

## Chain morphology of poly(*N*-*tert*-butylacrylamide)-based amphiphilic alternating multiblock copolymers in solution and relationship of block amphiphile

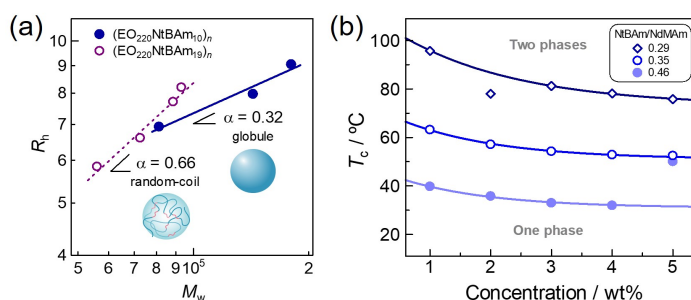
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**ABSTRACT:** Amphiphilic alternating multiblock (AMB) copolymers, in which solvophilic and solvophobic blocks are repeatedly connected to one another, may form various chain morphologies in a specific solvent such as unimer and multimer micelles [1]. The morphology of a unimer micelle of AMB copolymers should be correlated with the balance of solvophilic and solvophobic blocks. We have synthesized poly(ethylene oxide) (PEO)-poly(*N*-*tert*-butylacrylamide) (PNtBAm) AMB copolymers: (EO<sub>220</sub>NtBAm<sub>10</sub>)<sub>n</sub> and (EO<sub>220</sub>NtBAm<sub>19</sub>)<sub>n</sub>, where EO is the ethylene oxide unit, NtBAm is the *N*-*tert*-butylacrylamide unit, and *n* is the number of the PEO-PNtBAm repeating pair, respectively. Since PNtBAm is hardly dissolved into methanol, PEO-PNtBAm AMB copolymers may form a micelle-like structure in methanol. To investigate the chain morphology in methanol, the molecular-weight dependence on the hydrodynamic radius (*R<sub>h</sub>*) has been investigated.

The dynamic light scattering (DLS) measurements have revealed that PEO-PNtBAm AMB copolymers exist as unimers and aggregates in a dilute methanol solution. The *R<sub>h</sub>* of the unimer tended to increase with increasing *M<sub>w</sub>*. By plotting *R<sub>h</sub>* against *M<sub>w</sub>*, a power law is found between *R<sub>h</sub>* and *M<sub>w</sub>* as represented in Fig. 1(a): the index value  $\alpha = 0.32$  for (EO<sub>220</sub>NtBAm<sub>10</sub>)<sub>n</sub> and  $\alpha = 0.66$  for (EO<sub>220</sub>NtBAm<sub>19</sub>)<sub>n</sub>. The  $\alpha$  value suggest that (EO<sub>220</sub>NtBAm<sub>10</sub>)<sub>n</sub> form globule-like structure. The

index  $\alpha = 0.66$  for (EO<sub>220</sub>NtBAm<sub>19</sub>)<sub>n</sub> is slightly larger than that for a random-coil structure. Although we have tried to measure the small-angle X-ray scattering (SAXS) measurements, the profiles contain a large contribution from the aggregate, which suffers the detailed analysis



**Figure 1:** (a) Log-log plot of *R<sub>h</sub>* of the unimers vs. *M<sub>w</sub>* at 25 °C (the 0.1 wt% PEO-PNtBAm methanol solution). (b) Concentration dependence of the cloud point (*T<sub>c</sub>*) for the 1.0 wt% aqueous solution of P(NtBAm-co-NdMAM).

on the unimer morphology.

In order to control the solvophobicity of the AMB copolymer, we have prepared random copolymers of NtBAm and *N,N*-dimethylacrylamide (NdMAM) (NtBAm / NdMAM = 0.46, 0.35, 0.29). Figure 1(b) shows the phase diagram of the aqueous solution of P(NtBAm-co-NdMAM). The lower critical solution temperature (LCST)-type phase behavior has observed in these aqueous solutions. The higher NtBAm / NdMAM ratio, the lower phase separation boundary. SAXS measurements have revealed that three types of P(NtBAm-co-NdMAM) exist as a random-coil structure in aqueous solution. Therefore, we have considered that the solvophobicity of the block chain can be controlled by copolymerizing NdMAM.

**KEY WORDS:** alternating multiblock copolymer, chain morphology, solvophilic, solvophobic, light scattering

### References

1. K. Rikiyama et al., Polymer 156, 102-110 (2018).