Amphiphilic molecules: small and large

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Large amphiphilic molecules represent a new frontier in the field of surfactant science and technology. Their macromolecular nature affords a range of architectures, length scales, time scales, and levels of interactions much wider than those offered by small amphiphilic molecules. At the same time, such diversity poses great challenges in the characterization and understanding of the solution and surface properties of large amphiphiles. An obvious starting point is to utilize the arsenal accumulated over the last decades on the behavior of small amphiphiles. The evolution in self-assembly properties from small to large amphiphiles is outlined here, and the two classes of molecules are placed in perspective.

1. INTRODUCTION

Amphiphilic is an attribute which means "loving both" (or "having an affinity for both"). In the case of the molecules of particular interest here, this dual "affection" is usually expressed toward water and toward oil, but, in general, amphiphilicity can be expressed toward any two solvents which are incompatible with each other. For most purposes we consider as amphiphilic molecules those consisting of hydrophilic (water-loving) parts and hydrophobic (water-hating) parts, but in the present treatise we will include also molecules with two different parts being both hydrophilic. Typical amphiphilic molecules have molecular weights on the order of 500 and we would call them "small". Amphiphiles also come in "large" sizes, 10 - 1000 times bigger than the "small". These large amphiphiles are often block copolymers, where block(s) of one type of homopolymer are attached sequentially to block(s) of another type. There are two natural starting points for considering amphiphilic block copolymers in solvent environments, low molecular weight amphiphilic molecules in water and neat (solvent-free) block copolymers. In this introductory chapter we will present amphiphilic copolymers in such a broader context, and in doing so we will also compare amphiphilic block copolymers with other types of amphiphilic copolymers.

2. SELF-ASSEMBLY OF SMALL AMPHIPHILIC MOLECULES

Surfactants (surface-active agents) and (polar) lipids are representative examples of low molecular weight amphiphiles with distinct hydrophilic and hydrophobic parts. These classes, with broad technical applications and biological functions, have been extensively studied during the whole of the 20th century and a thorough understanding has emerged [1-6]. In the various applications, constant efforts are made to design new surfactants with an improved performance. It has been known since long time that the more amphiphilic a surfactant the more efficient it is. Since the hydrophilic head group is often fixed (e.g., a sulfate or amine ionic group, or oligo-ethylene oxide nonionic block), the desire to increase the amphiphilicity has prompted an enlargement of the hydrophobic group such as the lengthening of an alkyl chain.

Due to the amphiphilic nature of a surfactant or lipid, the two parts of the same molecule interact very differently with either a polar solvent or surface or a nonpolar solvent or surface. There are two different ways to render favorable intermolecular contacts possible in surfactants while eliminating unfavorable ones: self-assembly in solution (see Figure 1) and adsorption at a surface or an interface (examples shown in Figure 2). The self-assemblies can involve only the amphiphilic molecules, or there can be a mixed aggregate formed together with a low molecular weight cosolute or a macromolecule [2]; in fact, self-assembly is quite sensitive to a range of cosolutes. During the recent years, we have learnt that amphiphile adsorption at different interfaces is also best considered as a self-assembly process promoted by the interface and that there is considerable organisation of amphiphilic molecules at interfaces.

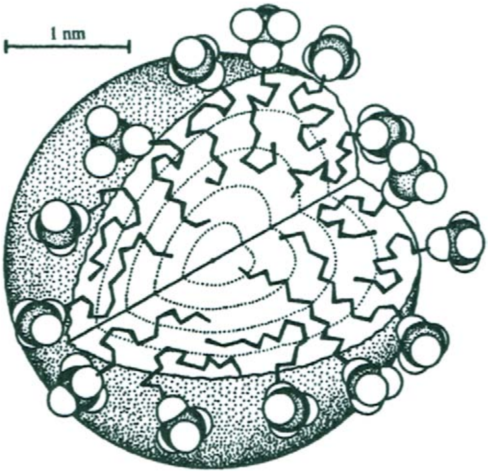


Figure 1. An illustration of a spherical micelle (for dodecyl sulphate) emphasizing the liquid like character with a disordered hydrocarbon core and a rough surface. (adapted from J. Israelachvili, Intermolecular and Surface Forces, Academic Press, London, 1985, p. 215)

