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Multiblock Copolymers at Interfaces: Concentration and Selectivity Effects

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ABSTRACT: We consider the adsorption of mutiblock copolymers made of a regular succession of 2*N* consecutive sequences of *Z* monomers of alternating species A and B, respectively. These eventually adsorb at the interface between two immiscible, good but selective solvents for the different species. We consider the various surface regimes that may occur as selectivity and surface concentration are changed. These range from flat to hairpin conformations for large selectivities and small concentrations. These progressively crossover to adsorbed configurations with very polydisperse loop distribution of sizes for intermediate selectivities and large surface concentrations.

I. Introduction

Large polymers always interact strongly with surfaces and interfaces. This is due to the fact that even when the interaction of a single monomer with the surface is weak, the total interaction energy between the surface and the polymer may be strong[1−5] because a large number of units are interacting with the surface. The shape and composition profile depend on the exact nature of the surface and of the chain. Two types of surface, namely penetrable or impenetrable, may be considered. The first one is found when a chain is attracted by the interface between two solvents, for instance, whereas the second one involves a solid surface. The latter case was mainly studied, so far, and has applications in colloidal stabilization and flocculation. The former case is also interesting because multiblock copolymers may be used as adhesives between the corresponding homopolymers. They also have a large potential as emulsifiers. The interest in mutiblocks is that their selectivity may be low and that they may be manufactured to suit many liquid mixtures. (We thank one of our referees for pointing this out.) Another potential application concerns the possibility of making foams by choosing a copolymer and a solvent of only one type of sequence.

The difference between solid and liquid interfaces lies in the number (N_s) of monomers that are located on the surface when the polymer is not adsorbed, when excluded volume interactions are taken into account. For penetrable surfaces, or interfaces between solvents, we have $N_s \sim N^{2/5}$ (*N* being the total number of monomers), whereas the exponent is close to $^3/_5$ for solid surfaces.[6] From this knowledge, it is possible to get, using a scaling approach, the various surface regimes, the characteristic properties of the chains and the concentration profile for each type of surface.[7,8] More recently, a lot of work was devoted to the structure of polymers and copolymers at surfaces.[9−25] In what follows, we will consider the special case of multiblock copolymers at the interface between two immiscible solvents.[26−30] We were initially motivated, at least partly, by the adsorption of proteins such as β-casein at the interface between water and oil. Such a molecule may be roughly described as being a succession of hydrophobic and hydrophilic sequences.[9] The simplest way to describe this system is to assume that we are dealing with a regular copolymer, made of *N* sequences of *Z* monomers each. Actual proteins sequences are rather random, with a distribution of values for *Z*. This might be considered in a second approach. Because of the selectivity of the solvents, the polymers have a strong tendency to go to the interface. In our first study, we assumed that the difference in selectivities was very large, so that the junction points between sequences were located on the interface between the solvents.[31] However it is interesting to see what happens when the difference in selectivities is not so large. The case of infinitesimal difference in selectivities was studied recently by Sommer et al.[32,33] This led us to consider the case of variable selectivity in order to understand how a multiblock copolymer is first adsorbed and how the junctions between sequences are progressively localized on the interface when selectivity is increased or temperature changed. As the presence of many polymers on the interface usually leads to the presence of large loops, it was also interesting to consider the influence of surface concentration on the structure of the adsorbed copolymers.

In what follows, we will first review the results for the adsorption of polymers on a penetrable surface. Then we will consider in section 3 the case of the adsorption of a multiblock copolymer at the interface between two good solvents. The origin of the attraction of the chain by the interface is the difference in selectivities between the solvents for both sequences of the copolymer (see below). We will then progressively increase this attraction and study how the copolymer adheres to the interface. Section 4 will deal with the many-chain problem. The main difficulty in that section is to reconcile the results found in the adsorption and in the strong selectivity cases: For large surface concentrations, in the so-called plateau regime, the adsorbed polymers are made of a very polydisperse distribution of loops. In the latter case, if we force the junction points to be located on the surface, the conformation of the sequences tends to be hairpins for large concentrations. As we will see, this difference is resolved simply by allowing some junction points to leave the surface. As a result, the excluded volume energy of the chains does not increase, rather the system adapts its interaction energy with the interface by forming large loops.

