

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/278325668>

Control of Self-Assembled Structure through Architecturally and Compositionally Complex Block Copolymer Surfactant Mixtures

ARTICLE *in* MACROMOLECULES · OCTOBER 2014

Impact Factor: 5.8 · DOI: 10.1021/ma5012667

CITATIONS

4

READS

15

5 AUTHORS, INCLUDING:



[Xu Wang](#)

State University of New York Upstate Medical ...

11 PUBLICATIONS 247 CITATIONS

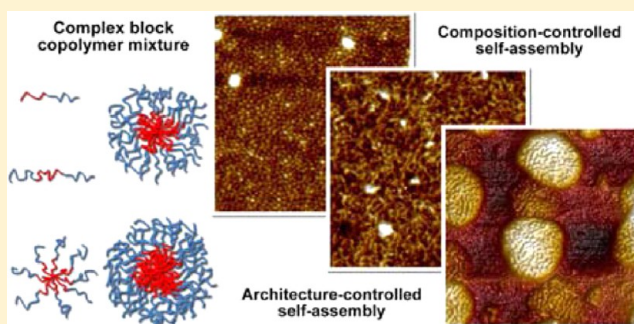
SEE PROFILE

Control of Self-Assembled Structure through Architecturally and Compositionally Complex Block Copolymer Surfactant Mixtures

Xu Wang,^{†,⊥} Jesse L. Davis,^{†,⊥} Juan Pablo Hinestrosa,[‡] Jimmy W. Mays,[†] and S. Michael Kilbey, II^{*,†,§}[†]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States[‡]Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States[§]Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States

S Supporting Information

ABSTRACT: The self-assembly of binary mixtures of architecturally and compositionally diverse surfactant-like polystyrene–poly(2-vinylpyridine) (PS–PVP) block copolymers (BCPs) in solution and in thin films has been systematically studied. PS–PVP BCPs of different molecular architecture synthesized by living anionic polymerization, including linear diblocks, triblocks, and branched star-like copolymers all having different block sizes, styrene to 2-vinylpyridine ratios, and variations in numbers of arms, were employed as constituent building blocks for the construction of advanced copolymeric ensembles. While ensembles formed from monomodal PS–PVP BCPs exhibit simple spherical aggregate structures in the PS-selective solvent toluene, aggregates created by mixing PS–PVP BCPs of different architecture display structures that include spherical, worm-like and large compound micellar aggregates. This result is attributed to the complex, architecture-induced diversity of microphase segregation in the mixed systems, wherein the fine-scale structures of the resultant ensembles can be further controlled by adjusting the blend composition. For example, unique hierarchically structured large compound micellar aggregates with spherical primary structures and worm-like secondary structures that resemble a brain coral were directly created when a 1:1 mixture (by weight) of a triblock copolymer and a star BCP that was cast in thin film form. The present study is valuable for illuminating the range of structures that may be created through architecture- and composition-controlled self-assembly of amphiphilic copolymer mixtures, which generally benefits the development of self-assembly as a method to make soft matter building blocks, as well as connections between self-assembled structures in solution and their thin films.



■ INTRODUCTION

Self-assembly of copolymeric systems^{1,2} is viewed as a driver of technological advances that rely on the capacity of block copolymers (BCPs) to microphase segregate into well-defined and sometimes complex structures in solution, in bulk, and in thin films.^{3–9} Amphiphilic BCPs are widely studied due to their surfactant-like nature that promotes self-assembly as well as their ability to straddle interfaces. The combination of the extraordinary ability to control the chemical composition and integrate different monomeric building blocks through advanced polymerization methods inspires their use in many applications, such as templates for preparing inorganic constructs,^{10–13} nanocarriers for delivery of therapeutic agents¹⁴ or bioactive materials,¹⁵ fabrication of tunable optical materials,^{16,17} or films with self-healing characteristics,¹⁸ to name a few. As a result, elucidating links between BCP design, assembly conditions, and structure continues to be an important theme in soft matter science.^{2,3a,19} In terms of solution behavior, efforts over the past 2 decades have been devoted primarily to the self-assembly of well-defined linear polymer amphiphiles;^{1,20,21} the self-assembly behaviors of

architecturally complex BCPs^{22–24} or mixtures of polymer amphiphiles have been studied much less in comparison.^{25–42}

In contexts other than biological systems, polymers contain a mixture of chain lengths. While a large polydispersity can drive macrophase segregation of diblock copolymer melts,⁴³ BCPs are generally robust in the sense that low levels of polydispersity are tolerated within their microphase segregated structures. In amphiphilic systems self-assembled in solution, mixing chains of different degrees-of-polymerization or composition can alter the size and shape of micellar aggregates,⁴⁴ sometimes allowing exotic ensemble structures marked by undulations or distortions to be formed. For example, Mahanthappa and co-workers showed that polydispersity in the core block of poly(ethylene oxide-*block*-1,4-butadiene-*block*-ethylene oxide) (PEO–PB–PEO) triblock copolymers affects the interfacial curvature, allowing ellipsoidal-shaped micelles to form.^{44b} This ability of BCPs to balance

Received: June 18, 2014

Revised: September 21, 2014

Published: October 13, 2014

Table 1. Molecular Characteristics and Self-Assembly Properties of Surfactant-Like PS–PVP BCPs in Toluene[†]

sample ID	BCP	M_w (kg/mol) ^a	PDI	S/V	dn/dc (mL/g)	concentration (mg/mL)	micellization property ^b	R_{h1} (nm) ^c	R_{h2} (nm) ^c
D1	PS-PVP	[100-60]	1.08	1.7	0.199	1.0	I, M	11	166
D2	PS-PVP	[54-14]	1.11	3.9	0.195	1.0	I, M	6	88
D3	PS-PVP	[255-24]	1.06	10.6	0.189	1.0	I, M	14	142
T1	PVP-PS-PVP	[31.25-62.5-31.25]	1.40	1	0.099	8.0	I, M	9	285
T2	PVP-PS-PVP	[12-96-12]	1.20	4	0.113	8.0	I, M	8	130
T3	PVP-PS-PVP	[6.2-124-6.2]	1.20	10	0.108	8.0	I, M	8	134
S1	[PS-PVP] ₈	[27-27] ₈	1.18	1	0.086	8.0	I, M	19	102
S2	[PS-PVP] ₈	[42-14] ₈	1.09	3	0.117	8.0	I, M	16	189
S3	[PS-PVP] ₈	[42-6] ₈	1.23	7	0.086	8.0	U	26	
S4	[PS-PVP] ₂₆	[50-50] ₂₆	1.23	1	0.104	1.0	U	40	
S5	[PS-PVP] ₂₆	[102.5-20.5] ₂₆	1.45	5	0.097	1.0	U	61	
S6	[PS-PVP] ₂₆	[103.8-11.5] ₂₆	1.36	9	0.106	1.0	U	53	
S7	[PS-PVP] ₄₀	[53.75-53.75] ₄₀	1.26	1	0.107	1.0	U	52	
S8	[PS-PVP] ₄₀	[106.25-21.25] ₄₀	1.16	5	0.106	1.0	U	75	
S9	[PS-PVP] ₄₀	[108-12] ₄₀	1.30	9	0.085	1.0	U	77	

[†]Key: (a) Total molecular weight of linear copolymers is the sum of the values in square brackets (individual block molecular weights), and total molecular weight of star copolymers is the product of the sum of the block molecular weights (in square brackets) and the average number of arms (subscript). (b) Micellization properties of BCPs in toluene at concentrations above the CMCs (using I for isolated chains, M for multimolecular micelles, and U for unimolecular micelles). (c) Results obtained from DLS in toluene at $c = 1.0$ mg/mL for diblocks, 26- and 40-arm stars, and at $c = 8.0$ mg/mL for triblocks and 8-arm stars.

interfacial curvature and stretching of the core and corona blocks has been shown to give rise to even more complex structures in mixed systems: Bates and Jain showed that binary mixtures of nearly monodisperse PEO–poly(1,2-butadiene) diblock copolymers having different compositions and molecular weights in aqueous solution could form sophisticated structures.^{25a} For example, around compositions where single-chain systems formed branched worm-like micelles or network structures, bimodal mixtures formed interesting octopus-like structures that appear to have cylindrical structures with varying local curvature radiating from a central disk-like core.

In terms of blending different types of amphiphilic BCPs, Zhu et al. recently reported the construction of multigeometry, soft nanoparticles consisting of disk–sphere and disk–cylinder shapes by blending of two different linear BCPs in a water/THF mixed solvent system. The multigeometry aggregates form because the incompatible solvophobic blocks locally phase segregate within the assembly, with each type of BCP contributing its characteristic phase segregated structure (bilayer vesicle, cylinder-like, or sphere) to the complex hybrid nanoparticle.⁴⁵ This strategy of kinetic control can be used to construct novel soft matter nanostructures with designed compositions and geometries from simple linear BCPs. The blending of more sophisticated chain architectures can also lead to multigeometry nanoparticles. Lodge and co-workers examined the morphology of 3-arm, ABC star-like terpolymers consisting of mutually immiscible blocks (ethyl–ethylene, ethylene oxide, and perfluoropropylene oxide), and mixed these with the corresponding AB diblock copolymer synthesized as an intermediate to the star terpolymer. The segregation behavior of the three arms of the star resulted in multicompartment worm-like micelles of various lengths. Most striking, when the sphere-forming AB diblock was mixed with the star terpolymer, fusion of the aggregates and chain rearrangements within the nanostructures led to the formation of “hamburger-like” micelles. In addition to this interesting structure, the slow evolution through aggregate fusion and breakup yielded asymmetric multicompartment micelles of various size.⁴⁶ In

total, these studies highlight the richness of mixing architecturally and compositionally diverse BCP amphiphiles.

Despite the potential for realizing new aggregate shapes and for tuning structure, understanding the self-assembly behavior of complex BCP mixtures is in its infancy. In particular, there have been no systematic studies of the self-assembly of BCP mixtures with both architectural and compositional variations. With this in mind, we examine the structures adopted in solution and in thin films when amphiphilic polystyrene–poly(2-vinylpyridine) (PS–PVP) BCP amphiphiles are self-assembled in the PS-selective solvent toluene. Binary mixtures created from pairs of diblock + triblock, diblock + star, and triblock + star copolymers are explored across a range of compositions and, in the case of the stars, with varying number of diblock copolymer arms. While self-assembly of the single component PS–PVP BCPs tends to yield spherical structures—either spherical micelles in the case of the linear BCPs or unimolecular micelles for the stars with a large number of arms—the mixtures adopt more complex architectures depending on the diversity of component architecture and macro-molecular composition.

