Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplemental Information

Complexation of Pluronic L62 (EO_6) -(PO_{34}) -(EO_6)/Aerosol-OT (sodium bis(2-ethylhexyl) sulfosuccinate) in aqueous solutions Investigated by Small Angle Neutron Scattering

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In this supplemental materials, we will show the scattering intensity data of solution (L62+AOT: $D_2O = 30wt\%$) and compare with the data of solution (L62+AOT:$D_2O = 5wt\%$), which we have discussed extensively in the paper.

Result of AOT:$D_2O = 30wt\%$

The SANS result of 30wt% solution of AOT (AOT: L62=100:0) at different temperatures is shown in the Fig.1. Two main scattering peaks are indicated with arrows and their positions satisfy $q_2 = 2 \times q_1$. The equality of $q_2 = 2q_1$ strongly suggests the presence of the lamellar structure (L_α). Fig. 1 compares the intensity data of 30wt.% and 5wt.% (AOT/D_2O). Based on the relative peak position, we conclude that AOT lamellar structure has formed at $10°C$ in $30wt\%$ sample, which is same as $5wt\%$ sample, but the lamellar layer is better ordered in $30wt\%$ than it of $5wt\%$ at same temperature. Also, for both trails, the peak positions move to the higher q range, so the lamellar d spacing decreases for both concentrations, but for $30wt.\%$ trail, the peak position

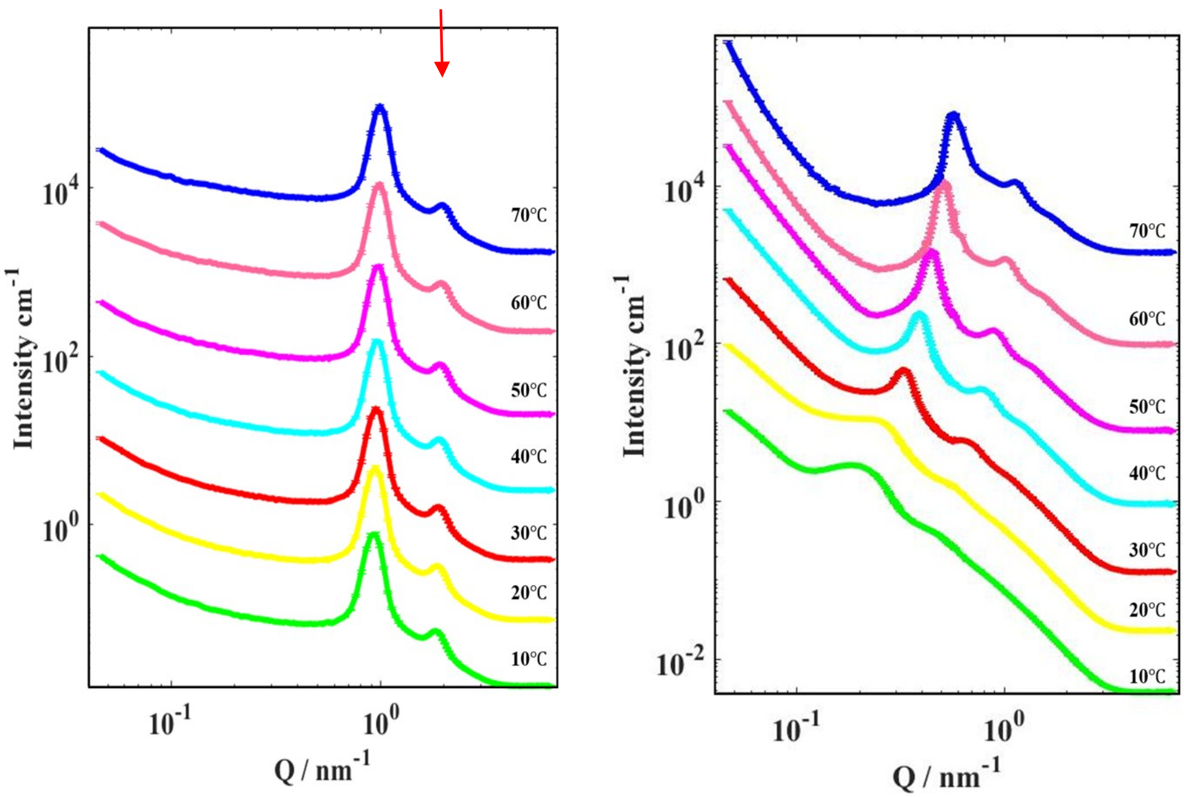

Fig. 1 The scattering intensity of AOT/$D_2O = 30wt\%$ solution (left) is compared with AOT/$D_2O = 5wt\%$ at temperature from 10℃ to 70℃. (right) The intensity has been rescaled for clarity.

shifts less significant.