II. Adsorption on a Penetrable Surface

Let us consider first the case of a homopolymer chain made of *N* monomers of size *a* in the vicinity of an

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attractive interface between two good solvents. We will assume that the surface is flat and neglect its roughness. Each monomer is attracted and has a free energy gain $kT\delta$ (k is Boltzmann's constant, T is the temperature, and δ is the dimensionless energy) when it is directly on the surface, where δ is assumed to be small. We further assume that the interaction is very short range and that only monomers located on the surface are attracted. Because we are considering the interface between two good solvents, the chain may be on either side, and we are dealing with a penetrable interface. This was already considered by de Gennes[34] and by Eisenriegler et al.,[6] who showed that, when the chain is not adsorbed, the number of monomers on the surface (N_s) is

$$N_s \sim N^{2/5} \tag{1}$$

where we used the Flory value for the excluded volume exponent. The free energy gain per chain is therefore $kT\delta N_s$ and is to be compared with the thermal energy of the polymer in order to decide whether it is adsorbed or not. Thus, when δN_s is small, the chain is basically isotropic. When it is larger than unity, the polymer is adsorbed and takes a flat configuration. Its width (D) may be derived by a simple scaling argument. Assuming that the size of the chain depends only on the dimensionless energy, we have

$$D = N^{3/5} a f(\delta N^{2/5}) \tag{2}$$

where the unknown function $f(x)$ is analytic for small x and has a power law behavior for large x: $f(x \to \infty) \sim x^{\alpha}$, where the exponent is determined by the condition that D should be independent of N. We find

$$D \sim \delta^{-3/2} a \tag{3}$$

A similar argument may be given for the radius of the polymer in the adsorption plane ($R_{||}$). The main difference with the previous one comes from the condition that determines the exponent: here, because the polymer is flat on the surface, the molecular weight dependence should be two-dimensional, so that $R_{||} \sim N^{3/4}$. We find:

$$R_{||} \sim N^{3/4} \delta^{3/8} a \tag{4}$$

Note that although the polymer is adsorbed, it is locally isotropic. Consequently, we may define blobs with size D, made of g monomers such as $\delta g^{2/5} \sim 1$, that are on the verge of being adsorbed. The polymer may be regarded as a two-dimensional array of blobs, so that

$$R_{||} \sim \left(\frac{N}{g}\right)^{3/4} D \tag{5a}$$

with

$$D \sim g^{3/5} a \tag{5b}$$

Above an overlap surface concentration Γ^*, the chains interpenetrate each other and large loops start forming. The overlap concentration is

$$\Gamma^* \sim \frac{N}{R_{||}^{\,2}} \sim N^{-1/2} \delta^{-3/4} \tag{6}$$

In the semidilute regime, the size D of the adsorbed layer may again be obtained by a direct argument. Assuming that the width depends only on the reduced concentration

$$D = \delta^{-3/2} g\left(\frac{\Gamma}{\Gamma^*}\right) \tag{7a}$$

and that $g(x)$ behaves as a power law for large x, we determine the exponent by the requirement that the width is proportional to $N^{3/5}$. We find

$$D \sim N^{3/5} (\Gamma^2/\delta)^{3/5} a \tag{7b}$$

Thus the width grows with surface concentration until it reaches the plateau value for

$$\Gamma_{\rm sat} \sim \delta^{1/2} \tag{8}$$

where the adsorbed layer has the size of an isotropic polymer. The surface is then saturated, and very few polymers more may still adsorb. Coming back to relations 3 and 5b, one can check that the surface is then saturated with isotropic blobs: $\Gamma_{\rm sat} \sim g/D^2$.

III. Adsorption of a Multiblock Copolymer

Let us now consider a multiblock copolymer made of $2N$ sequences of Z monomers each in the vicinity of the interface between two good solvents. We will consider only the symmetric case, where the two types of sequences have equal number of monomers. Although the solvents are good for both sequences, there is a slight selectivity: solvent α prefers monomers A while solvent β prefers B units. We first recall the results of Sommer et al.,[11] who also considered the asymmetric case. We assume that the difference in the quality of the solvents for each sequence is tiny. Let χ be the interaction parameter of monomers A and B in solvents α and β, respectively, and $\bar{\chi}$ that of monomers A and B in solvents β and α, respectively. We are thus considering the symmetric case. Finally let δ be the selectivity parameter, which is the difference between the quality of the solvents: $\delta = \chi - \bar{\chi}$. Because of this selectivity, each sequence has a tendency to be in its better solvent. This however would imply that the copolymer lies at the interface and therefore looses its translational entropy. Thus we have to compare these contributions to the free energy in order to determine whether the copolymer is at the surface or not. As mentioned above, the copolymer goes to the interface because each sequence is then in its favored solvent. This leads us to consider the multiblock as a special homopolymer, where the N diblocks act as monomers. Following Sommer et al., we evaluate the free energy gain per diblock: if no difference is present between both solvents, both A and B monomers would be equally present on both sides of the interface. Because of the slight selectivity of the solvents, there is a deformation of the monomer distribution, and each species is slightly in excess on one side of the surface. Because of this, the centers of gravity of the sequences no longer coincide but are on different sides of the surface. Therefore, they are at some distance x, to be determined. We may say that there is a polarization of the diblock in this sense. The free energy of such a configuration (F_s) is made of two parts. The first is an elastic contribution that tends to make the centers of gravity of a diblock coincide. In a Flory approximation, this may be written as $F_e \sim kT(x^2/R^2)$, where $R \sim Z^{3/5}$ is the average radius of a sequence. The second contribution is the free energy gain because a

