Structural properties of self-assembled polymeric micelles

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At present, the thermodynamic understanding of complex copolymer systems is undergoing important developments. Block copolymers aggregate in selective solvents into micelles of various form and size depending on molecular architecture and interaction parameters. The micelles constitute the basis for a variety of novel mesophases, including biocontinuous phases and networks of ordered cross-linking micelles. Research has focused on structural studies of block copolymer systems, using small-angle scattering of X-rays and neutrons.

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Abbreviations

AB	Diblock copolymer composed of an A and a B block
ABA	Symmetric triblock copolymer composed of A and B blocks where the A block is soluble in the relevant solvent
BAB	Symmetric triblock copolymer composed of A and B blocks where the A block is soluble in the relevant solvent
c	copolymer concentration
EO$_m$	poly(ethylene oxide) with m monomers
I	scattering intensity
PBO	poly(butylene oxide)
PDMS	poly(dimethyl siloxane)
PE	poly(ethylene)
PEB	poly(ethylene butylene)
PEE	poly(ethyl ethylene)
PEO	poly(ethylene oxide)
PEP	Poly(ethylene propylene)
PI	poly(isoprene)
PIB	poly(isobutylene)
PO$_n$	poly(propylene oxide) with n monomers
PPO	poly(propylene oxide)
PS	poly(styrene)
q	scattering momentum transfer
ϕ	micellar volume fraction
ϕ_c	critical micellar volume fraction for hard-sphere crystallization

Introduction

The physical properties of amphiphilic macromolecules constitute a rich topic which, in recent years, has attracted interests within both applied and basic science [1–3,4••–7••]. Currently, the field is extremely active, and a concise review of recent progress can include only limited aspects of the recent results.

When block copolymers are mixed in a solvent which dissolves only one of the blocks, the molecules self -associate into specific structures to avoid direct contact between solvent and the blocks which are insoluble. This self-association gives rise to a wide range of phase behavior, including the formation of micelles of various forms and sizes, complexly structured microemulsions, and liquid crystalline phases. A variety of block copolymers, including blocks of poly(styrene) (PS), poly(isoprene) (PI) poly(ethylene) (PE), poly(ethylene propylene) (PEP), and poly(ethylene butylene) (PEB), have been studied in this context when dissolved in selective organic solvents. In aqueous solutions, block copolymers based on poly(ethylene oxide) (PEO), as the water-soluble block have been investigated to a large extent. The insoluble or less-soluble blocks have, for example, been poly(propylene oxide) (PPO), poly(dimethyl siloxane) (PDMS), poly(butylene oxide) (PBO), PS, and poly(isobutylene) (PIB). In this paper I will review some of the recent progress on complex block copolymer systems, where the main focus has been on structural studies based on small-angle scattering of X-rays and neutrons.

