Well Ordered Polymer Melts from Blends of Disordered Triblock Copolymer Surfactants and Functional Homopolymers**

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Microphase segregated block copolymer melts and solids have long garnered significant scientific interest due to their ability to spontaneously form periodic morphologies at controllable length scales.[1–3] Their utility as stand-alone nanostructured functional materials[4–8] or as templates for the fabrication of hierarchical solids[9–12] is well documented. However, their deployment in large scale applications has often been limited by the cost and scalability of the living polymerization techniques necessary for the precise control of molecular parameters required to achieve well defined morphologies. Here, we report that well ordered, processible, and functional polymer melts with periodic nanostructures can be obtained in bulk quantity by simple blending of commercially available triblock copolymer surfactants with a series of commodity homopolymers that selectively associate with one of blocks through hydrogen bonding. While the neat surfactants are disordered in the melt, scattering measurements indicate that the blends undergo a disorder-to-order transition to yield stable microphase separated structures. Moreover, the functional groups present in the homopolymers provide a convenient handle for subsequent templating schemes including phase selective chemistries and depositions, chemical modifications, and binding of active dopants including nanoparticles. The results are general, and suggest a low cost, high volume strategy to produce ordered spherical, cylindrical, or lamellar microphase separated polymer melts for commercial use.
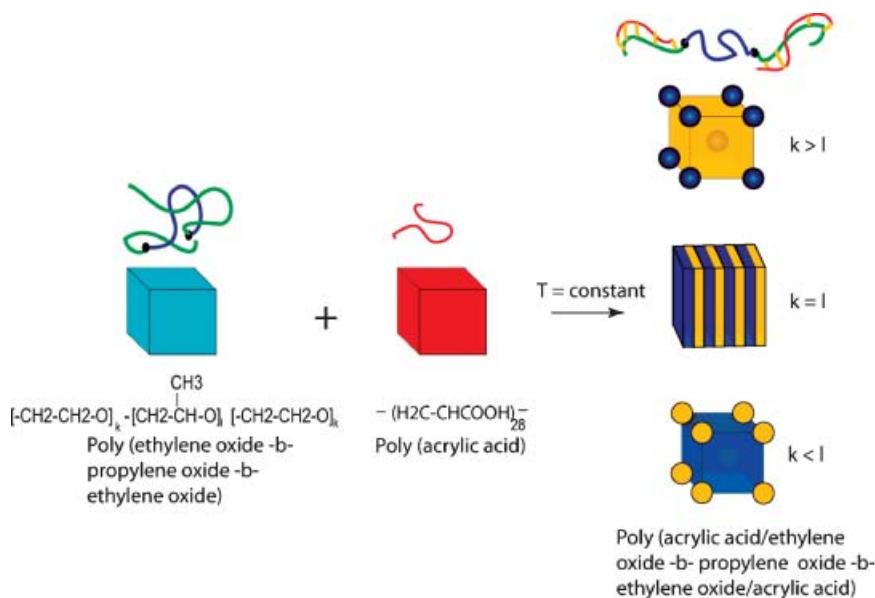
The microphase segregation of block copolymers is governed thermodynamically by the product of Flory–Huggins interaction parameter (χ) of the copolymer segments and the total number of monomers per copolymer chain (N).[13,14] Since the molecular interactions for a given copolymer are dictated by their chemical structure, the segregation strength (χN) of block copolymers can be tuned by changing the copolymer molecular weight (N). The segment-segment interaction parameter (χ) on the other hand, can be increased by altering the chemical composition of one of the blocks or by the selective chemical modification of the segments (e.g., sulfonation of styrenic groups). Additional structural control is afforded by manipulating the copolymer architecture through the use of linear and branched sequences.[15,16] The past twenty years of research has resulted in a remarkable palette of accessible phases and copolymer chemistry, including triply periodic bicontinuous structures.[17] This palette has been further expanded to generate hierarchical morphologies through the supramolecular assembly of well-defined block copolymers with small molecule amphiphiles that can hydrogen bond with one of the blocks.[17,18] While careful control of structure can be achieved through various protocols, each is relatively costly and well ordered, microphase separated functional copolymer melts are essentially unavailable at the bulk scale.

