
- (50) H. H. Lee, W. Y. Jeong, J. K. Kim, K. J. Ihn, J. A. Kornfield, Z.-G. Wang, and S. Qi, *Macromolecules*, **34**, 785 (2002).
- (51) D. A. Hajduk, S. M. Gruner, P. Rangarajan, R. A. Register, L. J. Fetters, C. Honeker, R. J. Albalak, and E. L. Thomas, *Macromolecules*, **27**, 490 (1994).
- (52) J. H. Ahn and W. C. Zin, *Macromolecules*, **35**, 10238 (2002).
- (53) Y.-L. Loo, R. A. Register, D. H. Adamson, and A. J. Ryan, *Macromolecules*, **38**, 4947 (2005).
- (54) C. Lai, Y.-L. Loo, R. A. Register, and D. H. Adamson, *Macromolecules*, **38**, 7098 (2005).
- (55) K. J. Hanley, T. P. Lodge, and C.-I. Huang, *Macromolecules*,

- 33, 5918 (2000).
- (56) T. P. Lodge, K. J. Hanley, and B. Pudil, *Macromolecules*, **35**, 4707 (2002).
- (57) J. Bang, T. P. Lodge, S. Wang, K. L. Briker, and W. R. Burghardt, *Phys. Rev. Lett.*, **89**, 215505 (2002).
- (58) T. P. Lodge, J. Bang, M. J. Park, and K. Char, *Phys. Rev. Lett.*, **92**, 145501 (2004).
- (59) M. J. Park, J. Bang, T. Harada, and K. Char, and T. P. Lodge, *Macromolecules*, **37**, 9064 (2004).
- (60) Y. Y. Huang, H.-L. Chen, and T. Hashimoto, *Macromolecules*, **36**, 764 (2003).
- (61) Y. Y. Huang, J.-Y. Hsu, H.-L. Chen, and T. Hashimoto, *Macromolecules*, **40**, 3700 (2007).
- (62) M. W. Matsen and F. S. Bates, *Macromolecules*, **29**, 1091 (1996).
- (63) E. W. Cochran, C. J. Garcia-Cervera, and G. H. Fredrickson, *Macromolecules*, **39**, 2449 (2006).
- (64) (a) J.-S. Lee, A. Hirao and S. Nakahama, *Macromolecules*, **21**, 274 (1988). (b) J.-S. Lee, A. Hirao and S. Nakahama, *Macromolecules*, **22**, 2602 (1989).
- (65) (a) G. Krausch, *Mater. Sci. Eng.*, **R14**, 1 (1995). (b) M. J. Fasolka and A. M. Mayes, *Annu. Rev. Mater. Res.*, **31**, 323 (2001).
- (66) I. W. Hamley, *Nanotechnology*, **14**, R39 (2003).
- (67) C. Park, J. Yoon, and E. L. Thomas, *Polymer*, **44**, 6725 (2003).
- (68) M. Lazzari and M. A. Lopez-Quintela, *Adv. Mater.*, **15**, 1583 (2003).
- (69) R. A. Segalman, *Mater. Sci. Eng.*, **R48**, 191 (2005).
- (70) C. J. Hawker and T. P. Russell, *MRS Bull.*, **30**, 952 (2005).
- (71) I. W. Hamley, *Ang. Chemie. Int. Ed.*, **42**, 1692 (2003).
- (72) S. Forste and T. Plantenberg, *Angew. Chem. Int. Ed.*, **41**, 688 (2002).
- (73) G. J. Doler-Illeia, E. L. Crepaldi, D. Grosso, and C. Sanchez, *Curr. Opin. Coll. Inter. Sci.*, **8**, 109 (2003).
- (74) S. B. Darling, *Prog. Polym. Sci.*, **32**, 1152 (2007).
- (75) G. Riess, *Progr. Polym. Sci.*, **28**, 1107 (2003).
- (76) L. F. Zhang and A. Eisenberg, *Science*, **268**, 1728 (1995).
- (77) S. Jain and F. S. Bates, *Science*, **300**, 460 (2003).
- (78) M. Yokoyama, M. Miyauchi, N. Yamada, T. Okano, Y. Sakurai, K. Kataoka, and S. Inoue, *J. Control. Release*, **11**, 269 (1990).
- (79) Y. Bae, S. Fukushima, A. Harada, and K. Kataoka, *Angew. Chem. Int. Ed.*, **42**, 4640 (2003).
- (80) L. Qi, H. Cölfen, and M. Antonietti, *Nano Lett.*, **1**, 61 (2001).
- (81) M. Möller and J. P. Spatz, *Curr. Opin. Colloid Interface Sci.*, **2**, 177 (1997).
- (82) S. Förster and M. Antonietti, *Adv. Mater.*, **10**, 195 (1998).
- (83) S. Förster and T. Plantenberg, *Angew. Chem Int. Ed.*, **41**, 688 (2002).
- (84) S. I. Yoo, J. H. Kwon, and B. H. Sohn, *J. Mater. Chem.*, **17**, 2969 (2007).
- (85) A. Philip and J. K. Kim, *Chem. Comm.*, 1193 (2008).
- (86) E. Helfand and Z. R. Wasserman, *Macromolecules*, **9**, 879 (1976).
- (87) E. Helfand and Z. R. Wasserman, *Macromolecules*, **11**, 960 (1978).
- (88) E. Helfand and Z. R. Wasserman, *Macromolecules*, **13**, 994 (1980).
- (89) E. Helfand and Z. R. Wasserman, *Polym. Eng. Sci.*, **17**, 535 (1977).
- (90) S. Krause, *J. Polym. Sci.: Part A-2*, **7**, 249 (1969).
- (91) S. Krause, *Macromolecules*, **3**, 84 (1970).
- (92) T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *J. Polym. Sci.: Part A-2*, **7**, 1283 (1969).
- (93) T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *Macromolecules*, **3**, 87 (1970).
- (94) J. D. Vavasour and M. D. Whitmore, *Macromolecules*, **25**, 5477 (1992).
- (95) J. D. Vavasour and M. D. Whitmore, *Macromolecules*, **26**, 7070 (1993).
- (96) M. W. Matsen and M. Schick, *Macromolecules*, **27**, 4014, 6761, 7157 (1994).
- (97) M. W. Matsen and M. Schick, *Phys. Rev. Lett.*, **72**, 2660 (1994).
- (98) A. K. Khandpur, S. Forster, and F. S. Bates, *Macromolecules*, **28**, 8796 (1995).
- (99) F. S. Bates and M. A. Hartney, *Macromolecules*, **18**, 2478 (1985); **19**, 2892 (1986).
- (100) M. Shibayama, T. Hashimoto, H. Kawai, H. Watanabe, and T. Kodaka, *Macromolecules*, **16**, 16 (1983).
- (101) T. Hashimoto, M. Shibayama, and H. Kawai, *Macromolecules*, **16**, 361 (1983).
- (102) T. Hashimoto, M. Shibayama, and H. Kawai, *Macromolecules*, **16**, 1093 (1983).
- (103) M. Shibayama, T. Hashimoto, and H. Kawai, *Macromolecules*, **16**, 1443 (1983).
- (104) T. Hashimoto, Y. Tsukahara, and H. Kawai, *Polymer J.*, **15**, 699 (1983).
- (105) K. Mori, H. Hasegawa, and T. Hashimoto, *Polymer J.*, **17**, 799 (1985).
- (106) R. J. Roe, M. Fishkis, and J. C. Chang, *Macromolecules*, **14**, 1091 (1981).
- (107) W. C. Zin and R. J. Roe, *Macromolecules*, **17**, 183 (1984).
- (108) E. V. Gouinlock and R. S. Porter, *Polym. Eng. Sci.*, **17**, 534 (1977).
- (109) C. I. Chung and J. C. Gale, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 1149 (1976).
- (110) C. I. Chung and M. I. Lin, *J. Polym. Sci. Polym. Phys. Ed.*, **16**, 545 (1978).