Block copolymer self-association into micellar aggregates

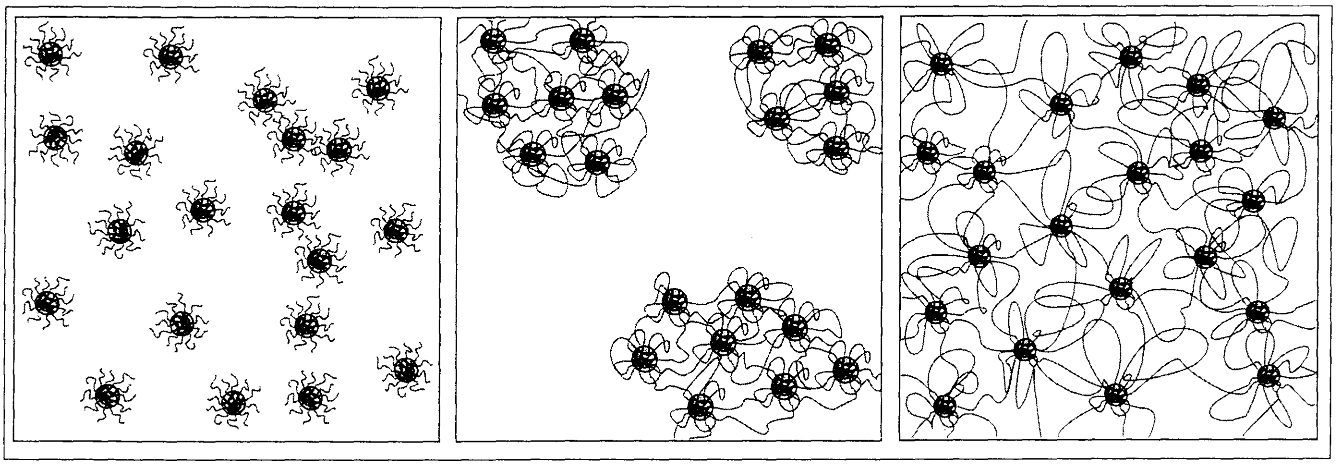
It is well established that a variety of block copolymers of AB or ABA type form micelles in solvents, which are thermodynamically good for the A block and precipitants for the B block. Such micelles constitute a liquid dispersion of hard-sphere interacting units. BAB copolymers may also form individual micelles, but this implies that all polymer chains start and end in the same micellar core having the middle A-block dispersed into the liquid. It is more likely that such micelles form interconnected networks, where cores are connected by the soluble A-polymer block, as shown schematically in Figure 1.

Critical micellization temperature and concentration

In general, micellization of block copolymers assumes an equilibrium between molecularly dispersed copolymers (unimers) and multimolecular aggregates (micelles). The thermodynamic approach for describing the aggregation process has been calculated based on lattice models with the mean-field Flory–Huggins type of segmental interactions [8,9•].

Ideal model systems for studying the micellization process and micellar interactions are aqueous systems of block copolymers composed of PEO with either PPO or PBO, because at low temperatures all these polymers are hydrophilic, but at higher temperatures PPO and PBO become hydrophobic. At low temperature aqueous solutions of PEO–PPO–PEO and PEO–PBO–PEO therefore appear as unimers. Structural studies based on scattering [5••] and ^{1}H-NMR relaxation [10] indicate that the PEO–PPO–PEO unimers resemble unimolecular micelles

Figure 1



Schematic representation of spherical micelles. Left: micelles of AB- or ABA-type of block copolymers, resulting in independent hard-sphere interacting aggregates. Middle: micelles of BAB-type block copolymers, with relative short middle-block chains, resulting in domains of interconneced networks of spherical aggregates. Right: micelles of BAB-type with large, flexible middle-blocks, resulting in a network extending over the whole sample volume, thus providing a macroscopic gel. Note that the micellar density is the same in the three examples.

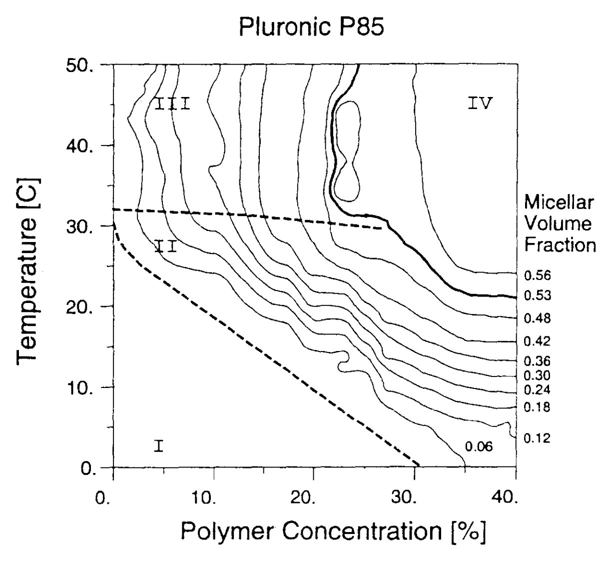
where the PPO blocks have a more compact structure than that of chains obeying Gaussian conformation.