We find that the domain segregation of low molar mass amphiphilic block copolymers, including samples with relatively broad molar mass distributions, can be dramatically increased by simply blending with a homopolymer that strongly associates with the hydrophilic segment through hydrogen bonding. The selective association of homopolymer increases the effective segregation strength as a result of significantly increased effective interaction parameter in the blend. Specifically, we apply this principle to the family of poly(oxyethylene-oxypropylene-oxyethylene) (PEO_mPPO_n-PEO_m, Pluronic™) triblock copolymers.[19] Pluronic™ or Poloxamer™ surfactants are inexpensive, commercially available from many companies in large quantities for use in a variety of detergent, pharmaceutical, and cosmetic applications, and can be melt-processed at reasonable temperatures ($T_m \approx 60\,°C$).[20] They are synthesized by base-catalyzed cationic polymerization using difunctional propylene glycol and monofunctional ethylene glycol reactants. The formation of monofunctional allylalcohol from PPO as a byproduct of the polymerization results in diblock copolymers and broadens the molar mass distribution ($M_w/M_n \approx 1.2$–1.3).[21] While the PEO-PPO-PEO architecture is nominally a tri-block copolymer, the surfactants are disordered in their melt state due to a low segregation strength that is both a result of their low molar mass (F108 has the highest mol. wt. of $14500\,g\,mol^{-1}$) and the weakly repulsive PEO-PPO interactions ($\chi_{PEO\text{-}PPO} \approx 0.066$–0.068 at $80\,°C$).[22,23]

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Scheme 1. Schematic representing the generation of ordered microphases with the addition of a homopolymer to a phase-mixed triblock copolymer melt. The phase-mixed copolymer is represented by the mixture of colors, *blue and green*, and the homopolymer is represented by the color *red*. The phase separated structures in the blend are thus represented by blue and yellow (≈red + green) after assessing the relative miscibility of homopolymer with the copolymer segments using neutron scattering. *k* and *l* represent the number of EO and PO blocks, respectively.

in the ODT that are expected and driven by the changes in apparent volume fraction.

In this work, three Pluronic copolymers spanning a range of volume fractions ($\phi_{EO} \approx 0.2–0.83$) are used to establish the generality of this approach to EO_m-PO_nEO_m triblock systems. Pluronic F108, P105, and L92 copolymers have 80, 50, and 20% oxyethylene by volume, respectively. The copolymers used, their total chain length, volume fraction of EO per chain, expected microphase morphology, mean-field segregation strength $(\chi N)_c$ and the corresponding ODT temperature required for their phase separation are given in Table 1. The $(\chi N)_c$ required for pure EO-PO-EO copolymers is estimated from mean-field theory to be 18 for lamellae, 20 for cylinders, and 23 for spheres.[26] From Table 1, we find that none of the polymers studied here, even if monodisperse, would have the χN necessary to form ordered microphases in the melt above 60 °C. Therefore, we measured the effect of added homopolymer on the melt-phase morphology of Pluronic

We first show that blending the disordered Pluronic copolymers with a functional homopolymer such as poly-(acrylic acid) (PAA) yields well ordered microphase-separated melts (Scheme 1). While mean field calculations based on the random phase approximation[3] suggest that blends of block copolymers with homopolymers that exhibit strong attractive interactions with one of the blocks can lead to microphase separated systems,[24] we believe the work reported here is the first to demonstrate generation of well ordered copolymer melts upon the addition of homopolymer to *disordered* copolymer systems. It is important here to draw the distinction between phase segregation induced by an increase in the effective interaction parameter and morphological transitions induced by changes in the apparent volume fraction.[25] The latter are well known: for example, the addition of homopolymer that is chemically identical to one of the blocks can lead to transitions between morphologies in systems that are inherently well segregated as well as result in modest increases

copolymers at 80 °C using small-angle X-ray scattering (SAXS).

In Figure 1, we plot the change in SAXS profiles of Pluronic copolymers F108 (Fig. 1a), P105 (Fig. 1b), and L92 (Fig. 1c) as a function of added PAA concentration. The full-width at half-maximum (FWHM) of the primary SAXS peak decreases in all three systems as the PAA concentration is increased. The broad scattering peak from Pluronic copolymer blends with less than 20% PAA by mass represents compositional fluctuations observed typically in disordered copolymer melts. The decreased FWHM suggests that the PEO-PPO compositional fluctuations are strongly correlated in blends than in the neat copolymer. In other words, the Pluronic triblock copolymers undergo a disorder-to-order transition (DOT) with the addition of PAA. In the Pluronic F108 copolymer, which has the highest χN among the systems studied, addition of PAA above 25% by mass also leads to two higher order scattering peaks at $\sqrt{2}q^*$ and $\sqrt{3}q^*$. These higher order

Table 1. Molecular parameters of oxyethylene-oxypropylene-oxyethylene triblock copolymers, $EO_mPO_nEO_m$.