- (111) G. Kraus and T. Hashimoto, *J. Appl. Polym. Sci.*, **27**, 1745 (1982).
- (112) F. S. Bates, *Macromolecules*, **17**, 2607 (1984).
- (113) F. S. Bates, J. H. Rosadale, H. E. Bair, and T. P. Russell, *Macromolecules*, **22**, 2557 (1989).
- (114) F. S. Bates, J. H. Rosadale, G. H. Fredrickson, and C. J. Glinka, *Phys. Rev. Lett.*, **61**, 2229 (1988).
- (115) K. Almdal, J. H. Rosadale, F. S. Bates, G. D. Wignall, and G. H. Fredrickson, *Phys. Rev. Lett.*, **65**, 1112 (1990).
- (116) K. I. Winey, E. L. Thomas, and L. J. Fetters, *Macromolecules*, **25**, 422 (1992).
- (117) J. L. Adams, W. W. Graessley, and R. A. Register, *Macromolecules*, **27**, 6026 (1994).
- (118) K. I. Winey, D. A. Gobran, Z. Xu, L. J. Fetters, and E. L. Thomas, *Macromolecules*, **27**, 2392 (1994).
- (119) G. Flodas, N. Hadjichristidis, H. Iatrou, T. Pakula, and E. W. Fisher, *Macromolecules*, **27**, 7735 (1994).
- (120) C. D. Han and J. Kim, *J. Polym. Sci.: Part B: Polym. Phys.*, **25**, 1741 (1987).

- (121) C. D. Han, J. Kim, and J. K. Kim, *Macromolecules*, **22**, 383 (1989).
- (122) C. D. Han, D. M. Baek, and J. K. Kim, *Macromolecules*, **23**, 561 (1990).
- (123) C. D. Han, D. M. Baek, S. Sakurai, and T. Hashimoto, *Polymer J.*, **21**, 841 (1989).
- (124) T. Hashimoto, T. Ogawa, and C. D. Han, *J. Phys. Soc. Jap.*, **63**, 2206 (1994).
- (125) C. D. Han, D. M. Baek, J. K. Kim, T. Ogawa, N. Sakamoto, and T. Hashimoto, *Macromolecules*, **28**, 5043 (1995).
- (126) N. P. Balsara, D. Perahia, C. R. Safinya, M. Tirrell, and T. P. Lodge, *Macromolecules*, **25**, 3896 (1992).
- (127) N. P. Balsara, H. J. Dai, P. K. Kesani, B. A. Garatz, and B. Hammouda, *Macromolecules*, **27**, 7406 (1994).
- (128) R. M. Kannan and J. A. Kornfield, *Macromolecules*, **27**, 1177 (1994).
- (129) D. J. Meier, *J. Polym. Sci.: Part C*, **26**, 81 (1969).
- (130) D. J. Meier, *Polym. Preprints*, **11**(2), 400 (1970).
- (131) D. J. Meier, in *Thermoplastic Elastomers*, N. R. Legge, G. Holden, and H. Schroeder, Eds., Hanser, New York, 1987, Chapter 11.
- (132) T. S. Bailey, C. M. Hardy, T. H. Eppps, and F. S. Bates, *Macromolecules*, **35**, 7007 (2002).
- (133) M. Takenaka, T. Wakada, S. Akasaka, S. Nishitsuji, K. Saijo, H. Shimizu, M. I. Kim, and H. Hasegawa, *Macromolecules*, **40**, 4399 (2007).
- (134) N. Sakamoto, T. Hashimoto, C. D. Han, D. Kim, and N. Y. Vaidya, *Macromolecules*, **30**, 1621 (1997).
- (135) C. D. Han, N. Y. Vaidya, D. Kim, G. Shin, D. Yamaguchi, and T. Hashimoto, *Macromolecules*, **33**, 3767 (2000).
- (136) S. Choi, K. M. Lee, C. D. Han, N. Sota, and T. Hashimoto, *Macromolecules*, **36**, 793 (2003).
- (137) J. K. Kim, H. H. Lee, S. Sakurai, S. Aida, J. Masamoto, S. Nomura, Y. Kitagawa, and Y. Suda, *Macromolecules*, **32**, 6707 (1999).
- (138) R. A. Segalman, A. Hexemer, R. C. Hayward, and E. J. Kramer, *Macromolecules*, **36**, 3272 (2003).
- (139) X. Wang, E. E. Dormidontova, and T. P. Lodge, *Macromolecules*, **35**, 9687 (2002).
- (140) G. H. Fredrickson and E. Helfand, *J. Chem. Phys.*, **87**, 697 (1987).
- (141) G. H. Fredrickson and E. Helfand, *J. Chem. Phys.*, **89**, 5890 (1988).
- (142) J. Barret and G. H. Fredrickson, *J. Chem. Phys.*, **95**, 1281 (1991).
- (143) C. D. Han, D. M. Baek, J. Kim, K. Kimishima, and T. Hashimoto, *Macromolecules*, **25**, 3052 (1992).
- (144) S. A. Brazovskii, *Sov. Phys. (JETP)*, **41**, 85 (1975).
- (145) W. Zha, C. D. Han, D. H. Lee, S. H. Han, J. K. Kim, J. H. Kang, and C. Park, *Macromolecules*, **40**, 2109 (2007).
- (146) B. Sthn, *J. Polym. Sci.; Part B: Polym. Phys. Ed.*, **30**, 1013 (1992).
- (147) D. A. Hajduk, S. M. Grunmer, S. Erramilli, R. A. Register, and L. J. Fetters, *Macromolecules*, **29**, 1473 (1996).
- (148) G. Floudas, N. Hadjichristidis, M. Stamm, A. E. Likthman, and A. N. Semenov, *J. Chem. Phys.*, **106**, 3318 (1997).
- (149) H. Soenen, A. Liskova, K. Reynders, H. Berghmans, H. H. Winter, and N. Overbergh, *Polymer*, **38**, 5661 (1997).
- (150) V. P. Voronov, V. M. Buleiko, V. E. Podneks, I. W. Hamley, J. P. A. Fairclough, A. J. Ryan, S. M. Mai, B. X. Kiao, and C. Booth, *Macromolecules*, **30**, 6674 (1997).
- (151) H. J. Kim, S. B. Kim, J. K. Kim, Y. M. Jung, D. Y. Ryu, K. A. Lavery, and T. P. Russell, *Macromolecules*, **39**, 408 (2006).
- (152) G. H. Fredrickson, *J. Chem. Phys.*, **85**, 5306 (1986).
- (153) G. H. Fredrickson and R. G. Larson, *J. Chem. Phys.*, **86**, 1553 (1987).
- (154) R. G. Larson and G. H. Fredrickson, *Macromolecules*, **20**, 1897 (1987).
- (155) C. D. Han and M. S. Jhon, *J. Appl. Polym. Sci.*, **32**, 3809 (1986).
- (156) C. D. Han and J. K. Kim, *Macromolecules*, **22**, 4292 (1989).
- (157) D. Patterson and A. Robard, *Macromolecules*, **11**, 690 (1978).
- (158) I. C. Sanchez and C. G. Panayiotou, in *Models for Thermodynamic and Phase Equilibria Calculation*, S. I. Sandler, Ed., Marcel Dekker Inc, New York, 1994, Ch. 3.
- (159) C. S. Hudson, *J. Phys. Chem.*, **47**, 113 (1904).
- (160) G. N. Malcolm and J. S. Rowlinson, *Trans. Faraday Soc.*, **53**, 921 (1957).
- (161) M. M. Abbott and J. M. Prausnitz, in *Models for Thermodynamic and Phase Equilibria Calculations*, S. I. Sandler, Ed., Marcel Dekker, New York, 1994, pp. 1-86.
- (162) T. Hashimoto and N. Sakamoto, *Macromolecules*, **28**, 4779 (1995).
- (163) N. Sakamoto and T. Hashimoto, *Macromolecules*, **31**, 3815 (1998).
