1418 *Macromolecules* 1991, *24*, 1418–1419

On the Collapse of Multiblock Copolymers

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Received July 27, 1990;
Revised Manuscript Received August 15, 1990

The phase behavior of multiblock copolymers received little attention. Its primary feature is, of course, the repression of macroscopic phase separation in favor of mesophase formation. A pioneering study, by Benoit and Hadziioannou, considered the melt case. It suggests that the microphase separation depends only weakly on the number of blocks.[1] Yet, in other situations qualitative effects are expected. Both kinetic and equilibrium phenomena are possible. For example, the number of blocks can radically modify the kinetics of phase separation. Thus, a quenched semidilute solution of linear multiblock copolymer can yield a physical gel.[2] The cross-links are due to aggregates of the insoluble blocks. This gel is viewed as arrested phase separation: The growth of the immiscible blocks' nuclei is frozen because of bridges of soluble blocks. In the following we consider the distinctive features of *dilute solutions* of multiblock copolymers. In particular, the behavior of *linear* $(AB)_n$ *multiblock copolymers* in a *highly selective solvent of low molecular weight*, specifically, a nonsolvent for the B blocks but a good solvent for the A coils. In this regime intramolecular aggregation may occur. Depending on the number blocks, their nature, and their size, one may expect the formation of a single molecular micelle or a string of such micelles.

We focus on flexible,[3] neutral copolymers, comprising monodispersed A and B blocks consisting, respectively, of N_A and N_B monomers. Under such conditions, a mixture of A and B homopolymers undergoes a macroscopic phase separation. The few soluble B blocks adopt a collapsed configuration, i.e., a globule of radius $N_B^{1/3}a$, where a is the monomer size. AB diblock copolymers exhibit a different behavior. The B block in isolated, free copolymers adopts the collapsed configuration of a free B homopolymer. However, the macroscopic phase separation is replaced by micellization. For finite concentrations, larger than the critical micelle concentration (cmc), the diblock copolymers aggregated into spherical micelles.[4] These consist of a meltlike inner core, comprising insoluble B blocks, and an exterior corona of soluble A blocks swollen by the solvent. For multiblock copolymers, different scenarios are possible. In particular, one must allow for the formation of "*molecular micelles*" incorporating blocks belonging to a *single* copolymer. These molecular micelles are structurally similar to micelles of diblock copolymers with the caveat that both core and coronal blocks form loops anchored to the core surface (Figure 1). We denote the number of incorporated AB pairs, the aggregation number, by f. The optimal f, f_e, corresponds to a minimum in the free energy per aggregated AB pair. f_e reflects the interplay of surface free energy of the core and free-energy penalties due to aggregation-induced deformations. It is now possible to distinguish two simple limiting cases: (i) $n \approx f_e$, when the multiblock copolymer "collapses" into a single molecular micelle, and (ii) $n \gg f_e$, when the copolymer rearranges into a linear string of molecular micelles. Loop formation is unlikely since it imposes overlap of micellar coronas at the loop junction. Such overlap is heavily penalized.[5] Also, loop formation results in loss of configurational entropy. When n is roughly an integer multiple of f_e, the molecular micelles are expected to be thermodynamically stable. This follows because the formation of competing, intermolecular micelles involves a loss of translational entropy in addition to the contributions listed above. Even when this requirement is not fulfilled, the molecular micelles may be long lived because of the colloidal stabilization provided by the coronal blocks. This last point applies in particular to multiblock copolymers in the range $1 \ll n < f_e$. This range is of special importance since synthetic capabilities are limited, at present, to the production of multiblock copolymers consisting of a dozen blocks or so.[6]

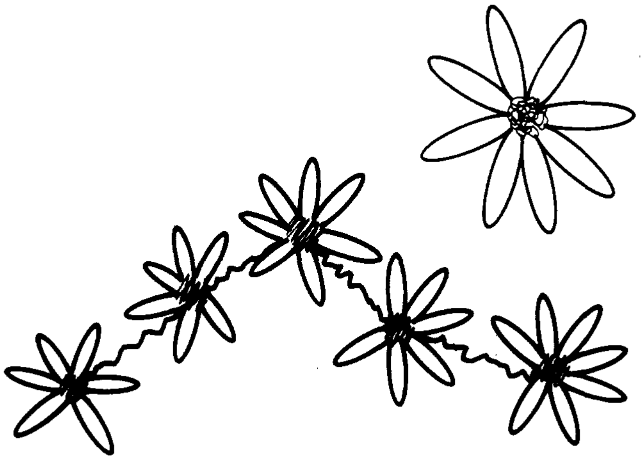

Figure 1. Schematic representation of a multiblock copolymer in a selective solvent showing cross sections of a single molecular micelle (inset) and a string of such micelles.

