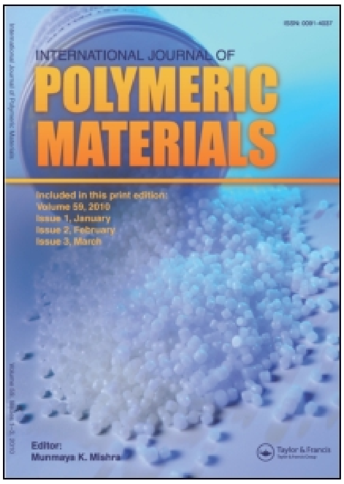

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Daoud, M. , Aguie-Beghin, V. and Douillard, R.(2002) 'Copolymers at Interfaces', International Journal of Polymeric Materials, 51: 1, 31 — 47
To link to this Article: DOI: 10.1080/00914030213029
URL: http://dx.doi.org/10.1080/00914030213029

International Journal of Polymeric Materials, 51:31 – 47, 2002

0091-4037/02 $12.00 + .00

Copolymers at Interfaces*

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(Received 18 November 2000; In final form 6 January 2001)

We discuss the adsorption of multiblock copolymers at the interface between two selective solvents of the constituent monomers. We consider two cases, namely when the blocks are regular, and when the copolymer is made of random sequences. In both cases, we discuss the various surface regimes, and we compare the properties of the layers. We find that the saturation concentration and the drop in surface tension are larger for the random case, except when selectivity and the number of sequences of the regular chain are both large.

Keywords: Interface; Adsorption; Copolymers; Random; Block

I. INTRODUCTION

The conformation of polymers and copolymers at interfaces has attracted some attention recently both from theoretical and experimental points of view [1 – 17]. This is related to the facts that many applications are possible for these systems. It is also related to the recent fundamental interest in the influence of surfaces on phase transitions. Homopolymers [1, 6, 18] were shown to build up a surface layer with a monomer density profile that decreases as a function of the distance from the surface as a power law. In the proximal region, close to the interface, the exponent is related to surface properties, while in the central region, further away from the surface the exponent

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* Dedicated to Prof. Fakisok in honor of his 65th birthday.

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is related to bulk properties, and the profile was shown by de Gennes to be self-similar [1]. Also, it was shown that two different cases may be considered. These depend on the nature of the surface. It was shown that the exponents are different for an impenetrable surface, and for a penetrable surface between two immiscible solvents for instance. For all cases, the various surface regimes were determined, as well as the corresponding density profiles. Adsorption of diblock copolymers at surfaces was also considered. Motivated by studies about beta casein at the air/water interface, regular multiblock copolymers were studied very recently [12, 13]. In what follows, we would like to consider the case of random copolymers, made of a random succession of monomers A and B of different chemical nature. The latter was considered by Garel and Orland [19, 20] in the single random, non correlated chain case. But the influence of concentration was not studied so far. Similarly, the case of correlated random distributions of monomers along the copolymer was not considered so far to our knowledge. This is what is done here, together with a comparison between the regular and random cases. In what follows, we will first remind the main results for homopolymers and for the regular, symmetric multiblock copolymers. We will then discuss the random, non correlated and correlated cases. The comparison between both cases is given in the last chapter.

II. REGULAR MULTIBLOCKS

Let us consider a regular, symmetric multiblock copolymer, made of 2N successive blocks of two different monomer species A and B. Each block has the same number Z of monomers. This copolymer is assumed to be at the interface between two immiscible solvents. The interface is supposed to be flat. Each of the solvents has a preference for one of the constituents Solvent 1 (resp.2) slightly prefers monomer A (resp.B). This was considered recently by Sommer *et al.* [21]. It may be discussed in terms of monomer–solvent interaction parameters. Let $\chi_{\mathrm{i}\alpha}$ be the interaction between solvent i (1 or 2) and monomer α (A or B). We also assume that the interactions are symmetric: $\chi_{1\mathrm{A}} = \chi_{2\mathrm{B}} = \chi$ and $\chi_{1\mathrm{B}} = \chi_{2\mathrm{A}} = \overline{\chi}$. This implies that there is a single energy parameter that describes the problem, namely the energy gain δ when a monomer goes into its preferred solvent:

$$\delta = \chi - \overline{\chi} \tag{1}$$

In the following, we will consider the case of weak selectivity, when δ is small. In order to understand the behavior of the multiblock at the interface, one needs first to discuss that of a diblock: the entire copolymer may indeed be considered as a homopolymer, with a diblock as repeat unit. This was already considered by Sommer *et al.*, who provided a Flory approach to this problem. Because of the weak selectivity of the solvents, the centers of gravity of sequences A and B are slightly on either side of the interface. Let x be their distance. When the selectivity of the solvents is too weak, the centers of gravity come back on top of each other, and x vanishes. The free energy $\mathrm{F_d}$ of a diblock close to such selective interface is assumed to have two contributions

$$\mathrm{F_d} \sim \frac{x^2}{R_0^2} + Z\delta\frac{x}{R_0} \tag{2}$$

where the first term is an entropic energy that corresponds to restoring both centers of gravity at the same location. The second term is the energy gain because of the fact that a fraction of the monomers becomes located in its favorite solvent. It was assumed that this fraction is proportional to the ratio $\mathrm{x/R_0}$, where $\mathrm{R_0}$ is the Flory radius of the diblock, $\mathrm{R_0} \sim Z_{\mathrm{a}}^{\mathrm{v}}$, where a is the step length and v the excluded volume exponent, approximately 3/5. Minimization of this free energy with respect to x leads to

$$\mathrm{x \sim R_0\, Z\, \delta} \tag{3a}$$

and to a minimized free energy for a diblock

$$\mathrm{F_d - (Z\,\delta)^2} \tag{3b}$$

As mentioned above, the entire copolymer may be considered as a homopolymer, made of N diblocks, close to a penetrable interface. The unit of this is the diblock that we just considered above. The former problem was studied by Bray and Moore [24] some years ago, and they showed that when the interaction between the surface and each unit is weak, the average number N_S of units near the interface is

$$N_S \sim N^{2/5} \tag{4}$$

So that the free energy gain of a copolymer near the interface is, using relations (3b) and (4):

$$F \sim N^{2/5}(Z\,\delta)^2 \tag{5}$$

This has to be compared with a loss of entropy of order kT, related to the localization of the center of mass of the copolymer in the vicinity of the interface. We take the latter equal to unity in our discussion. Therefore, when $Z\,N^{1/5}\,\delta$ is smaller than unity, the selectivity is not large enough to induce any adsorption of the chains. In the opposite limit, on the contrary, the copolymer is adsorbed by the interface. This happens when selectivity is large enough (but still smaller than unity). It also occurs for a given selectivity when the number of sequences is large, or when each sequence is made of a large number of monomers. Thus the cross over [22] between the adsorbed and non adsorbed regimes is for

$$\delta^* \sim Z^{-1}\,N^{-1/5} \tag{6a}$$

Let M be the total number of monomers, $M = ZN$. The previous equation may be rewritten as

$$\delta^* \sim M^{-1}N^{4/5} \sim M^{-1/5}Z^{-4/5} \tag{6b}$$

The latter relation shows clearly that for a given total number of monomers, the number of sequences and their lengths have a very different effect on the crossover energy: increasing the number N of sequences leads to an increase of δ^*. On the other hand, increasing the length Z of each sequence lowers δ^* and therefore makes adsorption of a copolymer easier. Let us note that for values of the selectivity parameter δ larger than δ^*, the copolymer is adsorbed, but there remains isotropic parts made of N^* sequences, with energy of order kT, such that

$$N^* \sim (Z\delta)^{-5} \tag{7a}$$

These were called isotropic blobs, and have an energy of order unity, and a radius D such that

$$\mathrm{D} \sim (N^{*}\mathrm{Z})^{3/5} a \sim \delta^{-3} \mathrm{Z}^{-12/5} \tag{8}$$

This implies that the free energy gain of an adsorbed copolymer is, for $\mathrm{N}^{*} \gg 1$

$$\mathrm{F_a} \sim \mathrm{N/N^{*}} \tag{7b}$$

The above discussion dealt with the case of a single copolymer, or a dilute solution of adsorbed chains. Another situation of interest is when the interface is saturated with chains. It was shown that for small δ, this does not correspond to the occupancy of all the sites of the interface by monomers, but rather to its saturation by the isotropic blobs that were considered above. This implies that the surface concentration is identical to that in the isotropic blobs. Note that the former is the average concentration in the region of width D near the interface:

$$\Gamma_{\mathrm{sat}} \sim \mathrm{N^{*}Z/D^{2}} \sim Z^{4/5}\delta \tag{9}$$

When the surface is saturated, the profile extends to distances on the order of the radius of gyration of the chain because of the formation of very large loops. Because the interface is penetrable, the concentration profile is flat in the proximal region, for distances to the interface smaller than D. For larger distances, in the central regime, the profile is self similar, as shown by de Gennes [23]:

$$\Phi(\mathrm{z}) \sim \mathrm{z}^{-4/3} \quad (\mathrm{D} \ll \mathrm{z} \ll \mathrm{R}) \tag{10a}$$