- (164) J. Cho, *Macromolecules*, **37**, 10101 (2004); J. Cho and Y. K. Kwon, *J. Polym. Sci. Polym. Phys.*, **41**, 1889 (2003).
- (165) H. J. Kim, S. B. Kim, J. K. Kim, and Y. M. Jung, *J. Phys. Chem. B*, **110**, 23123 (2006).
- (166) H. Kasten and B. Stühn, *Macromolecules*, **28**, 4777 (1995).
- (167) D. A. Hajduk, S. M. Gruner, S. Erramilli, R. A. Register, and L. J. Fetters, *Macromolecules*, **29**, 1473 (1996).
- (168) D. Schwahn, H. Frielinghaus, K. Mortensen, and K. Almdal, *Phys. Rev. Lett.*, **77**, 3153 (1996).
- (169) V. Bartels, M. Stamm, and K. Mortensen, *Polym. Bull.*, **36**, 103 (1996).
- (170) H. Frielinghaus, D. Schwahn, K. Mortensen, K. Almdal, and T. Springer, *Macromolecules*, **29**, 3263 (1996).
- (171) A.-V. G. Ruzette, A. M. Mayes, M. Pollard, T. P. Russell, and B. Hammouda, *Macromolecules*, **36**, 3351 (2003).
- (172) B. Steinhoff, M. Rüllmann, M. Wenzel, M. Junker, I. Alig, R. Oser, B. Stuhn, G. Meier, O. Diat, P. Bosecke, and H. B. Stanley, *Macromolecules*, **31**, 36 (1998).
- (173) D. Schwahn, H. Frielinghaus, K. Mortensen, and K. Almdal, *Macromolecules*, **34**, 1694 (2001).
- (174) H. Frielinghaus, D. Schwahn, J. Dudowicz, K. F. Freed, and K. W. Foreman, *J. Chem. Phys.*, **114**, 5016 (2001).
- (175) J. Dodowicz, M. S. Freed, and K. F. Freed, *Macromolecules*, **24**, 5096 (1991).
- (176) K. F. Freed and J. Dudowicz, *J. Chem. Phys.*, **97**, 2105 (1992).
- (177) J. Dudowicz and K. F. Freed, *Macromolecules*, **26**, 213 (1993).
- (178) J. Dudowicz, K. F. Freed, and J. F. Fouglaas, *Phys. Rev. Lett.*, **88**, 095503 (2002).
- (179) K. F. Freed and J. Dudowicz, *Adv. Polym. Sci.*, **183**, 63 (2005).
- (180) T. Hino and J. M. Prausnitz, *Macromolecules*, **31**, 2636 (1998).
- (181) J. Cho, *Macromolecules*, **33**, 2228 (2000).

- (182) J. Cho, *Macromolecules*, **34**, 1001 (2001).
- (183) A. V. G. Ruzette and A. M. Mayes, *Macromolecules*, **34**, 1894 (2001).
- (184) A. V. G. Ruzette, P. Banerjee, A. M. Mayes, M. Pollard, and T. P. Russell, *J. Chem. Phys.*, **114**, 8205 (2001).
- (185) J. A. Gonzalez-Leon, M. H. Acar, S. W. Ryu, A. V. G. Ruzette, and A. M. Mayes, *Nature*, **426**, 424 (2003).
- (186) J. A. Gonzalez-Leon, S. W. Ryu, S. A. Hewlett, S. H. Ibrahim, and A. M. Mayes, *Macromolecules*, **38**, 8036 (2005).
- (187) D. H. Lee, H. J. Kim, and J. K. Kim, *Macromolecular Symposia*, **240**, 123 (2006).
- (188) Y. Matsushita, H. Choshi, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **13**, 1053 (1980).
- (189) Y. Mogi, H. Kotsuji, Y. Kaneko, K. Mori, Y. Matsushita, and I. Noda, *Macromolecules*, **25**, 5408 (1992).
- (190) Y. Mogi, H. Kotsuji, Y. Kaneko, K. Mori, Y. Matsushita, I. Noda, and C. C. Han, *Macromolecules*, **26**, 5169 (1993).
- (191) Y. Mogi, M. Nomura, H. Kotsuji, K. Ohnishi, Y. Matsushita, and I. Noda, *Macromolecules*, **27**, 6755 (1994).
- (192) C. Auschra and R. Stadler, *Polym. Bull.*, **30**, 257, 305 (1993); *Macromolecules*, **26**, 2171, 6364 (1993).
- (193) R. Stadler, C. Auschra, J. Beckmann, U. Krappe, I. Voigt-Martin, and L. Leibler, *Macromolecules*, **28**, 3080 (1995).
- (194) U. Krappe, R. Stadler, and I. Voigt-Martin, *Macromolecules*, **28**, 4558 (1995).
- (195) U. Breiner, U. Krappe, E. L. Thomas, and R. Stadler, *Macromolecules*, **31**, 135 (1998).
- (196) W. Zhang and Z. G. Wang, *Macromolecules*, **28**, 7215 (1995).
- (197) F. S. Bates and G. H. Fredrickson, *Physics Today*, **52**, 32 (1999).
- (198) T. S. Bailey, H. D. Pham, and F. S. Bates, *Macromolecules*, **34**, 6994 (2001).
- (199) T. H. Epps, E. W. Cochran, T. S. Bailey, R. S. Waletzko, C. M. Hardy, and F. S. Bates, *Macromolecules*, **37**, 8325 (2004).
- (200) T. H. Epps, J. Chatterjee, and F. S. Bates, *Macromolecules*, **38**, 8775 (2005).
- (201) F. S. Bates, *MRS Bulletin*, **30**, 525 (2005).
- (202) G. H. Fredrickson, V. Ganesan, and F. Drolet, *Macromolecules*, **35**, 16 (2002).
- (203) T. S. Bailey, H. D. Pham, and F. S. Bates, *Chem. Mater.*, **14**, 1706 (2002).
- (204) T. H. Epps, T. S. Bailey, R. Waletzko, and F. S. Bates, *Macromolecules*, **36**, 2873 (2003).
- (205) T. Goldacker, V. Abetz, R. Stadler, I. Erukhimovich, and L. Leibler, *Nature*, **398**, 137 (1999).
- (206) A. Takano, K. Soga, J. Suzuki, and Y. Matsushita, *Macromolecules*, **36**, 9288 (2003).
- (207) T. A. Shefelbine, M. E. Vigild, M. W. Matsen, D. A. Hajduk, M. A. Hillmyer, E. L. Cussler, and F. S. Bates, *J. Am. Chem. Soc.*, **121**, 8457 (1999).
- (208) F. S. Bates, G. H. Fredrickson, G. H. Hucul, and S. F. Han, *AIChE J.*, **47**, 762 (2001).
- (209) C. Y. Ryu, J. Ruokolainen, G. H. Fredrickson, E. J. Kramer, and S. F. Hahn, *Macromolecules*, **35**, 2157 (2002).
- (210) T. J. Hermel, S. F. Hahn, K. A. Chaffin, W. W. Gerberich, and F. S. Bates, *Macromolecules*, **36**, 2190 (2003).
- (211) T. Asari, S. Arai, A. Takano, and Y. Matsushita, *Macromolecules*, **39**, 2232 (2006).
- (212) K. Hayashida, W. Kawashima, A. Takano, Y. Shinohara, Y. Amemiya, Y. Nozue, and Y. Matsushita, *Macromolecules*, **39**, 4869 (2006).
- (213) K. Hayashida, A. Takano, S. Arai, Y. Shinohara, Y. Amemiya, and Y. Matsushita, *Macromolecules*, **39**, 9402 (2006).
- (214) Y. Matsushita, *Macromolecules*, **40**, 771 (2007).
- (215) K. Hayashida, N. Saito, S. Arai, A. Takano, N. Tanaka, and Y. Matsushita, *Macromolecules*, **40**, 3695 (2007).
- (216) K. Hayashida, T. Dotera, A. Takano, and Y. Matsushita, *Phys. Rev. Lett.*, **98**, 195502 (2007).