EXPERIMENTAL SECTION

Materials. The diblock, triblock, and star copolymers comprising polystyrene (PS) and poly(2-vinylpyridine) (PVP) blocks were synthesized via anionic polymerization using custom-built, all-glass reactors with break-seals. The synthesis of these materials has been published separately^{47–49} and, therefore, is not repeated here. The polymers were characterized by a combination of size exclusion chromatography, multiangle laser light scattering, ¹H NMR spectroscopy, and elemental analysis,^{47–49} and the results are summarized in Table 1. In terms of molecular topology, the triblocks have a center PS block connected to PVP end blocks, and the arms of the stars have a diblock structure with PS as the first block emanating from the central core and PVP as the outer block. The chemical structures of styrene and 2-vinylpyridine monomers are shown in the inset in Figure 1a. Throughout this paper we refer to the BCPs by the molecular weight of the PS and PVP blocks (in kg/mol), styrene to 2-vinylpyridine ratio (S/V), and architecture using D for diblock, T for triblock, and S for star.

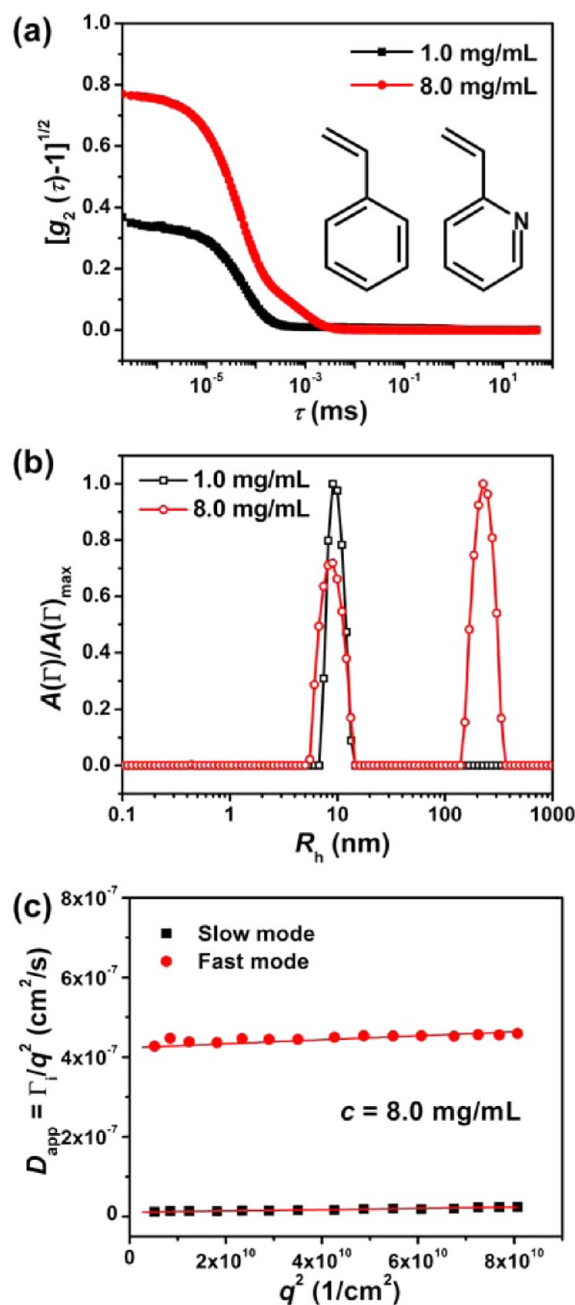


Figure 1. Light intensity autocorrelation functions (a), hydrodynamic radii, R_h , distributions (b), and apparent diffusion coefficient D_{app} versus q^2 (c) for sample T1 in toluene. Insets in part a are the chemical structures of styrene (left) and 2-vinylpyridine (right).

BCP Solution Preparation. Binary mixtures of BCPs were created using a premixing method in which the constituent BCPs were separately dissolved in the nonselective solvent THF at a concentration of 8.0 mg/mL. After equilibration for 3 days, the solutions were mixed together (in different proportions, including v:v = w:w = 1:1, 3:1, or 1:3) and subjected to ultrasonication for 10 min. The mixtures were dried at room temperature for 48 h and then dried further under vacuum at 60 °C for 6 h to completely remove any remaining THF. After cooling to room temperature, the blends were dissolved in toluene to make solutions having concentrations of either 1.0 or 8.0 mg/mL and then ultrasonicated for 10 min. These toluene solutions containing mixtures of BCPs were then stored in sealed vessels at room temperature for a minimum of 5 days before use. The structure adopted by self-assembly of each parent PS–PVP BCP was also characterized, and for these experiments, solutions of the BCPs in

toluene at 1.0 or 8.0 mg/mL were prepared gravimetrically, subjected to ultrasonication for 10 min to aid dissolution, and then allowed to equilibrate for at least 5 days.

Film Preparation. Diced silicon substrates obtained from Silicon Quest were ultrasonically cleaned successively in toluene, 2-propanol, methanol and deionized water, each for 15 min, and then immersed in a “piranha acid” solution (a 1:3 v/v mixture of 30% H₂O₂ and 98% H₂SO₄) and heated until no bubbles evolved. After this cleaning, the silicon substrates were rinsed with copious amounts of distilled water and then dried with N₂ flow. Thin films were made on silicon substrates by spin-coating 50 μ L of the polymer solution (in toluene at a polymer concentration of 8.0 mg/mL) at 2000 rpm for 1 min using a Laurell WS-400B-6NPP-LITE spin coater. The as-prepared film thicknesses are \sim 40 nm, as measured using a Beaglehole Instruments Picometer ellipsometer at multiple angles of incidence ranging from 80° to 60° using 1° increments.

Characterization. Dynamic light scattering (DLS) measurements were performed as described previously^{22,50} using a four-detector ALV goniometer system equipped with a linearly polarized 22 mW HeNe laser operating at a wavelength, λ , of 632.8 nm. The signal is processed using an ALV 7000 multiple tau digital correlator with an initial sampling time of 125 ns and the temperature is maintained at 25 ± 0.1 °C in all experiments. Approximately 1.5 mL of polymer solution was added to previously cleaned, dust-free 10 mm borosilicate glass cuvettes and these were sealed with a Teflon cap. DLS measurements were made at 16 angles ranging from 20° to 146° and a counting time of 600 s was used at each angle in order to obtain reliable statistics for the light intensity autocorrelation function, $g_2(q, \tau)$, defined by the Siegert relation as

$$g_2(q, \tau) = 1 + g_1(q, \tau)^2 = \frac{\langle I(q, t)I(q, t + \tau) \rangle}{\langle I(q, t) \rangle^2} \quad (1)$$

Here $I(q, t)$ is the scattered light intensity at time t and $g_1(q, \tau)$ is the first-order electric field time correlation function, which depends on the delay time τ and the scattering wave vector, q , which is determined from the scattering angle θ , λ and the solvent refractive index, n : $q = (4\pi n/\lambda) \sin(\theta/2)$. The autocorrelation functions obtained at each scattering angle were analyzed first by the CONTIN algorithm to determine the amplitude distribution of decay rates, $A(\Gamma)$, which provides insight into the population(s) of scatterers in solution. CONTIN uses a regularization method in order to resolve $A(\Gamma)$ such that it satisfies the expression

$$[g_2(\tau) - 1]^{1/2} = g_1(\tau) = \int_0^\infty A(\Gamma) e^{-\Gamma\tau} d\Gamma \quad (2)$$

For systems where the CONTIN analysis shows one peak in the distribution of decay rates, the method of cumulants is used to determine the mean decay rate, or first cumulant, Γ_1 , and the normalized variance, μ_2/Γ_1 , at each scattering angle according to

$$\frac{1}{2} \ln[g_2(\tau) - 1] = \Gamma_0 - \Gamma_1\tau + \frac{\mu_2}{2}\tau^2 \quad (3)$$

Γ_0 is a constant independent of τ . Solutions exhibiting two or three decay modes were analyzed using a double or triple exponential distribution according to eqs 4 or 5, respectively.

$$g_1(\tau) = A_1 \exp(-\Gamma_1\tau) + A_2 \exp(-\Gamma_2\tau) \quad (4)$$

$$g_1(\tau) = A_1 \exp(-\Gamma_1\tau) + A_2 \exp(-\Gamma_2\tau) + A_3 \exp(-\Gamma_3\tau) \quad (5)$$

Here A_1 , A_2 , and A_3 are the relative amplitudes of each characteristic decay mode Γ_1 , Γ_2 , and Γ_3 . The apparent diffusion coefficient, D_{app} , of scattering particles having a mean decay rate Γ_i can be determined by⁵¹

$$D_{\text{app}}(q) = \frac{\Gamma_i}{q^2} \quad (6)$$

The z-average diffusion coefficient, $\langle D \rangle_z$, is obtained by extrapolating $D_{\text{app}}(q)$ to $q^2 \rightarrow 0$, where particle form factors are unity and nondiffusional processes, such as segment fluctuations and rotation, do

not contribute to $g_1(q, \tau)$.⁵¹ Once $\langle D \rangle_z$ values are obtained, the hydrodynamic radius, R_h is calculated using the Stokes–Einstein equation as $R_h = kT/6\pi\eta_0\langle D \rangle_z$ where k is the Boltzmann constant, T is the absolute temperature, and η_0 is the solvent viscosity (0.555 cP for toluene and 0.454 cP for THF).⁵¹ It is emphasized here that the R_h values reported herein are *apparent* hydrodynamic radii determined at finite concentrations (either at 1 or 8 mg/mL); however, for convenience we refer to them simply as the hydrodynamic radius.

The refractive index increment, dn/dc , for each of the PS–PVP BCPs in toluene was obtained from refractive index measurements²² made using a Wyatt OptiLab Rex differential refractometer at $\lambda = 658$ nm. These dn/dc values are reported in Table 1.

Atomic force microscopy (AFM) images were collected using a Veeco Instruments Nanoscope IIIa multimode atomic force microscope in tapping mode using silicon cantilevers from Applied NanoStructures, Inc. (Mountain View, CA). Root mean square (RMS) roughness and particle size analysis of the images were performed using the NanoScope Analysis v140r1sr4 software.