For larger distances, the profile decreases exponentially towards the bulk concentration. Note that although the concentration at the interface is in the semi-dilute range, the bulk concentration may be in the dilute regime because of the Boltzmann weight related to the energy gain by adsorbed chains, (Eq. (7a)). Note also that the concentration in isotropic blobs is also self-similar. Equation (10a) may also be written in the following form:

$$\Phi(\mathrm{z})/\Phi(\mathrm{D}) \sim (\mathrm{z/D})^{-4/3} \tag{10b}$$

A final quantity that may be considered is the reduction in surface tension $\Delta\gamma$ due to the adsorption of the chains at the interface. In the dilute and semi dilute surface regimes, the change is proportional to the concentration in isotropic blobs. This gives

$$\Delta\gamma \sim \Gamma/^{\mathrm{N}*\mathrm{Z}} \sim \Gamma \mathrm{Z}^4\delta^5 \tag{11a}$$

In the plateau regime, it was shown [25] that the reduction $\Delta\gamma$ is composed of two contributions. The first one corresponds to the surface free energy of the chains. As discussed above, in the plateau, or saturated regime, the surface is covered with isotropic blobs. Each of these has an energy of the order of the thermal energy. Thus this first contribution is

$$\Delta\gamma_1 = -\mathrm{D}^{-2}$$

The second contribution is the so-called Gibbs contribution, and may be written, in the plateau regime, in the simple following form [11]:

$$\Delta\gamma_2 = -\Gamma_{\mathrm{sat}}\mu_{\mathrm{b}}$$

where μ_{b} is the bulk monomer chemical potential, and Γ is the surface concentration. Taking these two parts into account leads to a variation $\Delta\gamma$ of the surface tension

$$\Delta\gamma = -\delta^6 \mathrm{Z}^{24/5} - \phi_b^{5/4}\mathrm{Z}^{4/5}\delta \tag{11b}$$

where ϕ_{b} is the bulk monomer concentration in the solution, and where we used Eqs. (8) and (9) for D and Γ_{sat}. We also used the known fact that in a semi dilute solution, we have $\mu_{\mathrm{b}} = \phi_b^{5/4}$. The second term in relation (11) is present only when the bulk concentration is in the semi dilute range. It is smaller than the first one except for concentrated regimes that we are not considering here, where both terms become of the same order.

III. RANDOM MULTIBLOCKS

It is also interesting to consider random copolymers. These may either be synthetic or natural. An important example of the latter case is that of proteins. These are especially interesting because although they may be random, they provide solutions of random, but identical macromolecules. This is not the case for synthetic polymers, where randomness comes both in the sequences on a given copolymer, but also in the composition of the chains. It was already shown that surfaces act as a strong filter, adsorbing only symmetric chains and letting asymmetric copolymers in the bulk. Therefore, in what follows, we will consider only symmetric chains, made of the same number of monomers A and B. In the random non correlated case, it was shown by Garel *et al.* [19] that adsorption of one copolymer is due to a different mechanism: this is related to the fact that if one consider a sequence of n monomers on a chain, there is, on the average, an excess of one of the species of the order of $n^{1/2}$. A copolymer with N monomers may be considered as a diblock, with one of the blocks having an excess of one of the species. The other block has an excess of the other one. As N increases, these blocks tend to localize in their favorite solvent, and the chain becomes trapped at the interface. In what follows, we will consider both cases, for non correlated and correlated disorder of the monomers on the chain. We will first study the single copolymer case and then the concentration effects, and the important case when the interface is saturated.