- (217) R. Yin and T. E. Hogen-Esch, *Macromolecules*, **26**, 6952 (2003).
- (218) R. L. Lescanec, D. A. Hajduk, G. Y. Kim, Y. Gan, R. Yin, S. M. Gruner, T. E. Hogen-Esch, and E. L. Thomas, *Macromolecules*, **28**, 3485 (1995).
- (219) J. F. Marko, *Macromolecules*, **26**, 1442 (1993).
- (220) A. N. Morozov and J. G. E. M. Fraaije, *Macromolecules*, **34**, 1526 (2001).
- (221) W. H. Jo and J. Hur, *J. Chem. Phys.*, **111**, 1712 (1999).
- (222) A. Mayes and Olvera de la Cruz, *J. Chem. Phys.*, **91**, 7228 (1989).
- (223) D. E. Discher and A. Eisenberg, *Science*, **297**, 967 (2002).
- (224) J. S. Yoo, M. S. Kim, D. S. Lee, B. S. Kim, and J. H. Kim, *Macromol. Res.*, **14**, 117 (2006).
- (225) Y. P. Jung, Y. K. Son, and J. H. Kim, *Macromol. Res.*, **15**, 82 (2007).
- (226) S. J. Im, Y. M. Choi, E. Subramanyam, K. M. Huh, and K. Park, *Macromol. Res.*, **15**, 363 (2007).
- (227) S. J. Hwang, M. S. Kim, J. K. Han, D. S. Lee, B. S. Kim, E. K. Choi, H. J. Park, and J. S. Kim, *Macromol. Res.*, **15**, 437 (2007).
- (228) D. H. Kim, Y. S. Ko, and Y. K. Kwon, *Macromol. Res.*, **16**, 62 (2008).
- (229) K. Dayananda, M. S. Kim, and B. S. Kim, *Macromol. Res.*, **15**, 385 (2007).
- (230) Y. Y. Won, A. K. Brannan, H. T. Davis, and F. S. Bates, *J. Phys. Chem. B*, **106**, 3354 (2002).
- (231) D. J. Pochan, Z. Y. Chen, H. G. Cui, K. Hales, K. Qi, and K. L. Wooley, *Science*, **306**, 94 (2004).
- (232) H. Cui, Z. Chen, S. Zhong, K. L. Wooley, and D. J. Pochan, *Science*, **317**, 647 (2007).
- (233) Z. B. Li, E. Kesselman, Y. Talmon, M. A. Hillmyer, and T. P. Lodge, *Science*, **306**, 98 (2004).
- (234) Z. B. Li, M. A. Hillmyer, and T. P. Lodge, *Macromolecules*, **39**, 765 (2006).
- (235) Z. B. Li, M. A. Hillmyer, and T. P. Lodge, *Macromolecules*, **37**, 8933 (2004).
- (236) S. Y. Kim, S. H. Cho, Y. M. Lee, and L. Y. Chu, *Macromol. Res.*, **15**, 646 (2007).
- (237) K. M. Kim, S. Y. Choi, and H. J. Jeon, *Macromol. Res.*, **16**, 169 (2008).
- (238) Y. K. Joung, J. S. Lee, and K. D. Park, *Macromol. Res.*, **16**, 66 (2008).
- (239) B. Jeong, Y. H. Bae, D. S. Lee, and S. W. Kim, *Nature*, **388**, 860 (1997).
- (240) Y. Mohajer, G. L. Wilkes, I. C. Wang, and J. E. McGrath, *Polymer*, **23**, 1523 (1982).
- (241) R. Seguela and J. Prud'homme, *Polymer*, **30**, 1446 (1989).

- (242) R. E. Cohen, P. L. Cheng, K. Douzinas, P. Kofinas, and C. V. Berney, *Macromolecules*, **23**, 324 (1990).
- (243) K. C. Douzinas and R. E. Cohen, *Macromolecules*, **25**, 5030 (1992).
- (244) R. E. Cohen, A. Bellare, and M. A. Drzewinski, *Macromolecules*, **27**, 2321 (1994).
- (245) P. Rangarajan, R. A. Register, and L. J. Fetters, *Macromolecules*, **26**, 4640 (1993).
- (246) P. Rangarajan, R. A. Register, L. J. Fetters, W. Bras, S. Naylor, and A. J. Ryan, *Macromolecules*, **28**, 4932 (1995).
- (247) P. Rangarajan, R. A. Register, D. H. Adamson, L. J. Fetters, W. Bras, S. Naylor, and A. J. Ryan, *Macromolecules*, **28**, 1422 (1995).
- (248) A. J. Ryan, I. W. Hamley, W. Bras, and F. Bates, *Macromolecules*, **28**, 3860 (1995).
- (249) I. W. Hamley, J. P. A. Fairclough, F. S. Bates, and A. J. Ryan, *Polymer*, **39**, 1429 (1998).
- (250) D. J. Quiram, R. A. Register, and G. R. Marchand, *Macromolecules*, **30**, 4551 (1997).
- (251) I. W. Hamley, J. P. A. Fairclough, N. J. Terrill, A. J. Ryan, P. M. Lipic, F. S. Bates, and E. Towns-Andrews, *Macromolecules*, **29**, 8835 (1996).
- (252) I. W. Hamley, J. P. A. Fairclough, A. J. Ryan, F. S. Bates, and E. Towns-Andrews, *Polymer*, **37**, 4425 (1996).
- (253) P. C. Ashman and C. Booth, *Polymer*, **16**, 889 (1975).
- (254) C. Booth and D. V. Dodgson, *J. Polym. Sci.: Polym. Phys. Ed.*, **11**, 265 (1973).
- (255) S. M. Mai, J. P. A. Fairclough, K. Viras, P. A. Gorry, I. W. Hamley, A. J. Ryan, and C. Booth, *Macromolecules*, **30**, 8392 (1997).
- (256) A. J. Ryan, J. P. A. Fairclough, I. W. Hamley, S. M. Mai, and C. Booth, *Macromolecules*, **30**, 1723 (1997).
- (257) S. Nojima, K. Kato, S. Yamamoto, and T. Ashida, *Macromolecules*, **25**, 2237 (1992).
- (258) S. Nojima, M. Ono, and T. Ashida, *Polymer J.*, **24**, 1271 (1992).
- (259) S. Nojima, S. Yamamoto, and T. Ashida, *Polymer J.*, **27**, 673 (1995).
- (260) J. K. Kim, D. J. Park, M. S. Lee, and K. J. Ihn, *Polymer*, **42**, 7429 (2001).
- (261) M. D. Kempe, N. R. Scruggs, R. Verduzco, J. Lal, and J. A. Kornfield, *Nat. Mater.*, **3**, 177 (2004).
- (262) K. M. Lee and C. D. Han, *Macromolecules*, **35**, 3145 (2002).
- (263) Y. Tian, K. Watanabe, X. Kong, J. Abe, and T. Iyoda, *Macromolecules*, **35**, 3739 (2002).
- (264) Y. Morikawa, S. Nagano, K. Watanabe, K. Kamata, T. Iyoda, and T. Seki, *Adv. Mater.*, **18**, 883 (2006).
- (265) J. Li, K. Kamata, S. Watanabe, and T. Iyoda, *Adv. Mater.*, **19**, 1267 (2007).
- (266) A. Chen, M. Komura, K. Kamata, and T. Iyoda, *Adv. Mater.*, **20**, 763 (2008).
- (267) S. Watanabe, R. Fujiwara, M. Hada, Y. Okazaki, and T. Iyoda, *Angew. Chem. Int. Ed.*, **46**, 1120 (2007).
- (268) R.-M. Ho, Y.-W. Chiang, C.-C. Tsai, C.-C. Lin, B.-T. Ko, and B.-H. Huang, *J. Am. Chem. Soc.*, **126**, 2704 (2004).
- (269) Y.-W. Chiang, R.-M. Ho, B.-T. Ko, and C.-C. Lin, *Angew. Chem. Int. Ed.*, **44**, 7969 (2005).
