Solvent-regulated ordering in block copolymers

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Studies of the structural polymorphism exhibited by block copolymers in the presence of selective solvents are relatively recent, but very promising in terms of fundamental understanding and practical applications. Highlighting recent advances, this review progresses from ‘dry’ ordered copolymers to solvated ordered (gel-like) copolymers and lastly to solvated disordered (but locally organized) copolymers. Organic- and aqueous-solvent-based systems are concurrently examined to cross-fertilize polymer and colloid science.

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Introduction

Solvent regulation in block copolymer ordering

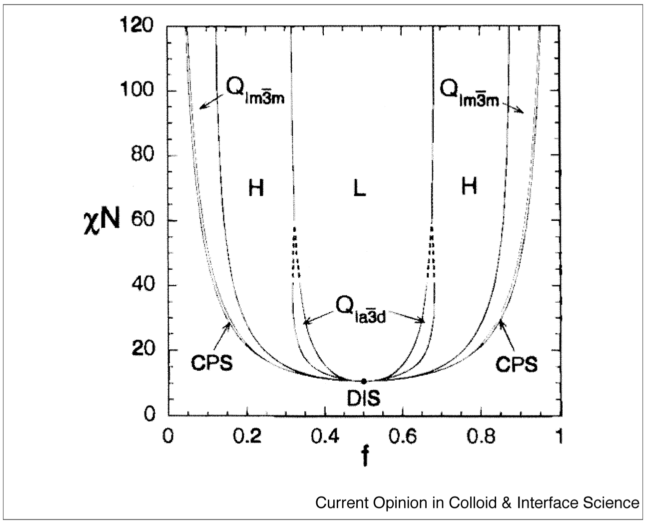
Block copolymers, macromolecules consisting of chemically different contiguous parts (blocks), have a fascinating tendency to attain, through block segregation and microphase separation, diverse ordered morphologies such as lamellae, cylinders and spheres, as well as bicontinuous minimal-surface microstructures [1•,2••]. These ordered morphologies exhibit rheological and other properties that differ considerably from those of the disordered state. Many applications derive from the ordered morphologies generated by block copolymers, especially since no special machining, other than combining the ‘right’ components under the ‘right’ conditions, is required to achieve self-assembled morphologies of well-defined order and characteristic dimensions at the nanometer scale. The various morphologies exhibited by linear block copolymers composed of two chemically distinct monomers have been extensively studied over the last decade and are now well understood [2••]. Current research interests are shifting toward more complex systems, such as non-linear block copolymers, multiblock copolymers, and block copolymer/homopolymer and block copolymer/block copolymer blends [1•,2••,3••]. These results greatly expand the range of microdomain sizes and morphologies that can be readily accessed. The ability to tune morphology by discerning the ‘right’ components and the ‘right’ conditions for a desired microstructure can be important in practical applications employing block copolymers. Of equal significance in applications is the ability to fix a desired microstructure so that it can endure operating conditions other than the equilibrium conditions under which it is stable.

Addition of a homopolymer or solvent to a block copolymer provides extra degrees of freedom useful in controlling morphology and, hence, structure/property relationships. Selective solvents also aid in the fundamental understanding of block copolymers by bringing many dynamic timescales to experimentally accessible windows and expediting equilibration. In terms of applications, solvents are already present in many applications employing self-ordered block copolymers, either in the final product or as an integral part of processing. Solvents can also facilitate the fixation of a desired or metastable microstructure through, e.g. solvent-phase polymerization/crosslinking or rapid solvent evaporation. Furthermore, selective solvents allow the creation of finite- (and controlled-) size polymeric assemblies (e.g. micelles), as well as nanoscale materials based on such assemblies, in disordered systems. While a relatively recent endeavor, the in-depth study of block copolymer phase behavior and microstructure in the presence of selective solvents therefore appears very promising in terms of fundamental understanding and practical applications. Throughout this review (which extends our complementary work addressing ‘dry’ self-ordered block copolymers [1•]), systems based on organic and on aqueous solvents will be examined in parallel to identify similarities and cross-fertilize two fields, originating from the schools of polymer physics and colloid science.

‘Dry’ block copolymers vs. surfactants in solution

The stability of different morphologies in block copolymers is the result of an interplay between enthalpic (e.g. contact between chemically different blocks) and entropic (e.g. chain stretching, confinement and frustration) contributions to the system free energy, and can be described in terms of a χN (tendency for block segregation, with χ being the Flory–Huggins interaction parameter and N proportional to molecular weight) vs. f (copolymer composition) diagram. Experimentally determined phase diagrams are now available for single-component block copolymer systems [4]. Recent advances in self-consistent field theory (SCFT) permit calculation of the free energy of ordered block copolymer phases possessing any symmetry, and show reasonable agreement with experiment [5••]. While varia-