Self-assembly involves the formation of domains of hydrophobic groups (in contact with a nonpolar solvent or surface if applicable) and domains of hydrophilic groups (in contact with water or another polar solvent or a hydrophilic surface). In general, in a system containing surfactant, water, and oil we have a segregation between water and oil domains and surfactant films (see Figure 3). The surfactant films can close on themselves and form discrete aggregates, or they can form "infinite" aggregates with connectivity over macroscopic distances, as shown schematically in Figure 4. A rich topological variation is possible as well as different intermicellar arrangements; examples of various self-assembled microstructures are given in Figure 5. This leads to a frequently complex phase behavior [5,6]. A general observation is that the phase behavior becomes richer as the size of the surfactant molecule increases.

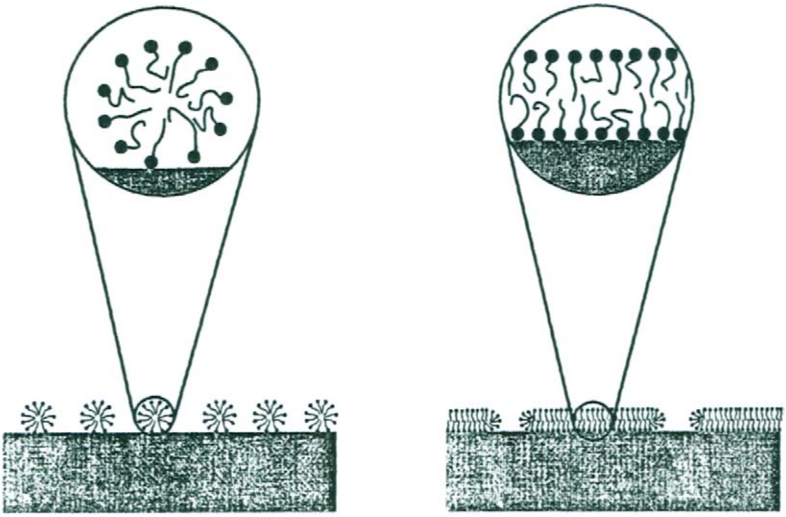


Figure 2. Surfactant molecules can self-assemble into discrete (spherical or cylindrical) micelles at a hydrophilic surface, in the absence of strong specific interactions between the surfactant head-group and the surface. (adapted from ref. [2], p. 60; © J. Wiley, 1998)

Both technical applications and biological functions may be enhanced by increasing the size of the amphiphilic molecule. Firstly, a stronger amphiphile has a low monomeric solubility, and thus has a stronger tendency to go to any interface. It is then more surface-active, and acts as a better detergent, a better stabiliser of dispersions or modifier of surfaces, and a better membrane-forming agent. Secondly, the richer self-assembly polymorphism gives a finer control over macroscopic and microscopic properties. Another point relates to the dynamic nature of the self-assemblies. Surfactant micelles and other aggregates are highly dynamic, with low residence times of surfactant molecules [1]. The residence times increase very strongly with increasing surfactant molecule size. An important incentive for increasing the molecular size is to decrease the lability of aggregates and making technical systems and biological structures more stable and less sensitive to perturbations.