- (270) W.-H. Tseng, P.-Y. Hsieh, R.-M. Ho, B.-H. Huang, C.-C. Lin, and B. Lotz, *Macromolecules*, **39**, 7071 (2006).
- (271) R.-M. Ho, C.-K. Chen, Y.-W. Chiang, B.-T. Ko, and C.-C. Lin, *Adv. Mater.*, **18**, 2355 (2006).
- (272) Y.-T. Tseng, W.-H. Tseng, C.-H. Lin, and R.-M. Ho, *Adv. Mater.*, **19**, 3584 (2007).
- (273) G. Hadziioannou, *Polymer*, **42**, 9097 (2001).
- (274) J. Liu, E. Sheina, T. Kowalewski, and R. D. McCullough, *Angew. Chem. Int. Ed.*, **41**, 329 (2002).
- (275) B. D. Olsen and R. A. Segalman, *Macromolecules*, **38**, 10127 (2005).
- (276) B. D. Olsen and R. A. Segalman, *Macromolecules*, **39**, 7078 (2006).
- (277) Y. F. Tao, B. D. Olsen, V. Ganesan, and R. A. Segalman, *Macromolecules*, **40**, 3320 (2007).
- (278) C.-A. Dai, W.-C. Yen, Y.-H. Lee, C.-C. Ho, and W.-F. Su, *J. Am. Chem. Soc.*, **129**, 411036 (2007).
- (279) J. H. Kim, M. S. Rahman, J. S. Lee, and J.-W. Park, *J. Am. Chem. Soc.*, **129**, 7756 (2007).
- (280) (a) M. S. Rahman, M. Changez, S. Samal, J.-S. Lee, *J. Nanoscience and Nanotechnology*, **7**, 3892 (2007). (b) Y.-D. Shin, S.-H. Han, S. Samal, and J.-S. Lee, *J. Polym. Sci.; Part A: Polym. Chem.*, **43**, 607 (2005).
- (281) M. S. Rahman, S. Samal, and J.-S. Lee, *Macromolecules*, **39**, 5009 (2006).
- (282) A. Urbas, R. Sharp, Y. Fink, E. L. Thomas, M. Xenidou, and L. J. Fetters, *Adv. Mater.*, **12**, 812 (2000).
- (283) M. Maldovan, C. K. Ullal, W. C. Carter, and E. L. Thomas, *Nat. Mater.*, **2**, 664 (2003).
- (284) M. Maldovan and E. L. Thomas, *Nat. Mater.*, **3**, 593 (2004).
- (285) Y. Kang, J. J. Walsh, T. Gorishnyy, and E. L. Thomas, *Nat. Mater.*, **6**, 957 (2007).
- (286) A. Urbas, Y. Fink, and E. L. Thomas, *Macromolecules*, **32**, 4748 (1999).
- (287) D. J. Kinning, K. I. Winey, and E. L. Thomas, *Macromolecule*, **21**, 3502 (1988).
- (288) K. I. Winey, E. L. Thomas, and L. J. Fetters, *J. Chem. Phys.*, **95**, 9367 (1991).
- (289) (a) K. I. Winey, E. L. Thomas, and L. J. Fetters, *Macromolecules*, **25**, 422 (1992). (b) K. I. Winey, E. L. Thomas, and L. J. Fetters, *Macromolecules*, **25**, 2645 (1992).
- (290) T. Hashimoto, H. Tanaka, and H. Hasegawa, *Macromolecules*, **23**, 4378 (1990).
- (291) H. Tanaka and T. Hashimoto, *Macromolecules*, **24**, 5713 (1991).
- (292) H. Tanaka, H. Hasegawa, and T. Hashimoto, *Macromolecules*, **24**, 240 (1991).
- (293) T. Hashimoto, K. Kimishima, and H. Hasegawa, *Macromolecules*, **24**, 5704 (1991).
- (294) T. Hashimoto, K. Yamasaki, S. Koizumi, and H. Hasegawa, *Macromolecules*, **26**, 2895 (1993).
- (295) S. Koizumi, H. Hasegawa, and T. Hashimoto, *Macromolecules*, **27**, 6532 (1994).
- (296) S. Koizumi, H. Hasegawa, and T. Hashimoto, *Macromolecules*, **27**, 7893 (1994).
- (297) R. J. Roe and W. C. Zin, *Macromolecules*, **17**, 189 (1984).
- (298) S. Nojima and R. J. Roe, *Macromolecules*, **20**, 1866 (1987).
- (299) M. M. Disko, K. S. Liang, S. K. Behal, R. J. Roe, and K. J. Jeon, *Macromolecules*, **26**, 2983 (1993).

- (300) C. K. Kang and W. C. Zin, *Macromolecules*, **25**, 3039 (1992).
- (301) R. J. Spontak, S. D. Smith, and A. Ashraf, *Macromolecules*, **26**, 956 (1993).
- (302) B. Löwenhaupt, A. Steurer, G. P. Hellmann, and Y. Gallot, *Macromolecules*, **27**, 908 (1994).
- (303) D. M. Baek, C. D. Han, and J. K. Kim, *Polymer*, **33**, 4821 (1992).
- (304) L. Leibler and H. Benoit, *Polymer*, **2**, 195 (1981).
- (305) K. M. Hong and J. Noolandi, *Macromolecules*, **16**, 1083 (1983).
- (306) M. D. Whitmore and J. Noolandi, *Macromolecules*, **18**, 2486 (1985).
- (307) M. W. Matsen, *Macromolecules*, **28**, 5765 (1995).
- (308) P. K. Janert and M. Schick, *Macromolecules*, **31**, 1109 (1998).
- (309) F. S. Bates, W. W. Maurer, P. M. Lipic, M. A. Hillmyer, K. S. Almdal, K. Mortensen, G. H. Fredrickson, and T. P. Lodge, *Phys. Rev. Lett.*, **79**, 849 (1997).
- (310) M. A. Hillmyer, W. W. Maurer, T. P. Lodge, F. S. Bates, and K. S. Almdal, *J. Phys. Chem. B.*, **103**, 4814 (1999).
- (311) N. Zhou, F. S. Bates, and T. P. Lodge, *Nano Lett.*, **6**, 2354 (2006).
- (312) H. S. Lee, A. Roy, and A. S. Badami, *Macromol. Res.*, **15**, 160 (2007).
- (313) M. J. Park, K. H. Downing, A. Jackson, E. D. Gomez, A. M. Minor, D. Cookson, A. Z. Weber, and N. P. Balsara, *Nano Lett.*, **7**, 3547 (2007).
- (314) M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schadler, and U. Wiesner, *Science*, **278**, 1795 (1997).
- (315) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science*, **279**, 548 (1998).
- (316) C. G. Goltner, S. Henke, M. C. Weisenberger, and M. Antonietti, *Agew. Chem. Int. Ed.*, **37**, 613 (1998).
- (317) A. C. Finnefrock, R. Ulrich, G. E. S. Toombers, S. M. Gruner, and U. Wiesner, *J. Am. Chem. Soc.*, **125**, 13084 (2003).
- (318) J. Lee, M. C. Orilall, S. C. Warren, M. Kamperman, F. J. Disalvo, and U. Wiesner, *Nat. Mater.*, **7**, 222 (2008).
- (319) P. R. L. Malenfant, J. Wan, S. T. Taylor, and M. Manoharan, *Nat. Nanotechnology*, **2**, 43 (2007).
- (320) Y. Gong, W. Joo, Y. Kim, and J. K. Kim, *Chem. Mater.*, **20**, 1203 (2008).
- (321) P. Mansky, P. M. Chaikin, and E. L. Thomas, *J. Mater. Sci.*, **30**, 1987 (1995).
- (322) M. Park, C. Harrison, P. M. Chaikin, R. A. Register, and D. H. Adamson, *Science*, **276**, 1401 (1997).
- (323) M. Park, P. M. Chaikin, R. A. Register, and D. H. Adamson, *Appl. Phys. Lett.*, **79**, 257 (2001).