Figure 1



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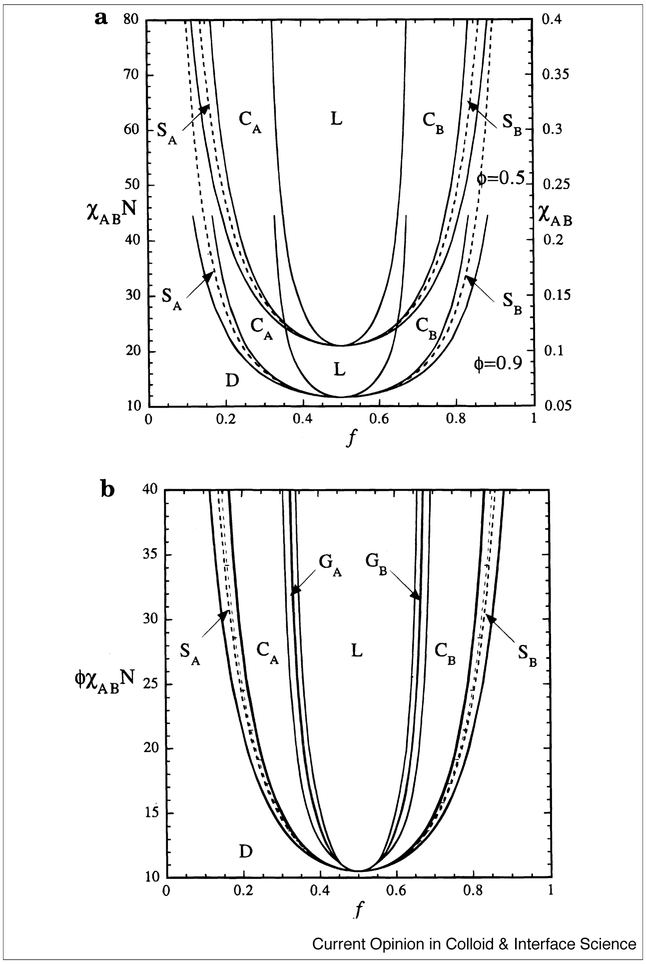
Mean-field χN vs. f phase diagram for conformationally symmetric AB diblock copolymer melts (one-component system). The different regions are labeled according to the block copolymer morphology: L (lamellar), H (hexagonally-packed cylinders), Q_{Ia3d} (bicontinuous cubic of the crystallographic spacegroup Q_{Ia3d}, gyroid), Q_{Im3m} (bcc spheres), CPS (close-packed spheres), and DIS (disordered). Dashed lines denote extrapolated phase boundaries, and the dot denotes the mean-field critical point. (Reproduced from Matsen and Bates, *Macromolecules* 1996, **29(4)**:1091–1098]; ©1996 American Chemical Society.)

tion in temperature may induce a change in microstructure (thermotropic polymorphism), f is most often varied (by synthesizing a new block copolymer) to attain a different morphology (see Figure 1).

Multicomponent systems, wherein other block copolymers, homopolymers, solvents or solutes are added to an initial block copolymer f, can order into a wide variety of morphologies. Self-consistent field theory is proving very useful in predicting the phase stability of a symmetric AB-block copolymer in the presence of a good solvent [6•] (Figure 2) or an A-homopolymer [7,8•] (Figure 3) to form a binary system, or both A- and B-homopolymers to form a ternary system (Figure 4) [9•]. These theoretical studies demonstrate that the addition of selective solvent(s) or short homopolymer(s) increases the structural (lyotropic) polymorphism, thereby reducing the need to synthesize a new block copolymer every time a specific morphology is required. As discussed later, new experimental studies corroborate the SCFT predictions (see Figures 5 and 6).

Figure 2



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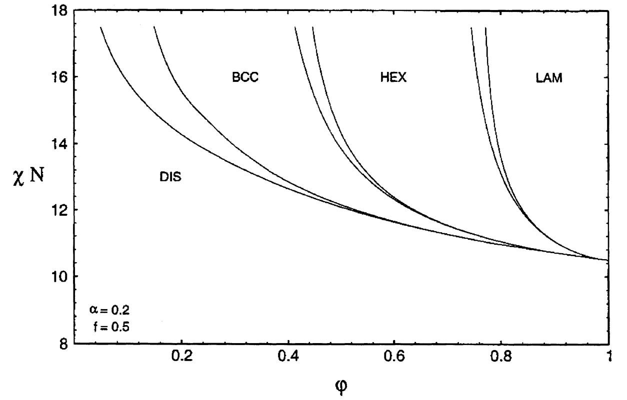
(a) Two-dimensional phase map for a diblock copolymer with N=200 in a neutral good solvent ($\chi_{AS}=\chi_{BS}=0.4$) for constant polymer concentration Φ (two-component system). (b) Rescaled phase maps from part a in comparison with the melt (see Figure 1). The different regions are labeled according to the block copolymer morphology: L (lamellar), C_A and C_B (hexagonally-packed cylinders), G_A and G_B (bicontinuous cubic of the crystallographic spacegroup Q_{Ia3d}, gyroid), and D (disordered). The melt calculation includes the G phase, whereas the solution ones do not. The dashed curves (S_A and S_B) correspond to the spinodal instability of the disordered state. (Reproduced from Ref. [6]; ©1998 American Chemical Society.)