3. OXYETHYLENE SURFACTANTS: SMALL BLOCK COPOLYMERS

Most surfactants have very small polar parts, a few Å, while the nonpolar part is an order of magnitude larger. For the important class of nonionic surfactants of the oxyethylene type the situation is different, the two parts being similar in size. These nonionic surfactants can be considered as short AB block copolymers and their behavior is a suitable starting point of our discussion; we adopt here the convention of denoting by A the (more) polar part. The nonionic surfactants show a complex phase behavior with several solution and liquid crystalline phases (see Figure 6 for a representative concentration-temperature phase diagram for a binary nonionic surfactant water system). Since the oxyethylene-water interaction is temperature dependent, and becomes less favorable at higher temperatures, we can control the self-assembly structure not only by the size of polar and nonpolar groups but

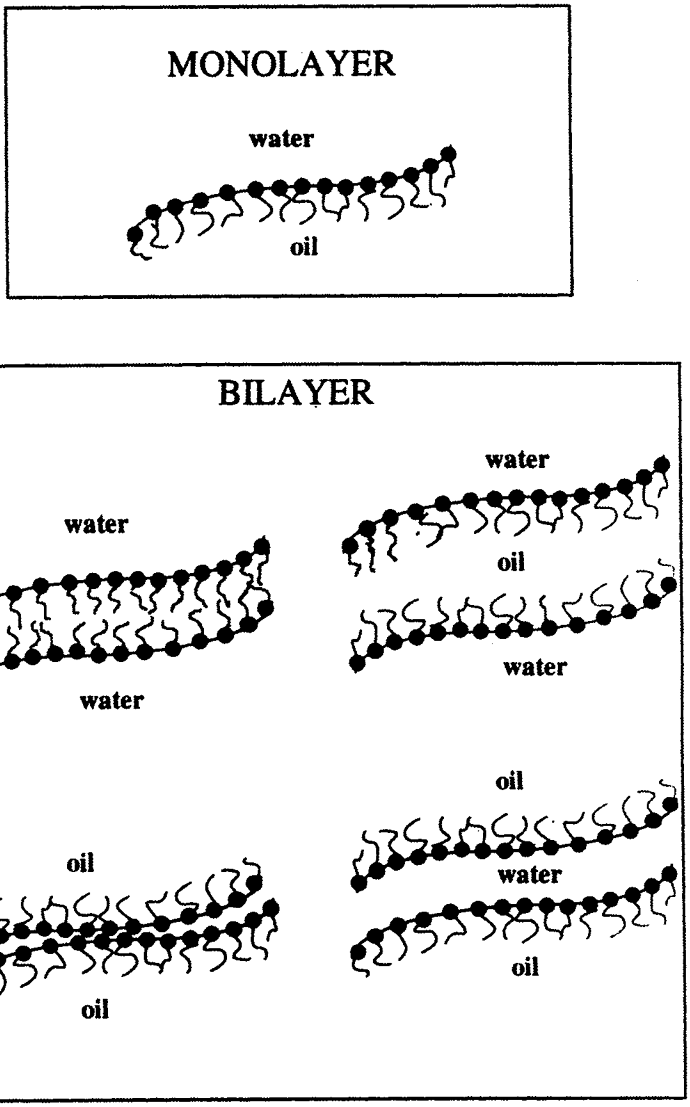


Figure 3. Surfactant monolayer (top panel) and bilayers (bottom panel). In any surfactant system we have a segregation into water-rich and oil-rich domains, as well as surfactant films. The latter can be pairwise correlated (into bilayers) or uncorrelated. (adapted from D.O. Shah, Ed., Micelles, Microemulsions, and Monolayers, Marcel Dekker, 1998, p. 105)

also by temperature. For binary surfactant-water systems, decreasing the polar head group size and increasing temperature give qualitatively the same change. For ternary systems with oil, we note that microemulsion structure is strongly dependent on temperature [4].