- (324) T. Hayakawa, T. Kouketsu, M. Kakimoto, H. Yokoyama, and S. Horiuchi, *Macromol. Res.*, **14**, 52 (2006).
- (325) D. H. Kim, Z. Lin, H.-C. Kim, U. Jeong, and T. P. Russell, *Adv. Mater.*, **15**, 811 (2003).
- (326) D. H. Kim, S. H. Kim, K. Lavery, and T. P. Russell, *Nano Lett.*, **4**, 1841 (2004).
- (327) D. A. Olson, L. Chen, and M. A. Hillmyer, *Chem. Mater.*, **20**, 869 (2008).
- (328) T. P. Russell, G. Coulon, V. R. Deline, and D. C. Miller, *Macromolecules*, **22**, 4600 (1989).
- (329) G. Coulon, T. P. Russell, V. R. Deline, and P. F. Green, *Macromolecules*, **22**, 2581 (1989).
- (330) S. H. Anastasiadis, T. P. Russell, S. K. Satija, and C. F. Majkrzak, *Phys. Rev. Lett.*, **62**, 1852 (1989).
- (331) P. Mansky, Y. Liu, E. Huang, T. P. Russell, and C. Hawker, *Science*, **275**, 1458 (1997).
- (332) P. Mansky, T. P. Russell, C. J. Hawker, J. Mays, D. C. Cook, and S. K. Satija, *Phys. Rev. Lett.*, **79**, 237 (1997).
- (333) E. Huang, T. P. Russell, C. Harrison, P. M. Chaikin, R. A. Register, C. J. Hawker, and J. Mays, *Macromolecules*, **31**, 7641 (1998).
- (334) D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, and T. P. Russell, *Science*, **308**, 236 (2005).
- (335) E. Drockenmuller, L. Y. T. Li, D. Y. Ryu, E. Harth, T. P. Russell, H. C. Kim, and C. J. Hawker, *J. Polym. Sci.; Part A: Polym. Chem.*, **43**, 1028 (2005).
- (336) E. Kim, C. Shin, H. Ahn, D. Y. Ryu, J. Bang, C. J. Hawker, and T. P. Russell, *Soft Matter*, **4**, 475 (2008).
- (337) J. Bang, J. Bae, P. Löwenhielm, C. Spiessberger, S. A. Givenbeck, T. P. Russell, and C. J. Hawker, *Adv. Mater.*, **19**, 4552 (2007).
- (338) K. Amundson, E. Helfand, S. S. Patel, X. Quan, and S. D. Smith, *Macromolecules*, **25**, 1935 (1992).
- (339) K. Amundson, E. Helfand, X. Quan, and S. D. Smith, *Macromolecules*, **26**, 2698 (1993).
- (340) K. Amundson, E. Helfand, X. Quan, S. D. Hudson, and S. D. Smith, *Macromolecules*, **27**, 6559 (1994).
- (341) T. L. Morkved, M. Lu, A. M. Urbas, E. E. Ehrichs, H. M. Jaeger, P. Mansky, and T. P. Russell, *Science*, **273**, 931 (1996).
- (342) P. Mansky, J. DeRouchey, T. P. Russell, J. Mays, M. Pitsikalis, T. Morkved, and H. Jaeger, *Macromolecules*, **31**, 4399 (1998).
- (343) T. Thurn-Albrecht, R. Steiner, J. DeRouchey, C. M. Stafford, E. Huang, M. Bal, M. Tuominen, C. J. Hawker, and T. P. Russell, *Adv. Mater.*, **12**, 787 (2000).
- (344) D. H. Kho, S. H. Chae, U. Jeong, H. Y. Kim, and J. K. Kim, *Macromolecules*, **38**, 3820 (2005).
- (345) T. Thurn-Albrecht, J. Schotter, G. A. Kastle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Block, M. T. Tuominen, and T. P. Russell, *Science*, **290**, 2126 (2000).
- (346) T. Grigorova, S. Pispas, N. Hadjichristidis, and T. Thurn-Albrecht, *Macromolecules*, **38**, 7430 (2005).
- (347) E. Sivaniah, Y. Hayashi, M. Iino, T. Hashimoto, and K. Fukunaga, E. J. Kramer, *Macromolecules*, **36**, 5894 (2003).
- (348) E. Sivaniah, Y. Hayashi, S. Matsubara, S. Kiyono, T. Hashimoto, K. Fukunaga, E. J. Kramer, and T. Mates, *Macromolecules*, **38**, 1837 (2005).
- (349) Y. Tsori and D. Andelman, *Macromolecules*, **36**, 8560 (2003).
- (350) Y. Tsori, E. Sivaniah, D. Andelman, and T. Hashimoto, *Macromolecules*, **38**, 7193 (2005).
- (351) G. Kim and M. Libera, *Macromolecules*, **31**, 2569 (1998).
- (352) G. Kim and M. Libera, *Macromolecules*, **31**, 2670 (1998).
- (353) K. Fukunaga, T. Hashimoto, H. Elbs, and G. Krausch, *Macromolecules*, **35**, 4406 (2002).
- (354) Y. Xuan, J. Peng, L. Cui, H. Wang, B. Li, and Y. Han, *Macromolecules*, **37**, 7301 (2004).
- (355) Z. Q. Lin, D. H. Kim, X. D. Wu, L. Boosahda, D. Stone, L. LaRose, and T. P. Russell, *Adv. Mater.*, **14**, 1373 (2002).
- (356) S. H. Kim, M. J. Misner, M. Kimura, T. Xu, and T. P. Russell, *Adv. Mater.*, **16**, 226 (2004).

- (357) S. H. Kim, M. J. Misner, and T. P. Russell, *Adv. Mater.*, **16**, 2119 (2004).
- (358) T. Xu, J. T. Goldbach, J. Leiston-Belanger, and T. P. Russell, *Colloid Polym. Sci.*, **282**, 927 (1994).
- (359) S. H. Kim, M. Misner, L. Yang, O. Gang, B. M. Ocko, and T. P. Russell, *Macromolecules*, **39**, 8473 (2006).
- (360) J. Ruokolainen, G. H. Fredrickson, E. J. Kramer, C. Y. Ryu, S. F. Hahn, and S. N. Magonov, *Macromolecules*, **35**, 9391 (2002).
- (361) V. Khanna, E. W. Cochran, A. Hexemer, G. E. Stein, G. H. Fredrickson, E. J. Kramer, X. Li, J. Wang, and S. F. Hahn, *Macromolecules*, **39**, 9346 (2006).
- (362) T. Xu, H. C. Kim, J. DeRouchey, C. Seney, C. Levesque, P. Martin, C. M. Stafford, and T. P. Russell, *Polymer*, **42**, 9091 (2001).
- (363) U. Jeong, H. Kim, R. L. Rodriguez, I. Y. Tsai, C. M. Stafford, J. K. Kim, C. J. Hawker, and T. P. Russell, *Adv. Mater.*, **14**, 274 (2002).
- (364) U. Jeong, D. Y. Ryu, J. K. Kim, D. H. Kim, X. Wu, and T. P. Russell, *Macromolecules*, **36**, 10126 (2003).
- (365) U. Jeong, D. Y. Ryu, D. H. Kho, D. H. Lee, J. K. Kim, and T. P. Russell, *Macromolecules*, **36**, 3626 (2003).
- (366) U. Jeong, D. Y. Ryu, J. K. Kim, D. H. Kim, T. P. Russell, and C. J. Hawker, *Adv. Mater.*, **15**, 1247 (2003).
- (367) Q. Wang, Q. Yan, P. F. Nealy, and J. J. de Pablo, *J. Chem. Phys.*, **112**, 450 (2000).
- (368) Q. Wang, P. F. Nealy, and J. J. de Pablo, *Macromolecules*, **34**, 3458 (2001).
- (369) Q. Wang, P. F. Nealy, and J. J. de Pablo, *Macromolecules*, **36**, 1731 (2003).