The predicted phase diagram for the binary AB-block copolymer/A-homopolymer displayed in Figure 3 (in which f constitutes the volume fraction of AB with respect to the AB + A mixture) [8•], and the ternary isothermal AB-block copolymer/A-homopolymer/B-homopolymer phase diagram presented in Figure 4 [9•], are highly reminiscent of the phase behavior of surfactants in solution: binary temperature–concentration surfactant–water and ternary isothermal surfactant–water–oil phase diagrams, respectively [10••,11••,12]. In the limit of dilute micellar solutions, the distinction between block copolymers and surfactants becomes diffuse, and the notation ‘amphiphilic block copolymers’ is often used to refer to block copolymers that self-assemble in aqueous solutions. The advances achieved over the past year with respect to the self-ordering of block copolymers in the presence of selective solvents confirm the

Figure 3



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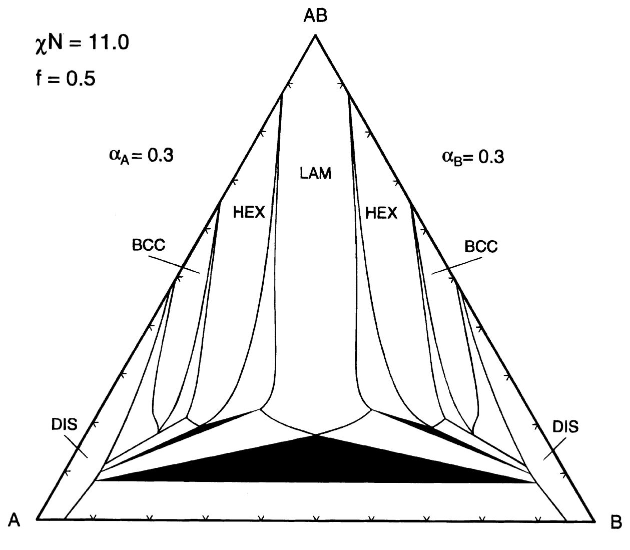
Predicted phase diagram for a symmetric AB diblock copolymer of N monomers blended with a homopolymer (two-component system). The copolymer volume fraction is denoted Φ. The ratio of the chain lengths $\alpha = N_A / N$ is $\alpha = 0.2$. The order/disorder transition for the pure diblock at $N = 10.495$ is continuous; all other transitions are first-order. The lamellar phase is denoted LAM, the phase of hexagonally arranged cylinders HEX, and the phase of spherical micelles on a body-centered-cubic lattice by BCC. The disordered DIS phase is assumed homogeneous. Regions of two-phase coexistence are unlabeled. Notice how the order/disorder transition occurs at larger values of N as homopolymer is added. This disordering effect is due to the large entropy of mixing of such short chains. (Reproduced from Ref. [8]; ©1998 American Chemical Society.)

Figure 4



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Predicted phase diagram for a symmetric AB-diblock copolymer of length N with an A-homopolymer of length $\alpha_A = 0.3N$ and a B-homopolymer of length $\alpha_B = 0.3N$ (three-component system). LAM denotes a lamellar phase; HEX, hexagonally arranged cylinders; BCC spheres on a body-centered-cubic lattice; and DIS, homogeneous phases. regions of three-phase coexistence are shaded, biphasic regions are unlabeled. (Reproduced from Ref. [9]; ©1997 American Chemical Society.)

foresight of de Gennes [13] in that ‘block copolymers can give us the best model of amphiphilic behavior’. Indeed, block copolymers afford more even flexibility than surfactants since they can be functionalized (without affecting their ability to self-order) and can organize at multiple levels and lengthscales [14••].

Gelation of block copolymers: solvent considerations

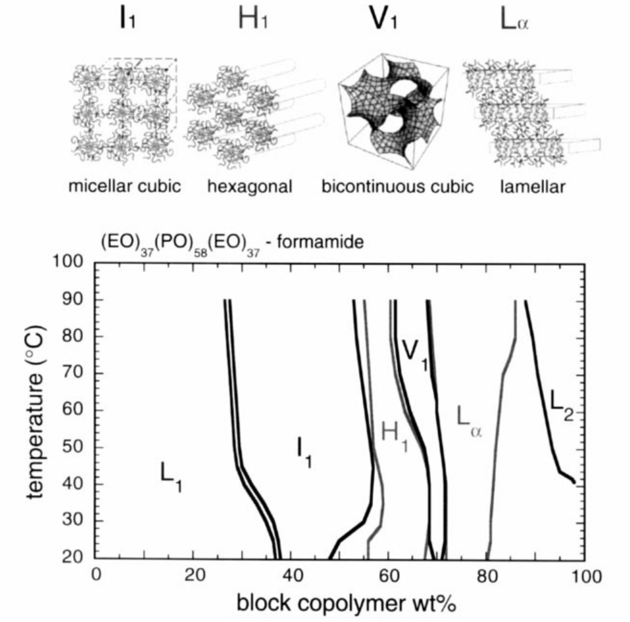
Binary block copolymer/selective solvent systems