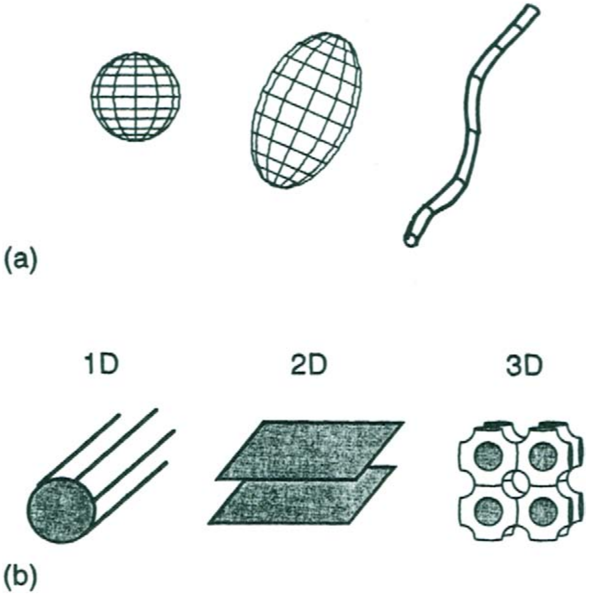
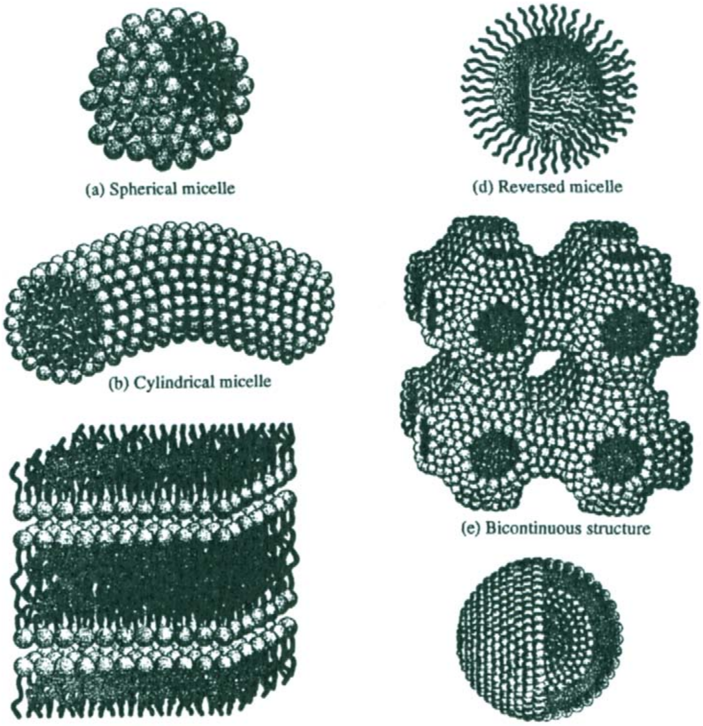


Figure 4. Examples of (a) discrete and (b) continuous surfactant self-assemblies. The latter can extend on 1 (cylinders), 2 (lamellae) or 3 (bicontinuous) dimensions. (adapted from D. O. Shah, Ed., Micelles, Microemulsions, and Monolayers, Marcel Dekker, 1998, p. 104)

The type of aggregate formed by a surfactant under specified conditions depends on the balance between hydrophilic and hydrophobic parts. This balance can be described by different parameters but the ones used more often are the surfactant number or critical packing parameter and the spontaneous curvature of the surfactant film (taken as positive if it is curved towards water) [1]. The surfactant number increases as the hydrophobic part gains in importance, while the spontaneous curvature decreases. For nonionics the surfactant number increases and the spontaneous curvature decreases as temperature increases (the temperature dependence of the spontaneous curvature is shown pictorially in Figure 7). The underlying less favorable oxyethylene-water interactions at higher temperatures have been discussed from different starting points. However, currently we understand these systems in terms of temperature induced conformational changes so that more polar conformers dominate at low temperatures and the less polar at high temperatures.

The simple diblock copolymer is the most direct analogue to conventional surfactants, but not the only one. Double-chain structures are found in many surfactants, like those used as textile softeners and developed for enhanced oil recovery, and many lipids are analogous to BAB block copolymers, while α,ω-surfactants are analogous to ABA copolymers.