Result o AOT/$D_2O = 30wt\%$).75

AOT/$D_2O = 5wt\%$

Fig. 2 compares the intensity data of $L62_{0.25}AOT_{0.75}$ trails for fixed 30wt.% and 5wt.% (solute/D_2O) solution. In this trail, lamellar phase exists from 10℃ to 70℃ even with L62 copolymer chains presented. The intensity data is very similar with the previous trail AOT/D_2O at 30wt.%. In addition, the lamellar structure is more robust than the trail ($L62_{0.25}AOT_{0.75}$) in the 5wt.% (solute/

D_2O), where lamellar phase is collapsed and replaced by the mixed micelle structures at higher temperature. Mentioned in this cited paper,[1] the lamellar(L_α)-Isotropic micelle(L_1) phase transition temperature has dependence with AOT concentration, $T \propto$ Concentration. At 30wt.%, the transition temperature is up to 130℃, as the result, the lamellar phase is favoured, whereas in 5wt.% (solute/ D_2O) solution trail, the micellar phase is preferred.

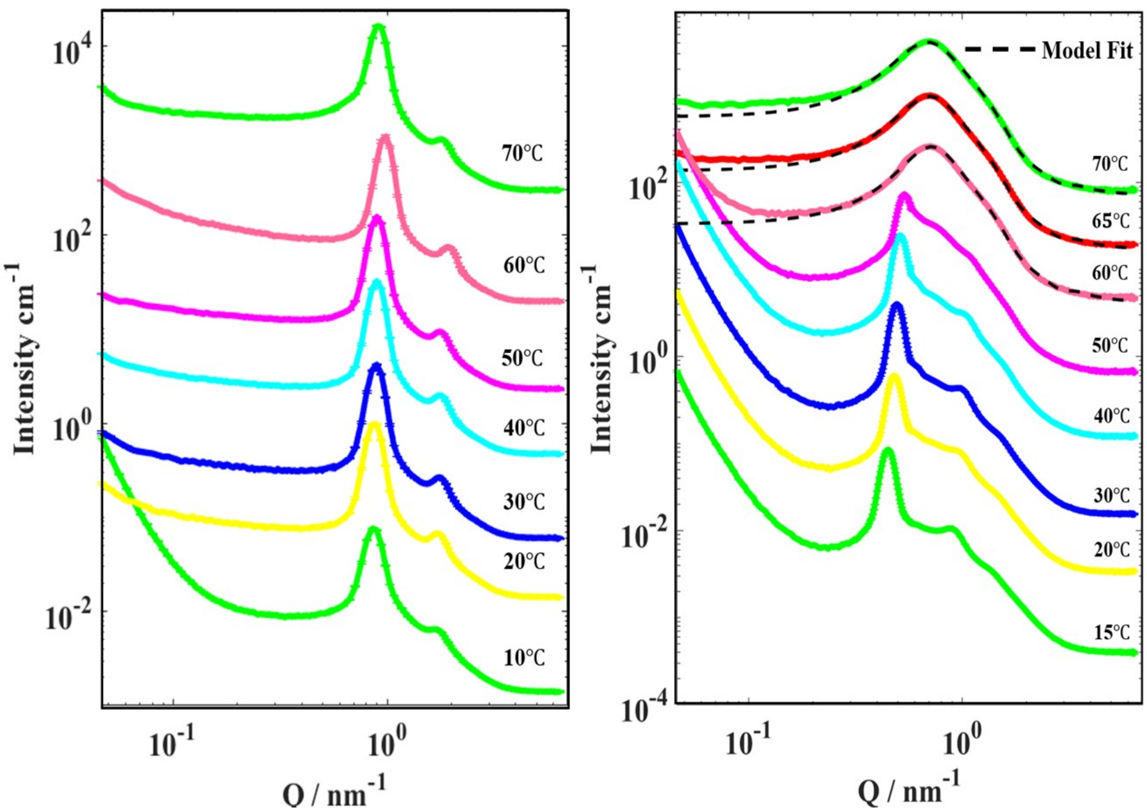

Fig. 2. The scattering intensity of $L62_{0.25}AOT_{0.75}$ trail at fixed (AOT+L62)/$D_2O = 30wt\%$ (left) is compared with the $5wt\%$ solution from 10℃ to 70℃. (right) The intensity has been rescaled for clarity.