Transmission electron microscopy (TEM) images were acquired using a Zeiss Libra 200 MC transmission electron microscope that is equipped with a Gatan UltraScan US1000XP CCD camera. For thin polymer films, the solution was spin-coated onto a carbon film grid that was affixed to a silicon wafer following the same procedure described for spin-coating on silicon substrates. The samples were stained by iodine vapor for 24 h. The iodine reacts preferentially with PVP, rendering the PVP microdomains dark in the TEM images. Images were acquired at the column temperature, which was close to room temperature.

For cryogenic-transmission electron microscopy (cryo-TEM), the toluene solution of polymer at a concentration of 8.0 mg/mL was cooled to 4 °C in order to slow the evaporation of the solvent while blotting excess liquid from the lacey carbon films. Droplets of the solution were placed on lacey carbon film grids. Excess fluid was blotted to create ultrathin layers of the suspension spanning the holes of perforated carbon films. The grids were immediately plunged into liquid nitrogen. Vitrified samples were transferred under liquid nitrogen into the transmission electron microscope using the Gatan 626 cryo-holder and stage. The sample temperature was held at −175 °C.

RESULTS AND DISCUSSION

Here the analysis of the structures adopted by the amphiphilic BCPs examined is segmented into two parts. In the first, the behavior of the parent PS–PVP BCPs is presented, beginning with their solution behavior in the selective solvent toluene and then in terms of the structures imaged when solutions are spin-cast into thin films. This is followed by sets of results obtained on binary mixtures of the copolymers. For the mixed systems, results obtained when the copolymers were mixed in equal parts (by mass) are presented first, followed by results obtained when the components are mixed in different ratios.

Self-Assembly of BCPs in Solution. Five groups of PS–PVP BCPs with various molecular architectures and S/V ratios were investigated, including three PS–PVP diblock copolymers (referred to as D1, D2, D3), three PVP–PS–PVP triblock copolymers (T1, T2, T3), three 8-arm stars (S1, S2, S3), three 26-arm stars (S4, S5, S6) and three 40-arm stars (S7, S8, S9). Among these BCPs, samples S1, T1, S1, S4, and S7 have small S/V in the range of $1 \leq S/V \leq 1.7$, samples S2, T2, S2, S5, and S8 have moderate S/V of $3.9 \leq S/V \leq 5$, and samples S3, T3, S3, S6, and S9 have large S/V ratios that range from $7 \leq S/V \leq 10.6$.

Generally speaking, the amphiphilic nature of PS–PVP BCPs drives their self-assembly in a selective solvent such as toluene, where the PS chains are well solvated and extended while the PVP blocks collapse and aggregate to avoid contact with the solvent. While the self-assembly properties of linear PS–PVP

BCPs in toluene have been studied,²⁰ to understand the structures adopted when mixtures of different copolymers are used, it is important to first investigate the parent BCPs. The results obtained from dynamic light scattering (DLS) measurements of the parent copolymers are summarized in Table 1. As an example, DLS results for sample T1 in toluene with polymer concentrations below and/or above the critical micelle concentration (CMC) are presented in Figure 1. DLS results for all of the other parent copolymers are presented in Figures S1–S14 in the Supporting Information file. Figure 1a shows the normalized light intensity autocorrelation function for T1 in toluene at the two concentrations studied. A single decay mode is observed at a concentration of 1.0 mg/mL while two decay modes are observed for the solution at 8.0 mg/mL. Additionally, the light intensity autocorrelation function acquired for T1 in toluene at 1.0 mg/mL begins at a much lower value (~ 0.4) and decays more rapidly as compared to that measured at 8.0 mg/mL. The R_h distributions presented in Figure 1b show a single, sharp distribution at 1.0 mg/mL but two well-resolved distributions at 8.0 mg/mL. The distribution centered at $R_h \approx 9$ nm is observed at both concentrations and is suggestive of single, isolated chains while the distribution appearing at $R_h \approx 200$ nm in the solution at 8.0 mg/mL suggests self-assembled aggregates. Figure 1c shows the apparent diffusion coefficients (determined by fitting the light intensity autocorrelation function with a double exponential decay) for T1 at 8.0 mg/mL as a function of q^2 . The characteristic hydrodynamic radii (R_{h1} for single chains, R_{h2} for micellar aggregates), which are presented in Table 1, are calculated using the Stokes–Einstein relation from the z -average diffusion coefficient. The R_{h1} value for the fast mode observed in Figure 1c, $R_{h1} = 9$ nm is similar to that obtained for sample T1 in the nonselective good solvent THF, $R_{h,THF} = 13$ nm (see Figure S30 in the Supporting Information). These results support the conclusion that at $c = 1.0$ mg/mL, T1 in toluene exists as isolated chains. In addition to isolated chains, the “slow” mode observed at $c = 8.0$ mg/mL is attributed to micellar aggregates that appear to be spherical in shape because D_{app} has no q -dependence over the q -range studied.⁵⁰ This finding of coexistence of single BCP chains and micellar aggregates indicates that these polymer amphiphiles follow the closed association model.²² The DLS results for other linear copolymers are similar to the behaviors exhibited by sample T1, and these are presented in the Supporting Information.

The results shown in Table 1 indicate that PS–PVP diblocks show bimodal size distributions in toluene at a low concentration (1.0 mg/mL), but triblocks only display well-defined bimodal size distributions at a higher concentration (8.0 mg/mL). This observation of the CMC of the triblocks being higher than that of the diblocks is in agreement with previous results showing that the CMCs for PS–PVP triblocks and heteroarm stars are several orders of magnitude higher than that for diblocks.^{24,52} This behavior arises due to unfavorable steric restrictions in triblocks and stars that makes bringing the solvophobic blocks into close proximity more difficult.

The hydrodynamic size distributions for the highly branched 26- and 40-arm stars in toluene at a concentration of 1.0 mg/mL are monomodal, and their correlation functions are fit well by a single exponential decay function. (See Figures S9 – S14 in the Supporting Information.) As expected and as reflected by the data in Table 1, the 40-arm stars (S7–S9) are larger than the 26-arm stars (S4–S6), and the hydrodynamic sizes for the stars having a constant number of arms at medium and large

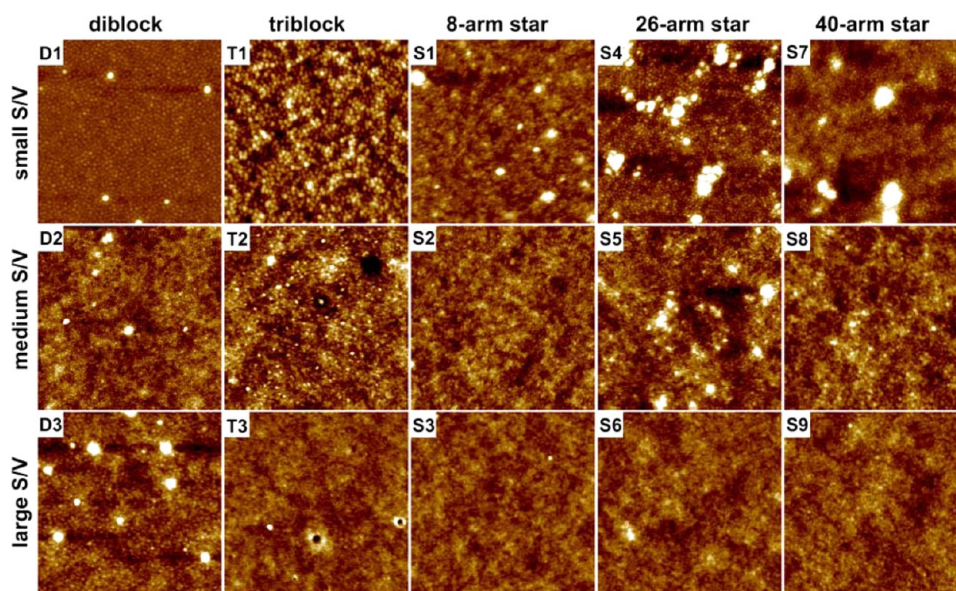


Figure 2. AFM height images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of BCP films. The sample IDs are corresponding to Table 1. Brighter areas are higher than darker areas. The Z scale is 15 nm for D1, T1, S1, S4, and S7 and 3 nm for others.

S/V are similar, but much larger than the R_h of the stars having a small S/V. Because R_h values for these stars range from 40 nm (26 arm, S/V = 1) to 77 nm (40 arm, S/V = 9), two samples were measured in the nonselective good solvent THF to determine if these complex macromolecules are aggregating in toluene at $c = 1.0\ \text{mg/mL}$. The narrow R_h distributions obtained for these 26- or 40-arm star copolymers (S6 and S8, respectively) in THF and the similarity in their R_h values in toluene and THF (see Figures S32 and S33 in the Supporting Information and results in Table 1) suggest that the 26- and 40-arm stars exist as unimolecular micelles in toluene. This behavior is believed to be due to the inability of the poorly solvated PVP to drive aggregation due to the dense topology resulting from the large number of arms and their high molecular weight.

While it is clear that the particular details of the BCP, including block sizes, composition, and architecture, strongly influence the tendency to undergo microphase segregation to form aggregates, in the context of the systems studied here the results given in Table 1 indicate that the 8-arm stars appear to be at the boundary of where centro-symmetric star-like copolymers transition from being able to form multimolecular aggregates to only forming unimolecular micelles. The 8-arm stars with small and medium S/V (samples S1 and S2) show multimolecular micellization behaviors similar to that displayed by the linear BCPs. However, the 8-arm star having a large S/V (sample S3) does not form aggregates; instead these stars remain as a unimolecular micelle, in a fashion analogous to the behavior observed for the 26- and 40-arm stars.