Organic solvents

Addition of an A-selective solvent to an AB-block copolymer modifies the ratio of A and B and increases the amount of A relative to that of B, thus shifting the phase stability in the direction of less B. A selective solvent would also change the order–disorder transition (but less so than a neutral good solvent) [6•]. Solvent-induced transitions from lamellar to hexagonally packed cylinders, to body-centered cubic packed spheres, and finally to disordered micelles (see Figure 4) are nicely confirmed in experimental studies of block copolymer/oligomer [15•] and block copolymer/solvent [16•] systems, the latter of which is shown in Figure 5. Notable in both systems are regions of cubic bicontinuous microstructures that are intermediate in curvature between the lamellar and the cylindrical structures. Bicontinuous morphologies are often encountered in the weak segregation limit of block copolymers wherein fluctuation effects are non-negligible [4]. The presence of selective solvent attenuates such fluctuation effects and facilitates the formation of bicontinuous morphologies (the absence of a bicontinuous regime in Figure 4 reflects the difficulty in modeling such microstructure and not its instability).

Of the various microstructures discussed above, the one based on spherical micelles is best known in the context of thermoplastic elastomers, in which triblock copolymers, with arms spreading over two adjacent micelles, provide physical crosslinks (elastomer) [17,18•] and form a gel in midblock-selective solvents. Such physical gels can be made permanent upon vitrification of the typically polystyrene micellar core below its glass transition temperature (T_g), but can readily be reformed at temperatures above T_g (thermoplastic) [19]. It should also be noted that, while block copolymer/selective solvent phase diagrams identify morphologies at equilibrium conditions, their utility extends to transient processes such as solvent evaporation from solvent-cast block copolymer films [20•] and solvent penetration into block copolymers during dissolution [21].

Figure 5



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The concentration-temperature phase diagram of the $(EO)_{37}(PO)_{58}(EO)_{37}$ block copolymer — formamide binary system (the concentrations are expressed in wt%). The block copolymer has 50% PEO and can be considered symmetric (and comparable to that modeled in Figure 3). The phase boundaries of the one-phase regions are drawn with solid lines. I_1, H_1, V_1, and $L\alpha$, denote micellar cubic, hexagonal (cylindrical), bicontinuous cubic, and lamellar (smectic) lyotropic liquid crystalline phases, respectively, while L_1 and L_2 denote formamide-rich and polymer-rich solutions. The samples whose compositions fall outside the one-phase regions are dispersions of two different phases. The tie-lines in the two-phase regions are parallel to the concentration axis (isothermal). Schematics of the different modes of self-organization of the amphiphilic block copolymers in the presence of the solvent are shown adjacent to the respective phases in the phase diagram. The Ia3d/Gyroid minimal surface is used as a representation of the microstructure in the V_1 phase. (Reproduced from Ref. [16]; ©1998 American Chemical Society.)

Aqueous solvents

Marvellous examples of block copolymer gels in selective solvent include poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO-PPO-PEO) block copolymers in water, which is a selective solvent for PEO. These copolymers have been used extensively as surfactants in dilute aqueous solutions, but their lyotropic polymorphism at high (30–90%) copolymer concentrations has only recently been recognized [22••]. Temperature–concentration phase diagrams have been reported for PEO-PPO-PEO block copolymers differing in molecular weight and composition [23], as well as for PPO-PEO-PPO block copolymers (which behave as elastomers due to PEO bridging) [24]. Copolymer composition provides a certain preference for morphology, but the presence of solvent can reverse this. In a recent study [25•], for instance, asymmetric PEO-PPO-PEO block copolymers with low-PEO content form two types of cylindrical morphologies with either PPO or water serving as the continuous medium.

The temperature–concentration stability range of these morphologies is predicted by SCFT that accounts specifically for the reduced solubility of both PEO and PPO in water with increasing temperature [25•]. Such theoretical modeling provides valuable information on block segregation, as well as the distribution of solvent in the microstructure. Block copolymers based on PEO and PPO moieties are not the only ones capable of forming gels in water. Aqueous phase diagrams of block copolymers possessing higher degrees of block segregation, such as PEO-poly(butylene oxide) [26,27] and PEO-poly(ethylethylene) [28•], are now available. It is noteworthy that these copolymers also order in the absence of water [27,28•], indicating that common physical principles govern block copolymer self-assembly in the presence and in the absence of solvent [10••].