Copolymer	M_n [g mol^{-1}][a]	M_w/M_n[a]	Volume Fraction of polyoxyethylene ϕ_{EO}	N[b]	$(\chi N)_{est.}$[c]	$(\chi N)_c$[d]	Estimated ODT Temperature [°C]
Pluronic L92	3,798	1.12	0.19	85.6	5.75	40	−159.5
Pluronic P105	5,971	1.263	0.48	157.9	10.5	19	1
Pluronic F108	14,984	1.233	0.79	325	21.85	32	30
$E_{70}(dP)_{31}E_{70}$	8,200	1.08	0.79	185.9	12.5	32	−46

[a]Private Communication, BASF. [b]Chain length (liquid), $N = m + 1.48n$ (see Ref. [22]); [c]$\chi(T) = (-0.122 \pm 0.022) + \frac{(66.8 \pm 8.2)}{T}$ (see Ref. [22]); [d]Ref. [24].
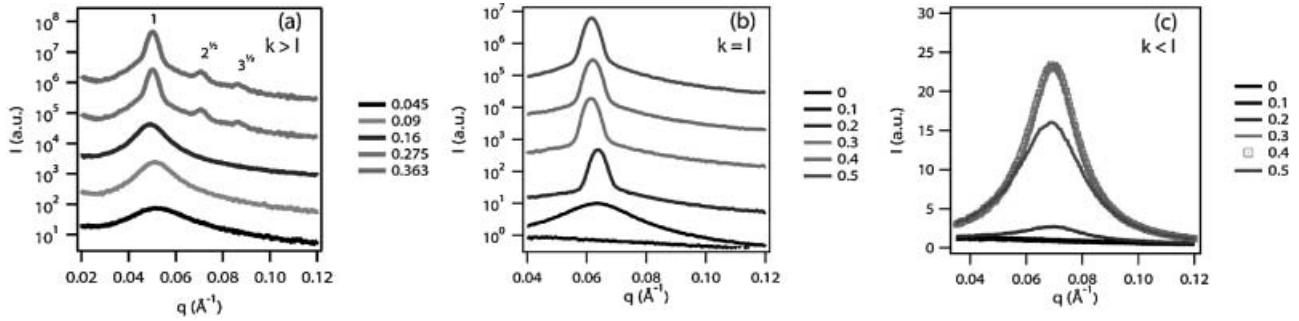
Figure 1. The change in SAXS profiles of bulk Pluronic a) F108, b) P105, and c) L92 copolymer melts obtained by blending with PAA at 80 °C. Scattering data in (a) and (b) are shifted in intensity for clarity.

reflections represent longer range correlations of a body-centered cubic lattice with minimum lattice distortions, which is an indication of significantly improved domain segregation. The ordered microphases in each copolymer correspond to a minimum increase in χN by 50% to 300%. Interestingly, the interdomain spacing ($d \approx 2\pi/q*$) in PAA/Pluronic copolymer blends does not significantly change (<5 Å) with blend composition, which implies a decrease in the interfacial area per block copolymer chain at the domain boundary.

A Pluronic-like dF68 copolymer (Table 1) with a perdeuterated PO (dPO) segments and well-defined polydispersity is employed to accurately ascertain the relative miscibility of PAA with EO and PO segments and the changes in blend morphology using small-angle neutron scattering (SANS) at beamlines NG7 and NG3 of the NIST Center for Neutron Research.[27] Since neutrons primarily scatter due to a difference in nuclear density, SANS from hydrogenous PAA/dF68 blends is only due to the correlation between dPO domains. Neutron measurements were performed on blend thin films with a view on technological implications of templates self-assembled on a silicon substrate.[28] The segregation strength of dF68 copolymer is estimated to be about 12.5 and the corresponding ODT temperature is well below 0 °C. The change in absolute intensity position and FWHM of the primary SANS peak from PAA/dF68 blends measured at 80 °C is shown in Figure 2a and b.[29] The increased SANS intensity from blends shows that PAA is strongly selectively miscible with the EO segments. The domain segregation in dF68 blends also increases