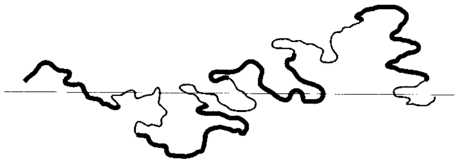

Figure 1. Adsorption of a mutiblock when the selectivity is sufficiently large. Note that large loops involving more than one sequence are present when the selectivity is not too high.

fraction of the monomers are on the "right" side. This may be written as $kT\delta(Zx/R)$, where we assumed that the fraction of monomers in their preferred solvent is proportional to x/R. Thus the free energy of a configuration with centers of masses at a distance x from the interface is

$$F = kT[x^2/R^2 + Zx(\delta/R)] \tag{9}$$

Minimizing this quantity with respect to x, we find $x \sim \delta ZR$ and the energy gain (ϵ) per diblock

$$\epsilon \sim (Z\delta)^2 \qquad (\delta Z \ll 1) \tag{10a}$$

Note that, when δZ is on the order of unity or larger, the sequences are located on each side of the interface, as will be discussed below, so that we expect x to be on the order of R and the energy gain per sequence becomes on the order of δZ

$$\epsilon \sim Z\delta \qquad (\delta Z \gg 1) \tag{10b}$$

Because the copolymer is in the vicinity of a penetrable interface, the number of such units near the surface is $N^{2/5}$, as shown in Figure 1. Thus the free energy gain per multiblock copolymer is

$$F \sim kTN^{2/5}(Z\delta)^2 \tag{11}$$

When this is larger than the thermal energy, the chain is confined to the interface. This implies a crossover selectivity parameter

$$\delta_c \sim Z^{-1}N^{-1/5} \tag{12}$$

For larger selectivity, the copolymer has a flat configuration at the interface. Assuming that the distances depend only on the reduced energy, we may write the following scaling relation

$$R \sim (NZ)^{3/5} f(ZN^{1/5}\delta) \tag{13}$$

The width D is found by assuming that $f(x)$ behaves as a power law for large x. The exponent is determined by the requirement that D be independent of the number (N) of sequences. We find

$$D \sim \delta^{-3} Z^{-12/5} \tag{14}$$

Note that this corresponds to the existence of isotropic blobs, made of n sequences, on the verge of being adsorbed. n is directly obtained from relations 12 or 13 as

$$n \sim (Z\delta)^{-5} \tag{14a}$$

with

$$D \sim (nZ)^{3/5} \tag{14b}$$

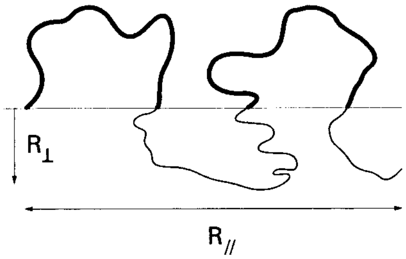

Figure 2. In the very large selectivity limit, the junction points between sequences are located in the interface, and each sequence is in its good solvent. No large loops as in Figure 1 are present.

The radius along the interface ($R_{||}$) is determined by the condition that if we define blobs with size D, the multiblock has to be in the interface and is therefore quasi-two-dimensional. With the same assumptions as before and the requirement that the exponent of N be $^3/_4$, we find

$$R_{||} \sim N^{3/4} Z^{27/20} \delta^{3/4} \tag{15}$$

The chain may considered as a two-dimensional arrangement of the isotropic blobs with radius D, so that

$$R_{||} \sim \left\{\frac{N}{n}\right\}^{3/4} D \tag{15a}$$

Finally, the free energy gain per chain is estimated directly by noting that it corresponds to kT per blob. Using relation 14a, we find

$$F_s \sim N/n \sim N(Z\delta)^5 \tag{16a}$$

corresponding to the number of diblocks on the surface (N_s)

$$N_s \sim N(Z\delta)^3 \tag{17}$$

where we used relation 10a for the energy of a diblock.

As selectivity is increased, the width D decreases until it reaches the size of a sequence. This occurs for $n = 1$ in relation 14a. This implies

$$\delta_L \sim Z^{-1} \tag{18}$$

For larger values of δ, the system reaches the large selectivity regime, and our previous argument breaks down because each sequence remains in its favored solvent: in the previous notations, $x \sim 1$. As noted above, the energy gain per sequence is then on the order of δZ, so the energy gain per multiblock is

$$F_s \sim NZ\delta \tag{16b}$$

The corresponding structure is shown in Figure 2. The width D of the layer is the radius of a sequence (R_s)

$$D \sim Z^{3/5} \tag{19}$$

and the extension in the interface is obtained by assuming that the multiblock is a two-dimensional chain of N sequences. Then we have

$$R_{||} \sim N^{3/4} Z^{3/5} \tag{20}$$

Finally, let us note that although relation 20 seems to imply that the structure is that of an isotropic chain, there is a part of the chain, around the junction points, that is still "polarized", as in the previous region. This may be understood by noting that although we have $\delta Z \gg 1$ for the entire sequence, we can find a part of the sequence, made of g elements, such that $\delta g \sim 1$. For this part, the previous analysis is still valid. This leads us to define an interfacial layer with width Δ, where both chemical species are present. Even though each block does not have large excursion in the unfavored solvent, parts made of g elements may do so. Generalizing eqs 19, we find that

$$\Delta \sim \delta^{-3/5} \qquad (21)$$

As δ decreases from unity to Z^{-1}, Δ increases from the size of a monomer to that of the whole sequence. When δ is unity or larger, in the very strong selectivity limit, the size of this interfacial layer is that of the monomer, and the junction points are strongly localized on the interface.