(a) Spherical micelle

(d) Reversed micelle

(b) Cylindrical micelle

(e) Bicontinuous structure

(c) Lamellar phase

(f) Vesicle

Figure 5. Surfactant self-assembly leads to a range of different structures of which a few are shown: (a) Spherical micelle with an interior composed of the hydrocarbon chains and a surface of the polar head-groups (depicted as spheres) facing water. The hydrocarbon core has a radius close to the length of the extended alkyl chain. (b) Cylindrical micelle with an interior composed of the hydrocarbon chains and a surface of the polar head-groups facing water. The cross section of the hydrocarbon core is similar to that of spherical micelles. The micellar length is highly variable so these micelles are polydisperse. (c) Lamellar phase consisting of surfactant bilayers. (d) Reverse micelle with a water core surrounded by the surfactant polar head-groups. The alkyl chains together with a non-polar solvent make up the continuous medium. (e) Bicontinuous structure with the surfactant molecules assembled into connected films characterized of two curvatures of opposite sign. (f) Vesicle built from bilayers similar to those of the lamellar phase, and characterized by two distinct aqueous domains, one forming the core and one the external medium. (adapted from ref. [2], p. 34; © J. Wiley, 1998)

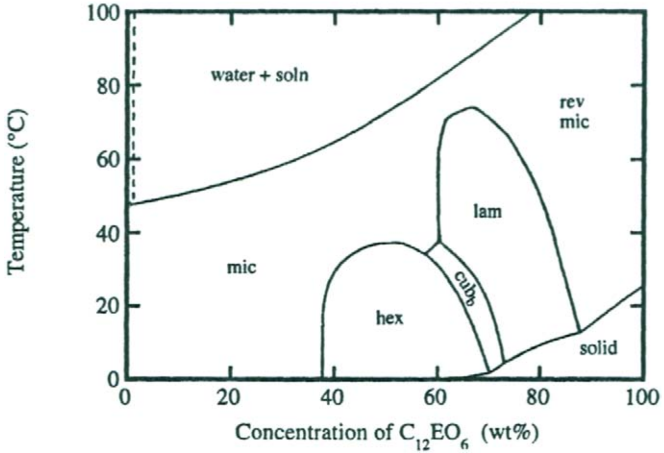


Figure 6. Binary concentration-temperature phase diagram for a nonionic surfactant with C12 hydrophobic chain and 6 oxyethylenes in the polar head group. Mic and rev mic denote micellar and reverse micellar solutions, respectively. Hex, cub, and lam, denote regions with hexagonal, cubic, and lamellar lyotropic liquid crystalline microstructure, respectively. (adapted from ref. [2], p. 99; © J. Wiley, 1998)

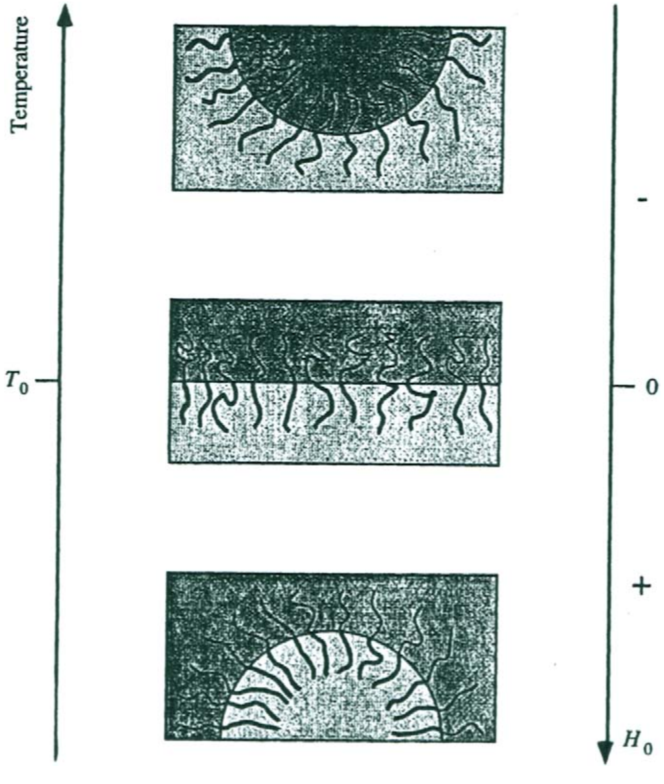


Figure 7. Spontaneous curvature, H, vs temperature for nonionic surfactants. H changes from positive at low temperature to negative at high temperatures. At some intermediate temperature, T_o, the spontaneous curvature is zero and the surfactant is termed balanced. (adapted from ref. [2], p. 101; © J. Wiley, 1998)

