Amphiphilic Poly(ethylene oxide)-Poly(propylene oxide) Alternating Multiblock Copolymers in Aqueous Solution

Yukiteru Katsumoto, Kenji Sakanaya, Keisuke Watanabe, Yusuke Sanada

Department of Chemistry, Fukuoka University, Fukuoka 814–0180, Japan

katsumoto@fukuoka-u.ac.jp

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. In this study, we have prepared two types of PEO–PPO AMB copolymers, $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_m$, where EO is the ethylene oxide unit, PO is the propylene oxide unit, and the subscripts indicate the number of repeat units. It is found that the aqueous solution of $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$ undergoes phase separation with a lower critical solution temperature (LCST). The precipitation fractionation enables us to prepare various samples having different molecular weight. The phase boundary of the aqueous solution for $(EO_{220}PO_{33})_n$ shifts to higher temperature region without changing its shape. On the other hand, the shape of those for $(EO_{68}PO_{33})_n$ significantly changes depending upon the molecular-weight. LCST of the aqueous solution of $(EO_{220}PO_{33})_n$ is much higher than that of $(EO_{68}PO_{33})_n$, because the latter has a shorter PEO block. The morphology of the unimer and associate of these copolymers are investigated by dynamic light scattering and small angle X-ray scattering techniques.

EXPERIMENTAL

The PEO-PPO AMB copolymer (Fig. 1) was prepared by a dehydrated condensation reaction according to the literature [1]. Briefly, α,ω-diamino PPO (JEFFAMINE D-2000; weight-average molecular weight, M_w, =2.0×10^3) was kindly supplied by Huntsman Corporation. α,ω-Disuccinimidyl PEO (SUNBRIGHT DE-100 HS; M_w=1.0×10^4)was purchased from NOF Corporation. The reaction was carried out in $CHCl_3$ at 0 °C. The crude sample was recovered by dialysis against water, followed by freeze-drying. Precipitation fractionation of the copolymer was performed by phase separation in an acetone/n-hexane mixture at 25-50°C. The characterization details can be found in previous reports [1,2].

