

Solution Properties of Amphiphilic Alternating Multiblock Copolymers in Water

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ABSTRACT: Poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO) alternating multiblock (AMB) copolymer is an amphiphilic macromolecules. Since its characteristic primary structure, the morphology of the polymer assemblies has attracted keen interests. It has been found that the aqueous solution of the PEO-PPO AMB copolymer undergoes phase separation with a lower critical solution temperature (LCST) [1]. Below the cloud point, the copolymer forms a multimer micelle [2]. The light scattering measurement suggests that the single chain behaves as a shrunk coil in water.

In this study, we have studied the effect of the number of repeat units on the solution properties of PEO-PPO AMB copolymers. Two types of PEO–PPO AMB copolymers have been prepared: $(\text{EO}_{220}\text{PO}_{33})_n$ and $(\text{EO}_{68}\text{PO}_{33})_n$, where EO is the ethylene oxide unit, PO is the propylene oxide unit, and the subscripts indicate the number of repeat units. The precipitation fractionation enables us to prepare various samples having different n .

The cloud point of the aqueous solution of $(\text{EO}_{220}\text{PO}_{33})_n$ is much higher than that of $(\text{EO}_{68}\text{PO}_{33})_n$, indicating that the latter is more hydrophobic. The phase boundary of the aqueous solution for $(\text{EO}_{220}\text{PO}_{33})_n$ shifts to higher temperature region with increasing n . This behavior has often been reported for amphiphilic polymers. The shape of the boundary does not change by n . The lower critical solution temperature (LCST) is considered to locate at the minimum of the curve, although the phase boundary curve at the higher concentration region is gradual. The n dependence of LCST for

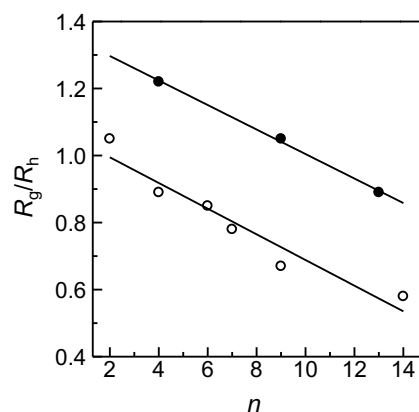


Figure 1. n dependence of R_g/R_h for $(\text{EO}_{220}\text{PO}_{33})_n$ and $(\text{EO}_{68}\text{PO}_{33})_n$ in water at 25 °C.

$(\text{EO}_{220}\text{PO}_{33})_n$ series can be analyzed by means of Shultz-Flory plots, which gives rise to the theta temperature (T_0) of 44 °C. This is in good agreement with the critical micellization temperature of the system reported previously [2]. On the other hand, the M_w dependence on the phase boundary for $(\text{EO}_{68}\text{PO}_{33})_n$ is relatively complicated; its shape significantly varies depending upon n , while LCST does not. LCST locates near 42 °C, irrespective of n .

The morphology of the unimer and associate of these copolymers are investigated by dynamic light scattering (DLS) and small angle X-ray scattering (SAXS) techniques. Both $(\text{EO}_{220}\text{PO}_{33})_n$ and $(\text{EO}_{68}\text{PO}_{33})_n$ exist as unimer at 0.1 wt % and 25 °C, even though a tiny amount of aggregate coexists. R_g and R_h estimated by DLS and SAXS become large as n increases. However, R_g/R_h clearly depends upon n . Fig. 1 represents the n dependence of R_g/R_h for $(\text{EO}_{220}\text{PO}_{33})_n$ and $(\text{EO}_{68}\text{PO}_{33})_n$ in water at 0.1 wt % and 25 °C. The results indicate that the single chain of the PEO-PPO AMB copolymers shrink with increasing n .

KEY WORDS: Amphiphilic alternating multiblock copolymer, chain length dependence, aqueous solution, DLS, SAXS

References.

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