DIBLOCK COPOLYMERS IN SELECTIVE SOLVENTS

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We review our recent work on diblock copolymers in highly selective solvents. This includes the static and kinetic properties of micelles, the thermodynamic description of a copolymer layer adsorbed on a wall and the kinetics of formation of an adsorbed layer.

Diblock copolymers are polymers formed by two blocks of monomers of different chemical nature A and B linked together. In many situations, they exhibit amphiphilic properties and can be considered as the macromolecular analogues of small chain surfactants. These amphiphilic properties find many applications, both as compatibilizing agents of molten polymer mixtures and as stabilizing agents of colloidal suspensions.

From the theoretical side, block copolymers can be studied using the statistical mechanical methods developed for homopolymers, and in a sense they can be considered as model surfactants. In our recent work [1, 2], we have studied the behavior of block copolymers in so-called highly selective solvents, using blob concepts and scaling ideas. We give here a brief outline of our results for micelle formation and for adsorption on solid surfaces.

In a highly selective solvent, one of the blocks, B, is in a good solvent, where it adopts a swollen configuration, and the other block, A, is in a very poor solvent. In general, A and B polymers are highly incompatible, so that the A block has a tendency to form molten regions, from which both the solvent and the B blocks are excluded. An isolated chain in solution thus adopts a configuration where the B block of N_B monomers of size a is swollen and has a radius given, in a Flory approximation, by $R_B \sim N_B^{3/5}a$, and the A block of N_A monomers forms a collapsed globule of radius $R_A \sim N_A^{1/3}a$.

As soon as the concentration of the solution has a finite value, the copolymer forms mesophases. If the molecular weight of the two blocks is such that the asymmetry ratio, defined by $\beta = N_B^{3/5}/N_A^{1/2}$, is larger than unity (the only case that we discuss here), the first mesophase that appears is a micellar phase. Each micelle has a spherical core, which is a molten A region, and a corona formed by the B blocks stretching outwards. When $\beta > 1$, the thickness of the

corona L is much larger than the core radius, and the micelles may be viewed as star polymers with a large number of arms equal to the aggregation number p. The value of the aggregation number is obtained by balancing the stretching energy of the arms in the corona (estimated from a blob model introduced by Daoud and Cotton [3]), with the energy of the core, which is governed by the surface tension γ between the insoluble A block and the solvent. This leads to an aggregation number which does not depend on the molecular weight of the soluble block B, and which scales with the molecular weight of the insoluble block as $p \sim N_A^{4/5}$. The critical micellar concentration (cmc) where the micelles appear is extremely small and decays exponentially with the molecular weight of the A block: $\log \phi_{cmc} \sim -N_A^{2/3}$. If the insoluble block is a true polymer ($N_A \gg 1$), the cmc value can be so low that it is unobservable in practice. A more refined theory [4] gives a micelle size distribution that is strongly peaked around the maximum $p \sim N_A^{4/5}$; above the cmc, the aggregation number is roughly constant and the concentration of free chains in equilibrium with the micelles remains approximately equal to the cmc value, the concentration of micelles increasing linearly with the total copolymer concentration.

Micelles are labile objects in equilibrium with their environment. Exchanges occur between free chains and micelles, as well as permanent destructions and reformations of micelles. For small surfactant micelles, these kinetic effects have been studied by measuring the relaxation towards thermodynamic equilibrium after the application of an external constraint. A very refined theoretical model has been constructed by Aniansson and Wall [5]. Two kinetic processes are distinguished: a fast process during which chains are expelled one by one from the micelle (the total number of micelles remaining constant) with a characteristic relaxation time T_1, and a slow process where the total number of micelles changes due to micelle destruction. The destruction of micelles is due either to chain by chain emptying, as in Aniansson's original work, or to fission of micelles as proposed later. The ideas of Aniansson were generalized to copolymers first by Halperin and Alexander [6], who used reptation theory to describe chain motions. Following their ideas, one can estimate the dependence of the two relaxation times T_1 and T_2 as a function of the molecular weights of the two blocks. Both for the fission mechanism and the chain by chain emptying mechanism, the relaxation time of the slow process increases very strongly with the molecular weight of the insoluble block of the copolymer $T_2 \sim \exp N_A^{6/5}$; this turns out to be longer than any realistic experimental time, and in block copolymer solutions, one can assume that micelles have an infinite lifetime. The relaxation time of the fast process increases also strongly with the molecular weight of the insoluble block, if the concentration is higher than the cmc, $T_1 = N_B^{9/5} N_A^{2/25} \exp(\alpha N_A^{2/3})$ (where α is a constant). For reasonable orders of magnitude of the parameters, T_1, although large (of the order of

minutes), retains a finite value. When perturbed, the micelle distribution can thus relax by releasing free copolymers from each micelle.