The temperature-induced change in hydrophobicity leads to a temperature above which micelles are formed with a core dominated by PPO (or PBO) and surrounded by a corona of hydrated PEO subchains. Model calculations have described this entropy driven micellization process [8,9•,11]. Equivalent temperature-induced micellization has been studied in PS–PI–PS triblock copolymer systems in dibutyl phthalate, which changes from a good to a bad solvent for PS when the temperature is reduced [12•].

Depending on the molecular architecture and the interaction parameters, various micellar forms can appear, such as spherical, rod-like and discoid shapes. In the $EO_mPO_nEO_m$ systems, changes from spherical to rod-like and discoid shapes can be followed by changing temperature or concentration. For high copolymer concentrations, corresponding transitions from cubic to hexagonal and lamellar liquid crystalline phases appear. In many of the $EO_mPO_nEO_m$ systems all three classical phases are present, but with reduced PEO size, first the spherical micelles and successively the rod-like and disc-like micelles vanishes [13,14•,15•], eventually leading to a bicontinuous microemulsion [16].

One of the important parameters obtained from the experimental scattering data [17] and other indirect techniques [18] is the micellar volume fraction, ϕ [17]. For example, in Figure 2 a contour plot of ϕ data of $EO_{25}PO_{40}EO_{25}$ (Pluronic 85® from BASF) is shown [5••,19]. The phase diagram for $EO_mPO_nEO_m$ looks the same for different values of this material; only the specific values of transition temperature (T_{cml}) and concentration change. The variation in ϕ separates into four regimes.

Figure 2



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Temperature versus polymer-concentration contour plot showing the experimental micellar volume fraction, ϕ, of aqueous solutions of $EO_{25}PO_{40}EO_{25}$ (reproduced with permission from [5••]). The solid line represents ϕ=0.53 and separates the micellar liquid (regimes II and III) and the cubic ordered phase (IV). The broken lines are guides separating these characteristic regimes: I, unimers; II, unimers and micelles and III, spherical micelles.

At low temperatures and concentrations (regime I), all polymers are dissolved as unimers. Above a line of critical micellization temperatures and concentrations a regime of coexisting micelles and unimers appears (regime II). The dispersion is totally dominated by micelles in regime III. In regime IV ϕ reaches a critical limit (ϕ_c) of the order of ϕ_c

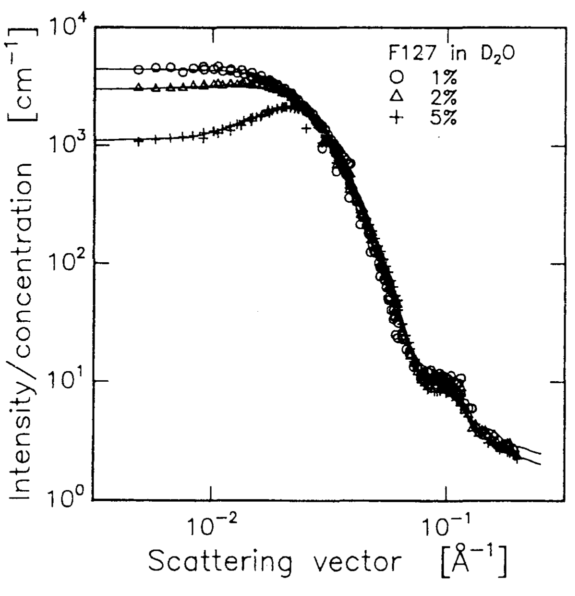
Micellar size and aggregation number

The micellar core radius of $EO_mPO_nEO_m$ copolymers is roughly independent of copolymer concentration, but shows temperature dependence reflecting changes in aggregation number [5••,13]. The change in micellar radius for different $EO_mPO_nEO_m$ copolymers shows very similar characteristics. The core size follows an empirical scaling relation relative to the reduced temperature: $R_c \sim (T\text{-}T_{cml})^{0.2}$. The aggregation number, N_{agg}, can, with similar results, be calculated independently both from the core dimensions, and based on the limiting volume fraction in regime III [17].

