6680 *Macromolecules* **2004,** *37,* 6680−6682

Access to the Superstrong Segregation Regime with Nonionic ABC Copolymers

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Received June 28, 2004
Revised Manuscript Received July 28, 2004

Block copolymers readily self-assemble into a rich variety of ordered phases, an attribute shared with other important soft materials such as surfactants and liquid crystals. The factors that govern the choice of ordered state symmetry, and the details of chain packing within a particular lattice, are rather well understood in the case of bulk, two-monomer "AB" diblock copolymers and also for analogous diblocks that undergo micellization in selective solvents. In both bulk and solution, the key free energy balance lies between minimizing interfacial area and satisfying the desire of the constituent blocks to be random coils. Thus, in the undiluted AB copolymer the interfacial tension scales as $\sqrt{\chi}$, where χ is the interaction parameter between A and B repeat units; the distortion ("stretching") of the individual blocks away from the preferred Gaussian conformation varies as L^2/Nb^2, where L is the microdomain periodicity, N is the number of repeat units, and b is the statistical segment length.[1] In a micelle formed from AB copolymers in a solvent favoring A, the interfacial tension γ can be related to an effective χ parameter between the B core and the solvated A corona. The conformational freedom of the A block in this case is dominated by the osmotic repulsion, i.e., excluded volume, between the well-solvated corona chains, which also leads to chain stretching away from the interface. The self-consistent mean-field theory (SCMFT) approach to describing the resulting phase behavior has become highly refined and capable of describing most experimental observations with near quantitative accuracy.[2]

The SCMFT now recognizes three distinct regimes, termed "weak", "intermediate", and "strong" segregation. The first imagines the individual coils to be at most weakly perturbed from the Gaussian state expected as $\chi \rightarrow 0$ and is not actually accessed within the ordered state. The last regime is obtained when the individual chains are large enough, and the interfacial tension high enough, that the inevitable interfacial zone between domains of pure A and B is negligible in thickness compared to the domain dimensions themselves. In practice, this regime corresponds to the dimensionless product $\chi N > 50-100$. However, a few years ago, Semenov, Khokhlov, and co-workers identified a new regime of phase behavior that they dubbed "superstrong segregation", in which the interactions between A and B become so strong that the interfacial energy overwhelms the conformational entropy (in the bulk) or the coronal crowding (in solution).[3,4] In this case flat interfaces are favored, and the minor block becomes nearly fully extended. To date, this regime has not been examined experimentally in a systematic fashion. Indeed, Semenov et al. suggested that it might only be experimentally accessible using ionic polymers to gain the requisite interaction strength.[3] It is the purpose of this communication to demonstrate that, in fact, it is possible to access this superstrong segregation regime (SSSR) with nonionic, flexible coil block copolymers, by use of three-monomer ABC triblock copolymers and judicious choice of chemical groups A, B, and C. The key aspect of this strategy is that the choice of a triblock copolymer can lead to internally segregated micelles with two interfaces (C/B and B/A + solvent), thereby significantly augmenting the role of interfacial tension. Furthermore, the A, B, and C monomers should be selected to maximize their mutual repulsion. In the nonionic case, a hydrophilic A, a lipophilic B, and a hydrophobic and lipophobic fluoropolymer C offer the necessary strong 3-fold philicity.

A prototypical experimental system that we propose affords access to the SSSR consists of a water-soluble poly(ethylene oxide) (O) block; a hydrocarbon, polystyrene (S); a fluoropolymer (F), obtained by grafting perfluorohexyl iodide groups to a 1,2-polybutadiene (B) backbone. A linear OSB triblock was prepared first by controlled anionic polymerization, with block molecular weights of 13 200 ($N_O = 300$), 4700 ($N_S = 45$), and 1300 ($N_B = 24$), respectively; the B block was then functionalized to produce OSF, with an F block molecular weight of 4600.[5] The micelles formed by dispersing 1% of each copolymer in aqueous solution were characterized by dynamic light scattering, small-angle neutron scattering, and small-angle X-ray scattering. These several experiments provided a consistent and quantitative characterization of the micellar shape and size.[5] The OSB micelles were spherical, consisting of a core of intermixed S and B segments within an O corona; the core radius R_c was about 20 nm and the overall micellar radius R about 50 nm. In contrast, the OSF micelles were flattened disks or oblate ellipsoids, containing an F core, an S shell, and an O corona. In this case the inner F core had principal radii of 25, 25, and 5 nm, and the S shell was about 5 nm thick. The overall hydrodynamic radius was also about 50 nm.

