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On the Adsorption Threshold of Multiblock Copolymers

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How does the adsorption behavior of multiblock copolymers differ from that of homopolymers? While the adsorption of homopolymers has been studied extensively,[1] comparatively little is known about the corresponding phenomenology of multiblock copolymers. Yet, this last system is of considerable interest: First, it provides a convenient starting point for the discussion on adsorbed copolymers in general. Second, as we shall see, the adsorption behavior of multiblock copolymers exhibits novel features of interest in its own right. A useful single-chain characteristic to study is the adsorption threshold, δ_c.[2,3] When the attractive energy per monomer at the surface, $-\delta kT$, is weaker than $\delta_c kT$, the configuration of a linear chain at the surface is isotropic. In essence, it retains the configuration of a free chain. In the opposite limit, $\delta \gg \delta_c$, the chain adopts a flattened, pancake-like configuration. δ_c of a linear, flexible, homopolymer comprising N monomers is specified by $\delta_c \sim N^{-\phi}$, where ϕ is a crossover exponent. N^{ϕ} is the number of monomers in contact with the surface. The adsorption threshold occurs when the adsorption free energy of the chain is of order kT; i.e., $F_{ads}/kT \approx N^{\phi}\delta \approx 1$. ϕ, the crossover exponent, assumes different values depending on the spatial dimensionality, the solvent quality, and the penetrability of the surface. In three dimensions, $\phi = 1 - v$ for penetrable surfaces[3,4] while for impenetrable surfaces $\phi \approx {}^{3}/_{5}$ in good solvents and $\phi = {}^{1}/_{2}$ in Θ solvents.[5] In the following we consider δ_c of a linear $(AB)_f$ multiblock copolymer consisting of $f \gg 1$ symmetric AB diblock copolymers joined "head to tail". Each A and B block comprises n monomers so that $2nf = N$. In this case we may consider the individual AB diblock as an effective monomer. The number of AB units at the surface is thus f^{ϕ}. In the following we compare the adsorption behavior of such multiblock copolymers with that of a linear homopolymer consisting of N identical monomers, each with a contact interaction of $-\delta kT$. δ_c of the multiblock copolymer *differs from that of a homopolymer* when the adsorption free energy per diblock, ϵ, is not given by $\epsilon \sim n^{\phi}\delta kT$. This Note concerns such a case. It involves the penetrable interface between two coexisting fluid phases α and β. α is the better solvent for the As while β is the preferential solvent for the Bs. For brevity, we limit the discussion to the symmetric case, i.e., $\chi_{A\alpha} = \chi_{B\beta} = \chi$ and $\chi_{A\beta} = \chi_{B\alpha} = \bar{\chi}$, where the subscripts specify the identity of the block and the phase described by the Flory χ parameter. We further assume that all monomer–monomer interactions are identical. Since our concern is with the adsorption threshold, the two fluids are only *weakly selective*; i.e., $|\delta kT| = |\chi - \bar{\chi}| \ll kT$. Finally, we focus on the sharp interface case, assuming that the weak adsorption of a single polymer does not modify its structure. As we shall see, in this situation δ_c assumes a novel form. In particular, $\delta_c \sim f^{-1/4}n^{-1}$ in a Θ solvent and $\delta_c \sim f^{-1/5}n^{-1}$ in a good solvent. In marked difference, the corresponding expressions for multiblock copolymers exhibiting homopolymer-like behavior are $\delta_c \approx f^{-1/2}n^{-1/2}$ and $\delta_c \approx f^{-2/5}n^{-2/5}$, respectively. These features reflect the novel scaling behavior of $\epsilon \approx n^2\delta^2$. In turn, this is due to the "polarization" of the constituting diblocks at the interface.

As noted above, the crucial ingredient in our discussion is the calculation of the average adsorption free energy of a single AB diblock, ϵ. A diblock at the $\alpha\beta$ interface is "polarized". In the bulk the A and B monomers are uniformly distributed within a sphere of radius $R_0 \approx n^{1/2}a$. This situation may be envisioned as the superposition of two spherical monomer "clouds" due respectively to the A and B blocks. At the interface the two clouds no longer fully overlap: The diblock assumes an ellipsoid-like configuration and an excess of A monomer is expected on the α side while on the β side there is an excess of B monomers. The free energy of such an "induced dipole" at the surface may be deduced via a simple scaling argument.[6] We argue that the relative surface excess is proportional to x/R_0, where x is the separation between the centers of the two monomer clouds. The limit of $x/R_0 = 1$ is attained only for highly selective α and β such that only one monomer species is found in each phase. The surface excess is of the form nx/R_0 and the associated free energy is thus $-kT\delta nx/R_0$. The polarization is countered by the Gaussian elastic free energy of the chain, kTx^2/R_0^2. Altogether the free energy per chain is $F_{chain}/kT \approx x^2/R_o^2 - \delta nx/R_0$. Minimization with respect to x yields $x \approx \delta n^{3/2}a$ and an equilibrium free energy of

$$\epsilon/kT \approx -n^2\delta^2$$

In the case of good solvent conditions $R_F \approx n^{3/5}a$ should replace R_0 in the above expressions. The validity of the resulting expression for the elastic free energy is limited to the linear response regime. With this modification one obtains $x \approx \delta n^{8/5}a$ but with no modification in ϵ. The distinctive scaling form of ϵ arises because all monomers within a diblock at the interface are involved in the surface interaction. Since this ϵ does not exhibit n^{ϕ} scaling, it leads to novel expressions for δ_c and the thickness of the strongly adsorbed multiblock. For the symmetric diblock copolymer, when $F_{ads} \approx \epsilon$, this suggests $\delta_c \approx n^{-1}$.