Scattering from spherical micelles

The scattering functions ($I[q]$, where I is the scattering intensity and q is the scattering momentum transfer) of $EO_{99}PO_{65}EO_{99}$ micelles for various copolymer concentrations (cs) are shown in Figure 3 [20]. The characteristics of the scattering functions are the concentration dependent correlation hole, in other words reduced intensity at low q, the side maximum near $q = 0.1$ Å^{-1} and the limiting $I \sim q^{-2}$ behavior at high q values, reflecting to first order the intermicellar correlations, the micellar core and the dispersed PEO chains respectively.

Figure 3



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Example of scattering functions, I(q), of different concentrations of spherical ABA triblock copolymer micelles ($EO_{99}PO_{65}EO_{99}$) obtained at T=35°C (reprinted with permission from [20]). The solid line represents the best fit to the analytical scattering function expressed by the micellar form factor [21•] and the structure factor with hard-sphere interacting spheres [22].

The micellar form factor can be expressed analytically, assuming a dense core and Gaussian chains in the corona [21•]. The solid lines in Figure 3 represent best fits to this formula, including smearing due to limited instrumental resolution and intermicellar correlations based on hard-sphere interactions in the Percus–Yevick approximations (discussed in [22]).

The spherical micellar conformations have been confirmed by direct imaging, using cryo-transmission electron microscopy [20]. The micellar characteristics as obtained from small-angle neutron scattering may also be compared to the micellar hydrodynamic radius, R_h, as obtained using dynamic light scattering [23,24]. Generally, the micellar hydrodynamic radius is larger than the core and smaller than the interaction radius.

Rod-, worm- (thread) and disc-like micelles

Depending on the block copolymer design and the specific interaction parameters between solvent and polymer blocks, micellar shapes other than spherical aggregates may form. In the $EO_mPO_nEO_m$ copolymers it is thermodynamically possible to follow a transition from spheres to rods and discs by changing the temperature and/or the size of the PEO blocks. Aqueous solutions of PEO–PPO–PEO show, at elevated temperatures, a form transformation from spherical to rod-like micelles [5••,13]. The origin of the sphere-to-rod transition is related to the size of the spherical aggregates. Close to the sphere-to-rod transition the core radius is large relative to the polymer backbone, resulting in either highly stretched PPO chains, or major mixing of PEO and PPO inside the core. Both possibilities lead to costs in free energy, the former result being entropically costly and the latter causing an increase in chemical potential, leading to the sphere-to-rod micellar shape transformation [5••,13].

In a recent study of a closely related block copolymer micellar system, consisting of PEO–PIB–PEO, coexistence of spherical and thread-like micelles was observed in a combined neutron scattering and cryo-electron microscopy study [25•].

At even higher temperatures disc-like micelles appear. Similar sequences in micellar form has been observed in micelles of low-molar mass glycol dodecyl ether, in which the shape is governed by changes in spontaneous curvature [26]. The changes in thermodynamic interaction parameters of aqueous PEO–PPO–PEO systems can equally be attributed to changes in an effective spontaneous curvature determining the shape of the micellar aggregates. In PEO–PPO–PEO block copolymer systems with only small hydrophilic PEO blocks, the spherical aggregates are not stable in any conditions. This is the case for the $EO_6PO_{62}EO_6$ system, where the micellar phase consists of disc-shaped aggregate [16].

Micelles with a crystalline core

A special class of disc-like micelles is based on crystalline block copolymers. Richter *et al.* [27••] and Lin and Gast

[28••] have shown that, in dilute solutions, semicrystalline diblock copolymers may form thin platelet structures consisting of chain-folded crystalline domain between solvated layers of the amorphous, tethered block chains. Examples of such systems are PE–PEP suspended in decane and PEO–PS in cyclopentane. The tethered chains make up a brush structure with a parabolic density profile, supporting self-consistent field theories. The core thickness is determined as being a compromise between the entropic contribution from brush stretching and the enthalpic input from crystalline chain folding. The large surface area enables the weak van der Waals interaction between the platelets to overcome the translational entropy, thus giving rise to needle-form macro-aggregates [27••].