Finally, the surface and bulk concentrations Γ and Φ may be related to each other by considering the chemical potentials μ_s and μ_b of the mutiblocks on the surface and in the bulk, respectively. The bulk potential has a translation term:

$$\frac{\mu_b}{kT} \sim \ln\left(\frac{\Phi}{NZ}\right) \qquad (22)$$

The surface potential has both a translational and an interaction contribution:

$$\frac{\mu_s}{kT} \sim \ln\left(\frac{\Gamma a}{NZD}\right) - N(Z\delta)^5 \qquad (\delta Z \ll 1) \qquad (23a)$$

where the second term is the energy gain when the copolymer is localized at the interface (relation 16). As noted above, the energy gain when $\delta Z \gg 1$ is $NZ\delta$, so

$$\mu_s = \ln\left(\frac{\Gamma a}{NZD}\right) - NZ\delta \qquad (\delta Z \gg 1) \qquad (23b)$$

Equating eqs 22 and 23, we find

$$\Gamma = \frac{a}{D}\Phi e^{N(Z\delta)^5} \qquad \text{for } \delta Z \ll 1 \text{ and } N^{1/5}\delta Z \gg 1 \qquad (24a)$$

and

$$\Gamma = \frac{a}{D}\Phi e^{NZ\delta} \quad \text{for } Z\delta \gg 1 \qquad (24b)$$

IV. Concentration Effects

When the surface concentration (Γ) increases, its effects are analytic corrections to the previous relations as long as the polymers are far from each other. This breaks down above an overlap concentration (Γ^*), where the chains fill the interface. Γ^* may be estimated from relations 15 and 20 in the regimes that we considered above.

$$\Gamma^* \sim \frac{NZ}{R_{\parallel}^{2}} \qquad (25a)$$

which leads to

$$\Gamma^*_1 \sim N^{-1/2}\delta^{-3/2}Z^{-17/10} \qquad (\delta Z \ll 1) \qquad (25b)$$

in the adsorption regime $\delta_c \ll \delta \ll \delta_L$ and to

$$\Gamma^*_2 \sim N^{-1/2}Z^{-1/5} \qquad (\delta Z \gg 1) \qquad (25c)$$

in the larger selectivity regime $\delta \gg \delta_L$, where the junction points are located at the interface.

1. The Weak Selectivity Limit. We consider first the weak selectivity regime where the copolymers are adsorbed. Above the overlap concentration Γ^*_1, large loops start forming because of excluded volume interactions. Thus the width of the adsorbed layer increases, and it was shown that it varies as $N^{3/5}$. The precise variation may be found by assuming that the width is a function of the reduced concentration Γ/Γ^*_1:

$$R_{\perp} = \delta^{-3}Z^{-12/5}f(\Gamma/\Gamma^*_1) \qquad (26a)$$

where we used eq 14 for the width in the dilute regime. Assuming further that the function $f(x)$ behaves as a power law in the semidilute range and using the constraint that $R_{\perp}$ varies as $N^{3/5}$, we find

$$R_{\perp} \sim (NZ)^{3/5}\{\Gamma\delta^{-1}Z^{-4/5}\}^{6/5} \qquad (\Gamma \gg \Gamma^*_1) \qquad (26b)$$

Thus the size of the loops and of the adsorbed layer increases with surface concentration until a second special concentration, Γ_1, where it becomes the same order of magnitude as the radius of a free copolymer. From relation 26b, we get

$$\Gamma_1 \sim Z^{4/5}\delta \qquad (27)$$

For this concentration, the width of the adsorbed layer is

$$R_{\perp} \sim (NZ)^{3/5} \qquad (26c)$$

The surface is saturated with isotropic blobs of radius D. Using relations 14 and 14a, one can check that $\Gamma_1 \sim nZ/D^2$. Therefore, the corresponding line in Figure 6 is a limit, because any further copolymer goes into the solution rather than on the surface. Note also that, in the concentration range between Γ^*_1 and Γ_1, the surface is saturated with blobs of size $\xi_{\parallel}$. The latter may be calculated by applying to $R_{\parallel}$ (relation 15) a scaling assumption similar to eq 26a for the width of the layer. The constraint in this case is that the screening length is independent of the total number of sequences. Therefore, in regime IV of Figure 6, we find

$$\xi_{\parallel} \sim \Gamma^{-3/2}\delta^{-3/2}Z^{-6/5} \qquad (26d)$$

Note that $\xi_{\parallel}$ varies from $R_{\parallel}$ (relation 26a) to D (relation 14) as the surface concentration Γ increases from Γ^*_1 to Γ_1. This corresponds to a saturation of the surface with objects ranging from the entire copolymer, at Γ^*_1, to the isotropic blob, at Γ_1, when the surface becomes completely saturated.

