# **Hierarchical Structures of Amphiphilic Polymers in Solution**

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## **1. INTRODUCTION**

Characteristic structures and functions of biopolymers are brought about by various specific interactions, i.e., hydrophobic interaction, electrostatic interaction, hydrogen bonding, acid-base complexation, and so on. Among them, the first two interactions play primary roles also in synthetic amphiphilic polymers bearing hydrophobic and electrolyte units. So far these amphiphilic polymers have been extensively studied as a primitive model for biopolymers. Although the amphiphilic polymers are much simpler systems than proteins in nature, they take hierarchical structures in aqueous solution and much more complex than normal synthetic polymers. In this study, we have investigated hierarchical structures of amphiphilic random copolymers in aqueous solution by static and dynamic light scattering, fluorescence, and viscosity.

#### 2. EXPERIMENTAL SECTION

Random copolymers shown in Scheme 1 were synthesized by radical polymerization. The copolymers possess the common hydrophobic monomer unit, but different electrolyte monomer units. The content x of the hydrophobic monomer unit and degree of polymerization n for each copolymer sample were determined by NMR (in

D<sub>2</sub>O) and sedimentation equilibrium (in methanol), respectively.

# **3. RESULTS AND DISCUSSION**

Light scattering and time-resolved fluorescence measurements demonstrated that most of the copolymers listed in Scheme 1 investigated form uni-core micelles consisting of 2 - 10 copolymer chains as a major component in dilute aqueous solution. Hydrodynamic radius data showed that the component is a flower micelle with a hydrophobic core but not all hydrophobic (C12) groups are included in the core. The loop size of the flower micelle was determined mainly by the main-chain stiffness.

Figure 1 shows the copolymer concentration c dependence of the self-diffusion coefficient  $D_{\text{fast}}$  of the major component and

the specific viscosity  $\eta_{sp}$  for aqueous solutions of a p(A/C12) sample with n = 264 and x = 0.06. The decrease of  $D_{fast}$  and increase of  $\eta_{sp}$  with increasing *c* indicate the further aggregation of the flower micelle maybe by the hydrophobic interaction among C12 groups outside the core.

### REFERENCE

1. Kawata, T. et al. "Micellar Structure of Amphiphilic Statistical Copolymers Bearing Dodecyl Hydrophobes in Aqueous Media," *Macromolecules*, **40**, 1631-1637 (2007).



Figure 1.