- (370) U. Jeong, D. Y. Ryu, D. H. Kho, J. K. Kim, J. T. Goldbach, D. H. Kim, and T. P. Russell, *Adv. Mater.*, **16**, 533 (2004).
- (371) K. A. Koppi, M. Tirrel, F. S. Bates, K. Almda, and R. H. Colby, *J. Phys II(France)*, **2**, 1941 (1992).
- (372) V. K. Gupta, R. Krishnamoorti, J. A. Kornfield, and S. D. Smith, *Macromolecules*, **28**, 464 (1995).
- (373) Z. R. Chen and J. A. Kornfield, *Polymer*, **39**, 4679 (1998).
- (374) R. J. Albalak and E. L. Thomas, *J. Polym. Sci.: Polym. Phys. Ed.*, **31**, 37 (1993).
- (375) R. J. Albalak and E. L. Thomas, *J. Polym. Sci.: Polym. Phys. Ed.*, **32**, 341 (1994).
- (376) S. Sakurai, *Polymer*, **49**, 2781 (2008).
- (377) D. E. Angelescu, J. H. Waller, J. H. Adamson, P. Deshpande, S. Y. Chou, R. A. Register, and P. M. Chaikin, *Adv. Mater.*, **16**, 1736 (2004).
- (378) D. E. Angelescu, J. H. R. A. Register, and P. M. Chaikin, *Adv. Mater.*, **17**, 1878 (2005).
- (379) T. Hashimoto, J. Bodycomb, Y. Funaki, and K. Kimishima, *Macromolecules*, **32**, 952 (1999).
- (380) J. Bodycomb, Y. Funaki, K. Kimishima, and T. Hashimoto, *Macromolecules*, **32**, 2075 (1999).
- (381) K. Mita, H. Tanaka, K. Saijo, M. Takenaka, and T. Hashimoto, *Macromolecules*, **40**, 5923 (2007).
- (382) C. De Rosa, C. Park, E. L. Thomas, and B. Lotz, *Nature*, **405**, 433 (2000).
- (383) C. De Rosa, C. Park, B. Lotz, J. C. Wittmann, L. J. Fetters, and E. L. Thomas, *Macromolecules*, **33**, 4871 (2000).
- (384) C. Park, C. De Rosa, L. J. Fetters, B. Lotz, and E. L. Thomas, *Adv. Mater.*, **13**, 724 (2001).
- (385) C. Park, C. D. Rosa, and E. L. Thomas, *Macromolecules*, **34**, 2602 (2001).
- (386) C. Park, J. Y. Cheng, M. J. Fasolka, A. M. Mayes, C. A. Ross, E. L. Thomas, and C. De Rosa, *Appl. Phys. Lett.*, **79**, 848 (2001).
- (387) R. A. Segalman, H. Yokoyama, and E. J. Kramer, *Adv. Mater.*, **13**, 1152 (2001).
- (388) (a) R. A. Segalman, K. E. Schaefer, G. H. Fredrickson, E. J. Kramer, and S. Magonov, *Macromolecules*, **36**, 4498 (2003). (b) R. A. Segalman, A. Hexemer, R. C. Hayward, and E. J. Kramer, *Macromolecules*, **36**, 3272 (2003).
- (389) (a) M. R. Hammond, E. Cochran, G. H. Fredrickson, and E. J. Kramer, *Macromolecules*, **38**, 6575 (2005). (b) M. R. Hammond and E. J. Kramer, *Macromolecules*, **39**, 1538 (2006).
- (390) J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, and G. J. Vancso, *Appl. Phys. Lett.*, **81**, 3657 (2002).
- (391) J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, and G. J. Vancso, *Adv. Mater.*, **15**, 1599 (2003).
- (392) J. Y. Cheng, A. M. Mayes, and C. A. Ross, *Nature Mater.*, **3**, 823 (2004).
- (393) P. Chuang, J. Y. Cheng, T. A. Savas, and C. A. Ross, *Nano Letters*, **6**, 2099 (2006).
- (394) P. Lambooy, T. P. Russell, G. J. Kellogg, A. M. Mayes, P. D. Gallagher, and S. K. Satija, *Phys. Rev. Lett.*, **72**, 2899 (1994).
- (395) T. P. Russell, P. Lambooy, G. J. Kellogg, A. M. Mayes, P. Lambooy, and T. P. Russell, *Macromolecules*, **27**, 6225 (1994).
- (396) D. G. Walton, G. J. Kellogg, and A. M. Mayes, *Physica B*, **22**, 213-214 (1995).
- (397) G. J. Kellogg, D. G. Walton, A. M. Mayes, P. Lambooy, T. P. Russell, and P. D. Gallagher, *Phys. Rev. Lett.*, **76**, 2503 (1996).
- (398) N. Koneripalli, N. Singh, R. Levichy, F. S. Bates, P. G. Gallagher, and S. K. Satija, *Macromolecules*, **28**, 2897 (1995).
- (399) K. Shin, H. Xiang, S. I. Moon, T. Kim, T. J. McCarthy, and T. P. Russell, *Science*, **306**, 76 (2004).
- (400) H. Xiang, K. Shin, T. Kim, S. Moon, T. J. McCarthy, and T. P. Russell, *Macromolecules*, **37**, 5660 (2004).
- (401) H. Xiang, K. Shin, T. Kim, S. Moon, T. J. McCarthy, and T. P. Russell, *J. Polym. Sci.: Part B: Polym. Phys.*, **43**, 3377 (2005).
- (402) H. Xiang, K. Shin, T. Kim, S. I. Moon, T. J. McCarthy, and T. P. Russell, *Macromolecules*, **38**, 1055 (2005).
- (403) Y. Wu, G. Cheng, K. Katsov, S. W. Sides, J. Wang, J. Tang, G. H. Fredrickson, M. Moskovits, and G. D. Stucky, *Nat. Mater.*, **3**, 816 (2004).
- (404) B. Yu, P. Sun, T. Chen, Q. Jin, D. Ding, B. Li, and A. C. Shi, *Phys. Rev. Lett.*, **96**, 138306 (2006).
- (405) P. Chen, H. Liang, and A. C. Shi, *Macromolecules*, **40**, 7329 (2007).
- (406) B. Yu, B. Li, Q. Jin, D. Ding, and A. C. Shi, *Macromolecules*, **40**, 9133 (2007).
- (407) H. Yabu, T. Higuchi, and M. Shimomura, *Adv. Mater.*, **17**, 2062 (2005).
- (408) J. Bang, S. H. Kim, E. E. Drockenmuller, M. J. Misner, T. P. Russell, and C. J. Hawker, *J. Am. Chem. Soc.*, **128**, 7622 (2006).
- (409) S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J.

- de Pablo, and P. F. Nealey, *Nature*, **424**, 411 (2003).
- (410) E. W. Edwards, M. F. Montague, H. H. Solak, C. J. Hawker, and P. F. Nealey, *Adv. Mater.*, **16**, 1315 (2004).
- (411) S. Xiao, X. M. Yang, E. W. Edwards, Y. H. La, and P. F. Nealey, *Nanotechnology*, **16**, S324 (2005).
- (412) E. W. Edwards, M. P. Stoykovich, H. H. Solak, and P. F. Nealey, *Macromolecules*, **39**, 3598 (2006).
- (413) M. P. Stoykovich, M. Muller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. de Pablo, and P. F. Nealey, *Science*, **308**, 1442 (2005).
- (414) M. P. Stoykovich and P. F. Nealey, *Materials Today*, **9**, 20 (2006).
- (415) L. Rockford, Y. Liu, P. Mansky, T. P. Russell, M. Yoon, and S. G. J. Mochrie, *Phys. Rev. Lett.*, **82**, 2602 (1999).
- (416) L. Rockford, S. G. J. Mochrie, and T. P. Russell, *Macromolecules*, **34**, 1487 (2001).
- (417) R. G. H. Lammertink, M. A. Hempenius, J. E. van den Enk, V. Z. H. Chan, E. L. Thomas, and G. J. Vancso, *Adv. Mater.*, **12**, 98 (2000).