Gel dynamics

The use of the word 'gel' to refer to ordered block copolymers in selective solvents reflects their rheological properties, since rheology is commonly utilized to characterize the ordered microstructure of such complex fluids [29••]. Most interesting in this respect are studies that combine shear alignment of microstructure with small-angle neutron, X-ray, or light scattering at different orientations with respect to the alignment director. Detailed information can thus be obtained on the crystallography of micellar cubic [30•,31•,32•,33], cylindrical [34,35], and lamellar [36•,37••] microstructures. Ordered block copolymers, when prepared by temperature quenching or mixing with (or casting from) a solvent, inherently consist of numerous grain boundaries.

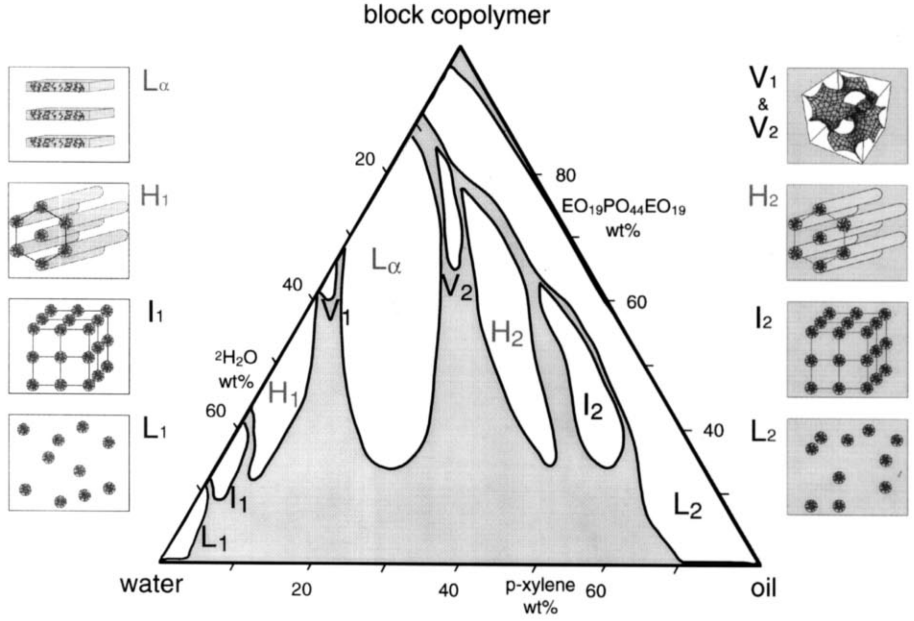
Different domains can be aligned by shear to create a monodomain (single texture) over macroscopic (cm) dimensions [38]. Furthermore, the level of shear can be used to modify the alignment (e.g. from parallel to perpendicular relative to the shear direction) in the case of lamellae. In this respect, ordered block copolymers in solvent behave similarly to 'dry' block copolymers [36•,37]. An exciting recent observation [37••] in a system of solvated block copolymers concerns the shear-induced formation of onion-like multilamellar vesicles, which have been previously observed in surfactants, but not in 'dry' block copolymers. Shear can therefore be used to generate new morphologies with finite dimensions and higher order organization.

Ternary block copolymer/solvent 1/solvent 2 systems

Diblock and triblock copolymers

Ternary systems that contain an AB-block copolymer and two solvents, one selective for the A-block and the other selective for the B-block, offer a prime example of

Figure 6



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The phase diagram of the $(EO)_{19}(PO)_{43}(EO)_{19}$–$^2H_2O$ (‘water’)–*p*-xylene (‘oil’) ternary system at 25°C. The phase boundaries of the one-phase regions are drawn with solid lines. I_1, H_1, V_1, L_α, V_2, H_2, and I_2, denote normal (oil-in-water) micellar cubic, normal hexagonal, normal bicontinuous cubic, lamellar, reverse (water-in-oil) bicontinuous cubic, reverse hexagonal, and reverse micellar cubic lyotropic liquid crystalline phases, respectively, while L_1 and L_2 denote water-rich (normal micellar) and water-lean/oil-rich (reverse micellar) solutions. The concentrations are expressed in wt%. The samples whose compositions fall outside the one-phase regions are dispersions of two or three (depending on the location in the phase diagram) different phases. Schematics of the different modes of self-organization of the amphiphilic block copolymers in the presence of solvents (‘water’ and ‘oil’) are shown adjacent to the respective phases in the phase diagram. The amphiphiles are localized at the interfaces between the water and oil domains (shaded). The Ia3d/Gyroid minimal surface is used as a representation of the microstructure in the V_1 and V_2 phases. (Adapted from Ref. [39]; ©1998 American Chemical Society.)

solvent-regulated ordering in block copolymers (see Figure 4). Poly(ethylene oxide)–poly(propylene oxide) block copolymers in mixtures with water and xylene as PEO- and PPO-selective solvents, respectively, exhibit remarkable microstructural polymorphism, with as many as nine independent morphologies — seven ordered: lamellar, water-continuous (oil-in-water, or ‘normal’) cylindrical, oil-continuous (water-in-oil, or ‘reverse’) cylindrical, water-continuous and oil-continuous micellar cubic, and two bicontinuous cubic; and two disordered: water-continuous micellar and oil-continuous micellar [39••]. That these morphologies can be formed by the same block copolymer at the same temperature (see Figure 6) is testimony to the diversity of solvated block copolymer systems. The macromolecular nature of block copolymers allows for fine-tuning of interfacial curvature and, hence, morphology through the degree of PEO and PPO block swelling by water and oil molecules, respectively.