BCP Assemblies in Thin Films. Spin coating of solution-assembled parent BCPs was used in order to image the nanostructures formed by AFM. As the removal of solvent toluene during spin coating is very rapid, the as-spun films are often regarded as representing the morphology of the aggregates in solution.^{10,36} AFM images of the resulting films of the aggregated PS–PVP BCP system formed by self-assembly are presented in Figure 2. The horizontal size (radii of the aggregates) and vertical height of the microdomains, as well as the RMS roughness values calculated for the films, which

were determined from a section analysis of the AFM images, are displayed in Figure 3. In general, the aggregates appear as circular microdomains (bright regions) covering the film surface, although there are clear differences in the size of the aggregates as the macromolecular architecture or S/V ratio are changed. The circular particles have horizontal dimensions of 40–80 nm (in diameter) for all the films made from BCPs with small S/V ratios, which includes samples D1, T1, S1, S4, and S7 (top row of images in Figure 2). It is also worth noting that the films created by spin-casting the self-assembled PS–PVPs having medium or large S/V (center and bottom rows of images in Figure 2) are flatter and the particles are smaller than those created using the BCPs having low S/V. Parts a and b of Figure 3 also show that the horizontal radius and the vertical height of surface deposited aggregates forming the films generally decreases with increasing S/V. In the case of the systems that are able to form micelles in solution, we believe that this is as a direct result larger S/V ratios leading to micelles with smaller PVP cores and larger PS coronae in toluene. We speculate that the PVP domains play a leading role in the morphologies adopted in thin films because the soluble PS domains lose a large amount of solvent and spread on the surfaces during the solvent removal process, as depicted in Scheme S2 of the Supporting Information. In particular, the “softness” of the larger PS corona facilitates the coverage and spreading of the micelles on the surface, as suggested by Scheme 1, leading to smoother, more uniform films. This behavior is also reflected in the RMS roughness values calculated for the films. As Figure 3c shows, the RMS roughness of the films made by spin-casting the self-assembled triblocks and stars tends to decrease with the increased S/V for BCPs having total molecular weights that are similar. While sample D3 shows a larger roughness compared to sample D2, the former has a much larger total molecular weight and PVP molecular weight as compared to the latter. Presumably, the morphology and the roughness of the films are affected by both the molecular composition (S/V) and the molecular weight of the BCPs.

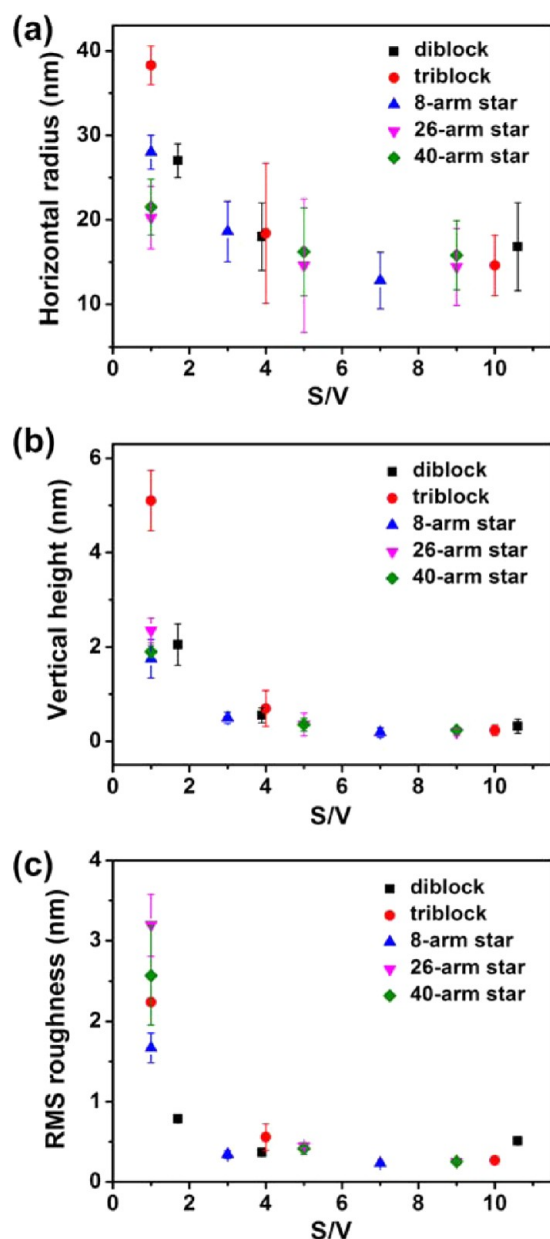


Figure 3. Horizontal radius (a) and vertical height (b) of the microdomains, and RMS roughness values calculated for the films (c) as a function of S/V ratio. Error bars computed from the standard deviation of replicate measurements ($n = 3$ for roughness, $n = 20$ for radius and height).

Overall and as expected, self-assembly in thin films of the single component PS–PVP BCPs from the selective solvent toluene leads to formation of simple spherical aggregate structures regardless of the molecular architecture and composition. In order to demonstrate that the structures imaged from spin-cast films are representative of their solution structure, disperse unimolecular micelles on a silicon substrate prepared by drop-casting from sample S7 toluene solution at $c = 3.0 \mu\text{g/mL}$ were imaged by AFM. As shown in Figure S34 of the Supporting Information, an individual unimolecular micelle on a substrate surfaces has a hemispherical shape with a horizontal radius of ~ 50 nm, which is in good agreement with DLS results ($R_h = 52$ nm). However, the characteristic dimension of an individual micelle is larger than the aggregate

sizes captured by AFM imaging of thin films made by spin-casting: the corresponding film made by spin-casting S7 has horizontal feature size of 21.5 ± 3.2 nm. As depicted in Scheme S2 (of the Supporting Information) we believe that this discrepancy arises because the thin film structures imaged by AFM are mainly the noncollapsed parts of the micelles (the “hilltops”), because of how the aggregates spread and cover the surface when forming continuous films. This also manifests in the difference between the hydrodynamic sizes measured by DLS for the micellar aggregates, which are much larger than the characteristic dimensions measured for the thin films.

Architecturally Complex Binary BCP Mixtures. Because of their ability to form spherical micelles in toluene and stability when deposited in thin films diblock D1, triblock T1, and 8-arm star S1, all of which have small S/V ratios, were selected as the common constituents for binary mixtures. Table 2 identifies the variety of binary mixtures made. Diblock sample D1 was mixed with triblocks T1, T2, and T3 and 8-arm stars S1, S2, and S3, which represents blending at varying S/V ratios. Binary mixtures at small S/V were also examined by mixing D1 with stars S1, S4, and S7, which span a range in number of arms, f , from 8 to 26 to 40. Similarly, triblock T1 was mixed with stars S1, S2, S3, S4, and S7, and binary mixtures of star S1 with triblocks T1, T2, and T3 were also made. In all of these experiments, the copolymers were combined at a mixing ratio of 1:1 by weight using the premixing strategy described earlier. Mixing at different ratios is discussed later.

The morphology of the self-assembled structures formed by premixing the amphiphilic BCPs was investigated in thin film form using AFM. Figure 4 displays the AFM topography images of thin films resulting from binary mixtures of linear copolymers, namely diblock + triblock mixtures D1 + T1, D1 + T2, and D1 + T3, as well as of diblock + star mixtures D1 + S1, D1 + S2, D1 + S3, D1 + S4, and D1 + S7. The films of diblock + triblock copolymer pairs show spherical aggregate structures, and the particle sizes slightly decrease as the average composition expressed through the average S/V ratio (given in Table 2) of the blends increases. This trend is similar to that for the pure triblocks (T1, T2, T3), but the differences in characteristic particle sizes (radius as measured by AFM) of the diblock + triblock copolymer mixtures are smaller than those determined for the pure triblocks. This finding is similar to the report of Yoo et al.,³³ who showed that when two different micelle-forming diblock copolymers were combined by premixing the copolymers in a common good solvent, the resultant micelles were of a “hybridized” (intermediate) size. Remarkably, most films of diblock/star copolymer mixtures exhibit spherical aggregate structures, only the spin-cast film of aggregates formed by premixing D1 + S1 (Figure 4b) shows cylindrical microdomains oriented parallel to the substrate, which can be described as worm-like or bicontinuous structures. These distorted worm-like structures, which usually exist in films created from blending BCPs,^{33,34} have been proposed by Hashimoto and co-workers to originate from a cosurfactant effect and blending.³⁴

As captured by the data presented in Table 2, for films created from binary mixtures of diblock and star copolymers, the general trend is that the RMS roughnesses of these films decrease with increasing average S/V ratios. This behavior, which is consistent with trends observed for the parent materials, is most clearly observed in mixtures D1 + S1, D1 + S2, and D1 + S3, where the number of arms is held constant at $f = 8$. Also, the data in Table 2 show that there is also an increase

Scheme 1. Model Structures of BCP Micelles with Different Core and Corona Sizes Formed in Selective Solvents and on Solid Surfaces through Spin-Assisted Assembly

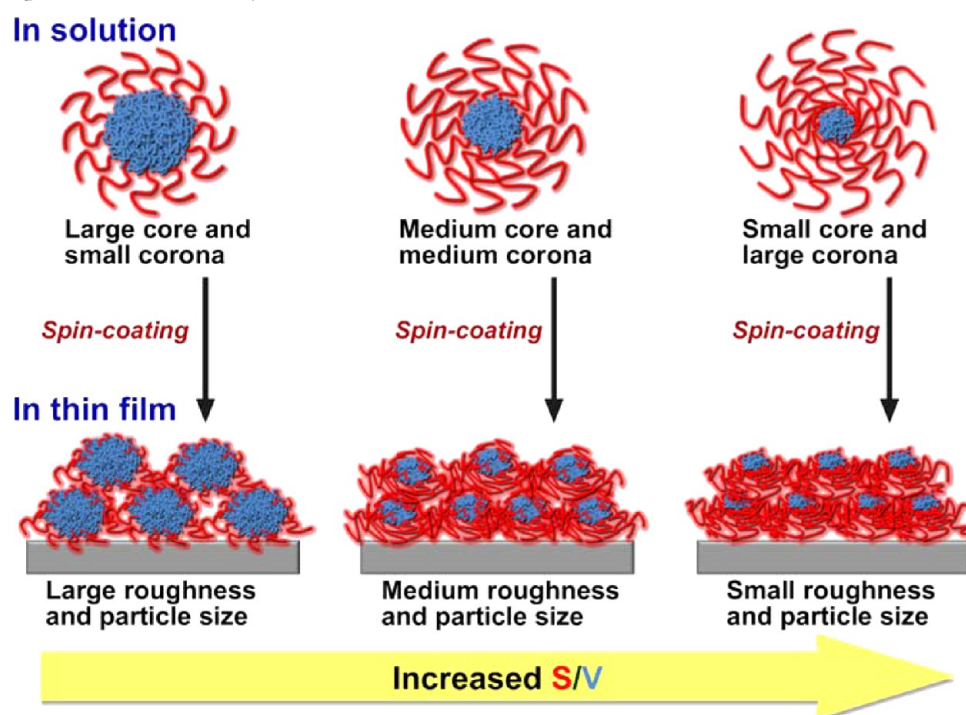


Table 2. Mixing Strategy by Varying Component Architecture and Self-Assembly Properties of PS–PVP BCP Mixtures at a Mixing Ratio of 1:1 (by Weight) in Toluene Solutions and in Thin Film Form

