The micellization of amphiphilic copolymers can result in two different types of micelles, depending on whether the hydrophobic portion is randomly bound to the hydrophilic polymer or grafted to one end of the hydrophilic portion. When terminal hydrophobic groups associate to form micelles, the water clusters immobilized around the hydrophobic segments are excluded from the core and no direct interaction exists between the core and the hydrophilic shell that remains as mobile linear chains in the micellar structure (Winnik et al., 1992; Chung et al., 1999). Randomly modified polymers, however, associate in such a manner that hydrophobic and hydrophilic segments of the polymer are entangled, allowing possible contact between the core and the aqueous media. In this case, the hydrophilic chains forming the shells are less mobile (Chung et al., 1999). This is an important issue, since exposed hydrophobic cores may result in secondary aggregation of polymeric micelles (Gao and Eisenberg, 1993; Yokoyama et al., 1994; La et al., 1996).

Gadelle et al. (1995) investigated the solubilization of various aromatic solutes in PEO-*b*-PPO-*b*-PEO (ABA)/PPO-*b*-PEO-*b*-PPO (BAB) triblock copolymers. According to the experimental results, they indicated two different solubilization processes. To understand better the mechanism for solubilization in the polymeric surfactant solutions, it was postulated that (1) the addition of apolar solutes promotes micellization of the polymeric surfactant molecules, (2) the central core of the polymeric micelles contains some water molecules, and (3) solubilization is initially a replacement process in which water molecules are displaced from the micellar core by the solubilizate. A detailed discussion of the solubilization process can be found in the next section and the pharmaceutical application section of this chapter.

Modeling of Micellization and Solubilization

Diblock Copolymeric Micelles

In an early diblock copolymeric micellar model, an isolated chain in solution was described as having a tadpole configuration with a short collapsed head-block connected to a solvent swollen tail. Each solvent-phobic head is assumed to be a molten liquid globule that merges with other heads in order to minimize exposure to the poor solvent. The resulting micellar aggregate is thus a molten spherical core surrounded by the swollen tails (Daoud and Cotton, 1982; Kwon and Kataoda, 1995; Marques, 1997) (Figure 13.3). The liquid nature of the core allows for mixing the chains and enables the assembly to reach a thermodynamic equilibrium state where the balance between core-solvent interfacial tension and stretching of the chains can be achieved. Under these equilibrium conditions, the micelle aggregation number has been theoretically predicted (Halperin, 1987; Marques et al., 1988) with reasonable agreement in experimental data.

There is evidence to suggest that the hypothesized liquid nature of the core does not generally hold (Antonietti et al., 1994; Marques, 1997). If the core is not a molten globule but is instead in a glass-like state, Marques (1997) indicated that two possible core structures can be considered, and the structure formed depends on the preparation method. First, for micelles prepared in an equilibrium solution (usually at high temperature) and then quenched, the molten core will undergo a glassy transition leading to a final structure that carries the signature of the micellization temperature and of the quenching process. The central glassy region is then likely to have a uniform monomer density of entangled glassy chains. The initial aggregation number is defined by the micellization that occurs at the equilibrium solution state before quenching. Faster quenching rates produce micelles closer to the initial state.

The second possible geometry will arise if the micellization proceeds by aggregation of copolymer chains that already have a glassy head. Although little is known about the structure of individual glassy chains in solution, the characteristic relaxation time of the chain is likely to depend on the amount of solvent actually present in the collapsed globule. In the extreme case of zero solvent content (zero plasticizing effect) and infinite relaxation time, the core will have a porous structure (Figure 13.4), and the pores are filled with solvent and copolymer tails. This bunchy aspect leads to a new distribution of monomers in the micelles and provides simple geometric rules determining