Each of these morphologies can be formed by surfactants or lipids in the presence of water and organic solvents, but they have never all been observed together as in Figure 6. Unlike PEO-PPO-PEO block copolymers, surfactants reside in the strong segregation regime and are of comparable size to that of solvent molecules, in which case solvents cannot swell the surfactant chain and modify the preferred interfacial curvature. Ternary systems consisting of PEO-PPO-PEO block copolymers, water and oil, have been used to study the effects of copolymer molecular weight [39••,40], copolymer composition [41•,42,43], and solvent quality [41•,44] on morphology. The phase behavior exhibited by these copolymers in selective solvents is general and has also been observed [44] in PEO-poly(butylene oxide) and PEO-polystyrene block copolymers, and also in mixtures of polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene with asphaltene and maltene (components of asphalt) [45•].

Micellization of block copolymers: contemporary issues

Micelles in organic and aqueous solvents

In contrast to the ordered morphologies of solvated block copolymers, the formation of disordered (dilute) block copolymer micellar solutions represents a mature field. Several reviews have recently addressed block copolymer micelle formation and morphology in organic [46–48] and aqueous [48–52••] solutions. Issues of ongoing interest include the formation of multimolecular micelles, the characteristics and interactions of micelles, and the temperature–concentration conditions favoring micellization [48,49]. A common feature of block copolymers in apolar solvents is that micelles form with decreasing temperature, indicating that micellization is driven by enthalpic interactions [48,53,54], which is an important consideration in the design of micellar systems (e.g. for applications in lubricants). Formation of polystyrene-*b*-poly(ethylene-*r*-butylene)-*b*-polystyrene copolymers (SEBS) micelles in *n*-octane, selective for the middle EB block, is also facilitated by an increase in copolymer molecular weight [54] and by changing from the triblock to diblock architecture [55•]. At high temperatures, triblock copolymers dissolved in a poor solvent for the endblocks (similar to thermoplastic elastomer gels) form loose aggregates with a small association number. Upon decreasing temperature, the aggregates form well-defined micelles that may be connected in a network [56].

In marked contrast, heat-induced micellization has been observed [22••,49,50,57] in PEO-PPO block copolymers in water. Such entropy-driven micellization is related to the decreased solubility of PEO (and PPO) in water with increasing temperature, but its molecular origin remains in dispute [22••]. The structure of PEO-PPO-PEO micelles is a weak function of concentration, but changes rapidly with temperature [58], with the association number increasing, and micelles becoming drier, as the temperature is increased and water is expelled from the micelle core [59•]. Gradual replacement of water by polymer in the micelle core explains the broad nature of the observed transition from block copolymer unimers to micelles [59•]. While PEO-PPO-PEO micelles are typically spherical, a sphere → cylinder transition has also been documented [60•] at high temperatures.

Another distinction between block copolymers in apolar and aqueous solvents is the large difference in polarity between water and the chemical moieties comprising most block copolymers. This difference restricts the variety of block copolymers that can form micelles in water. Non-ionic PEO enjoys a unique position as a convenient hydrophilic block, but ionized polymers, e.g. poly(acrylic acid), may also be used [51,52••,61••]. Above a certain hydrophobic block size (and corresponding degree of segregation), most block copolymers become too hydrophobic, and the critical micelle concentration (CMC) becomes vanishingly small. Aggregates can still form, but not in a thermodynamically reversible fashion. Recent studies are interested in the micellization of block copolymers with relatively short PEO blocks, such as PEO-polystyrene [62•,63], PEO-poly(isobutylene) [64], and PEO-poly(ethylene-*co*-propylene) [65]. The hydrophobic scale between ethylene oxide (EO), butylene oxide (BO) and styrene (S) segments [62•], EO:BO:S = 1:4:12, provides an indication of the rapidly increasing segregation between the block copolymer and aqueous solvent.

