Effect of local chain deformability on the temperature-induced morphological transitions of polystyrene-*b*-poly(*N*-isopropylacrylamide) micelles in aqueous solution

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Introduction

In the spherical star-like micelles, the ability of polymer chains exhibiting different conformations at different positions inside the micelles as "local deformability" (**Scheme 1**). The free energy of the corona (F_{corona}) is related to not only the overall size of the soluble block but also its local deformability. To our best knowledge, the local deformation of the soluble block is rarely considered in literature while discussing the micellar morphology of BCPs. In order to demonstrate the effect of local deformability of the soluble block, we designed two polystyrene-b-poly(N-isopropylacrylamide) (PS-b-PNIPAM) BCPs and temperature was utilized to alter the conformation of PNIPAM in the PS-*b*-PNIPAM BCPs. The effects of the overall coil size and local deformability on micellar morphology were discussed and compared with the theoretical prediction.

Scheme 1. Schematic illustration of different local deformation of spherical star-like micelle.

Results

Table 1. The molecular characteristics of two PS-*b*-PNIPAM BCPs.

Sample	PDI [b]	Chemical composition [a]	f_{ps} [c]
1	1.16	PS_{65}-*b*-$PNIPAM_{108}$	36%
2	1.26	PS_{65}-*b*-$PNIPAM_{360}$	15%

[a] Calculated from ^{1}H-NMR spectra. [b] PDI = M_w/M_n, determined by GPC. [c] Volume fraction of the PS block.

Preparation of the Micelles: The PS-*b*-PNIPAM BCP (1.5 mg) was first dissolved in 12.0 mL of THF to obtain a homogeneous solution, then the solution was sealed in a dialysis tube (cutoff molecular weight = 3500 g mol^{-1}) and dialyzed against deionized water at 25 °C for 3 days to remove THF. The resulting block copolymer solution was used for both DLS and TEM analysis.

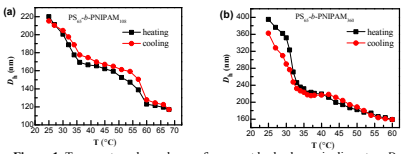


Figure 1. Temperature dependence of apparent hydrodynamic diameters D_h of PS-*b*-PNIPAM micelles: (a) PS_{65}-*b*-$PNIPAM_{108}$ (b) PS_{65}-*b*-$PNIPAM_{360}$.

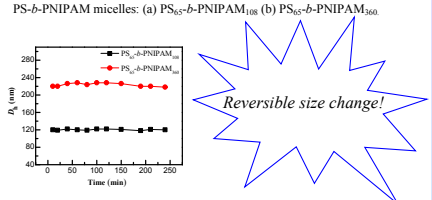


Figure 2. The apparent hydrodynamic diameters D_h of PS-*b*-PNIPAM micelles as a function of heating time at specified temperatures. 60 °C for PS_{65}-*b*-$PNIPAM_{108}$ and 40 °C for PS_{65}-*b*-$PNIPAM_{360}$.

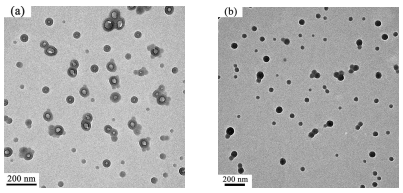


Figure 3. TEM images of PS_{65}-*b*-$PNIPAM_{108}$ micelles at 25 °C (a) and 60 °C (b).

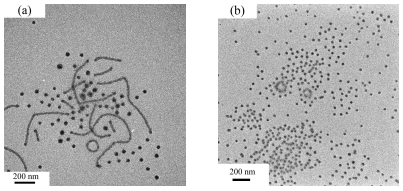


Figure 4. TEM images of PS_{65}-*b*-$PNIPAM_{360}$ micelles at 25 °C (a) and 40 °C (b).

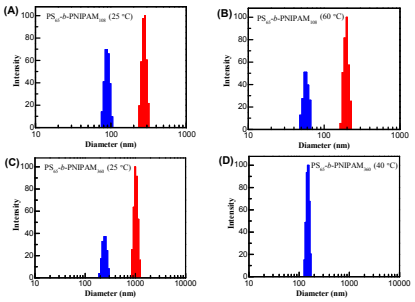


Figure 5. CONTIN size distributions of PS-*b*-PNIPAM micelles measured at the scattering angle of 90°. (A) PS_{65}-*b*-$PNIPAM_{108}$ micelles at 25 °C; (B) PS_{65}-*b*-$PNIPAM_{108}$ micelles at 60 °C; (C) PS_{65}-*b*-$PNIPAM_{360}$ micelles at 25 °C; (D) PS_{65}-*b*-$PNIPAM_{360}$ micelles at 40 °C.

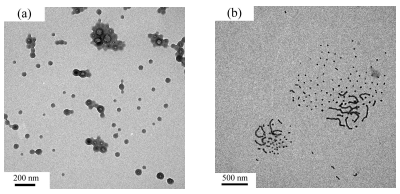


Figure 6. TEM images of PS_{65}-*b*-$PNIPAM_{108}$ micelles (a) and PS_{65}-*b*-$PNIPAM_{360}$ micelles (b) after being cooled back to 25 °C from elevated temperature.

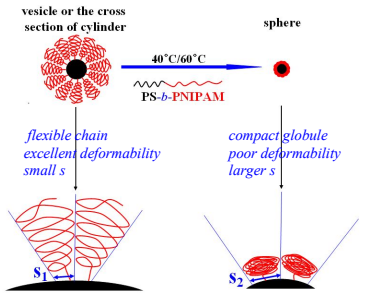
Reversible morphological transitions!

The cylinder → sphere and vesicle → sphere transitions are opposed to the theoretical prediction.

Table 2. The estimated values of the area occupied by per PNIPAM chain (*s*) in the PS-*b*-PNIPAM micelles.

	25 °C		60 °C (or 40 °C)
PS_{65}-*b*-$PNIPAM_{108}$	1.23 nm² (vesicle)	1.80 nm² (sphere)	2.14nm² (sphere)
PS_{65}-*b*-$PNIPAM_{360}$	1.54 nm² (cylinder)	1.90 nm² (sphere)	2.33 nm² (sphere)

larger s → more crowded → formation of spherical micelles



the interfacial area per chain: $S_2 > S_1$

Scheme 2. Schematic illustration of the morphological transition in the process of arising temperature.

Conclusions

1. Reversible morphological transitions takes place for two PS-*b*-PNIPAM BCPs in aqueous solution solely by changing the temperature.

2. The transitions are opposed to the theoretical prediction when only the overall volume change is taken into account. We proposed that the local deformability of the PNIPAM chains varies with temperature, which can well interpret the morphological transition.

References

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Acknowledgement

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