When a micellar solution is in contact with a wall, the copolymer chains may adsorb on the wall. Their adsorption behavior is governed by the relative values of the interaction energies between the wall, the solvent and the monomers forming the two blocks. We consider here only the case where the insoluble block is strongly adsorbed by the wall and the soluble block is strongly repelled by the wall. This is the configuration where one may expect the formation of thicker layers, and thus where the copolymer should be most efficient as a stabilizing agent of colloidal dispersions. In this limit,the adsorbed copolymer layer has the double layer structure shown in fig. 1. The A block forms a thin molten film of thickness d on the surface, and the soluble B block forms a polymer brush of thickness L dangling into the solvent. The geometry of the adsorbed layer and the surface coverage σ (the total number of polymer chains per unit area) are obtained by balancing the chemical potential of the adsorbed copolymer with that of the external micellar solution. The chemical potential of the adsorbed copolymer includes contributions from the two
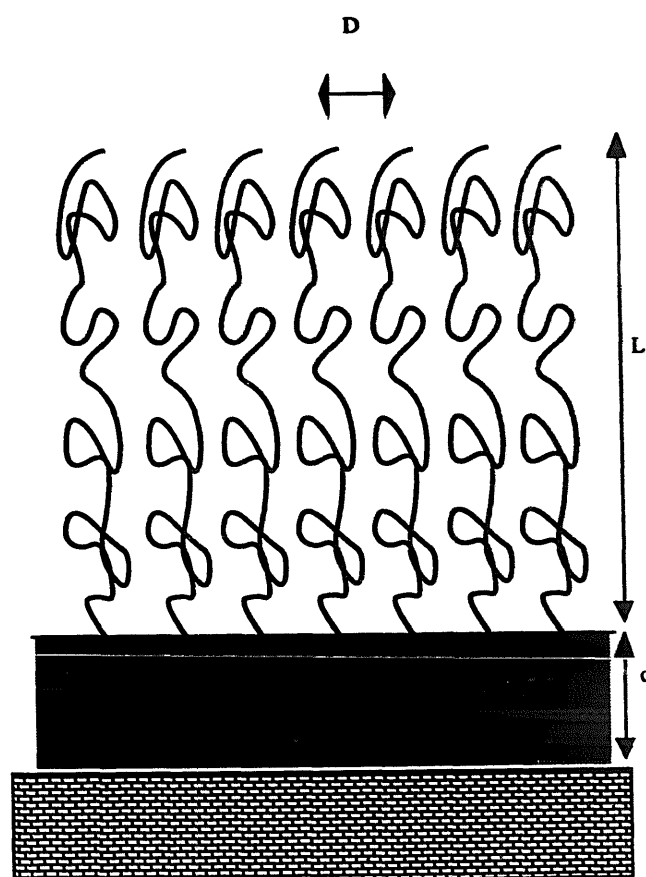

Fig. 1. Structure of an adsorbed copolymer layer.

blocks. The contribution of the soluble block is due to the stretching of the B chains, and is calculated in the framework of the Alexander blob model [7]; this term favors thinner layers and lowers the surface coverage. The contribution of the A block to the chemical potential is that of a thin liquid film of thickness d. The polymer entropy of a confined melt vanishes, and the chemical potential is dominated by the direct interaction between the polymer and the wall; to model these interactions, we choose the non-retarded van der Waals interactions, which are in general repulsive (negative Hamaker constant) when the A monomers are attracted towards the wall, and tend thus to thicken the film and increase the surface coverage. The geometry of the adsorbed copolymer layer is then essentially governed by the asymmetry β of the copolymer. If the copolymer is symmetric $(1 < \beta < N_A^{7/50})$, the contribution of the van der Waals free energy is small, and the surface coverage varies as $\sigma = N_A^{-13/25} \beta^{-2}$. If the copolymer is dissymmetric $(N_A^{7/50} < \beta)$, the chemical potential of the external micellar solution is small compared to the van der Waals energy and the stretching energy of the B chains. The surface coverge increases then as $\sigma = N_A^{-17/23} \beta^{-10/23}$. A variation of surface coverage in agreement with this law has recently been observed by Parsonage et al. [8] for the adsorption of polystyrene–polyvinylpyridine copolymers on silica or mica from a toluene solution. This is the first experiment that suggests the importance of the van der Waals forces for block copolymer adsorption.

The structure of the adsrobed layer sketched in fig. 1 and that we just described is the structure at thermodynamic equilibrium; however, in the external B layers, the chains are elongated and the energy cost to bring new chains into this layer is much larger than kT. This means that there is a high energy barrier to overcome in the adsorption process. The adsorption kinetics is thus very slow and it is not clear whether equilibrium can be reached within reasonable experimental times. The question of the respective role of the free chains and the micelles in the adsorption kinetics is also of interest.

In the early stages of the adsorption, the coronas of the micelles are strongly repelled by the solid surface, and the energy barrier for micelle adsorption is huge. Although the concentration of micelles is much higher than that of free chains, the flux of free chains towards the surface is larger by orders of magnitude than that of micelles. In a first approximation, one can thus ignore direct adsorption of micelles. This does not mean, however, that micelles do not play any role in the adsorption kinetics. As the free chains adsorb, a depletion layer of these free chains is created in the vicinity of the solid surface; the concentration in this depletion layer falls below the cmc value, and the equilibrium between free chains and micelles is broken. The micelles relax towards equilibrium by releasing free chains with a relaxation time T_1. The released free chains may themselves adsorb, and the adsorption kinetics is

considerably accelerated compared to what it would be for a solution of independent copolymer chains.

In the initial times of the adsorption kinetics ($t < T_1$), micelle relaxation is negligible and the adsorption is dominated by the diffusion of the free chains towards the surface; the increase of surface coverage with time follows the classical law for diffusion limited adsorption $\sigma \sim t^{1/2}$. At times larger than T_1, micelle relaxation becomes important and a steady state is reached where all the chains released by the micelles adsorb on the surface; the surface coverage increases then as $\sigma \sim t$. During this process, the outer B brush of the adsorbed layer builds up, and the energy barrier against adsorption increases. At longer times, the crossing of the barrier becomes the limiting step for adsorption, and the surface coverage increases extremely slowly with time $\sigma \sim (\log t)^{6/5}$ [9]. These predictions for the adsorption kinetics have been compared to recent experiments by Tassin et al. for adsorption of polystyrene–polyvinylpyridine copolymer solutions on silver surfaces [10]. A two-step kinetics is observed with a fast process corresponding to the micelle limited adsorption and a slow process where σ increases logarithmically with time; this leads to a micelle relaxation T_1 of order one minute for polymers with a molecular weight of 5000 for the insoluble block and 60 000 for the soluble block.

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