dramatically with PAA concentration as observed from the decrease in FWHM. The actual increase in effective χN ($\sim 1/$ ODT) is measured as an increase in the ODT temperature. The neat dF68 copolymer is phase-mixed at room temperature but compositional fluctuations emerge in the disordered melt and remain stable until 150 °C (Fig. 2c). Its blend with PAA at 40% by mass, on the other hand, remains highly ordered throughout the entire temperature range 25–150 °C (Fig. 2d).[30] Note that the PAA used is "off-the-shelf" and exhibits a broad molar
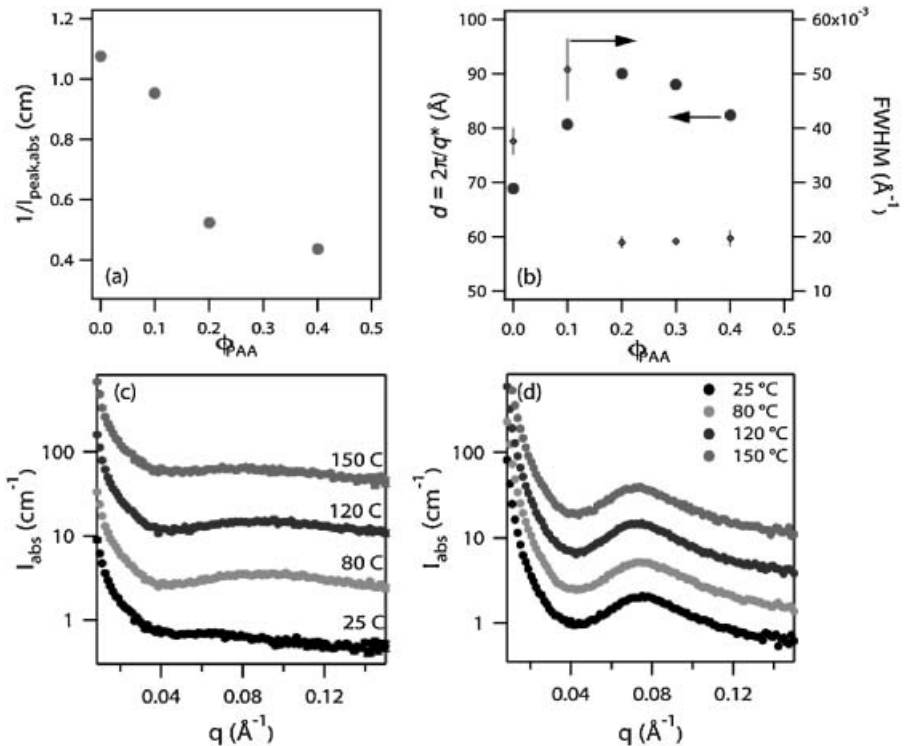

Figure 2. Change in a) absolute intensity, b) full-width at half-maximum, and interdomain spacing calculated from the primary neutron scattering peak in dF68 copolymer as a function of PAA concentration at 80 °C. The dF68 copolymer corresponds to Scheme 1a, as discussed in Scheme 1. SANS profiles from c) neat dF68 copolymer and d) its PAA blend thin film at 40% by mass as a function of temperature in the range 25 to 150 °C. Data in (c) and (d) are in absolute units at 25 °C while those at higher temperatures are offset in intensity by factors (100, 200, and 300) cm^{-1} in (c) and (50, 100, and 150) cm^{-1} in (d), respectively.

Table 2. Molecular parameters of homopolymers used in this study.

Polymer	M_n [g mol^{-1}]	M_w/M_n
PAA (off-the-shelf)	1,000	1.8
PAA (narrow)	8,500	1.07
PVPh	8,000	1.2
PAMPS	45,000	1.43

mass distribution. The actual increase in ODT is much higher when PAA with narrow molar mass distribution ($M_n \approx 8,500$ g mol^{-1}; $M_w/M_n \approx 1.07$) is used. The ordered morphology in that case remains stable even up to 175 °C (not shown here). These results show that blending with PAA increases the ODT of PEO-PPO-PEO triblock copolymers by at least 150 °C.