III.1. Random Non Correlated Case

Let us consider a copolymer made of the random, non correlated succession of two monomer species A and B. This is at the interface between two immiscible solvents 1 and 2 with same characteristics as above. We assume both solvents to be good for either species, but with a preference for one or the other. When the selectivity of the solvents is too low, the copolymer retains an isotropic configuration in both solvents. As selectivity increases, there is a tendency for each species to go into its preferred solvent, so that the center of mass of the chain localizes near the interface. The cross over between these situations was evaluated in the following way: on the average, if we consider a sequence of n monomers along the chain, there is an excess of one of the species which is on the order of $n^{1/2}$. This implies that there is a cross-over length N^*, such that

$$N^{*1/2}\delta \sim 1 \tag{12}$$

where the random copolymer may be considered as a diblock with each block having an excess of monomer species in its preferred solvent such that the energy gain is of the same order as the thermal energy. For larger lengths, the copolymer may be subdivided into pieces with N^* monomers that lie alternatively on each side of the interface. This may be described in terms of isotropic blobs made of N^* monomers and size

$$\mathrm{D} \sim N^{*3/5} \sim \delta^{-6/5} \tag{13}$$

And the radius of the copolymer along the interface is:

$$R_{\|} \sim (N/N^*)^{3/4} D \tag{14a}$$

The energy gain per chain is

$$\mathrm{E} \sim \mathrm{N/N^*} \tag{14b}$$

As surface concentration Γ increases, the copolymers overlap at Γ^* such that

$$\Gamma^* \sim N/R_{\|}^2 \sim N^{-1/2}\delta^{-3/5} \tag{15}$$

for larger concentrations, one gets a semi dilute surface regime, where one has to define a screening length ξ in addition to the radius on the surface. Both lengths may be obtained by assuming a scaled form for the concentration dependence of the various lengths:

$$R_{\|}, \sim N^{3/4}\delta^{3/10}\mathrm{f}(\Gamma N^{1/2}\delta^{3/5}) \tag{16a}$$

and

$$R_{\perp} \sim \mathrm{D}\,\mathrm{g}(\Gamma N^{1/2}\delta^{3/5}) \tag{16b}$$

where f(x) and g(x) are unknown scaling functions, with known asymptotic behaviors: they are analytical for small arguments, and behave as power laws for large x.

This leads respectively to

$$R_{\|} \sim (\mathrm{N}/\Gamma)^{1/2} \tag{17a}$$

$$\xi \sim \Gamma^{-3/2}\,\delta^{-3/5} \tag{17b}$$

$$\mathrm{R}_{\perp} \sim \mathrm{N}^{3/5}\,\Gamma^{6/5}\,\delta^{-12/25} \tag{17c}$$

where we assumed that $R_{\|}$ varies as $N^{1/2}$ because of screening in the semi dilute range, and that ξ is independent of the size N of the chains. We also assumed in relation (17c) that large loops are present because of the interactions between chains in the semi dilute surface regime. This implies that the molecular weight dependence of the width of the adsorbed layer varies as $N^{3/5}$.

As surface concentration increases, one gets into the saturated regime. The cross over concentration Γ_{sat} may be found for instance by comparing the size D of the isotropic blobs, relation (11) and that of the surface concentration blob ξ, relation (17b). We remind that the isotropic blob corresponds to a part of the chains that gains an attractive energy from the surface on the order of the thermal energy. The surface blob corresponds to a part of the copolymer that has a repulsive interaction energy of the same order. Therefore, equality of these lengths corresponds to a compensation between the attractive and repulsive energies of the adsorbed macromolecules. Trying to increase the surface concentration Γ above Γ_{sat} would increase the repulsive energy per chain without any gain.

Using Eqs. (11) and (17b), we get

$$\Gamma_{sat} \sim \delta^{2/5} \tag{18}$$

The corresponding phase diagram is shown on Figure 2.

III.2. The Random Correlated Case

Finally let us consider a random symmetric copolymer, made of the same number N/2 of monomers of two different species A and B. The difference with the previous section lies in the fact that we assume now that although the monomers are distributed at random along the chain, there is a strong correlation in their positions: if we assume that a site is occupied by one of the species, then the probability P(n) that a site at a curvilinear distance n from that site is occupied by the same species decreases as a power law of the distance:

$$P(n) \sim n^{-x} \quad (0 < x < 1) \tag{19}$$

This implies that if we consider a sequence made of n monomers along the macromolecule, the excess of one of the species is [26], on the