We discuss very briefly the partition of the polymers between the bulk and the interface. The chemical potential of the chains in the bulk is still given by eq 22. Those that are adsorbed on the surface have, in addition to the translational contribution in 23a two other ones, related to the interaction and confinement energies. The repulsive energy is directly estimated from the number of blobs on the surface. This may be obtained by noting that their size, $\xi_{\parallel}$ (relation 26d), has formally the same form as $R_{\parallel}$ (relation 15), with N replaced by the number n of sequences in a blob. This leads to a repulsive energy per chain

$$F_{\text{int}} \sim N/n \sim N\Gamma^2\delta^3 Z^{17/5} \qquad (23c)$$

The confinement energy per chain is

$$F_{\text{conf}} \sim NZ(a/D)^{5/3} \sim N(\delta Z)^5 \qquad (23d)$$

where we used eq 14 for D. Thus F_{conf} is on the same order as the surface energy. The ratio of the latter energies is

$$F_{\text{int}}/F_{\text{conf}} \sim \{\Gamma\delta^{-1}Z^{-4/5})^2$$

and is small for $\Gamma \ll \Gamma_1$. Therefore, we find that eq 24a is valid until saturation of the surface, for $\Gamma \sim \Gamma_1$, when both contributions become similar.

2. The Large Selectivity Limit. The previous results hold as long as the selectivity is weak and the single copolymer is adsorbed. We expect changes when selectivity is higher: for $\delta Z > 1$, in the dilute surface regime, the copolymer chain has a flat configuration. All the junction points between sequences are located near the interface. It is then more difficult to make large loops as concentration is increased beyond the overlap concentration Γ^*_2 (relation 25c). As a result, we find that there is first a semidilute regime where the width of the surface layer remains constant before large loops start developing.

2a. The Constant Width Regime. For concentrations larger than Γ^*_2, the copolymers overlap, and the regime is semidilute. Because the selectivity is large, junction points tend to remain close to the interface as long as the excluded volume interaction energy is not too high. Therefore, the width of the surface layer remains constant as long as the concentration is not too large. The crossover to the high concentration regime is discussed below, in section 2b. In the constant width regime, region III of Figure 6, the local behavior of the copolymers is the same as in the dilute regime for distances smaller than the size ($\xi_{\parallel}$) of a blob. The latter is obtained by a scaling argument similar to the previous ones. Assuming that all distances depend only on the relative concentration Γ/Γ^*_2, we have

$$\xi_{\parallel} \sim N^{3/4}Z^{3/5}g(\Gamma N^{1/2}Z^{1/5}) \qquad (28a)$$

where we used relations 20 and 25c. In the semidilute range, $g(x)$ behaves as a power law, with an exponent determined by the condition that $\xi_{\parallel}$ is a local parameter that should be independent of the mass of the copolymer. This leads to

$$\xi_{\parallel} \sim \Gamma^{-3/2}Z^{3/10} \qquad (28b)$$

It is interesting for later use to determine also the number g of blocks in such blob. This is obtained for instance from relation 25c, which gives

$$g \sim \Gamma^{-2}Z^{-2/5} \qquad (28c)$$

Therefore the energy of a copolymer chain in this regime is

$$F_1 \sim N/g \sim N\Gamma^2 Z^{2/5} \qquad (29)$$

Finally, using similar arguments, the radius of a copolymer in this screened regime is

$$R_{\parallel} \sim \left[\frac{NZ}{\Gamma}\right]^{1/2} \qquad (28d)$$

while $R_{\perp}$ is given by relation 19.

We can also estimate the chemical potentials and the surface concentration as above. One finds that the relation between the surface and bulk concentrations crosses over from relation 24a to 24b for $\delta Z \sim 1$.

2b. The Large Loop Regime. As the surface concentration increases in the semidilute regime III, the interaction energy (eq 29) increases. In principle, the argument for the latter to leave the interface is that this happens when it becomes the same order of magnitude as the energy gained by the localization of the junction points at the interface. However, we argue that this happens much before and that junctions leave the interface as soon as the repulsive energy is on the order of the energy of individual junctions. This allows the system to form locally large loops and stabilize the repulsive energy. Another way of describing this is to consider the extra length that becomes available when a junction leaves the surface as an "excitation". Therefore, as long as the interaction energy (relation 29) is smaller than the energy gained by a diblock when it is located at the interface, the system does not make large loops. On the other hand, when the converse becomes true, junction points leave the interface, and the copolymers develop loops with sizes larger than D. Therefore, comparing the energy of relation 29 with the gain per diblock at the interface (relation 10b) leads to the crossover line Γ_2 between regime III, where the chains are localized at the interface, and regime IV, where large loops are present. We find