The effective χN in PAA/Pluronic copolymer blends is much higher than that in the neat copolymer due probably to the selective hydrogen bonding (H-bonding) interactions between AA and EO segments. H-bonding between AA and EO could increase the EO-PO repulsion and result in a higher effective segment-segment interaction parameter ($\chi_{PAA/EO-PO} > \chi_{EO-PO}$). To extend the applicability of this approach to any homopolymer with H-bonding interactions, we measured the melt phase morphology of dF68 blended with different homopolymers using SANS (Table 2). Homopolymers with varying affinity and strength of hydrogen bonding are chosen: (i) poly(4-vinylphenol) (PVPh), (ii) poly(styrene sulfonate) (PSS), and (iii) poly(2-acrylamido-2-methy-l,1-propanesulfonic acid) (PAMPS). PVPh is highly polarizable and is well known for its hydrogen bonding with EO segments. PAMPS and PSS are both negatively charged but the styrenic backbone on the latter increases the entropy due to mixing. In Figure 3b, we compare the change in position and FWHM of the primary scattering peak in blends of dF68 with different homopolymers at 40% by mass. That the addition of any homopolymer with selective H-bond interactions will significantly improve the domain segregation of dF68 copolymer melt is clearly evident from the decrease in FWHM of the scattering peak. The improved domain segregation is due to an increase in the effective $\chi_{(homopolymer/EO)-PO}$ resulting from the selective homopolymer/EO enthalpic interactions ($\chi_{homopolymer/EO} < 0$). The difference in the H-bonding affinity of added homopolymers is thus an additional variable to further tune the template morphology. For example, the dF68 copolymer template is better

ordered when blended with PAMPS than with PAA at 40% by mass, as observed from the second order peak in SANS (Fig. 3c). This difference can be attributed to the higher number of H-bonding sites accessible in PAMPS (–CONH and SO$_3$H) compared to that in PAA (–COOH).

The selective miscibility of PAA with EO segments also leads to order-order transitions in its blends of commercial Pluronic copolymers such as P123 and P105 (not shown here).[31] The observed order-order transitions are driven more by an increase in the effective interaction parameter, $\chi_{(AA/EO-)-PO}$, than from a simple increase in the effective chain length, N_{AA+EO}. The decrease in peak intensity of PAA/L92 blend at 50% PAA could similarly correspond to a change in morphology from spheres-to-cylinders. Our results conclusively demonstrate that nanostructured templates with characteristic spacing ≤ 10 nm can be generated by simply mixing inexpensive Pluronic copolymer melts with a functional homopolymer. Blending with a homopolymer is an efficient approach to selectively functionalize amphiphilic block copolymer melts. We note that increasing the molar mass of Pluronic-like analogues will increase segregation strength further and provide access to broad range of domain sizes. We also expect the blending strategy to be generally applicable to amphiphilic copolymer systems in which hydrogen bonding is possible (e.g., polyoxyalkylene-based copolymers). When combined with methods such as shear-induced ordering, our approach could readily yield nanostructured templates with good long-range order in industrially relevant quantities and
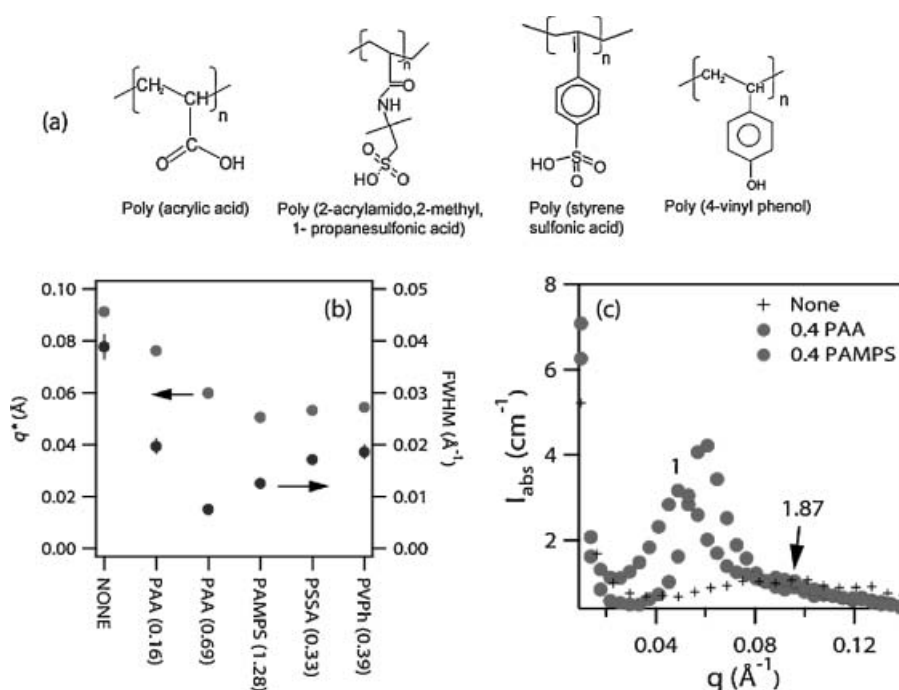