Micelles with a glassy core

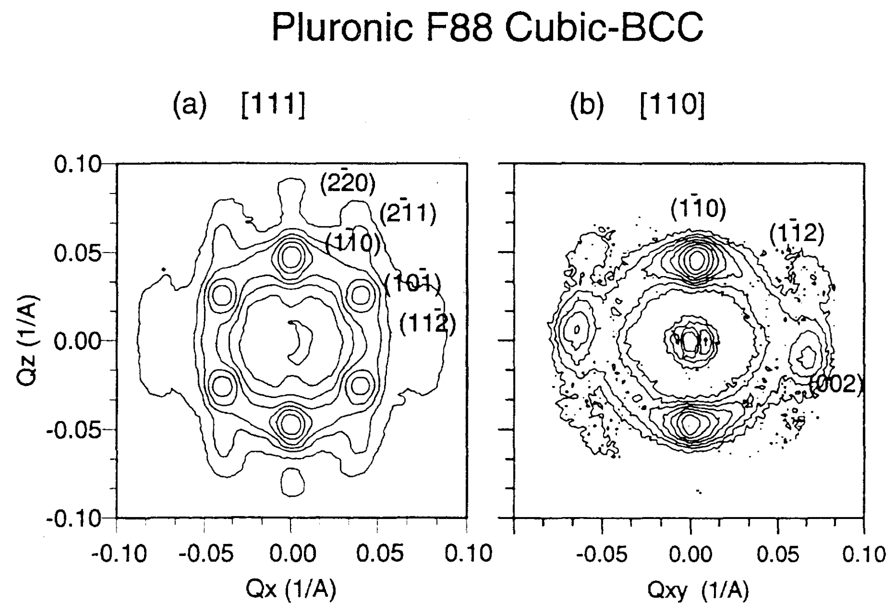
A number of micelles are composed of block copolymers in which the insoluble block is a glass at relevant temperatures. Any dynamics involving molecules jumping from one micelle to another or involving micellar shape transformations are frozen out. Block copolymers of PS are examples of such systems. Mixing PS–PEO block copolymers with water at ambient temperatures leads to large plate or rod-like micelles present in the original lamellar sheets of the bulk PS–PEO. Only when annealed above the glass transition of the PS block do the micelles relax to the spherical equilibrium structure ([29•]; K Mortensen, unpublished data). In a triblock copolymer of the BAB type, the glassy cores have a particularly strong influence, as they make up a permanent physical network structure, as discussed further below.

Cubic phase of spherical ABA and AB block copolymer micelles

In the contour plot of ϕ shown in Figure 2, we see that the limiting value of the saturation point is of the order of $\phi_c = 0.53$. When this ϕ_c border line is crossed the micellar liquid undergoes a first order phase transition to a cubic crystal [30] with the elastic shear modulus of the order of 10^4–10^5 Pa [23,24]. The liquid and crystalline domains coexist in the range of $\phi_c = 0.47$–0.53 [31], in agreement with simple hard sphere crystallization [32].

Shear has a marked effect on the crystalline texture, as it aligns the polycrystalline powder into one macroscopic monodomain. Both bcc [5••,19] and fcc [33•] phases have been reported in the $EO_mPO_nEO_m$ and related micellar systems [34], depending on the detailed micellar structure. The shear dependence on the $EO_mPO_nEO_m$ cubic phase seems to depend on the specific material used. While an earlier study showed only minor shear dependence [5••], more recent experiments have shown shear thinning and structural dislocation ([35•,36]; C Glinka *et al.*, personal communication) in analogy to the results of Gast and co-workers on PS–PI [34]. The local crystalline lattice undergoes a deformation which eventually develops into a bcc twin structure. At higher shear rates, loss of long-range order is observed which is associated with shear melting.

