by the tails will depend on the exact packing geometry of the solid heads and on how deformable the solid is. For an infinitely rigid head, the porosity may vary from a minimum of 26%, when spherical heads close pack in a crystal hexagonal close packed or face centered cubic structure, to the most likely case, corresponding to an amorphous structure of approximately 45% porosity. A particular feature of these micelles is that the exchange of a bead from the central core region to the bulk is practically forbidden. At a given moment, only the surface beads may be easily exchanged. This contradicts with the classical micelles where all the micelle chains are *surface chains* and may then be directly exchanged with the bulk. Marques (1997) has shown that the calculated scaling form for the aggregation number in diblock copolymers with a glassy head is in close agreement with results by Antonietti et al. (1994). This suggests that bunchy micelles are good candidates for modeling micellization in that system. However, care should be exerted when extracting information from a single set of data, because alternative explanations could be invoked.

The configuration of the polymers in the micelle has also been studied within the framework of the Daoud-Cotton model (Daoud and Cotton, 1982) for star polymers. However, this model assumes that all the chain ends lie at the outer surface of the corona, therefore overlooking the possibility of a chain-end distribution Marques (1997).

Solubilization by block copolymers has been investigated by Nagarajan and Ganesh (1989) who developed a theory of solubilization of low molecular weight compounds in micelles of AB diblock copolymers in a selective solvent. The theory predicts that the solubilization behavior of the micelles and their geometrical characteristics are significantly influenced by the interactions between the solubilizate and the solvent-compatible block of the copolymer as well as by the solubilizate-solvent interfacial tension. The scaling relationship obtained was compared with previous experimental data where the micellar core was composed of poly(propylene oxide)/PST. This polymer core showed substantial solubilization of aromatic hydrocarbon solubilizates in contrast to negligible solubilization of aliphatics. The conclusion was made that the solubilizate that is more compatible with the polymer block that constitutes the core of the micelle is solubilized to a greater extent.

Triblock Copolymeric Micelles

Hydrophilic terminal blockmicelles: Water-soluble poly(EO)-poly(PO)-poly(EO) (PEO-*b*-PPO-*b*-PEO) triblock copolymers can aggregate to form micelles with a core presumably dominated by PPO and a corona dominated by hydrated PEO blocks. Hurterr et al. (1993a) developed a self-consistent mean field lattice theory to predict the aggregation behavior of PEO-*b*-PPO-*b*-PEO block copolymers and the solubilization of naphthalene in these micelles as a function of polymer composition and molecular weight. The predictions compared favorably with experimental results. It was found that the dependence of the micelle-water partition coefficient on polymer composition is not simply related to the proportion of the hydrophobic constituent but depends on the details of the micelle structure. A strong effect of the molecular weight and PPO content of the polymer on the amount of naphthalene solubilized was observed. A more detailed discussion of Pluronics and other ABA triblock polymers can be found in the next section and the pharmaceutical application section in this chapter.

Hydrophobic terminal blockmicelles: Xing and Mattice (1998) applied Monte Carlo simulation techniques to study the models of BAB triblock copolymeric micelles with solubilizates in a selected solvent. They focused on a microscopic picture regarding the locus of solubilizates in BAB triblock copolymer micelles when the solubilizate molecules are energetically equivalent to a segment of the insoluble block. This situation is of practical interest since monomer or homopolymer impurities are hard to eliminate from block copolymer synthesis.

Two models for micelle structure were identified in their studies (Xing and Mattice, 1998). In analogy with the structural models for systems involving low molecular weight surfactants, two kinds of aggregates of spherical shape can be pictured, depending on how the solubilizates are located inside the block copolymer micelles. Solubilization takes places in two steps in the Xing and Mattice's simulations (1998).