4. LARGE AMPHIPHILIC MOLECULES

The connection to surfactants, described above to some length both in order to introduce various self-assembly structures and to indicate the ubiquitous special temperature effects displayed for systems containing poly(oxyethylene) chains, is but one basis for the rapid development of the field of water-soluble amphiphilic polymers and for their scientific understanding. The relation to neat block copolymers and their rich phase behavior, and to block copolymers in the presence of selective solvents is another such basis. For neat block copolymers there is an increasing tendency for segregation between the blocks as the interblock interaction becomes less favorable (the interaction being described by a Flory interaction parameter, χ) as block molecular weight (~N) increases and as temperature decreases (generally, $\chi \sim 1/T$). Composition (that of the two blocks in the block copolymer molecule) - temperature phase diagrams can be generated in terms of the interaction parameter and molecular weight (Figure 8).

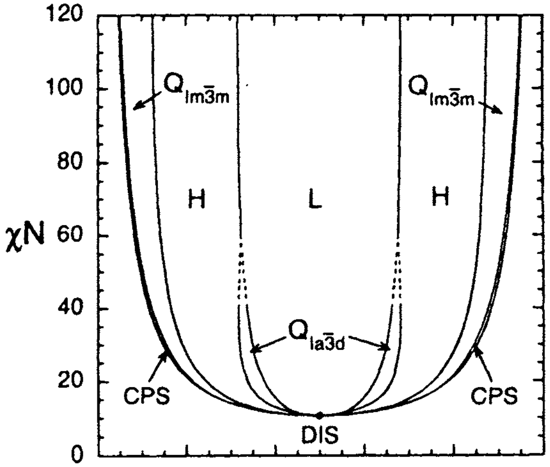


Figure 8. Mean-field phase diagram (χN vs f) for conformationally symmetric diblock copolymers. The notation for the different microstructures is: L, lamellar; H, cylinders in a hexagonal array; Q_{Ia3d}, bicontinuous cubic; Q_{Im3m}, micellar (discrete) cubic; CPS, close-packed spheres; and DIS, disordered melt. (adapted from M.W. Matsen and F.S. Bates, Macromolecules 29 (1996) 1091; © American Chemical Society, 1996)

For small amphiphilic molecules, the chemical structures are basically limited to the AB, ABA and BAB types, while enlarging the molecules gives much richer possibilities. It is also a major advantage in moving to higher molecular weight amphiphiles that the molecular architecture may be much more diverse: block, graft, and star copolymers are possible.

Amphiphilic polymers, which have already received major scientific attention and very extensive industrial use, are block copolymers of the AB, ABA or BAB types, and different graft copolymers (see Figure 9). Particular attention among the latter is directed towards hydrophobically-modified graft copolymers, where a low number (on the order of 1%) of hydrophobic groups have been grafted onto a linear water-soluble polymer, for example a polysaccharide or poly(acrylate). These polymers, used inter alia for rheology control in modern paints and coatings, may instructively be termed polymer-modified surfactants; thus it is very useful to consider them as conventional surfactants coupled together by the polymer back-bone (the converse structure also exists, where hydrophilic groups are grafted onto a nonpolar backbone). We should note the relation of these HM-polymers or polymer-modified surfactants with polysurfactants, like the since long known polysoaps. In fact a related principle of enlarging surfactant molecules of considerable current interest has been by polymerization of simple surfactants to create polymerized surfactants. Most studies have so far examined moderately sized molecules, like dimeric, or gemini, surfactants, trimeric surfactants etc.