For brevity we focus most of the discussion on the two simple cases noted earlier, that is, $n \approx f_e$ and $n \gg f_e$. Our analysis utilizes scaling arguments. We assume thus that N_A and N_B are large. As is customary in scaling arguments, numerical prefactors are ignored. To simplify the calculation, we ignore the effects of loops. In particular, a loop is replaced by two coils obtained by cutting it in half.[7] The molecular micelles are thus assumed to be identical with micelles of AB diblock copolymers. Finally, we limit the discussion to starlike micelles[4,8] with coronas of thickness, H, much larger than the core radius, R_{core}.[3]

The equilibrium structure of such micelles corresponds to a minimum in F, the free energy per aggregated AB pair. In this limit, F accounts for two contributions: $F_{surface}$, the surface free energy, is proportional to the core area per AB pair, R_{core}^2/f. Since $R_{core}^3 \approx fN_Ba^3$, we have $F_{surface}/kT \approx (\gamma a^2/kT)f^{-1/3}N_B^{2/3}$, where γ is the core's "surface tension". This term favors micellar growth. The second term, F_{corona}, allows for the deformation of the coronal loops. Within our model the corona is pictured as a spherical grafted layer, reminiscent of the corona of star polymers. It characteristics may be found through a blob ansatz due to Daoud and Cotton.[9] The corona is assumed to consist of concentric shells of close-packed blobs such that a grafted A coil contributes a single blob to each shell. This last requirement accounts for the stretched configurations adopted by densely grafted chains. The blob's size varies with the shell's radius so that $r^2\xi(r) \approx f\xi^3(r)$ or $\xi \sim r/f^{1/2}$. The coronal thickness, H, is found by utilizing the monomer conservation requirement in the form $N_A \approx \int_{R_{core}}^{R_{core}+H}(\xi/a)^{5/3}\xi^{-1}\,dr$ where $(\xi/a)^{5/3}$ is the number of monomers per blob. In the limit of interest, of $H \gg R_{core}$, H is given by $H \approx f^{1/5}N_A^{3/5}a$. F_{corona} is obtained by the kT per blob ansatz $F_{corona}/kT \approx \int_{R_{core}}^{R_{core}+H}\xi^{-1}\,dr \approx f^{1/2}\ln\,(R_{core} + H)/R_{core} \approx f^{1/2}$. Minimization of F with respect to f yields $f_e \approx N_B^{4/5}$ and the corresponding H, $H_e \sim$

0024-9297/91/2224-1418$02.50/0

$N_B^{4/25}N_A^{3/5}a$.[10] We are now in a position to specify the characteristics of an $(AB)_n$ multiblock copolymer in a selective solvent. Since we limited our analysis to starlike molecular micelles, the copolymer must satisfy the following inequalities: If $n \lesssim f_e$, we must have $N_A \gg n^{2/9}N_B^{5/9}$, while in the opposite limit, of $n >> f_e$, we require $N_A \gg N_B^{4/5}$. In the first case, $n \approx f_e$, the copolymer forms a single molecular micelle. Since the micelle is starlike, its radius, R, is dominated by H and we have

$$R \approx H \approx n^{1/5}N_A^{3/5}a \tag{1}$$

$$R_{\text{core}} \approx n^{1/3}N_B^{1/3}a \tag{2}$$

In the opposite limit of $n \gg f_e$, the copolymer collapses into a string of n/f_e starlike micelles. Each molecular micelle is characterized by $H \approx N_B^{4/25}N_A^{3/5}a$ and $R_{\text{core}} \approx N_B^{3/5}$. For large n/f_e, the string of micelles is expected to exhibit self-avoidance and we have $R \approx (n/f_e)^{3/5}H$ or

$$R \approx n^{3/5}N_A^{3/5}N_B^{-8/25}a \tag{3}$$

It is helpful to compare relations (1) and (3) with R of the AB diblock copolymer obtained by grouping the individual A and B blocks, i.e., an A diblock copolymer comprising an A block of nN_A A monomers and a B block of nN_B B monomers. Since the radius of a diblock copolymer is dominated by the swollen A block, we have

$$R \approx n^{3/5}N_A^{3/5}a \tag{4}$$

Thus, R of a multiblock in the case $n \approx f_e$ is smaller by a factor of $n^{-2/5}$. In the opposite limit of $n \gg f_e$, the multiblock copolymer radius is smaller by a factor of $N_B^{-8/25}$. It is also important to note the differences between the behavior of the B blocks in the isolated copolymers. In a diblock copolymer it collapses into a globule of radius $N_B^{1/3}a$ while in the molecular micelles, the B block configuration is nearer to that of an ideal B coil. Finally, in the regimes considered multiblock copolymers do not aggregate into intermolecular micelles. In marked distinction to the diblock copolymer, the number of free multiblock copolymers in a selective solvent is identical with their number in a nonselective solvent. In conclusion, a somewhat similar behavior was observed in graft polymers comprising a hydrophobic homopolymer carrying short amphiphilic side chains.[11-13] In extreme solvent conditions such polymers adopt a micellar configuration. Depending on the nature of the solvent, the amphiphilic chains populate the core or the corona; i.e., the polymer can form the counterpart of a regular or of an inverted molecular micelle. Internal micelles also appear in weak polyelectrolytes immersed in a poor solvent.[14,15] A chain carrying monomeric stickers capable of pair formation exhibits somewhat similar features.[16]

Acknowledgment. It is a pleasure to acknowledge helpful discussions with Professors H. Benoit, J. M. Guenet, and J. Herz, who introduced the author to multiblock copolymers. The hospitality of Prof. E. W. Fischer and the Max-Planck-Institut für Polymerforschung is gratefully acknowledged.

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