Figure 4



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Two-dimensional scattering pattern of $EO_{96}PO_{39}EO_{96}$, as obtained **(a)** with the shear axis parallel to the beam, and **(b)** when the sample is rotated by 35° around the vertical axis.

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Single crystal crystallography

Diat *et al.* [37•] have studied the influence of shear and found that by applying an oscillating shear of strain amplitude less than unity, twinned free single crystals of millimeter scale can be obtained. The monodomain cubic phase of $EO_mPO_nEO_m$ micelles has, typically, a mosaicity of the order of 10° [5••]. With shear-oriented crystals, it is possible to perform crystallographic studies and to index the observed Bragg reflections. For example, the two-dimensional scattering pattern of $EO_{96}PO_{39}EO_{96}$ is shown in Figure 4. The scattering pattern is in agreement with a bcc lattice, as indicated by the associated Miller indices. When the limit of high temperature and/or high polymer concentration is reached, the cubic phase of the $EO_mPO_nEO_m$ micelles melts near the transition from spherical to rod-like form.

Nematic phases of micelles

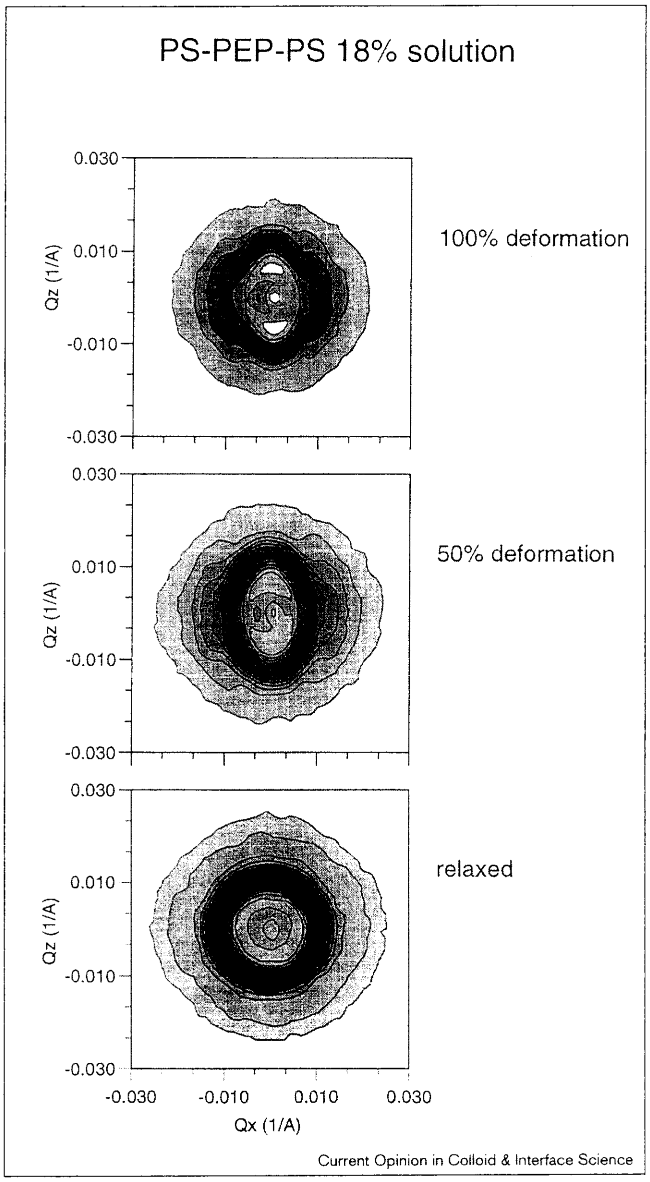
Both the rod-like and the disc-like micelles form potentially nematic phases above certain concentration limits. It has been shown that in steady shear rod-like and worm-like micelles align to various degrees depending on polymer concentration and shear rate. The degree of alignment can be quantified by the ratio between scattered intensity parallel and perpendicular to the shear. For concentrations above 15–20%, the $EO_mPO_nEO_m$ systems form hexagonal rod structures [5••,19]. Disc and platelet micelles, like the crystalline micelles discussed above, also form nematic phases with near lamellar-like structures [27••].