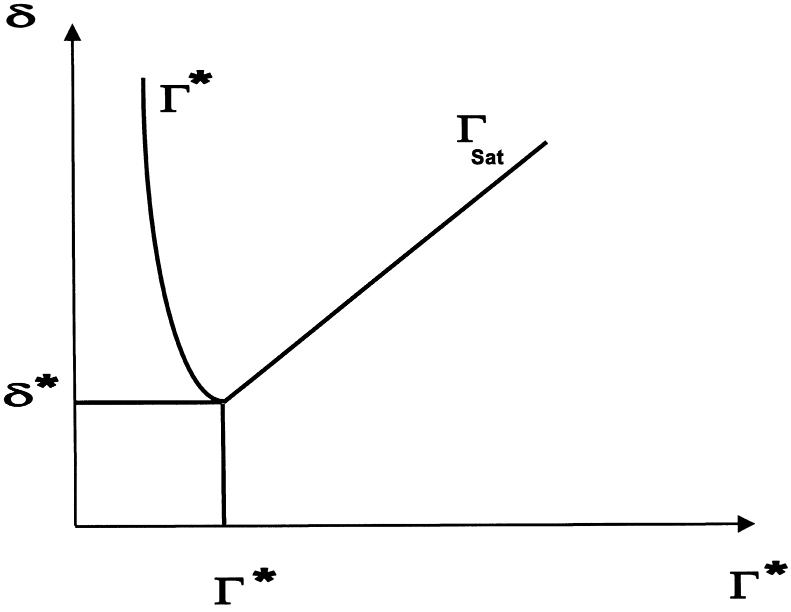

FIGURE 1 Phase diagram showing the various regimes of adsorbed regular copolymers. I is the dilute surface regime; II is semi dilute. Γ_{sat} is the saturation concentration for the surface. Regions in the lower part of the diagram correspond to isotropic chains.

average, on the order of $n^{1-X/2}$. The Brownian case that we considered above is recovered for $x = 1$. Thus the same arguments as above may be given for the adsorption of a copolymer at the interface between two selective, immiscible, solvents. When the chain is short, the fluctuations are not sufficiently important to induce the localization at the interface. This happens for a length N^* such that the energy gain is of order unity:

$$N^{*1-x/2}\delta \sim 1 \tag{20}$$

For larger chains, the copolymer lies on the interface and has characteristic dimensions $R_{||}$ along the surface and D in the normal direction. These may be obtained by a direct scaling argument, where we assume that both lengths depend only on the dimensionless energy given in Eq. (20)

$$R \sim N^{3/5} f(N^{1-x/2}\delta) \tag{21a}$$

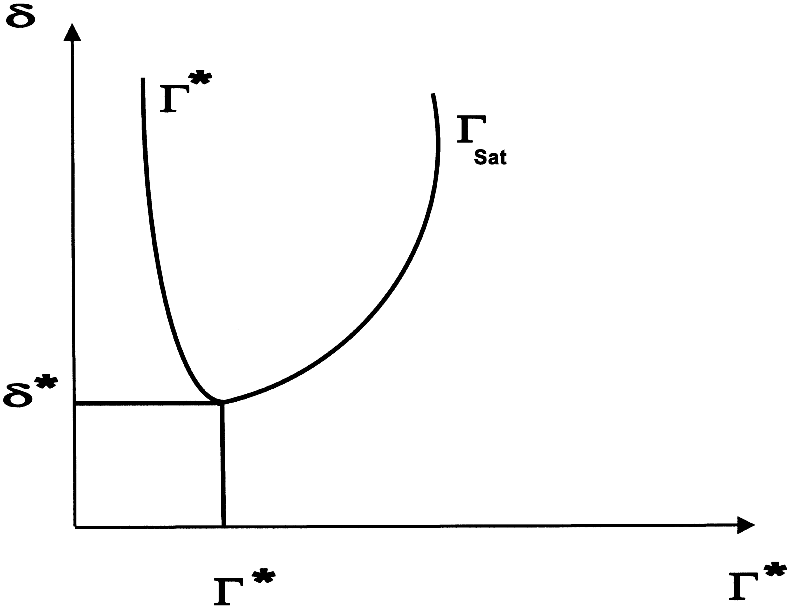

FIGURE 2 Phase diagram for a random copolymer in the general case. The various regimes are the same as in Figure 1.

leading to

$$R_{\parallel} \sim N^{3/4} \delta^{3/20\phi} \tag{21b}$$

And

$$D \sim \delta^{-3/5\phi} \tag{21c}$$

where $\phi = (2 - x)/2$. (thus ϕ varies from 1 to 1/2 as x varies from 0 to 1). Note that we can define an isotropic blob as above, made of N^* elements, and such that its size is D. The free energy gain E of the copolymer at the interface is the number of such blobs per chain:

$$E \sim N/N^* \sim N\,\delta^{1/\phi} \tag{21d}$$

Note that this implies that the surface concentration is exponentially larger than the bulk concentration. Thus even when the bulk concentration is very low, the surface concentration may be in a concentrated range.