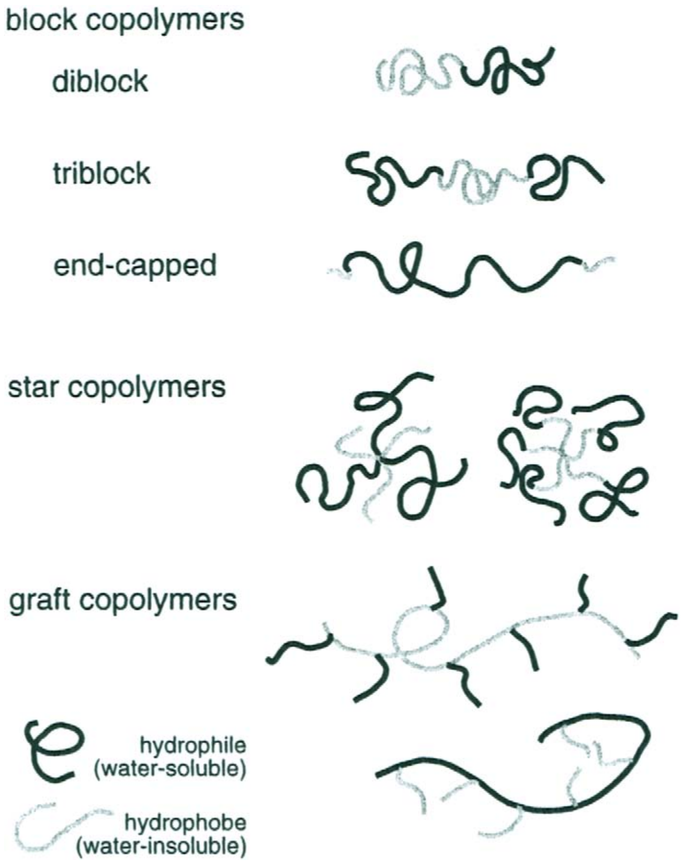


Figure 9. Schematics of block, star, and graft amphiphilic block copolymers.

We should also note that Nature makes frequent use of amphiphilic polymers. Some glycolipids can be considered as short diblock copolymers. Lipopolysaccharides are examples of strongly amphiphilic graft copolymers. One example is Emulsan, the trade name of a bacterially produced polyanionic lipopolysaccharide which is exceptionally efficient as emulsifier (Figure 10). In the polysaccharide field there are also many examples of copolymers which are composed of different hydrophilic parts, like proteoglucans in connective tissue built up of dermatan sulfate and chondrotin sulfate. Proteins have hydrophobic and hydrophilic domains and their character can be more or less block-like. One recent illustration of their amphiphilic character is that they cross-link to form amphiphilic graft copolymers (hydrophobically modified water-soluble polymers) very much in the same way as surfactant micelles. Sometimes Nature introduces special hydrophilic groups, like in glycoproteins, to enhance the amphiphilic character and we modify biopolymers to make them more amphiphilic.

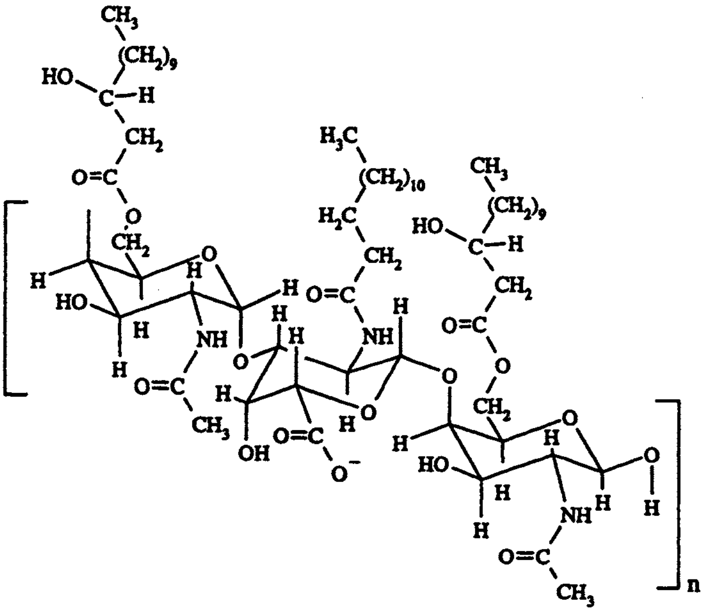


Figure 10. Chemical structure of Emulsan, a bacterially produced polyanionic lipopolysaccharide.