mixture ID	polymer I ^a	polymer II ^a	average S/V ^b	R_{h1} (nm) ^c	R_{h2} (nm) ^c	R_{h3} (nm) ^c	RMS roughness (nm) ^d	horizontal radius (nm) ^e	vertical height (nm) ^e	morphology ^f
D1 + T1	D1	T1	1.3	21	492		2.0 ± 0.5	29.5 ± 4.4	3.3 ± 0.5	S
D1 + T2	D1	T2	2.5	13	325		0.8 ± 0.4	27.6 ± 4.6	1.1 ± 0.3	S
D1 + T3	D1	T3	3.3	20	381		0.8 ± 0.3	24.5 ± 2.1	1.1 ± 0.4	S
D1 + S1	D1	S1	1.3	16	248	686	2.1 ± 0.3			W
D1 + S2	D1	S2	2.2	13	224	456	1.2 ± 0.6	24.2 ± 6.0	1.1 ± 0.3	S
D1 + S3	D1	S3	3	13	82	432	0.9 ± 0.4	23.8 ± 4.5	1.0 ± 0.2	S
D1 + S4	D1	S4	1.3	31	436		2.3 ± 0.5	25.3 ± 7.1	2.7 ± 0.8	S
D1 + S7	D1	S7	1.3	66	670		4.4 ± 0.1	23.3 ± 7.5	1.3 ± 0.6	S
T1 + S1	T1	S1	1	22	328		1.9 ± 0.9			W
T1 + S2	T1	S2	1.7	12	114		9.5 ± 1.7			H
T1 + S3	T1	S3	2.2	14	476		7.1 ± 0.1			H
T1 + S4	T1	S4	1	15	68		4.6 ± 1.6			W
T1 + S7	T1	S7	1	22	81		2.4 ± 0.5			W
S1 + T2	S1	T2	1.9	17	160	595	2.4 ± 0.4	26.8 ± 3.3	1.8 ± 0.8	S
S1 + T3	S1	T3	2.4	13	121	347	7.6 ± 0.8			H

^aSample IDs of polymer I and polymer II correspond to the parent BCPs listed in Table 1. ^bAverage composition of the blend. ^cDetermined by DLS in toluene at $c = 8.0$ mg/mL. ^dAcquired by AFM roughness analysis with uncertainty expressed by the standard deviation ($n = 3$). ^eMeasured by AFM section analysis of the films with homogeneous spherical aggregate structures with uncertainty expressed by the standard deviation ($n = 20$). ^fMorphology of aggregates observed in thin film: S for spherical aggregate structures, W for worm-like structures, and H for hierarchical structures.

in the RMS roughness as the number of arms of the stars increases, as evidenced through the mixed systems of D1 + S1, D1 + S4, and D1 + S7, which have a constant average composition (average S/V = 1.3). Mixtures of D1 with stars of small S/V, namely D1 + S1, D1 + S4, and D1 + S7, produce films that entirely cover the surface and have large roughness values. This is especially true for D1 + S7 mixture, where the RMS roughness is ~4.4 nm due to the present of large bulges on the film surface. The small S/V ratio (large PVP content), highly branched architecture and large molecular weight of S7 seem to facilitate aggregation (as observed in Figure 2 for

copolymer S7), and as a result, blending of S7 with D1 leads to rougher surfaces (Figure 4h) compared to the films made from the parent BCPs.

Aggregates formed from mixtures of triblocks and star copolymers seem to be more complex in structure than those formed by mixing diblocks and stars. As shown in Table 2, the film RMS roughnesses for triblock + star copolymer are large in comparison and they also do not follow the trend established by the diblock + star mixtures of decreasing with increasing S/V. Moreover, the films cast from mixtures of T1 with stars at a constant S/V = 1 (T1 + S1, T1 + S4, T1 + S7) exhibit worm-

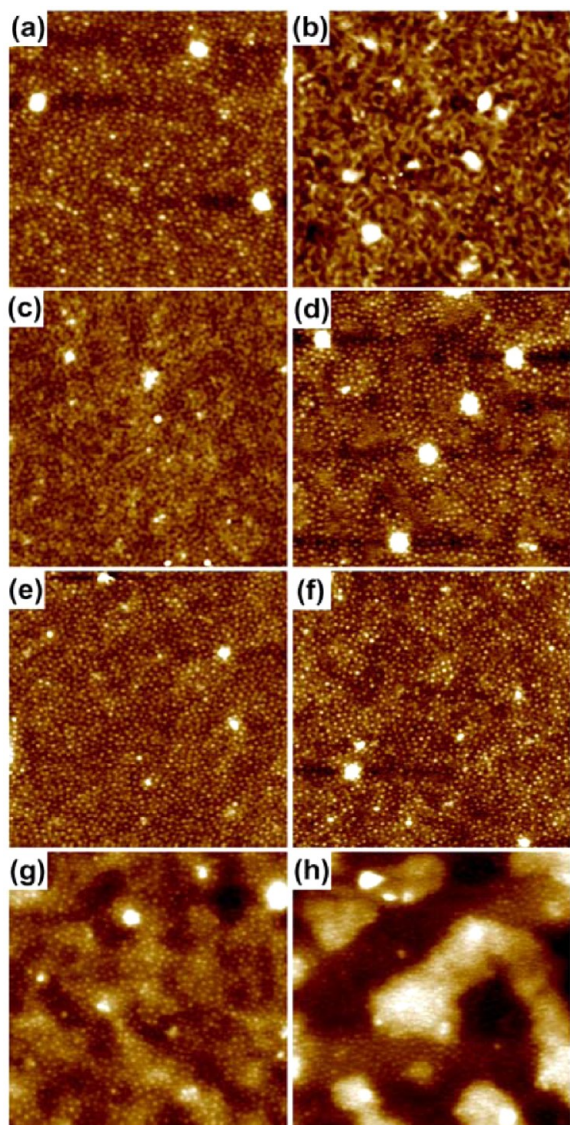


Figure 4. AFM height images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the films of BCP mixtures of D1 + T1 (a), D1 + S1 (b), D1 + T2 (c), D1 + S2 (d), D1 + T3 (e), D1 + S3 (f), D1 + S4 (g) and D1 + S7 (h) at a mixing ratio of 1:1 by weight. The Z scale is 15 nm (a, b), 5 nm (c, d, e, and f), and 20 nm (g, h).

like structures (Figure 5a–c), similar to the film morphology for D1 + S1. The lengths of the cylinders in these films generally decrease with increasing number of arms in the star BCP. As shown in Figure 5d, the film of S1 + T2 mixture exhibits nearly spherical aggregates (that may be described as intermediate between spheres and short cylinders) with a horizontal particle radius of $\sim 26.8\ \text{nm}$ and a vertical particle height of $\sim 1.8\ \text{nm}$. Moreover, some of the triblock + star copolymer mixtures—specifically T1 + S2, S1 + T3, and T1 + S3 mixtures—can form what appear to be hierarchical morphologies with distinct primary and secondary structures when spin-cast as films, as shown in Figures 5e–g. The primary structures of these hierarchical morphologies are large-scale cylinders (Figure 5e) or spheres (Figure 5g) with a secondary structure that appears to be thin worm-like domains on the surfaces of the large aggregates. Among these, aggregates in thin films created from the mixture T1 + S3 are remarkable for their hierarchical structure that consists of a spherical primary

structure and worm-like secondary structure, which gives the aggregates the appearance of a brain coral or a walnut. This structure has a horizontal diameter of $\sim 600\ \text{nm}$ and a vertical height of $\sim 16\ \text{nm}$ (Figure 5g). We note that of the pairs of copolymers studied, the parent polymers of T1 and S3 have the largest discrepancy in their R_h values. Similar walnut shaped hierarchical structures made of a network of polyaniline nanofibers polymerized on cationic surface-decorated PS microspheres have been reported; however the operative process that leads to the interesting hierarchical structure springs from adsorption of cationic surfactant and its ability to direct the oxidative polymerization.⁵³ A similar hierarchical structure consisting of a sphere with striated domains was created by microphase separation of fluorine-containing diblock copolymers: Zhang and co-workers demonstrated that by controlling the addition of the poor solvent water into a homogeneous solution of the copolymer in THF, soft nanoparticles having diverse internal and hierarchical structures could be created.⁵⁴ As demonstrated here, spin-casting binary mixtures of complex PS–PVP BCPs, i.e., triblock + star copolymer pairs, appears to be another path toward creating supramolecular, hierarchically structured aggregates via self-assembly.

In order to provide additional detail of the structure of these hierarchical aggregates, the film of T1 + S3 mixture was characterized by TEM after using iodine to stain the PVP segments selectively. As shown in Figure 5h and its inset, the PVP blocks (darker regions) are generally organized into spherical domains separated by the brighter PS phase, and the large compound micelles have diameters ranging from ~ 500 to $\sim 1000\ \text{nm}$ that appear to consist of an aggregation of simple spherical micelles having PVP cores and PS coronae. There are some smaller compound micelles comprised of several simple micelles around the large ones that also can be seen in the AFM image (Figure 5g). In total, the results suggest that there are three typical morphologies adopted in films comprised of self-assembled PS–PVP BCP mixtures, namely (i) spherical, (ii) worm-like, and (iii) hierarchical structures, each of which is represented by the binary mixtures D1 + T1, D1 + S1, and T1 + S3, respectively.