As will be discussed below, the appearance of the disk shape for a micelle formed from flexible coil polymers is a signature of the SSSR. Note that this behavior is fundamentally distinct from disklike micelles formed as a result of core block crystallization[6] or from rod−coil copolymers[7] and that fluorination of the butadiene block does not generate a rodlike conformation.[8] The OSF micelles have more recently been examined by cryogenic transmission electron microscopy (cryo-TEM), in which thin (<200 nm thick) free-standing films of aqueous solution are vitrified by rapid immersion in liquid ethane prior to imaging. Figure 1 shows a representative cryo-TEM image. The round objects correspond to micellar cores viewed along the minor axis. The uniform shade of gray suggests projections of an object of approximately constant thickness (as opposed to, say,

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10.1021/ma048708b CCC: $27.50

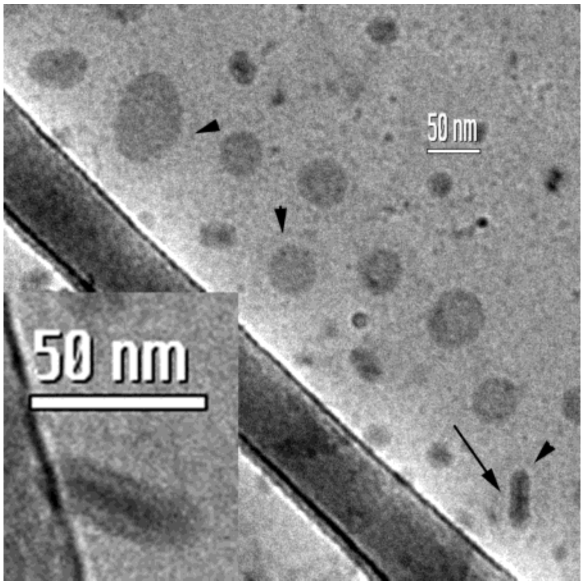

Figure 1. Cryo-TEM images of OSF micelles. Arrowheads indicate the extent of the "O" corona; the long arrow identifies a micelle viewed side-on. The inset presents an expanded side view, revealing the F core and S shell.

a sphere). The corona blocks are well solvated and not directly visible, but the arrowheads indicate the characteristic halo of O that has undergone some beam damage; in addition, an "exclusion zone" between micelles reflects the extent of the corona. Most importantly, however, some micelles were adventitiously locked in place while "standing on edge"; an example is expanded in the inset. In this case the dark F core and the gray S shell can be clearly resolved and the flattened disk structure unambiguously confirmed.

The fact that the OSF micelles are disklike could be taken as prima facie evidence that the SSSR has been achieved. However, the case would be more compelling if the distinction between OSB spheres and OSF disks could be reconciled at least semiquantitatively with the predicted criteria for the SSSR, and that is the main purpose of this paper. The situation is illustrated schematically in Figure 2. The first image (a) corresponds to the spherical OSB micelle and the middle image (b) the OSF disk; the dimensions are approximately to scale. The image (c) is of a hypothetical core–shell–corona spherical micelle, which OSF might be expected to form if it were not in the SSSR. Thus, in the following we estimate the free energies of structures (a) and (c) and show that OSB is expected to form (a), whereas OSF should not form structure (c). To begin, it is helpful to recall the principal free energy competition that governs "normal" micelles, in the relevant case where the corona blocks are longer than the core blocks. The size of a spherical micelle is determined by the interfacial tension at the core–corona interface, balanced against the osmotic crowding of the corona chains.[1,9]