Effect of block copolymer architecture

Studies investigating the effect of copolymer architecture on copolymer association in solution are now being extended to starblock copolymers with arms of different chemical composition [66•,67•]. Polystyrene-polyisoprene $(PS)_8(PI)_8$ copolymers have been found [66•] to form multimolecular micelles in *n*-decane, a selective solvent for the PI arms, while polystyrene-poly(2-vinyl pyridine) $(PS)_6(P2VP)_6$ copolymers form micelles in toluene, which is a selective solvent for PS [67•]. Because of the conformational constrains imposed by the multiple arms, starblock copolymers exhibit a much higher CMC, and a correspondingly lower association number, compared to analogous AB diblock copolymers [66•,67•]. The emerging synthesis of tricomponent block copolymers creates opportunities for new micellization behavior, beyond that of the bicomponent copolymers discussed above. A comparison of the solution properties of water-soluble ABC triblock copolymers consisting of methyl vinyl ether, ethyl vinyl ether, and methyl tri(ethylene glycol) vinyl ether of various block sequences suggests that the location of the hydrophilic block has a profound effect on copolymer association [68]. A poly(2-ethylhexyl acrylate)–poly(methyl methacrylate)–poly(acrylic acid) triblock copolymer has been shown [69•] to form spherical, stratified micelles in water.

Block copolymer micelles in novel solvents

Two novel solvent media, nematic liquid crystals and supercritical carbon dioxide, augment the antithesis between the properties of ‘water’ and ‘oil’ discussed above. The solution behavior of block copolymers with a liquid crystalline side-chain (LC) block and an isotropic (I) block has been studied [70•] in dilute nematic solutions composed of low-molar-mass liquid crystals. Copolymers with a high fraction of the I-block are insoluble in the nematic solvent, while copolymers with a high fraction of the LC-block are completely soluble. If the weight fraction of the LC-block lies in the range 0.46–0.85, thermoreversible thread-like aggregates are formed, with their long axis oriented along the director field of the nematic matrix.

Supercritical CO_2 continues to attract attention as a benign polymerization medium. The recent design and synthesis of surfactants capable of forming micelles in CO_2 opens the doors for use of surfactant-modified CO_2 in heterogeneous polymerizations. Polystyrene-fluoropolymer block copolymers, employed as emulsifying agents in supercritical CO_2, form small (association number 6–7) micelles with a CO_2-phobic PS core and a CO_2-philic fluoropolymer corona [71]. In this case, the pressure of supercritical CO_2 serves to control micellization. Three regions have been observed [72,73] in the phase diagrams of fluorinated block copolymers in supercritical CO_2: (i) a two-phase region at low CO_2 density; (ii) solutions of spherical micelles at intermediate CO_2 densities; and (iii) solutions of individual copolymers at high CO_2 densities. Increasing pressure and decreasing temperature increase the density of CO_2 and thus improve its solvent quality [72,73]. Micellization in CO_2 has been discerned [73] to be endothermic and entropy-driven, surprisingly similar to that of amphiphilic block copolymers in water.