Figure 3. b) Change in the position (q^*) and the FWHM of the primary SANS peak from dF68 obtained by blending with homopolymers shown in (a) at 40% by mass. Abscissae represent the homopolymer degree of polymerization relative to that of dF68 copolymer. c) compares the SANS from dF68 blended with PAA and PAMPS homopolymers at 40% by mass.

may broaden their applicability to the fabrication of materials with improved functionalities. For example, mesoporous silica films synthesized from PAA/F127 blends exhibit exceptional order and increased porosity which may translate into better mechanical properties and lower dielectric constant.[32]

Experimental

Materials: Pluronic copolymers were kindly donated by BASF Corporation. Poly(acrylic acid) (PAA) and poly(4-vinyl phenol) (PVPh) homopolymers were purchased from Sigma–Aldrich Chemical Company and E. I. du Pont de Nemours and Company, respectively. Homopolymers PAA and poly(styrenesulfonic acid) with well-defined molar mass distribution were purchased from Polymer Source Incorporation. Poly(2-acrylamido-2-methyl-1-propanesulfonic acid) was synthesized in Prof. Lynn Loo's laboratory at the University of Texas, Austin, by Joung Eun Yoo. All the chemicals were used as-is without further purification.

Blends of block copolymer and homopolymer were prepared by codissolving them at a given weight ratio in ethanol. Bulk samples (≈ 2 mm thickness) used in X-ray scattering and thin film samples ($\approx 0.5 \mu$m thickness) used in neutron scattering were prepared by respectively solvent-casting and spin-coating on silicon wafers from solution.

X-Ray Scattering: Small-angle X-ray scattering (SAXS) [33] experiments were performed using the Rigaku-Molecular Metrology SAXS equipment at the W. M. Keck Nanostructures Laboratory (a NSF-MRSEC supported open access user facility), University of Massachusetts Amherst. Bulk blend samples were vacuum-dried overnight to remove residual traces of ethanol. SAXS of the bulk samples encapsulated between two kapton windows was then measured in the temperature range 80 °C after annealing at 130 °C for 30 min. Scattered X-rays were collected onto a 2-D wire array detector located at a distance of 1.195 m that corresponds to the measured q-range, 0.06 nm$^{-1} < q < 1.6$ nm^{-1}. Scattering data is presented in arbitrary units.

Neutron Scattering: Small-angle neutron scattering (SANS) experiments were performed at 30 m small-angle neutron scattering instruments NG7 and NG3 at the NIST Center for Neutron Research. The self-assembled morphology of blends was measured under vacuum from stacks of (10 to 14) thin films. The silicon wafers supporting the films are transparent to incident neutrons allowing direct characterization of the microphase morphology. The scattered intensity was measured at a sample-to-detector distance of 4.5 m using neutrons of wavelength, $\lambda \approx 0.6$ nm and wavelength spread $\Delta\lambda/\lambda = 0.11$. The measured q-range was 0.085 nm$^{-1} < q < 1.5$ nm^{-1}, where $q = (4\pi/\lambda)\sin(\theta)$ and 2θ is the scattering angle. The data were corrected for scattering from instrument background, blank silicon wafers, detector sensitivity, and was converted into absolute intensity units (cm^{-1}).

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[31] X-ray reflectivity measurements on blend thin films show that (i) the PAA/P123 blends undergo a cylindrical-to-lamellae transition between 26.5 to 28.5% PAA by mass, and (ii) PAA/P105 blends undergo a lamellae-to-cylindrical transition when PAMPS instead of PAA is added at 20% by mass. The observed order-order transitions are driven more by an increase in the effective interaction parameter, χ(homopolymer/EO-)-PO, than from a simple increase in the effective chain length, $N_{homopolymer + EO}$.

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