BAB block copolymer architecture

The phase behavior of a triblock copolymer of BAB type in a solvent selective for the midblock (polymer A) results in quite different structures relative to the AB and ABA types. These polymers may also form micellar aggregates. It is frequently observed, however, that systems of dilute polymer concentration,rather than miclles, make up loose structures of less well defined associates [7••,38,39].

In the micellar phase, the A-midblocks of the BAB copolymers form either loops or bridges between micelles. The intermicellar bridging gives rise to clusters of highly interconnected micelles. Such behavior has been reported for aqueous $PO_{15}EO_{156}PO_{15}$ micellar systems where an excess of water is present at up to 50% copolymer concentration [38]. For a certain copolymer concentration, the micellar networks extend over the whole sample volume, thus providing a macroscopically isotropic physical gel. This concentration depends critically on the size and flexiblilty of the midblock chain, and may vary from a few percents, as observed for PS-PEB-PS (Kraton) in oil [40,41] to 50% as observed in PPO-PEO-PPO Reverse-Pluronics in water. In $PO_{15}EO_{156}PO_{15}$ at low temperatures, a cubic ordered structure is observed in the isotropic phase [42]. Equivalent results were recently obtained for a variety of poly(butylene oxide)–poly(ethylene oxide), $BO_nEO_mBO_n$, based system [43,44,45].

Figure 5



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Two-dimensional scattering pattern of PS–PEP–PS when (top) stretched 100% (middle) stretched 50% and (bottom) relaxed [57].

The usual Pluronics, $EO_mPO_nEO_m$, might be of the BAB type if dispersed in nonpolar solvents. Alexandridis *et al.* [46,47] and Chu and co-workers [48,49] have studied the aggregation behavior of $EO_mPO_nEO_m$ in xylene and found micelles with the classical cubic, hexagonal in the oil-rich phase has significant influence on the micellization [49]. Ternary systems of both $EO_mPO_nEO_m$ and $PO_nEO_mPO_n$ molecular architecture include the bicontinuous gyroid phase [46,51•,52] well known from both low molar weight surfactants and bulk block copolymer systems. The gyroid structure has not yet, however, been observed in simple aqueous systems of PEO-PPO based block copolymers.

Micellar networks

Depending on the lifetime of the polymer blocks associated with a given core, BAB material may show a finite elastic response. Systems with glassy micellar cores are ideal for such elastomers cross-linked by self-association. A number of studies have focused on the PS type of block copolymers, including PS–PI–PS [39,53,54•], PS–PEP–PS [40] and PS–PEB–PS [41,55•]. Scattering experiments, as well as electron microscopy imaging, have clearly revealed the spherical PS cores with, effectively, hard sphere interactions [41,55•].

The microscopic response to macroscopic deformation of the three-dimensional network was studied by neutron scattering. Upon stretching, of up to 100%, additional correlations appear in specific directions, resembling induced paracrystalline order, as shown in Figure 5 [56]. Further stretching gave rise to an anisotropic pattern of the butterfly type, indicating nonhomogeneous connectivity [57].

With increasing temperature, the structure factor of PS–PEB–PS systems becomes clearly more pronounced, revealing increased effective volume fraction. For polymer concentrations of 15% or more, this causes ordering above $T \approx 55°C$ [58•]. At even higher 6temperatures, the structure factor becomes even broader, showing that the ordered structure is stable within a limited temperature window only. It has also been shown that ordering into cubic phases of PS–PI–PS block copolymers can occur [54•].