$$\Gamma_2 \sim N^{-1/2}\delta^{1/2}Z^{3/10} \qquad (30)$$

The width of the adsorbed layer is obtained by a similar scaling argument: assuming

$$R_{\perp} = Z^{3/5}f(\Gamma/\Gamma_2) \qquad (30a)$$

and that $f(x)$ behaves as a power law, the exponent is determined by the requirement that $R_{\perp}$ behaves as $N^{3/5}$ in this large loop region. We find, in region IVa,

$$R_{\perp} \sim (NZ)^{3/5}(\Gamma\delta^{-1/2}Z^{-3/10})^{6/5} \qquad (30b)$$

Note that this crosses over smoothly to relation 26b for $\delta Z \sim 1$. Note also that there seems to appear in relation 30b a special concentration, $\Gamma'_1 \sim \delta^{1/2}Z^{3/10}$, which would correspond to the saturation of the interface. As we will see, however, another crossover takes place for $\Gamma \sim \Gamma^{**}$.

This may also be understood by considering the width (Δ) of the interface, where the junction points are located. Because of the interactions, this width increases. We may assume that it depends only on the ratio Γ/Γ^*_2:

$$\Delta \sim \delta^{-3/5}f(\Gamma/\Gamma^*_2) \qquad (21a)$$

Assuming that $f(x)$ behaves as a power law, the exponent is determined by the requirement that, for $\Gamma \sim \Gamma_2$, the junctions points are no longer localized, so Δ is on the order of $Z^{3/5}$. This leads to

$$\Delta \sim \delta^{-3/5}(\Gamma N^{1/2}Z^{1/5})^{6/5} \qquad (21b)$$

Note that Δ depends on N. This implies that in order to have a wide interface, one needs many sequences.

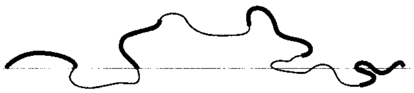

Figure 3. In region IVa of the diagram, large loops are present and the width of the surface layer is that of adsortion. Still, trains made of sequences with junction points at the surface are also present.

The effect is cooperative, and for a small number of sequences, the interface is not wide. This will be analyzed below. Thus for a given value of the interaction energy δ and for surface concentrations larger than Γ_2, large loops start forming. The structure of the chains is similar to the adsorption problem, and large loops are present. There are differences between this large interaction and the small interaction (adsorption) regime. The first one is that whereas in the latter case the large loops start forming as soon as the chains reach the semidilute regime, there is a constant width regime here first. In other words, whereas loops form immediately because there is no cost in energy for adsorption, it is necessary to have concentration blobs in this case in order to compensate for the energy loss when a diblock leaves the surface. A second difference between regime IVa in Figure 6 and the conventional semidilute adsorption, regime IV, is that the local screening lengths are not the same in both cases. This may be realized by comparing relation 26c, which is valid in region IV, and eq 28a, which remains valid in region IVa. This difference reflects the fact that, for smaller distances, the behavior of the copolymer is either that of an adsorbed polymer or a flat succession of sequences. The crossover from one behavior to the other takes place for $\delta Z \sim 1$. Finally, using relation 30, we may introduce a length which may be interpreted as the size of trains on the surface, such as shown in Figure 3: for any concentration $\Gamma > \Gamma_2$, we find a number n of sequences such that

$$\Gamma \sim n^{-1/2}\delta^{1/2}Z^{3/10} \tag{30a}$$

If we consider a part of the chain made of a number of sequences smaller than n, we may assume that it behaves as in regime III, where the copolymer is localized at the interface: its energy is smaller than the energy gained by a junction when it is localized at the interface. We are thus led to define a blob with size $L_{||}$ such that

$$L_{||} \sim \left[\frac{nZ}{\Gamma}\right]^{1/2} \sim {}^{-3/2}\delta^{1/2}Z^{4/5} \tag{31}$$

As discussed above, the local behavior for distances shorter than $L_{||}$ is similar to what happens at concentrations smaller than Γ_2, and therefore, we may assume that these blobs are confined within a distance $Z^{3/5}$ near the surface. The latter width may be obtained by generalizing relation 30b to sequences with n units, with n given by eq 30a. In this respect, we may consider them as trains localized at the surface, as opposed to the large loops that extend to much larger distances. Finally, one may check that they cross over smoothly to the adsorption blob in the semidilute range (relation 26c) for $\delta Z \sim 1$, and to the radius of the entire copolymer for $\Gamma \sim \Gamma_2$, as expected. We finally note that relation 24b between surface and bulk concentrations is valid in region IVa.