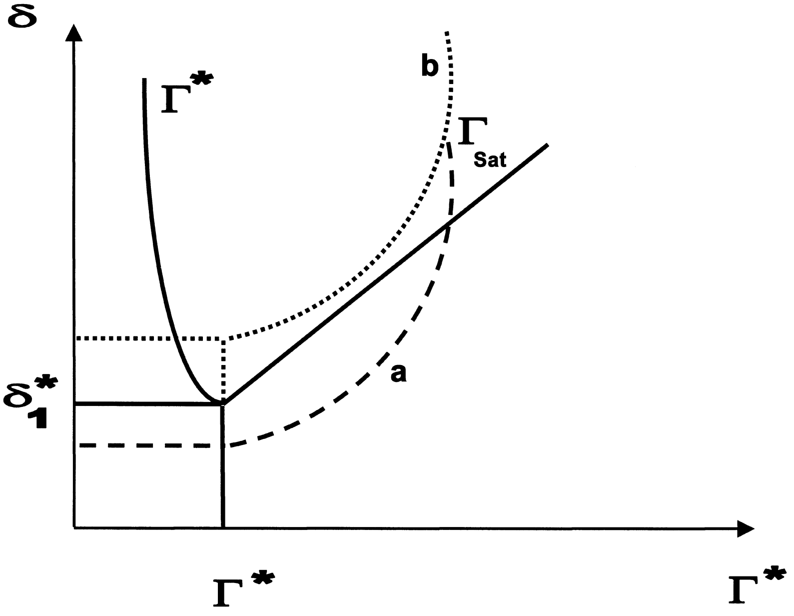

FIGURE 3 Comparison of the surface concentrations for regular and random copolymers. Two different cases may be present: The saturation concentration is larger for the random case except when the number N of sequences in the regular copolymer δ is large (curve b), and the selectivity is also large- or, equivalently, temperature is low.

As one increases the surface concentration, the isolated adsorbed copolymers come closer to each other, and eventually start overlapping. This occurs for concentrations larger than an overlap concentration

$$\Gamma^* \sim N/R_{\|}^2 \sim N^{-1/2}\delta^{-3/10\phi} \tag{22}$$

For larger concentrations, in the semi dilute surface regime, one is led to define two more distances, namely a screening length ξ and the width $R_\perp$ of the adsorbed layer. The latter increases because the presence of excluded volume interactions between different macromolecules leads to the formation of very large loops. Ultimately, in the saturation regime to be discussed below, the latter have the size of the polymer itself. This implies that the width varies as $N^{3/5}$. Using the same type of scaling arguments as in the previous section, we find

$$\mathrm{R}_{\parallel} \sim (N/\Gamma)^{1/2} \tag{23a}$$

$$\xi \sim \Gamma^{-3/2}\delta^{-3/10\phi} \tag{23b}$$

$$\mathrm{R}_{\perp} \sim N^{3/5}\Gamma^{6/5}\delta^{-6/25\phi} \tag{23c}$$

Note that for $\phi = 1/2$, we recover the results of Section II.1 for the non correlated case, Eqs. (17).

The cross over to the saturated surface regime occurs when the repulsive and attractive interactions are of the same order of magnitudes. This is found by comparing ξ and D. Using Eqs. (21c) and (23b), we find

$$\Gamma_{\mathrm{sat}} \sim \delta^{1/5\phi} \tag{24}$$

Note that in the saturated regime, very large loops are present, so that the width of the adsorbed layer is on the same order as the free radius of the chain, $\mathrm{R}_{\perp} \sim \mathrm{N}^{3/5}$.

Finally, the change in tension may be estimated following the same lines as for the regular multiblocks, see discussion above Eqs. (11). In the dilute regime, it is proportional to the concentration in isotropic blobs,

$$\Delta\gamma \sim \Gamma/\mathrm{N}^{*} \sim \Gamma\delta^{1/\phi} \tag{25a}$$

In the plateau regime, when the interface is saturated, the change $\Delta\gamma$ may be written as the sum of two contributions:

$$\Delta\gamma = -D^{-2} - \mu_b\Gamma_{\mathrm{sat}} \tag{25b}$$

where the first term is the surface free energy gain, and the second one is the Gibbs contribution. Using relations (21c) and (24), we find

$$\Delta\gamma = -\delta^{6/5\phi} - \phi_b^{5/4}\delta^{1/5\phi} \tag{26}$$

The second term is present only when the bulk is a semi dilute solution, and is smaller than the first one as long as the solution is not too concentrated, $\phi_{\mathrm{b}} \leq \delta^{4/5\phi}$, which is the case we are considering here.