RESULTS & DISCUSSION

Fig.2 shows the phase boundary curve for the aqueous solution of $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$, which are estimated by the measurement of the cloud point. The phase boundary of $(EO_{68}PO_{33})_n$ locates a lower temperature region, indicating that the copolymer is more hydrophobic. The phase boundary for $(EO_{220}PO_{33})_n$ shifts to a higher temperature region with decreasing M_w, which has often been reported for amphiphilic polymers. On the other hand, the M_w dependence on the phase boundary for $(EO_{68}PO_{33})_n$ is relatively complicated. The lower critical solution temperature (LCST) for the system can be obtained as the minimum of the phase boundary curve. The M_w dependence of LCST for $(EO_{220}PO_{33})_n$ series can be analyzed by means of Shultz-Flory plots [3], which gives rise to the theta temperature (T_θ) of 44 °C. The $(EO_{220}PO_{33})_n$ may form a micelle above the temperature. Fig. 3 represents the M_w dependence of the hydrodynamic radius for $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$ in water at 0.1 wt % and 25 °C. The results indicate that the single chain of $(EO_{220}PO_{33})_n$ forms a shrunk coil in water under T_θ, whereas that of $(EO_{68}PO_{33})_n$ exists as an anisotropic coil.
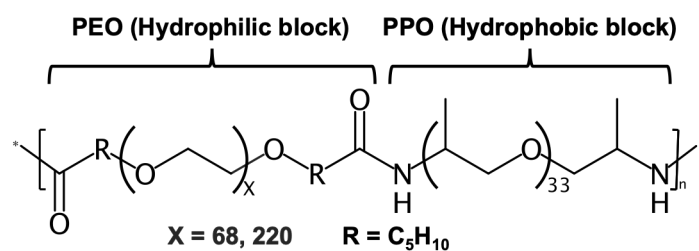
Figure 1: Chemical structure of PEO-PPO AMB copolymer.
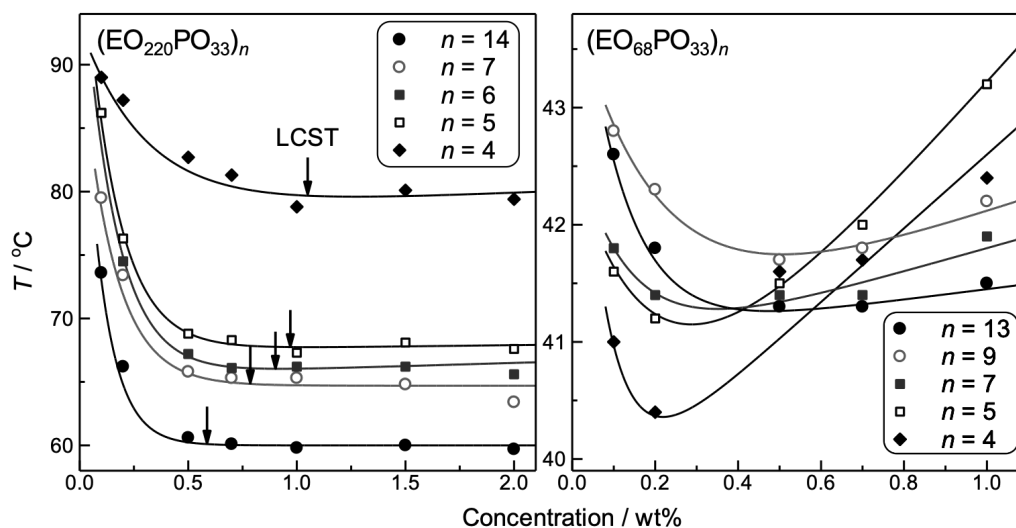
Figure 2: (Left)Phase diagram for the aqueous solution of $(EO_{220}PO_{33})_n$. (Right) that of $(EO_{68}PO_{33})_n$.
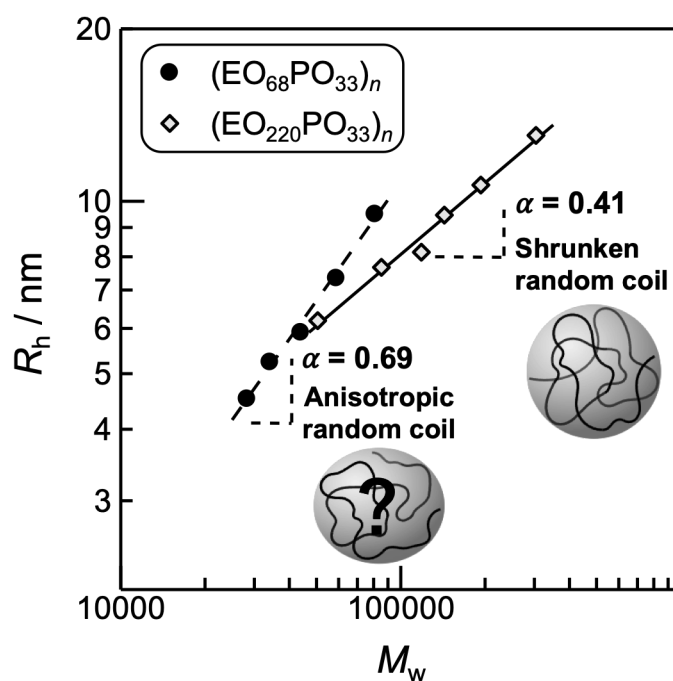
Figure 3: M_w dependence of the hydrodynamic radius for $(EO_{220}PO_{33})_n$ and $(EO_{68}PO_{33})_n$ in water at 0.1 wt % and 25 °C.

REFERENCES

[1] T. Horiuchi, et al. Langmuir 33 (2017) 14649-14656.

[2] K. Rikiyama, et al. Polymer(Guildf) 156 (2018) 102-110.

[3] A. R. Shultz and P. J. Flory, J. Am, Chem. Soc. 74 (1952) 4760-4767.