2c. The Hairpin Region. Regimes III and IVa that we just considered are valid as long as selectivity and surface concentration (Γ) are not too high. For very high selectivities and large surface concentrations, we are led to introduce more regions in the phase diagram of Figure 6. These are related to the fact that, so far, we only considered the cases where the screening length $\xi_{||}$ is larger than the size of a sequence. Above a concentration Γ^{**}, and for sufficiently large selectivities, this does not hold anymore. The crossover concentration

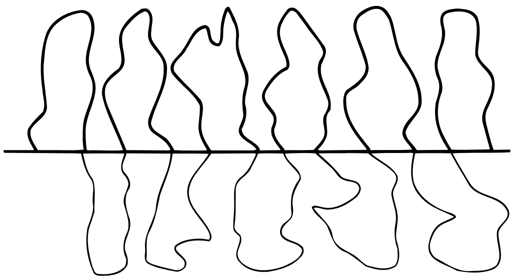

Figure 4. In region V of the diagram in Figure 6, for large selectivities and relatively large concentrations, the sequences adopt the shape of hairpins as long as the interaction energy is smaller than the selectivity.

$$\Gamma^{**} \sim \frac{Z}{Z^{6/5}} \sim Z^{-1/5} \tag{32}$$

corresponds to the saturation of the surface by sequences. Above this concentration, free sequences would overlap. For very large selectivities, however, the junction points are constrained to be on the surface. The situation is very similar to that of grafted polymers when the grafting density is high. This leads us to assume that the structure of each sequence becomes stretched. As they have to come back onto the surface, they adopt hairpin structures, shown in Figure 4. Therefore the width of the surface layer increases with concentration. Using a scaling argument, we may estimate that

$$R_{\perp} \sim Z^{3/5}f(\Gamma/\Gamma^{**}) \tag{33a}$$

In regime V, where these hairpins are assumed to be present, the width should be linear in Z. This leads to

$$R_{\perp} \sim Z\Gamma^{2} \tag{33b}$$

Similarly, the screening length $\xi_{||}$ now becomes the average distance between junction points on the surface. It may be calculated using the same methods as before. We get

$$\xi \sim \Gamma^{-3} \tag{34}$$

Note that because this corresponds to distances smaller than the radius of a sequence, the local structure has become isotropic: anisotropy came from the fact that the sequences had their junction points at the interface in the previous regions. Note also that relation 33b may be obtained directly from 34 if we assume that the sequence is a stretched ensemble of blobs:

$$R_{\perp} \sim \frac{Z}{g}\xi \tag{33c}$$

where g is the number of monomers per blob and is related to ξ by the usual excluded volume relation:

$$\xi \sim g^{3/5}$$

Finally, we note that in this regime the surface is saturated with these isotropic blobs of size ξ. Comparing the latter with the isotropic adsorption blob of size D (relation 14), we find that

$$\frac{\xi}{D} \sim \left\{\frac{\Gamma}{\Gamma_1}\right\}^3$$

where we used eq 27 for Γ_1. This shows that ξ is larger than D. Therefore, the radius of the blobs that are saturating the surface decreases in region V as surface concentration increases and becomes on the order of the adsorption blob for $\Gamma \sim \Gamma_1$.

The radius of a copolymer in the interface is

$$R_{\|} \sim N^{1/2}\xi \qquad (35)$$

where the value of the exponent is related to the fact that this is a semidilute regime. In order to determine the crossover from this hairpin region V to a large loop regime, we may use the same argument as in section 2b. We are led to compare the energy of a junction δZ (relation 10b) with the energy of a hairpin. This is the number (NZ/g) of blobs per copolymer. Using relation 28, we get $NZ\Gamma^5$. These two energies become comparable for

$$\Gamma_3 \sim N^{-1/5}\delta^{1/5} \qquad (36)$$

For a given concentration, and for values of δ smaller than the one that corresponds to Γ_3, loops start developing because the system gains entropy by letting sequences go into their less favored solvent. This situation is very interesting because the interfacial layer changes from a rather monodisperse distribution of loops in regime V to the polydisperse distribution that is present in the adsorption case. The width of the layer may be obtained by a scaling argument as before: assuming that it depends only on Γ/Γ_3, we have

$$R_{\perp} \sim Z\Gamma^2 f(\Gamma/\Gamma_3) \qquad (37)$$

using the same argument as for relation 30b, we find in region Va

$$R_{\perp} \sim (NZ)^{3/5}\{\Gamma^5\delta^{-3/5}Z^{2/5}\} \qquad (37a)$$

Note that this crosses over to relation 30b for $\Gamma \sim \Gamma^{**}$. Note also that the radius of the free copolymers is recovered for $\Gamma \sim \Gamma'_1$. From eq 37a, we find

$$\Gamma'_1 \sim \delta^{3/25}Z^{-2/25} \qquad (38)$$

Note that Γ_1 and Γ'_1 merge for $\Gamma \sim \Gamma^{**}$. However, as discussed below, it seems that saturation is not reached for this concentration, but at a higher one.