Note that for $\phi = 1/2$, Eq. (26) gives the non correlated case of the previous section: $\Delta\gamma_G = -\delta^{12/5} - \phi_b^{5/4}\delta^{2/5}$.

IV. DISCUSSION

Let us now compare the various results that we obtained above. In what follows we will consider copolymers made of a total number of M Monomers. So with our previous notations, M = N Z for the regular case, and M = N for the random case. For the single copolymer case, the cross over from isotropic to adsorbed states, equation occurs for

$$\delta^*_{\mathrm{reg}} \sim M^{-1}N^{4/5} \sim M^{-1/5}Z^{-4/5} \tag{6b}$$

This may be compared first with the cross over for adsorbing a homopolymer at an interface between two solvents. For the latter case, we know that the corresponding cross over occurs for

$$\delta^*_{\mathrm{homo}} \sim M^{-2/5} \tag{27}$$

The ratio

$$\delta^*_{\mathrm{reg}}/\delta^*_{\mathrm{homo}} \sim M^{-3/5}N^{4/5} \sim M^{1/5}Z^{-4/5} \tag{28a}$$

This ratio is of order unity for a special mass

$$M^* \sim N^{4/3} \sim Z^4 \tag{28b}$$

When the ratio (28a) is smaller than unity, a regular copolymer adsorbs at the interface more easily than a homopolymer with same mass. This happens for large masses, $M > M^*$, for a given number N of sequences in the copolymer. It happens for small masses on the contrary, $M < M^*$, for a given size Z of the sequences.

Let us now consider the random copolymer cases. For the latter, we found

$$\delta^*_{\mathrm{ran}} \sim M^{-\phi} \tag{20a}$$

where ϕ is defined below Eq. (21c), and has value between 1/2 and 1. Comparing Eqs. (27) and (20a), we find that because ϕ is larger than 1/2, the cross over for random copolymers always occurs for smaller values of the parameter δ. It is always easier to adsorb a random copolymer than a homopolymer with same mass. Comparing relations (6b) and (20a) for the regular and random copolymer cases, we find

$$\delta^*_{\text{ran}}/\delta^*_{\text{reg}} \sim M^{1-\phi}N^{-4/5} \sim M^{(1-5\phi)/5}Z^{4/5} \tag{29}$$

where the exponent for the total mass, M, variation is positive in the middle part and negative in the last part of the equation because of the restriction on the value of the cross over exponent ϕ mentioned above. Both systems are equivalent, and the cross over values are comparable for a special value of M, M* such that

$$\mathrm{M}^* \sim N^{4/5(1-\phi)} \sim Z^{4/5(\phi-1)} \tag{30}$$

Therefore, for a given value of the selectivity δ, it is easier to adsorb a random than a regular copolymer when M is smaller than M* for a given number N of sequences. This implies that the sequences in the regular copolymer are short. It is also easier when M is smaller than M* when the size of the sequences is given. This implies a large number of sequences.

The previous discussion was about a single chain at the interface. We consider now the saturation – or plateau-regimes. In both cases, for regular and random copolymers, the width of the adsorbed layer is of the same order, namely the radius of gyration $\mathrm{M}^{3/5}$, of the isotropic chains. But surface concentrations and surface tension drops are not similar: Using relations (9), (11), (24) and (26), we find:

$$\Gamma_{\text{reg}}/\Gamma_{\text{sat}} \sim (\mathrm{Z}/Z^*)^{4/5} \tag{31a}$$

and

$$\delta\gamma_{\text{reg}}/\delta\gamma_{\text{ran}} = (\mathrm{Z}/Z^*)^{24/5} \tag{31b}$$