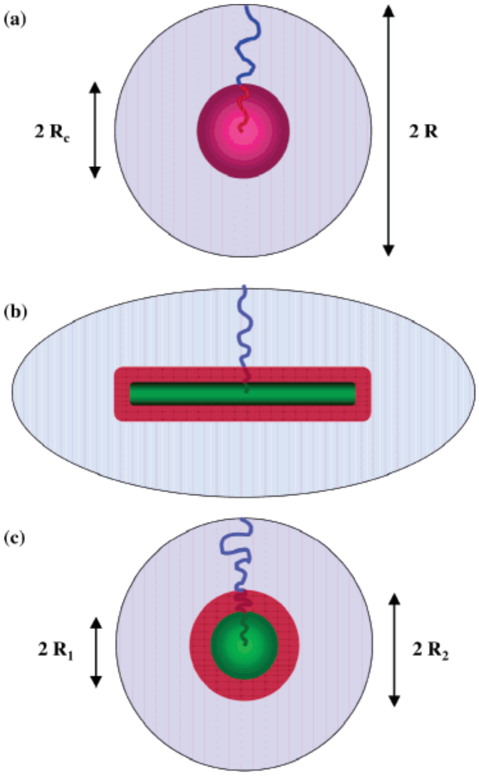

Figure 2. Schematic drawings of (a) a simple spherical core–corona micelle from an AB diblock copolymer, (b) a core–shell–corona oblate ellipsoid (disk) micelle from a linear ABC triblock copolymer, and (c) a core–shell–corona spherical micelle from a linear ABC triblock copolymer. All images show a representative block copolymer chain.

The free energy per micelle in units of kT is given by the sum of the interfacial energy and corona stretching terms:[3]

$$F = F_{\text{int}} + F_{\text{corona}} = 4\pi R_c^{\,2}\gamma + \frac{1}{\sqrt{2\pi}} f^{3/2}\ln(R/R_c) \qquad (1)$$

where f is the aggregation number. The core radius and aggregation number are directly linked via the core block density (assuming no solvent penetration), and minimizing the free energy per chain with respect to f gives the preferred aggregation number

$$f^* = \gamma^{6/5}(N_c v_c)^{4/5} 4\pi \frac{2^{3/5}}{3^{2/5}} (\ln[R/R_c])^{-6/5} \qquad (2)$$

where N_c and v_c are the degree of polymerization and monomer volumes for the core block, respectively. This leads to the following expression for the core radius

$$R_c = \gamma^{2/5}(N_c v_c)^{3/5} 6^{1/5} (\ln[R/R_c])^{-2/5} \qquad (3)$$

If γ increases, then both f and R_c increase; a transition to a cylindrical micelle, with smaller area per chain but greater corona crowding, is also possible if the corona block is not too long. The transition from strong segregation to the SSSR arises when the core block becomes fully stretched without transforming to cylinders; according to Semenov et al., this corresponds to $R_c \approx N_c b_c/2$, where b_c is the statistical segment length of the core block.[3] This occurs at a critical value of γ^* obtained from eq 3:

$$\gamma^* = N_c \frac{b_c^{\,5/2}}{v_c^{\,3/2}} \ln(R/R_c) \frac{1}{8\sqrt{3}} \qquad (4)$$

When this criterion is exceeded, a disklike micelle becomes the preferred morphology, rather than a cylinder, as the interfacial area per chain is less in the former. Thus, the key element of the SSSR is that the interfacial tension dictates the morphology, rather than a balance between interfacial tension and chain crowding. However, as Semenov et al. show, the corona blocks can still exert some influence by limiting the lateral extent of the disks;[3] the additional space available to the corona reduces the average chain stretching.