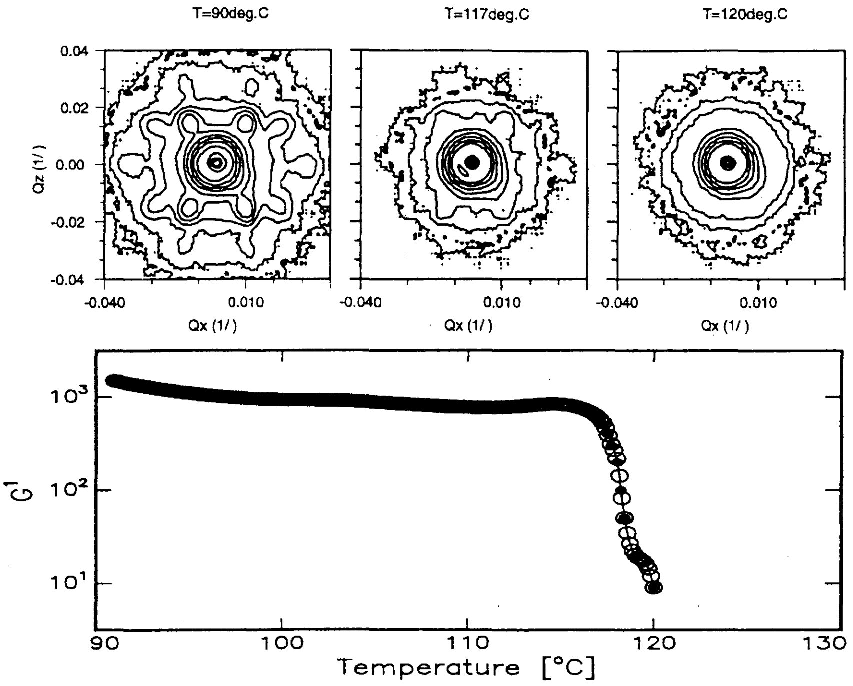
Shear alignment of BAB copolymer ordered networks

As in the AB and ABA systems, the BAB ordered gels might align into a monodomain cubic structure upon application of shear [42,59•]. In BAB networks of PS–PEB–PS micelles, the scattering pattern resembles a twinned bcc morphology with lattice constants of the order of 400 Å, as shown in Figure 6. Upon cooling to ambient temperatures, the characteristic bcc pattern remains, even though the peaks may broaden. This may reflect that although the bcc structure is thermodynamically unstable in this range, the twinned bcc structure is frozen because of the glassy poly(styrene) micellar cores.

Conclusions

In this review I have attempted to provide an overview of recent experimental studies of block copolymer micellar structures and mesophases. It is clear that the field is extremely active and a large variety of materials with novel

Figure 6



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Simultaneous results of scattering pattern (above) and rheology (below) near the cubic order-disorder transition in PS–PEB–PS gels.

properties can be designed based on the basic understandings gained. An example is the polymer networks where all cross-links are formed by self-association and positioned on a perfect lattice.

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• of special interest
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Combined neutron and light scattering and rheological measurements give detailed information on the aggregation behavior of block copolymer micelles in the melt, as well as in solution.

30. Mortensen K, Brown W, Nordén B: **Inverse melting transition and evidence of three-dimensional cubatic structure in a block-copolymer micellar system.** *Phys Rev Lett* 1992, **68**:2340-2343.

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Berret and co-workers present experimental data on the shear-related texture in a lyotropic crystalline micellar system. The good resolution of the X-ray technique enables the authors to study in detail the transition between shearing flows dominated by oriented textures at low shear rates and flows mediated by the mechanisms of layer sliding at higher rates.

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38. Mortensen K, Brown W, Jørgensen E: **Phase behavior of poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide) triblock copolymer melts and in aqueous solutions.** *Macromolecules* 1994, **27**:5654-5666.

39. Lairez D, Adam M, Raspaud E, Carton JP, Bouchaud JP: **Triblock copolymers in a selective solvent. 1. Aggregation process in dilute solutions.** *Macromolecules* 1994, **27**:2956-2964.

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