While it is generally accepted that there is correspondence between the structures imaged in thin film form and those present in solution,^{20,34,35} the thin film structures imaged by AFM may be affected by changes in morphology due to solvent evaporation, surface interactions and spreading. Therefore, cryo-TEM imaging provides more direct information regarding the morphologies adopted by the BCP mixtures in solution.^{20,45} The representative mixtures of D1 + T1, D1 + S1, and T1 + S3 were imaged by cryo-TEM at $-175\ ^\circ\text{C}$, and representative images are presented in Figure 6a–c. As shown in Figure 6a, simple spherical micelles with an average diameter of $36.7 \pm 7.3\ \text{nm}$ are clearly seen in the vitrified solution of D1 + T1 mixture. The size of the micelles present in the solution as determined from the cryo-TEM images is slightly smaller than the horizontal particle size extracted from images of thin films acquired by AFM. We suspect this discrepancy is because the micelles spread horizontally as they collapse on surfaces due to the transverse shear stress and solvent evaporation during spin-coating. In the D1 + T1 mixture, the diblocks and triblocks jointly participate in self-assembly and make up the hybrid micelles which generally consist of a spherical PVP core surrounded by PS coronal chains in toluene. In the case of the D1 + S1 mixture, no cylindrical aggregates are observed in the

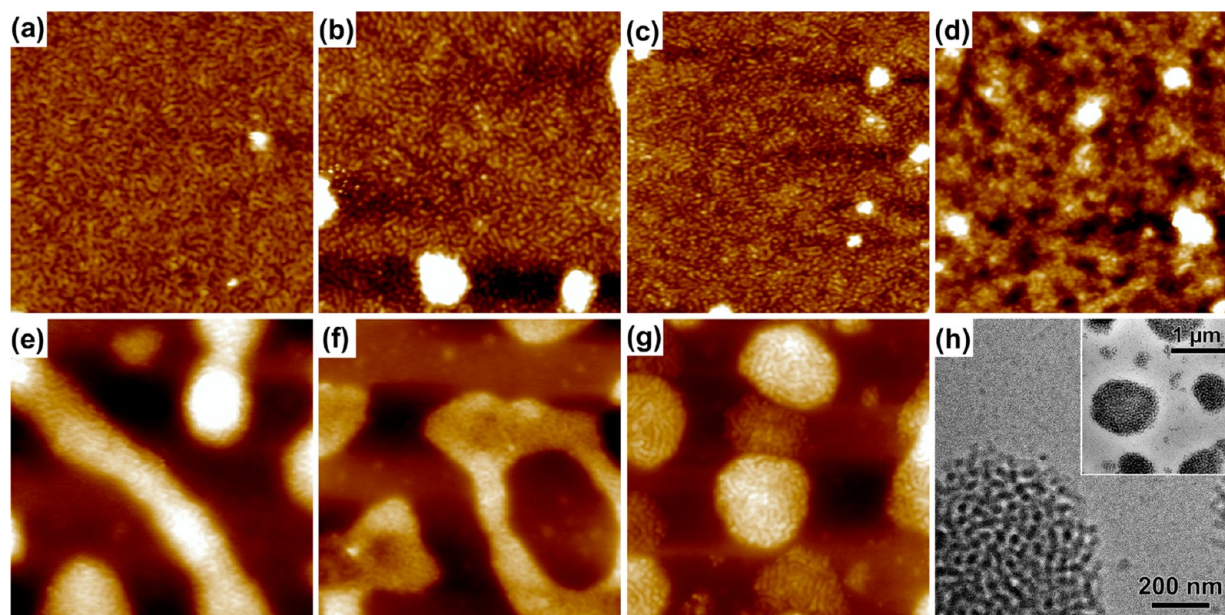


Figure 5. AFM height images ($2\ \mu\text{m} \times 2\ \mu\text{m}$) of the films of triblock/star copolymer mixtures of T1 + S1 (a), T1 + S4 (b), T1 + S7 (c), S1 + T2 (d), T1 + S2 (e), S1 + T3 (f) and T1 + S3 (g) at a mixing ratio of 1:1 by weight. The Z scale is 15 (a–d) and 40 nm (e–g). (h) TEM image of the film in part g with PVP blocks stained by iodine vapor. The inset is the large area TEM image.

bulk solution—only spheres with an average diameter of $24.0 \pm 4.6\ \text{nm}$ are observed, as shown in Figure 6b. This fact indicates that the worm-like structures observed when thin films were imaged are mainly due to the merging of spherical micelles during the spin coating process. The obvious morphological reconstruction in thin films occurs in specific BCP mixed systems and appears to be linked to certain component architectures. For the T1 + S3 mixture, as shown in Figure 6c, large compound micelles with a diameter of $\sim 350\ \text{nm}$ are observed, their sizes are much larger than those of simple spherical micelles, and are highly polydisperse. Notably, no hierarchical structures can be seen on the swollen large compound micelles in toluene solution. Therefore, the hierarchical structures in thin films as shown in Figure 5g are also formed during the solvent removal process, due to the substantial collapse of PS microdomains.

The self-assembly properties of PS–PVP BCP binary mixtures in toluene at $c = 8.0\ \text{mg/mL}$ were also investigated by DLS. They exhibit bimodal and even trimodal R_h distributions, as observed from results presented in the Supporting Information. In Table 2 the hydrodynamic sizes of the aggregates are presented using R_{h1} and R_{h2} for the systems with bimodal distributions and R_{h1} , R_{h2} , and R_{h3} for the systems having trimodal R_h distributions. The R_{h2} and R_{h3} values in the bimodal or trimodal systems that adopt simple spherical micelles are usually much larger than the sizes deduced from AFM and cryo-TEM imaging (e.g., D1 + T1 mixture), suggesting the formation of aggregates. The R_{h2} values corresponding to the large compound aggregates present in the bimodal systems are sometimes much smaller than the sizes obtained by AFM (e.g., T1 + S2 mixture); we believe this is due to the problem of multiple scattering by the large particles, which leads to a falsification of the angular distribution of scattered light that impacts the measured particle size distribution.⁵⁵ While multiple scattering can be avoided by using solutions of low concentration (e.g., at $1.0\ \text{mg/mL}$), the micellar aggregates disassemble or the mixtures

show different self-assembly behaviors at this concentration (see Table S1 in the Supporting Information), due to the high CMCs for the parent BCPs.

Compositionally Complex Binary BCP Mixtures. The average composition of the blend is known to be an important variable that strongly affects the self-assembled structures in systems where the parent BCPs have the same molecular architecture (e.g., diblock + diblock copolymer mixtures).^{25a} In this study, the mixtures are made from two BCPs with different macromolecular architectures. As shown in Table 2, BCP mixtures with different component architectures display diverse self-assembled structures in thin films, even though they have an identical average composition. This points to component architecture as a significant factor in the self-assembly behaviors of BCP mixtures, rather than the average composition of the blend. To support this contention, the composition-controlled self-assembly of BCP mixtures is illustrated using three PS–PVP BCP mixtures with BCP components of different architecture. Table 3 lists components used and the mixing strategy, and for convenience, we substitute the average composition of the blend for the mass fraction of the component. In the binary mixtures, the mass fractions of polymer I gradually decrease from 100% to 75% to 50% to 25% to 0%, with the mass fractions of polymer II increasing correspondingly.

As shown in parts a and b of Figure 7 (as well as results presented in Figures 2 and 4), thin films made by mixtures of D1 + T1 produce films with spherical aggregate structures for all blend compositions. Figure 8a presents the horizontal radii and the vertical heights of the aggregates in the films versus the mass fraction of T1 in D1 + T1 mixtures. Both the horizontal and the vertical sizes of the particles formed from D1 + T1 mixtures increase with the increasing fraction of T1 component, mainly because of the larger micelle size for T1 than that for D1. As the spherical particles formed from binary BCP mixtures usually show particle sizes that are intermediate or approximately equal to the ensembles made from the parent BCPs

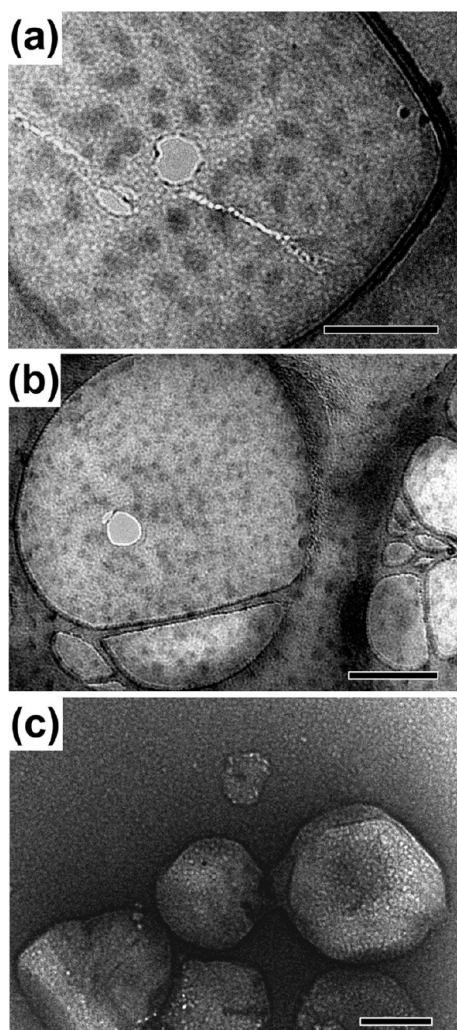


Figure 6. Cryo-TEM images of the BCP mixtures of D1 + T1 (a), D1 + S1 (b), and T1 + S3 (c) at a mixing ratio of 1:1 by weight in toluene, and the scale bar is 200 nm.

(see Tables 1 and 2), the results show that the particle sizes can be adjusted in a small range by tailoring the mixing ratio.