We now treat OSB as a diblock with S and B forming a single core block. The scattering measurements gave $R_c \approx 20$ nm and $R \approx 50$ nm, and an aggregation number $f \approx 3400$.[5] The large values of R and R_c suggest that the OSB system is quite strongly segregated, and consistent with that inference, the experimental values (including $v_c \approx 0.14$ nm^3) inserted into eq 2 suggests $\gamma \approx 22$ nm^{-2}. For comparison purposes, the surface tension of water is about 17 nm^{-2} in these units, whereas for hydrocarbon polymer blends γ is usually less than 1 nm^{-2}. Consequently, this value is probably too high, although a reasonable order of magnitude. With $b_c \approx 0.68$ nm, eq 4 gives

$$\gamma^* \approx 33 \text{ nm}^{-2} \tag{5}$$

as the necessary interfacial tension to access the SSSR. This is greater than the inferred value of γ, but by less than a factor of 2, which suggests that OSB is within striking distance of the SSSR.

We now turn to the core−shell−corona micelle in Figure 2c and modify the interfacial contribution as there are now two interfaces per micelle:

$$F_{\text{int}} = 4\pi R_1^{\,2}\gamma_1 + 4\pi R_2^{\,2}\gamma_2 \tag{6}$$

Here subscripts 1 and 2 denote the inner and outer surfaces of the shell, respectively. The core and shell radii are linked, namely

$$R_2^{\,3} = \left(f\frac{3}{4\pi}(N_c v_c + N_s v_s)\right) = R_1^{\,3}\left(1 + \frac{N_s v_s}{N_c v_c}\right) \tag{7}$$

where subscript s denotes the shell-forming block. Minimizing F/f with respect to f as before and applying the fully stretched criterion to the inner core yields

$$(\gamma_1 + x\gamma_2)^* = N_c \frac{b_c^{\,5/2}}{v_c^{\,3/2}} \ln(R/R_s)\frac{1}{8\sqrt{3}} \tag{8}$$

where

$$x = \left(1 + \frac{N_s v_s}{N_c v_c}\right)^{2/3} \tag{9}$$

Note that the full stretching criterion must be applied to the inner block in this case, as the shell block can adjust its conformation as necessary.

As structure (c) for OSF is only hypothetical, some assumption must be made as to the micellar size. Assuming that f is the same as for OSB, then we may also expect $R \approx 50$ nm and $R_2 \approx 20$ nm. The other necessary parameters $N_c = 24$, $b_c \approx 0.68$ nm, $v_c \approx 0.18$ nm^3, and $x \approx 1.8$ yield the critical value for the combined interfacial tensions as

$$(\gamma_1 + 1.8\gamma_2)^* \approx 8 \text{ nm}^{-2} \tag{10}$$

The remarkable result is that the required net interfacial energy for the SSSR is lower by a factor of 4 compared to that of the diblock. As the value of γ_2 estimated above is 22 nm^{-2}, it is apparent that OSF should indeed be well into the SSSR, independent of the value of γ_1. The factor of 4 reduction in the requisite critical interfacial tension between eqs 5 and 10 arises from the doubling of the number of interfaces in the ABC micelle and the reduction in N of the core block. The latter factor is enabled by the choice of the highly repulsive S and F segments. Note the interesting feature that γ should be essentially equal at the core/corona interface in OSB and the shell/corona interface in OSF; therefore this parameter is not, in itself, the origin of the change in behavior.

These results demonstrate that an entirely new domain of block copolymer phase behavior, the super-strong segregation regime, can be accessed in a controlled fashion with nonionic triblock copolymers. The SSSR offers new possibilities in terms of self-assembled structures and associated physical properties from relatively simple molecular architectures as well as an opportunity for further interplay of theory and experiment in block copolymer self-assembly.

Acknowledgment. This work was supported primarily by the MRSEC Program of the National Science Foundation under Award DMR-0212302. The cryo-TEM work was performed at the Hannah and George Krumholz Laboratory for Advanced Microscopy at the Technion.

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(9) The stretching of the core blocks is relatively insignificant when the corona blocks are longer, as is the case here; inclusion of stretching terms would modify our numerical estimates slightly but not affect the conclusions.

MA048708B