- (418) J. Y. Cheng, C. A. Ross, V. Z. H. Chan, E. L. Thomas, R. G. H. Lammertink, and G. J. Vancso, *Adv. Mater.*, **13**, 1174 (2001).
- (419) D. Zschech, D. H. Kim, A. P. Milenin, R. Scholz, R. Hillebrand, C. J. Hawker, T. P. Russell, M. Steinhart, and U. Gösele, *Nano Lett.*, **7**, 1516 (2007).
- (420) K. Naito, H. Hieda, M. Sakurai, Y. Kamata, and K. Asakawa, *IEEE Trans. on Magnetics*, **38**, 1949 (2002).
- (421) C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, T. P. Russell, and M. T. Tuominen, *Appl. Phys. Lett.*, **79**, 409 (2001).
- (422) K. W. Guarini, C. T. Black, Y. Zhang, H. Kim, E. M. Silorski, and I. V. Babich, *J. Vac. Sci. & Tech. B*, **20**, 2788 (2002).
- (423) C. T. Black, *Appl. Phys. Lett.*, **87**, 163116 (2005).
- (424) S. Y. Yang, I. Ryu, H. Y. Kim, J. K. Kim, S. K. Jang, and T. P. Russell, *Adv. Mater.*, **18**, 709 (2006).
- (425) S. Y. Yang, J. H. Yoon, M. H. Ree, S. K. Jang, and J. K. Kim, *Adv. Funct. Mater.*, **18**, 1371 (2008).
- (426) D. H. Kim, K. H. A. Lau, W. Joo, J. Peng, U. Jeong, C. J. Hawker, J. K. Kim, T. P. Russell, and W. Knoll, *J. Phys. Chem. B*, **110**, 15381 (2006).
- (427) D. H. Kim, K. H. A. Lau, J. W. F. Robertson, O.-J. Lee, U. Jeong, J. I. Lee, C. J. Hawker, T. P. Russell, J. K. Kim, and W. Knoll, *Adv. Mater.*, **17**, 2442 (2005).
- (428) K. H. A. Lau, D. H. Kim, and W. Knoll, *Macromol. Res.*, **15**, 211 (2007).
- (429) J. H. Yoon, S. Y. Yang, B. D. Lee, W. C. Joo, K. Y. Heo, J. K. Kim, and M. H. Ree, *J. Appl. Cryst.*, **40**, 305, (2007).
- (430) W. Joo, M. S. Park, and J. K. Kim, *Langmuir*, **22**, 7960 (2006).
- (431) C. Park, M. Rhue, J. Lim, and C. Kim, *Macromol. Res.*, **15**, 39 (2007).
- (432) Y. K. Lee, S. M. Hong, J. S. Kim, J. H. Im, H. S. Min, E. Subramanyam, K. M. Huh, and S. W. Park, *Macromol. Res.*, **15**, 330 (2007).
- (433) C. Choi, M. K. Jang, and J. W. Nah, *Macromol. Res.*, **15**, 623 (2007).
- (434) G. P. Kim, Y. S. Jung, S. B. Yoon, D. W. Kim, and S. H. Baeck, *Macromol. Res.*, **15**, 693 (2007)
- (435) B. J. Kim, D. K. Oh, and J. Y. Chang, *Macromol. Res.*, **16**, 103 (2008).
- (436) M. Haupt, S. Miller, A. Ladenburger, R. Sauer, K. Thonke, J. P. Spatz, S. Riethmuller, M. Moller, and F. J. Banhart, *Appl. Phys.*, **91**, 6057 (2002).
- (437) J. Cornelissen, R. van Heerbeek, P. C. J. Kamer, J. N. H. Reek, N. Sommerdijk, and R. J. M. Nolte, *Adv. Mater.*, **14**, 489 (2002).
- (438) J. P. Spatz, S. Mossmer, C. Hartmann, M. Moller, T. Herzog, M. Krieger, H. G. Boyen, P. Ziemann, and B. Kabius, *Langmuir*, **16**, 407 (2000).
- (439) G. Kästle, H. G. Boyen, F. Weigl, G. Lengel, T. Herzog, P. Ziemann, S. Riethmüller, O. Mayer, C. Hartmann, J. P. Spatz, M. Moller, M. Ozawa, F. Banhart, M. G. Garnier, and P. Oelhafen, *Adv. Funct. Mater.*, **13**, 853 (2003).
- (440) G. Boyen, G. Kästle, K. Zürn, T. Herzog, F. Weigl, P. Ziemann, O. Mayer, C. Jerome, M. Möller, S. J. Patz, M. G. Garnier, and P. Oelhafen, *Adv. Funct. Mater.*, **13**, 359 (2003).
- (441) S. I. Yoo, B.-H. Sohn, W. C. Zin, S. J. An, and G. C. Yi, *Chem. Commun.*, 2850 (2004).
- (442) B. H. Sohn, S. I. Yoo, S. H. Yun, and S. Park, *J. Am. Chem. Soc.*, **123**, 12734 (2001).
- (443) S. H. Yun, B. H. Sohn, J. C. Jung, W. C. Zin, J. K. Lee, and O. Song, *Langmuir*, **21**, 6548 (2005).
- (444) S. H. Yun, S. I. Yoo, J. C. Jung, W. C. Zin, and B. H. Sohn, *Chem. Mater.*, **18**, 5646 (2006).
- (445) A. Ethirajan, U. Wiedwald, H. G. Boyen, B. Kern, L. Han, A. Klimmer, F. Weigl, G. Kästle, P. Ziemann, K. Fauth, J. Cai, R. J. Behm, A. Romanyuk, P. Oelhafen, P. Walther, J. Biskupek, and U. Kaiser, *Adv. Mater.*, **19**, 406 (2007).
- (446) S. Park, B. Kim, J. Y. Wang, and T. P. Russell, *Adv. Mater.*, **20**, 681 (2008).
- (447) A. Frümsdorf, A. Kornowski, S. P. Pütter, H. Stillrich, and L. T. Lee, *Small*, **3**, 880 (2007).
- (448) Y. Guo and M. G. Moffitt, *Macromolecules*, **40**, 5868 (2007).
- (449) H. Zhao, E. P. Douglas, B. S. Harrison, and K. S. Schanze, *Langmuir*, **17**, 8428 (2001).
- (450) M. Moffitt, L. McMahon, V. Pessel, and A. Eisenberg, *Chem. Mater.*, **7**, 1185 (1995).
- (451) S. W. Yeh, T. L. Wu, and K. H. Wei, *Nanotechnology*, **16**, 683 (2005).
- (452) C. W. Wang and M. G. Moffitt, *Chem. Mater.*, **17**, 3871 (2005).
- (453) Y. Boontongkong and R. E. Cohen, *Macromolecules*, **35**, 3647 (2002).
- (454) W. Hwang, M. Ham, B. Sohn, J. Huh, Y. S. Kang, W. Jeong, J. Myoung, and C. Park, *Nanotechnology*, **16**, 2897 (2005).
- (455) X. Li, S. Tian, Y. Ping, D. H. Kim, and W. Knoll, *Langmuir*, **21**, 9393 (2005).
- (456) X. Li, K. H. A. Lau, D. H. Kim, and W. Knoll, *Langmuir*, **21**, 5212 (2005).
- (457) J. N. Cha, Y. Zhang, H. S. P. Wong, S. Raoux, C. Rettner, L. Krupp, and V. Deline, *Chem. Mater.*, **19**, 839 (2007).
- (458) M. Aizawa and J. M. Buriak, *Chem. Mater.*, **19**, 5090 (2007).
- (459) S. Zou, R. Hong, T. Emrick, and G. C. Walker, *Langmuir*, **23**, 1612 (2007).
- (460) Y. Kang, K. J. Erickson, and T. A. Taton, *J. Am. Chem. Soc.*, **127**, 13800 (2005).
- (461) J. Peng, W. Knoll, C. Park, and D. H. Kim, *Chem. Mater.*, **20**, 1200 (2008).