As for the self-assembly of D1 + S1 copolymer mixtures in thin films, the parent D1 and S1 copolymers adopt simple spherical aggregate structures, as seen in Figure 2. The D1 + S1 mixture at a mixing ratio of 3/1 by weight (Figure 7c) shows spherical aggregate structures with an average horizontal radius (in the plane of the film) of 30.7 ± 5.6 nm and an average height (out of the plane of the film) of 3.0 ± 0.8 nm, while D1 + S1 mixtures at mixing ratios of 1:1 (Figure 4b) and 1:3 by weight (Figure 7d) produce films with cylindrical aggregate (worm-like) structures having horizontal diameters of the cylinders of ~ 34 and ~ 22 nm, respectively. The complex

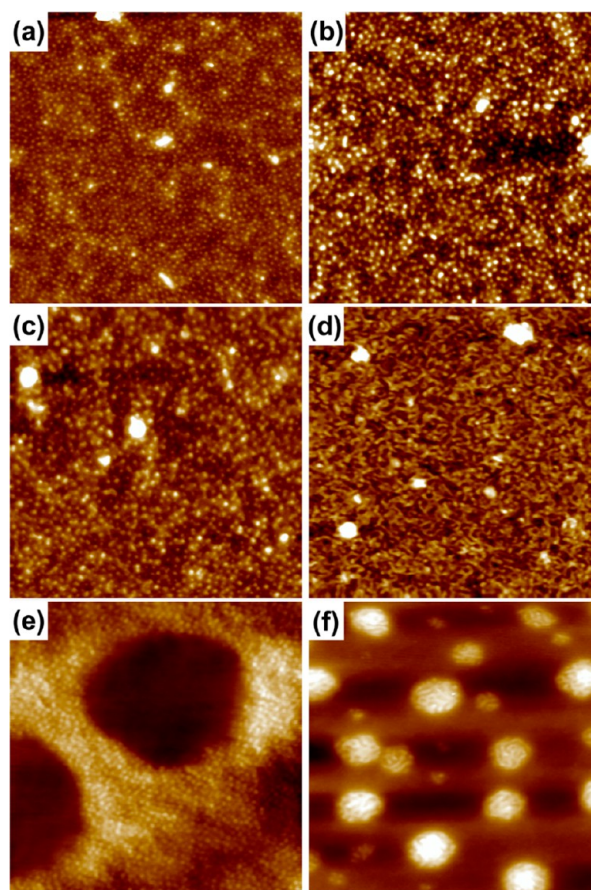


Figure 7. AFM height images ($2 \mu\text{m} \times 2 \mu\text{m}$) of the films of BCP mixtures of D1 + T1 (a, b), D1 + S1 (c, d), and T1 + S3 (e, f) at mixing ratios of 3:1 (a, c, e) and 1:3 (b, d, f) by weight. The Z scale is 15 (a–d) and 40 nm (e, f).

molecular architecture of the star copolymers is likely the origin of structural variation that is realized in their micellar aggregates. The introduction of a small amount of diblock D1 into the star S1 system allows them to change their structure from spherical to cylindrical aggregates. This is reflected in the small cylindrical aggregates formed when D1 + S1 mixture at a mixing ratio of 1:3 by weight is cast into thin films. Further addition of D1 to 50 wt % causes a maximum degree of hybridization in the mixed systems, and the mixture microphase segregates into large cylindrical aggregates. When the fraction of D1 in the mixture reaches 75 wt %, the self-assembly behavior of the mixed system is dominated the self-assembly behavior of D1, and the mixed system recovers the spherical aggregate structures.

Previously it was shown that spin-casting the 1/1 mixture of T1 + S3 creates the unusual, hierarchically structured

Table 3. Mixing Strategy by Varying Blend Composition

polymer I	polymer II	morphology ^a	mass fraction of polymer II in the blend				
			0%	25%	50%	75%	100%
D1	T1	S	1.7 ^b	1.5	1.3	1.1	1
D1	S1	W	1.7	1.5	1.3	1.1	1
T1	S3	H	1	1.4	2.2	3.6	7

^aMorphology of aggregates in thin films at a mixing ratio of w:w = 1:1, using S for spherical aggregate structures, W for worm-like structures, and H for hierarchical structures. ^bAverage composition (average S/V) of the blend.

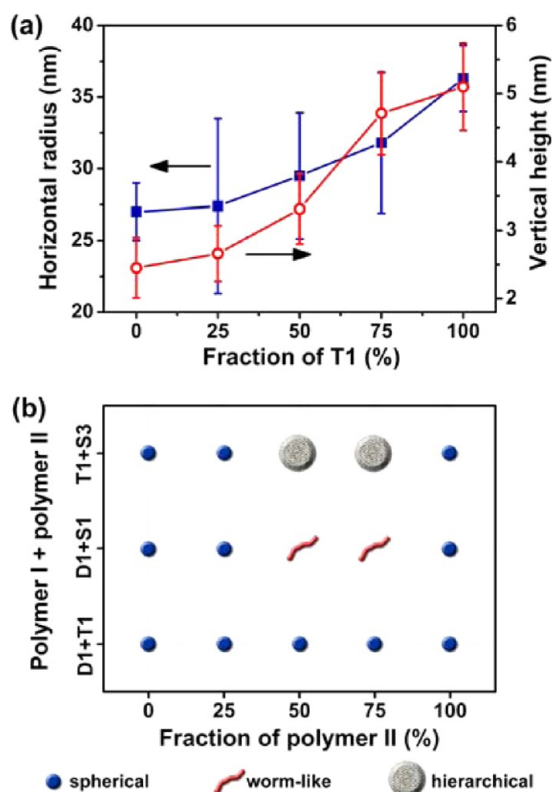


Figure 8. (a) Horizontal radius and vertical height of the microdomains in the films of D1 + T1 BCP mixtures as a function of the mass fraction of T1. The error bars reflect the standard deviation of replicate measurements ($n = 20$). (b) Dependence of film morphologies of three typical BCP mixtures as a function of the mass composition of the blended BCPs.

aggregates that resemble a brain coral. Self-assembled mixtures of T1 + S3 with a T1 fraction of 75 wt % adopt spherical structures when cast as thin films (Figure 7e), with the aggregates having an average in-plane radius of 28.1 ± 4.5 nm. In contrast to other mixtures, this film does not completely cover the surface—there are micropores with a horizontal radius of ~ 600 nm and a vertical depth of ~ 40 nm (Figure 7e). When the relative amount of S3 is increased to 75 wt %, as shown in Figure 7f, hierarchical morphologies with spherical primary and worm-like secondary structures are observed. The primary particles have an average horizontal diameter of 286 ± 94 nm, which is smaller than the brain coral-like aggregates made from the T1 + S3 copolymer mixture at a mixing ratio of 1:1 (by weight), due to the low degree of hybridization for the 1/3 mixture of T1 + S3.

The film morphologies observed from the three BCP mixtures as a function of blend composition are summarized and presented in Figure 8b. As shown in Figure 8b, the mixtures exhibit spherical aggregate structures when the mass fraction of linear BCPs—either diblock D1 or triblock T1—exceeds 50%. However, D1 + S1 and T1 + S3 copolymer mixtures can form worm-like and hierarchically structured aggregates, respectively, when the fraction of star copolymer in the blend reaches or exceeds 50 wt %. We suspect that these complex microphase separated film structures arise because mixing the linear and star block copolymers provides additional degrees-of-freedom in terms of how the macromolecules balance chain stretching and segregation and interface creation during self-assembly.⁵⁶ From the results of three typical BCP

mixtures at different compositions, we can conclude that linear BCPs have the tendency to guide the mixtures to form spherical aggregate structures. In contrast, and although star copolymers tend to adopt spherical aggregate structures on their own, the complex architecture endows them with the latent capacity to dominate the formation of ensembles, steering the mixed system toward more complex shapes. Moreover, while the architectures of the component block copolymers has primary influence on the structure adopted by the micellar aggregates in binary mixtures, minor changes in the structures can be achieved by adjusting the average composition of the blend.

CONCLUSIONS

We have presented a systematic study on self-assembly of complex surfactant-like BCPs and their binary mixtures that are diverse in their architectures and compositions. Our findings demonstrate that the combination of mixing chains of different architectures and compositions changes the self-assembly behavior, leading in some cases to more complex aggregate structures, particularly upon reconstruction during spin-casting, which allows worm-like structures and exotic hierarchical aggregates to be formed. The origin of these behaviors is attributed to the ability of the mixed systems to mediate interfacial curvature and chain stretching. Within this, two heuristics emerging from these studies are that complex and often polydisperse aggregates are observed when there is a significant difference between aggregate sizes of the parent copolymers, and perhaps require that one of the parent copolymers micellizes only weakly so that its chains can be recruited into the unusual structure. While the rules governing self-assembly of complex BCPs and the relationships between solution and thin film structures are yet to be elucidated, this study points toward new approaches for making unusual and sophisticated structures from simpler building blocks and the development of useful novel nano- and meso-structures and devices based on soft matter.

ASSOCIATED CONTENT

Supporting Information

Schemes showing BCP architecture and structural evolution during spin-casting, DLS results on single-component and binary mixtures, AFM images of thin films, and a table of hydrodynamic radii of PS–PVP block copolymer mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Author

*(S.M.K.) E-mail: mkilbey@utk.edu

Author Contributions

[†]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support for this work from the National Science Foundation (Award No. 1131252) is gratefully acknowledged. Some of the methods developed for TEM imaging benefitted from activities supported by the U.S. Army Research Office through Grant No. W911NF-11-1-0417. Access to light scattering capabilities was enabled by the User program of the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National

Laboratory, by the Office of Science, Department of Energy. Dr. John Dunlap of the Advanced Microscopy and Imaging Center at the University of Tennessee—Knoxville is gratefully acknowledged for assistance with TEM studies, and Paul Russo is thanked for helpful discussions.

