Hydrophobically associating water-soluble polymers are of interest because of their unusual properties in solution; e.g. enhanced viscosification efficiency, shear-thickening rheology, shear stability, and salt stability. However, such macromolecules are difficult to prepare and analyze. This chapter reviews synthetic routes designed to overcome the problems of mixing and reacting oil-soluble and water-soluble reagents/monomers. Both direct copolymerization and post-polymerization methods are described. It also presents methods for determining the amounts of hydrophobe incorporated by NMR, UV, and degradation/GC.

1.1 Introduction

Hydrophobically associating water-soluble polymers are of interest because of their unusual properties in solution. Even small levels of hydrophobic groups on water-soluble polymer backbones can have a profound effect on aqueous solution rheology. For example, solutions of such polymers show enhanced viscosification efficiency, shear-thickening rheology, as well as improved shear and salt stability [1–19].

Nevertheless, hydrophobically associating water-soluble polymers present challenges to both the synthetic and characterization chemists. Hydrophobically associating water-soluble polymers are often difficult to synthesize because of problems associated with mixing oil-soluble and water-soluble reagents/monomers. Similarly, since only small levels of hydrophobe are needed for rheology control, characterization of hydrophobe contents often stretch the detection limits of conventional polymer characterization methods.

This chapter reviews recent advances in the synthesis and characterization of hydrophobically modified water-soluble polymers. The synthetic part describes both direct synthesis via copolymerization and post-polymerization methods. The characterization section presents methods for measuring/estimating hydrophobe incorporation.

1.2 Synthesis

There are basically two ways to incorporate hydrophobic moieties into water-soluble polymer chains; i.e. direct copolymerization of hydrophobic and water
soluble monomers and post-polymerization functionalization. Each method has its advantages and disadvantages.

1.3 Copolymerization

Direct copolymerization of both oil-soluble and water-soluble monomers is difficult because of the phase incompatibility of hydrocarbon and water soluble monomers. Thus, simply dispersing the hydrophobic monomers in the aqueous phase with the hydrophilic monomer leads to a heterogeneous product with low hydrophobe incorporation.

Use of mutual solvents (e.g. alcohols) or solvent mixtures to dissolve both the water and oil-soluble monomers also has some serious limitations [4]. For example, even though a common solvent can be found for the monomers, it is unlikely that the polymer will also be soluble in such a medium. Thus, the polymer will precipitate before it has built up a sufficient molecular weight for use as a viscosifier. In addition, most of the possible water miscible solvents (e.g. alcohols, ether, acetone) are chain transfer agents for free radical polymerization, and their presence leads to low molecular weight products.

Better direct polymerization methods involve the use of micellar copolymerization or use of surfactant macromonomers. In the micellar copolymerization method [8, 13], an oil-soluble acrylamide; (e.g. C₈-alkyl acrylamide) is solubilized in the aqueous phase by appropriate surfactant(s) and copolymerized with water-soluble acrylamide (AM) monomer (Eq. 1.1). The resulting product is a copolymer of acrylamide and C₈-alkyl acrylamide (RAM).

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\begin{align*}
\text{CH}_2=\text{CH} & \quad + \quad \text{CH}_2=\text{CH} & \quad \xrightarrow{\text{Surfactant}} \\
\quad \quad \quad \quad \quad \text{C}=\text{O} & \quad \quad \quad \quad \quad \text{C}=\text{O} \\
\quad \quad \quad \quad \quad \text{NH}_2 & \quad \quad \quad \quad \quad \text{NH} \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{R} & \\
\text{R} = \text{C}_6-\text{C}_{12} \text{ alkyl group}
\end{align*}
\]

Typical surfactants for neutral or anionically charged hydrophobic polymers are sodium dodecyl sulfate or nonionic ethoxylates. For cationic polymers, either cationic or nonionic surfactants are used. Fluorinated surfactants are