As in section 2b, we may introduce in regime Va blobs made of n units, where n is deduced from relation 36:

$$n \sim \Gamma^{-5}\delta \qquad (36a)$$

These blobs have the same behavior as hairpins. As before, one may interpret them as trains, shown in Figure 5. The difference with section 2b comes from the fact that, in the present case, their width is given by relation 33b because they behave as hairpins. Generalizing relation 35, we find the size of such trains

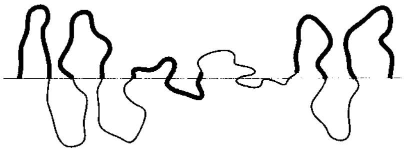

Figure 5. In region Va of the diagram, loops are coexisting with hairpins. Note that the loops are very polydisperse in size.

$$L_{\|} \sim n^{1/2}\xi \sim \delta^{1/2}\Gamma^{-11/2} \qquad (39)$$

which decreases very fast as surface concentration increases. Here again, we find that relation 24b applies to the relation between surface and bulk concentrations. The interaction energy is, in regime V,

$$F_{\text{int}} \sim NZ/g \sim NZ\Gamma^5 \qquad (40)$$

Similarly, in region Va, F_{int} is $Z\delta$ per blob, so that the interaction energy per copolymer is given by relation 40 above. This implies that the ratio of the latter to the energy gain $NZ\delta$ is

$$F_{\text{int}}/F_{\text{s}} \sim \Gamma^5\delta \qquad (41)$$

This implies that saturation is reached in both regimes for

$$\Gamma''_1 \sim \delta^{1/5}$$

Thus, we find that, at saturation in this high-energy regime, for $\Gamma \sim \Gamma''_1$, the radius of the layer is larger than the size of the free copolymer and is

$$R_{\perp} \sim (NZ)^{3/5}(Z\delta)^{2/5} \qquad (Z\delta \gg 1;\quad \Gamma > \delta^{1/5}) \qquad (42)$$

V. Conclusion

We considered the structure of an interfacial layer of multiblock copolymers between two immiscible, good solvents, with slightly different selectivity (δ). As a function of δ and of the surface concentration (Γ), we found various regimes that we summarize. For low values of Γ, we found three dilute regimes. For very low δ, the copolymer is not sufficiently attracted by the surface. For intermediate values, it is adsorbed and forms large loops. The corresponding structure is like a pancake. Its thickness, given by relation 14, is related to δ and is independent of the number of sequences. Finally, for large values of δ, the junction points are localized in the vicinity of the surface, and the width of the copolymer is directly related to the size of a single sequence, as shown by relation 19.

For larger concentrations, in the semidilute regimes, we found several regions. For very large selectivities, a first regime with constant width is followed by a second one where the sequences adopt hairpin-like configurations when the concentration on the surface is such that the distance between contacts is smaller than the size of a sequence.

For intermediate selectivities, we find, in addition to the “conventional” adsorption case, three regimes that allow for a smooth crossover to the large selectivity regimes. In regime IVa, large trains that have hairpin-like configurations are present, and the distribution of loops that is basically monodisperse in region V progressively becomes polydisperse. The layer becomes polydisperse as in the adsorption case for saturation,

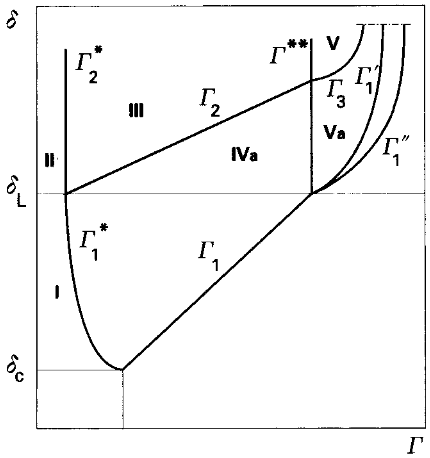

Figure 6. the phase diagram in a selectivity (δ)−surface concentration (Γ) plane. The various regimes are discussed in the text.

on line Γ'_1. The difference between both cases lies in the size of the objects (blobs) that are saturating the surface.

Our main assumption is worth mentioning here. It concerns the condition for a strongly adsorbed polymer to leave the surface when the concentration is increased. We assumed in section IV.2.b that we have to compare the energy gain of a *monomer* constrained to be at the surface with the energy loss of a *chain* due to the interaction with the other polymers at the interface. This implies the existence of a semidilute regime at the interface where the width of the layer remains constant and polymers pack until the two energies mentioned above become of the same order. Loops start then forming, and the flat configurations progressively cross over to the wider ones that are present in the adsorption case. In the diagram of Figure 6, this corresponds to the existence of regions III and IVa.

Finally, it seems that for high interactions, for $Z\delta \gg 1$, the width of the layer at saturation is larger than the size $(NZ)^{3/5}$ of a free copolymer.

We discuss briefly the decrease of surface tension. As surface concentration increases, we expect the surface tension to drop. This is expected to happen as long as saturation is not reached. Therefore, the best regimes for practical uses of copolymers as emulsifiers is in the vicinity of the saturation lines Γ_1 and Γ'_1: adding more copolymers will essentially lead to an increased bulk concentration without substantial decrease of the surface tension.

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