5. SELF-ASSEMBLY OF AMPHIPHILIC BLOCK COPOLYMERS

Large amphiphilic molecules such as diblock and triblock copolymers, as well as graft copolymers with sufficiently long grafts and flexible backbones, have been known to self-assemble in the form of micelles when dissolved in selective solvents [7,8] and also to adsorb on surfaces. The earlier studies were concerned primarily with block copolymers in organic solvents [7], but more recent studies have examined the formation of block copolymer micelles in aqueous solutions [8]. The energetics of micelle formation in organic solvents are generally different than these in aqueous solvents: block copolymer micelle formation in organic solvents is an exothermic (enthalpy-driven) process and micelles tend to "dissolve" at higher temperatures; in aqueous solvents micelle formation is often endothermic (entropy driven), a phenomenon more pronounced in oxyethylene-containing amphiphilic block copolymers where micelles form at elevated temperatures [8]. The ability of temperature to trigger the formation or dissolution of block copolymer micelles finds a number of technological applications. Block copolymer micelles differ from micelles formed by small amphiphiles in terms of size (polymeric micelles being larger) and degree of segregation between the blocks that form the micelle core and these that form the shell or corona (the surfactant tail and head group are strongly segregated), but most functional properties are common in micelles formed by both large and small amphiphilic molecules.

More recently, the self-assembly studies on block copolymers have been extended to cover a wide composition space in mixtures of block copolymers with selective solvents [9]. Such studies have identified various ordered block copolymer structures related to those found in block copolymers in the absence of solvents (see, e.g., Figure 8) as well as to the lyotropic liquid crystals formed in mixtures of small amphiphiles (surfactants and lipids) with water and (possibly) oil or cosurfactant (Figures 5 and 6). Scaling theories and mean-field lattice models developed for polymer blends have been extended to cover block copolymer solutions with encouraging results [9]. Still, the self-assembly of amphiphilic block copolymers remains an uncharted territory, and considerable effort is being extended on studies of the self-assembly of different classes of block copolymers (e.g., polyethers, polyelectrolytes) in various environments (e.g., in water, in non-aqueous solvents, or in the absence of solvents) [9]. A variety of experimental tools, ranging from static (e.g., small angle neutron scattering) to dynamic (e.g., rheology), are proving beneficial to this end. Concurrent with (and sometimes preceding) the fundamental efforts, applications of amphiphilic block copolymers are being explored in areas such as formulations, pharmaceutics, and separations [9].

6. OUTLOOK

Systems containing amphiphilic molecules, small (surfactants) or large (block copolymers), are notable in that they self-assemble (under appropriate conditions) to form morphologies of very well-defined structural order and nanometer scale dimensions. The challenge and the opportunity is in controlling and tuning the morphology, i.e., in determining the appropriate components and conditions leading to the desired microstructure. The importance of self-assembly studies becomes thus apparent. In addition to the numerous studies on small amphiphilic molecules already published (and expected to be published in the future), studies on large amphiphiles will become more prominent in the years to come and will significantly enhance our fundamental understanding and ability to manipulate self-assembly for the common good.

Large amphiphiles such as block copolymers are very flexible in attaining a great variety of micro-structures in the absence or in the presence of solvents and/or other additives. Furthermore, their macromolecular nature allows access to a wide range of length scales and time scales. Amphiphilic block copolymers thus have a potential of great contributions to diverse applications such as synthesis of functional nanoporous materials or formulations of coatings, paints, pharmaceuticals, and personal care products.

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