Consider first the adsorption of an ideal chain, i.e., when both α and β are Θ solvents for both A and B. The adsorption threshold, $F_{ads}/kT \approx 1$, is specified by $f^{1/2}n^2\delta^2 \approx 1$, leading to

$$\delta_c \approx f^{-1/4}n^{-1}$$

In the limit of $\delta_c \ll \delta \ll 1$ the adsorbed chain adopts a flattened, pancake-like configuration. The thickness of this "pancake", W, can be deduced by means of a scaling argument. W is assumed to have the form $W \approx R_0 g(F_{ads}/kT)$, where $R_0 \approx f^{1/2}n^{1/2}a$ is the radius of the free, ideal chain, a is a typical monomer size, $F_{ads}/kT \approx f^{1/2}\epsilon/kT$, and g is a scaling function. When $\delta \ll \delta_c$ and $\epsilon/kT \ll 1$, $g(F_{ads}/kT) \approx 1$ so that $W \approx R_0 \approx f^{1/2}n^{1/2}a$. On the other hand, when $\delta \gg \delta_c$, W is expected to be independent of f. Assuming that $g(F_{ads}/kT)$ exhibits a power law form in this limit, that is, $g(F_{ads}/kT) \approx (f^{1/2}\epsilon/kT)^{\alpha}$, we obtain $W \approx f^{1/2}n^{1/2}a(f^{1/2}\epsilon)^{\alpha}$, leading to $\alpha = -1$ and thus

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$$W \approx n^{-3/2}\delta^{-2}a$$

This is in marked contrast to the $W \approx \delta^{-1}a$ behavior expected for linear homopolymers. This result may also be obtained by minimization of an appropriate free energy. Following de Gennes[2] we assume a uniform, step-like, monomer concentration profile. The fraction of diblocks at the surface is thus $n^{1/2}a/W$. In a Θ solvent monomer–monomer interactions do not play a role and the chain is assumed to be ideal. The flattened configuration adopted by the coil is due to interplay between the adsorption term, $(n^{1/2}a/W)f\epsilon$, and the confinement penalty $R_0{}^2/W^2$. Altogether the free energy per chain is

$$F_{\text{chain}}/kT \approx fna^2/W^2 - (n^{1/2}a/W)fn^2\delta^2$$

and minimization with respect to W yields the equilibrium value quoted above. This result applies while $W > n^{1/2}a$ or $\delta < n^{-1/2}$. When $W \approx n^{1/2}a$ all the AB junctions are constrained to the interface and an increase in δ will cause no further decrease in W.

A somewhat different scenario is found in good solvent conditions, when ϕ of a penetrable surface is $\phi = 1 - \nu = {}^2/_5$. In this case the number of diblocks at the surface is $f^{2/5}$ and $F_{\text{ads}}/kT \approx f^{2/5}n^2\delta^2$. The adsorption threshold, as determined from $F_{\text{ads}}/kT \approx 1$, is thus

$$\delta_c \approx f^{-1/5}n^{-1}$$

The scaling argument for W now involves the form $W \approx R_F g(F_{\text{ads}}/kT)$ with $R_F \approx f^{3/5}n^{3/5}a$. Imposing the same requirements as before, we obtain $\alpha = {}^3/_2$ and the thickness of the adsorbed pancake in the $\delta \gg \delta_c$ regime is

$$W \approx n^{-12/5}\delta^{-3}a$$

As in the Θ solvent case, one may obtain this result by minimization of F_{ads}. However, to allow for the good solvent conditions, it is necessary to introduce two modifications: (i) The fraction of AB diblocks at the surface should be written as $n^{3/5}a/W$ rather than $n^{1/2}a/W$. (ii) The "scaling form"[7] of the confinement free energy, $N(a/W)^{5/3}kT$, should replace the ideal chain form. In this case the lowest width is $W \approx n^{3/5}a$, corresponding to $\delta \approx n^{-1}$.

The polymeric architecture can modify the associated adsorption behavior. Such is the case with topological features such as branching and closure, i.e: star[8] and ring[9] polymers. For multiblock copolymers, the similarity to homopolymers is expected to grow with the number of blocks. Yet, even in this limit their molecular architecture can give rise to distinctive phenomenology. One such case is their adsorption at a liquid–liquid interface.

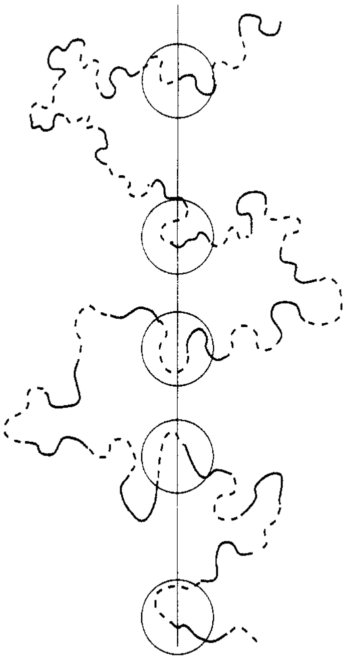

Figure 1. Schematic cross section of a multiblock copolymer at a penetrable, liquid–liquid interface. The diblocks at the interface, marked by circles, are depicted as fully polarized.

References and Notes

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(6) This result may also be obtained by analyzing the Schrodinger type equation governing the propagator of the ideal chain at an interface. A detailed discussion may be found in: Sommer, J. U.; Halperin, A.; Daoud, M. *Phys. Rev. E*, submitted.

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