Frozen micelles and other microstructured solutions

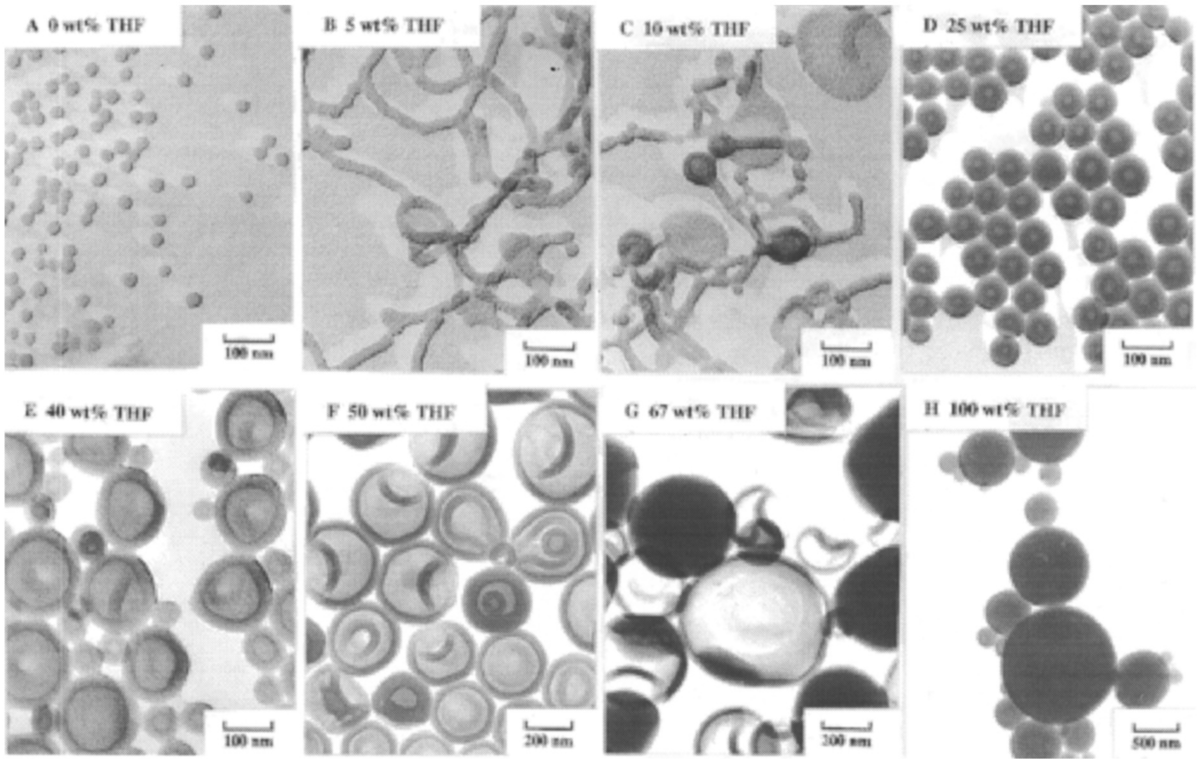
Micellar dynamics

Reasonably fast dynamics of micelle formation and amphiphile exchange between micelles are important in reaching and establishing equilibrium. If the microstructure is to be maintained beyond equilibrium (as in the case of liposomes), then the exchange dynamics must be slow. Block copolymers in solution offer the whole gamut of timescales, from millisecond [74•,75•,76,77] to hours (or longer) [78], depending on solubility and molecular weight. Fluorescence quenching techniques have proven useful in studying the exchange of block copolymers between micelles formed by polystyrene-*b*-poly(2-cinnamoylethyl methacrylate) diblock copolymers in THF/cyclopentane [79] and poly[(dimethylamino)alkyl methacrylate]-*b*-poly(sodium methacrylate) diblock copolymers in aqueous solution [80]. In the latter case, the exchange rate slows when either the hydrophilic or hydrophobic moiety of the diblock copolymers was divided into two endblocks, rendering a triblock copolymer.

Frozen micelles and other microstructures

A wide range of bilayer aggregates, among them tubules and vesicles, as well as more complex tubular or vesicu-

Figure 7



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The solvent effect can be a versatile tool of morphological control when a mixture of solvents is used. Gradual changes in the aggregate morphology can result from a progressive change in the nature of the common solvent. Figures A–H show that with increasing THF content in the DMF-THF solvent mixture, the morphology of the PS_{200}-*b*-PAA_{18} aggregates changes progressively from (A) spheres in 0 wt.% THF to: (B) interconnected rods in 5 wt.% THF; (C) a mixture of rods, lamellae, and vesicles in 10 wt.% THF; (D) only small vesicles in 25 wt.% THF; (E) medium-sized vesicles in 40 wt.% THF; (F) larger vesicles in 50 wt.% THF; (G) to a mixture of vesicles and large compound micelles in 67 wt.% THF; and finally (H) to large compound micelles in pure THF (the initial polymer concentration was 0.5 wt.%). (Reproduced from Ref. [82]; ©1998 American Chemical Society.)

lar aggregates (e.g. starfish-like vesicles, budding vesicles and vesicles consisting of one or more vesicles internalized within a larger one, as shown in Figure 7), have been prepared from various PS-*b*-PEO [81] and PS-poly(acrylic acid) (PAA) diblock copolymers [82•]. Aggregates of various morphologies can be prepared from a single block copolymer by (i) changing the solvent; (ii) adding electrolytes; or (iii) operating at subambient temperatures [81]. The morphologies and other characteristics of crew-cut aggregates of PS-*b*-PAA diblock copolymers are related to the nature of the initial common solvent in which the micelle-like aggregates were prepared [82•]. By matching the solubility parameters of the solvent and core-forming block, the solvent content of the core, as well as the degree of core chain stretching, can be controllably increased. As the degree of core chain stretching increases, the morphology of the aggregates can change progressively from spheres to cylinders, vesicles or large compound micelles [82•]. Multiple diblock copolymer morphologies, ranging from spherical micelles to vesicles, have likewise been observed [83•,84] in organic solvents. In the presence of a binary solvent mixture, identical micellar morphological transitions can be induced for the same copolymer by increasing the content of the block-selective solvent in the mixture [83•].

Conclusions

The high degree of observed morphological complexity, combined with an ascending level of understanding on how to reign such complexity, render solvated block copolymers a fertile field of investigation. Recent advances in the past year address the establishment of phase behavior and microstructure in ordered block copolymer gels and their connection to 'dry' block copolymers, and the discovery of aggregates of various morphologies in block copolymer solutions. The detailed control of morphology outlined in this review suggests that solvated block copolymers offer opportunities for novel applications that extend beyond their established uses as gels and solutions [85] into areas such as the synthesis of nanoporous materials using block copolymer assemblies as templates [61••,86•], as well as targeted drug delivery [87•] and stimuli-responsive controlled drug release [88•]. For the reasons provided here, it can certainly be said that solvated (amphiphilic) block copolymers bridge the fields of polymer physics and colloid science.

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References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

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