REFERENCES

- (1) Mai, Y.; Eisenberg, A. *Chem. Soc. Rev.* **2012**, *41*, 5969–5985.
- (2) Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H. *Science* **2012**, *336*, 434–440.
- (3) (a) Schacher, F. H.; Rupar, P. A.; Manners, I. *Angew. Chem., Int. Ed.* **2012**, *51*, 7898–7921. (b) Ahmed, R.; Patra, S. K.; Hamley, I. W.; Manners, I.; Faul, C. F. J. *J. Am. Chem. Soc.* **2013**, *135*, 2455–2458.
- (4) Cai, Y.; Aubrecht, K. B.; Grubbs, R. B. *J. Am. Chem. Soc.* **2011**, *133*, 1058–1065.
- (5) Ramanathan, M.; Kilbey, S. M.; Ji, Q.; Hill, J. P.; Ariga, K. *J. Mater. Chem.* **2012**, *22*, 10389–10405.
- (6) (a) Ma, N.; Li, Y.; Xu, H.; Wang, Z.; Zhang, X. *J. Am. Chem. Soc.* **2010**, *132*, 442–443. (b) Ren, L.; Hardy, C. G.; Tang, C. *J. Am. Chem. Soc.* **2010**, *132*, 8874–8875.
- (7) (a) Dou, H.; Jiang, M.; Peng, H.; Chen, D.; Hong, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 1516–1519. (b) Zhang, K.; Jiang, M.; Chen, D. *Angew. Chem., Int. Ed.* **2012**, *51*, 8744–8747.
- (8) (a) Jang, S. G.; Kramer, E. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 16986–16996. (b) Jang, S. G.; Audus, D. J.; Klinger, D.; Krogstad, D. V.; Kim, B. J.; Cameron, A.; Kim, S.-W.; Delaney, K. T.; Hur, S.-M.; Killops, K. L.; Fredrickson, G. H.; Kramer, E. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2013**, *135*, 6649–6657.
- (9) Li, Z.; Zhang, Y.; Fullhart, P.; Mirkin, C. A. *Nano Lett.* **2004**, *4*, 1055–1058.
- (10) Kästle, G.; Boyen, H. G.; Weigl, F.; Lengel, G.; Herzog, T.; Ziemann, P.; Riethmüller, S.; Mayer, O.; Hartmann, C.; Spatz, J. P.; Möller, M.; Ozawa, M.; Banhart, F.; Garnier, M. G.; Oelhafen, P. *Adv. Funct. Mater.* **2003**, *13*, 853–861.
- (11) Suntivich, R.; Choi, I.; Gupta, M. K.; Tsitsilianis, C.; Tsukruk, V. *Langmuir* **2011**, *27*, 10730–10738.
- (12) Gu, X.; Liu, Z.; Gunkel, I.; Chourou, S. T.; Hong, S. W.; Olynick, D. L.; Russell, T. P. *Adv. Mater.* **2012**, *24*, 5688–5694.
- (13) Hardy, C. G.; Ren, L.; Ma, S.; Tang, C. *Chem. Commun.* **2013**, *49*, 4373–4375.
- (14) (a) Kim, B.-S.; Park, S. W.; Hammond, P. T. *ACS Nano* **2008**, *2*, 386–392. (b) Kim, J. O.; Kabanov, A. V.; Bronich, T. K. *J. Controlled Release* **2009**, *138*, 197–204. (c) Rösler, A.; Vandermeulen, G. W. M.; Klok, H.-A. *Adv. Drug Delivery Rev.* **2012**, *64*, 270–279.
- (15) Ternat, C.; Ouali, L.; Sommer, H.; Fieber, W.; Velazco, M. I.; Plummer, C. J. G.; Kreutzer, G.; Klok, H.-A.; Månson, J.-A. E.; Herrmann, A. *Macromolecules* **2008**, *41*, 7079–7089.
- (16) Kang, Y.; Walsh, J. J.; Gorishnyy, T.; Thomas, E. L. *Nat. Mater.* **2007**, *6*, 957–960.
- (17) (a) Cho, J.; Hong, J.; Char, K.; Caruso, F. *J. Am. Chem. Soc.* **2006**, *128*, 9935–9942. (b) Joo, W.; Park, M. S.; Kim, J. K. *Langmuir* **2006**, *22*, 7960–7963. (c) Lu, Y.; Choi, Y. J.; Lim, H. S.; Kwak, D.; Shim, C.; Lee, S. G.; Cho, K. *Langmuir* **2010**, *26*, 17749–17755.
- (18) Hentschel, J.; Kushner, A. M.; Ziller, J.; Guan, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 10561–10565.
- (19) (a) Riess, G. *Prog. Polym. Sci.* **2003**, *28*, 1107–1170. (b) Matyjaszewski, K.; Tsarevsky, N. V. *Nat. Chem.* **2009**, *1*, 276–288. (c) Rupar, P. A.; Chabanne, L.; Winnik, M. A.; Manners, I. *Science* **2012**, *337*, 559–562. (d) Stals, P. J. M.; Li, Y.; Burdyńska, J.; Nicolay, R.; Nese, A.; Palmans, A. R. A.; Meijer, E. W.; Matyjaszewski, K.; Sheiko, S. S. *J. Am. Chem. Soc.* **2013**, *135*, 11421–11424. (e) Petzetakis, N.; Robin, M. P.; Patterson, J. P.; Kelley, E. G.; Cotanda, P.; Bomans, P. H. H.; Sommerdijk, N. A. J. M.; Dove, A. P.; Epps, T. H.; O'Reilly, R. K. *ACS Nano* **2013**, *7*, 1120–1128.
- (20) Zamfir, M.; Patrickios, C. S.; Montagne, F.; Abetz, C.; Abetz, V.; Oss-Ronen, L.; Talmon, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1636–1644.
- (21) Hayward, R. C.; Pochan, D. J. *Macromolecules* **2010**, *43*, 3577–3584.
- (22) Hinestrosa, J. P.; Uhrig, D.; Pickel, D. L.; Mays, J. W.; Kilbey, S. M. *Soft Matter* **2012**, *8*, 10061–10071.
- (23) (a) Tsitsilianis, C.; Voulgaris, D.; Štěpánek, M.; Podhájecká, K.; Procházka, K.; Tuzar, Z.; Brown, W. *Langmuir* **2000**, *16*, 6868–6876. (b) Štěpánek, M.; Matějček, P.; Humpolíčková, J.; Havráňková, J.; Podhájecká, K.; Špírková, M.; Tuzar, Z.; Tsitsilianis, C.; Procházka, K. *Polymer* **2005**, *46*, 10493–10505.
- (24) Voulgaris, D.; Tsitsilianis, C.; Esselink, F. J.; Hadzioannou, G. *Polymer* **1998**, *39*, 6429–6439.
- (25) (a) Jain, S.; Bates, F. S. *Macromolecules* **2004**, *37*, 1511–1523. (b) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Macromolecules* **2003**, *36*, 953–955.
- (26) Kang, N.; Perron, M.-E.; Prud'homme, R. E.; Zhang, Y.; Gaucher, G.; Leroux, J.-C. *Nano Lett.* **2005**, *5*, 315–319.
- (27) Cai, P.; Wang, C.; Ye, J.; Xie, Z.; Wu, C. *Macromolecules* **2004**, *37*, 3438–3443.
- (28) Koňák, Č.; Helmstedt, M. *Macromolecules* **2003**, *36*, 4603–4608.
- (29) (a) Štěpánek, M.; Podhájecká, K.; Tesařová, E.; Procházka, K.; Tuzar, Z.; Brown, W. *Langmuir* **2001**, *17*, 4240–4244. (b) Tian, M.; Qin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Procházka, K. *Langmuir* **1993**, *9*, 1741–1748.
- (30) Esselink, F. J.; Dormidontova, E. E.; Hadzioannou, G. *Macromolecules* **1998**, *31*, 4873–4878.
- (31) Borovinskii, A. L.; Khokhlov, A. R. *Macromolecules* **1998**, *31*, 7636–7640.
- (32) Honda, C.; Yamamoto, K.; Nose, T. *Polymer* **1996**, *37*, 1975–1984.
- (33) Yoo, S. I.; Sohn, B.-H.; Zin, W.-C.; Jung, J. C.; Park, C. *Macromolecules* **2007**, *40*, 8323–8328.
- (34) Court, F.; Yamaguchi, D.; Hashimoto, T. *Macromolecules* **2006**, *39*, 2596–2605.
- (35) van Zoelen, W.; ten Brinke, G. *Soft Matter* **2009**, *5*, 1568–1582.
- (36) Lefevre, N.; Daoulas, K. C.; Müller, M.; Gohy, J.-F.; Fustin, C.-A. *Macromolecules* **2010**, *43*, 7734–7743.
- (37) Stoykovich, M. P.; Müller, M.; Kim, S. O.; Solak, H. H.; Edwards, E. W.; de Pablo, J. J.; Nealey, P. F. *Science* **2005**, *308*, 1442–1446.
- (38) Greenall, M. J.; Schuetz, P.; Furzeland, S.; Atkins, D.; Buzzza, D. M. A.; Butler, M. F.; McLeish, T. C. B. *Macromolecules* **2011**, *44*, 5510–5519.
- (39) Liu, X.; Wu, J.; Kim, J.-S.; Eisenberg, A. *Langmuir* **2006**, *22*, 419–424.
- (40) Zhu, S.; Liu, Y.; Rafailovich, M. H.; Sokolov, J.; Gersappe, D.; Winesett, D. A.; Ade, H. *Nature* **1999**, *400*, 49–51.
- (41) Han, S. H.; Kim, J. K.; Pryamitsyn, V.; Ganesan, V. *Macromolecules* **2011**, *44*, 4970–4976.
- (42) Han, Y.; Jiang, W. *J. Phys. Chem. B* **2011**, *115*, 2167–2172.
- (43) Matsen, M. W. *Phys. Rev. Lett.* **2007**, *99*, 148304.
- (44) (a) Widin, J. M.; Schmitt, A. K.; Schmitt, A. L.; Im, K.; Mahanthappa, M. K. *J. Am. Chem. Soc.* **2012**, *134*, 3834–3844. (b) Schmitt, A. L.; Repollet-Pedrosa, M. H.; Mahanthappa, M. K. *ACS Macro Lett.* **2012**, *1*, 300–304.
- (45) Zhu, J.; Zhang, S.; Zhang, K.; Wang, X.; Mays, J. W.; Wooley, K. L.; Pochan, D. J. *Nat. Commun.* **2013**, *4*, 2297–2303.
- (46) Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2006**, *39*, 765–771.
- (47) Kilbey, S. M.; Watanabe, H.; Tirrell, M. *Macromolecules* **2001**, *34*, 5249–5259.
- (48) Alonzo, J.; Huang, Z.; Liu, M.; Mays, J. W.; Toomey, R. G.; Dadmun, M. D.; Kilbey, S. M. *Macromolecules* **2006**, *39*, 8434–8439.
- (49) Ji, H.; Sakellariou, G.; Advincula, R. C.; Smith, G. D.; Kilbey, S. M.; Dadmun, M. D.; Mays, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3949–3955.
- (50) Hinestrosa, J. P.; Alonzo, J.; Osa, M.; Kilbey, S. M. *Macromolecules* **2010**, *43*, 7294–7304.
- (51) Schärfl, W. In *Light Scattering from Polymer Solutions and Nanoparticle Dispersions*; Springer: Berlin, 2007.

- (52) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1991**, *24*, 1975–1986.
- (53) Jiang, N.; Xu, Y.; He, N.; Chen, J.; Deng, Y.; Yuan, C.; Han, G.; Dai, L. *J. Mater. Chem.* **2010**, *20*, 10847–10855.
- (54) Qin, S.; Li, H.; Yuan, W. Z.; Zhang, Y. *Soft Matter* **2012**, *8*, 2471–2476.
- (55) Urban, C.; Schurtenberger, P. J. *Colloid Interface Sci.* **1998**, *207*, 150–158.
- (56) Zhulina, E. B.; Adam, M.; LaRue, I.; Sheiko, S. S.; Rubinstein, M. *Macromolecules* **2005**, *38*, 5330–5351.