with

$$\mathrm{Z}^* \sim \delta^{-(5\phi-1)/4\phi} \tag{31c}$$

Thus both surface concentration and surface tension drop are larger for regular copolymers when the number of monomers per sequence is large. The latter result is valid both when the bulk solution is dilute or semi dilute. Figure 2 shows both diagrams for the regular and random cases. One can see that for $N < N^*$, or $Z > Z^*$, $\delta^*_{\text{ran}} < \delta^*_{\text{reg}}$, and there is no intersection of the saturation curves. In this case, the saturation concentration for the random case is always larger than the one for the regular case. In the opposite case, for $N > N^*$, or $Z < Z^*$ there is an intersection, and regular copolymers lead to a more concentrated surface if the selectivity of the interface is large enough, $\delta > \delta_\Gamma \sim Z^{-4\phi/(5\phi-1)}$. Although this does not appear clearly in relation (31a) above, it may be shown in the following way: the surface concentration corresponding to the crossing of both curves is

$$\Gamma_\Gamma \sim \delta_\Gamma^{1/5\phi} \sim Z^{-4/5(5\phi-1)}$$

The latter concentration has to be larger than the overlap concentration Γ^* for the isotropic polymers, $\Gamma^* \sim M^{-1/5}$. Taking this condition into account leads to a crossing only in the case discussed above. We conclude this discussion by noting that the surface concentration at saturation is larger for random copolymers than for regular ones, except for both large selectivity and large number of sequences. Using Eqs. (11) and (25), one can show that similar arguments hold for the change in surface tension.

References

[1] de Gennes, P. G. (1976). *J. de Physique*, **37**, 1445.
[2] Pincus, P. and de Gennes, P. G. (1983). *J. de Phys. Lett.*, **44**, 241.
[3] Eisenriegler, E., Binder, K. and Kremer, K. (1982). *J. Chem. Phys.*, **77**, 6296.
[4] Joanny, J. F. (1998). *Macromolecules*, **31**, 8297.
[5] Polymers at interfaces, Fleer, G. J., Cohen Stuart, M., Schjeutjens, J. M. H. J., Cosgrove, T. and Vincent, B. Editors, Chapman and Hall, London, 1993.
[6] Guiselin, O., *Thesis*, Université Paris VI, available from LLB; C. E. Saclay; 91191 France.
[7] Aubouy, M. and Raphael, E. (1994). *Macromolecules*, **27**, 5182.
[8] Huang, K. and Balasz, A. C. (1991). *Phys. Rev. Lett.*, **66**, 620.
[9] Zajac, R. and Chakrabarty, A. (1996). *J. Chem. Phys.*, **104**, 2418.
[10] Johner, A. (1999). *Macromolecules*, **32**, 825.
[11] Bouchaud, E. and Daoud, M. (1987). *J. de Physique*, **48**, 1991.
[12] Leclerc, E., *Thesis*, Université Paris VI, 1997, available from L. L. B.; C. E. Saclay; F91191 Gif/Yvette cedex.
[13] Aguié-Béguin, V., Leclerc, E., Daoud, M. and Douillard, R. (1999). *J. Coll. Interface Science*, **33**, 329.
[14] Auroy, P. and Auvray, L. (1992). *Macromolecules*, **25**, 4134.

[15] Jean, B., Lee, L. T. and Menelle, A. (1999). *Langmuir*, **15**, 3267.

[16] Fleer, G. J. (1999). *Macromolecules*, **32**, 487.

[17] Guenoun, P., Delsanti, M., Gazeau, D., Mays, J. W., Cook, D. C., Tirrell, M. and Auvray, L. (1998). *Eur. Phys. J. B*, **1**, 77.

[18] Auvray, L. and Cotton, J. P. (1987). *Macromolecules*, **20**, 202.

[19] Garel, T., Huse, D. A., Leibler, S. and Orland, H. (1989). *Europhys. Lett.*, **8**, 9.

[20] Monthus, C., Garel, T. and Orland, H., submitted to *Eur. Phys. J. B*.

[21] Sommer, J. U., Halperin, A. and Daoud, M. (1994). *Macromolecules*, **27**, 6991.

[22] Leclerc, E. and Daoud, M. (1997). *Macromolecules*, **30**, 293.

[23] de Gennes, P. G. (1981). *Macromolecules*, **14**, 1637.

[24] Bray, A. and Moore, M. A. (1977). *J. Phys.*, **A 10**, 1927.

[25] Defay, R., Prigogine, I., Bellemans, A. and Everett, D. H., *Surface adsorption*, Longmans, Green, and Co., London, 1966.

[26] Mandelbrot, B. B., *The fractal geometry of nature*, Freeman, San Francisco, 1977.