Result of $L62_{0.5}AOT_{0.5}$

As the fraction of L62 increases to 50wt%, the intensities of $L62_{0.5}AOT_{0.5}$ mixture at lower temperatures show very sharp peaks, which resemble to the lamellar features and intensity data cannot be fitted by ellipsoid model. When temperature increases, the sharp peak becomes broader, and data eventually can be fully described by Ellipsoid form factor with MPB-RMSA structure factors from 40℃. Different from the result of $L62_{0.5}AOT_{0.5}$ trail in 5wt.% solution, where the mixed

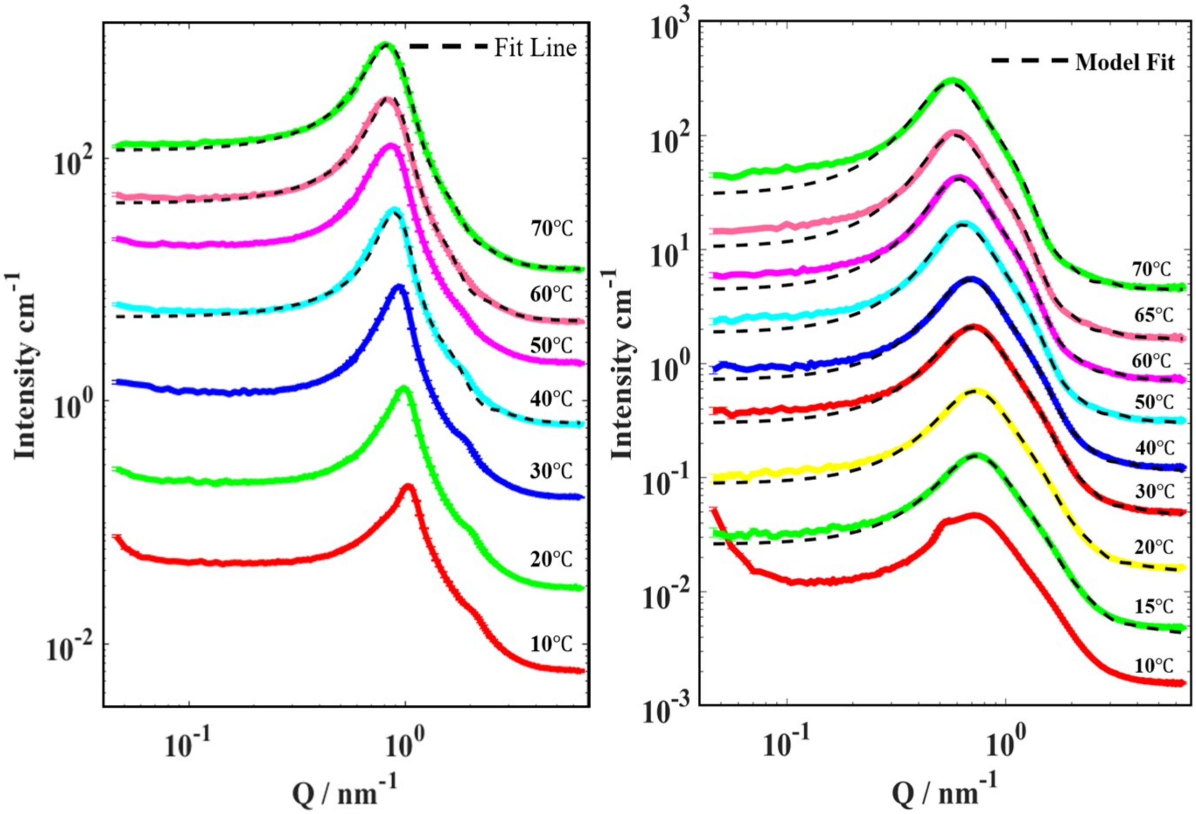

Fig. 3. The scattering intensity of $L62_{0.5}AOT_{0.5}$ trail at fixed (AOT+L62)/$D_2O = 30wt\%$ (left) is compared with the $5wt\%$ solution at temperature from 10°C to 70°C. (right) The intensity has been rescaled for clarity.

micelle structure appears at 15℃, in this trail the mixed micelle structure forms around 40℃. However, the general behaviour of this mixture is very similar with its comparison trail from the 5wt.% solution.

Result of $L62_{0.75}AOT_{0.25}$

In $L62_{0.75}AOT_{0.25}$ trail, there is no sign of lamellar structure at lower temperature. The intensities from 10℃ to 70℃ are fitted using Ellipsoid form factor with MPB-RMSA structure and we conclude mixed micelle structure are formed, as shown in **Fig. 4**. As temperature increases, the

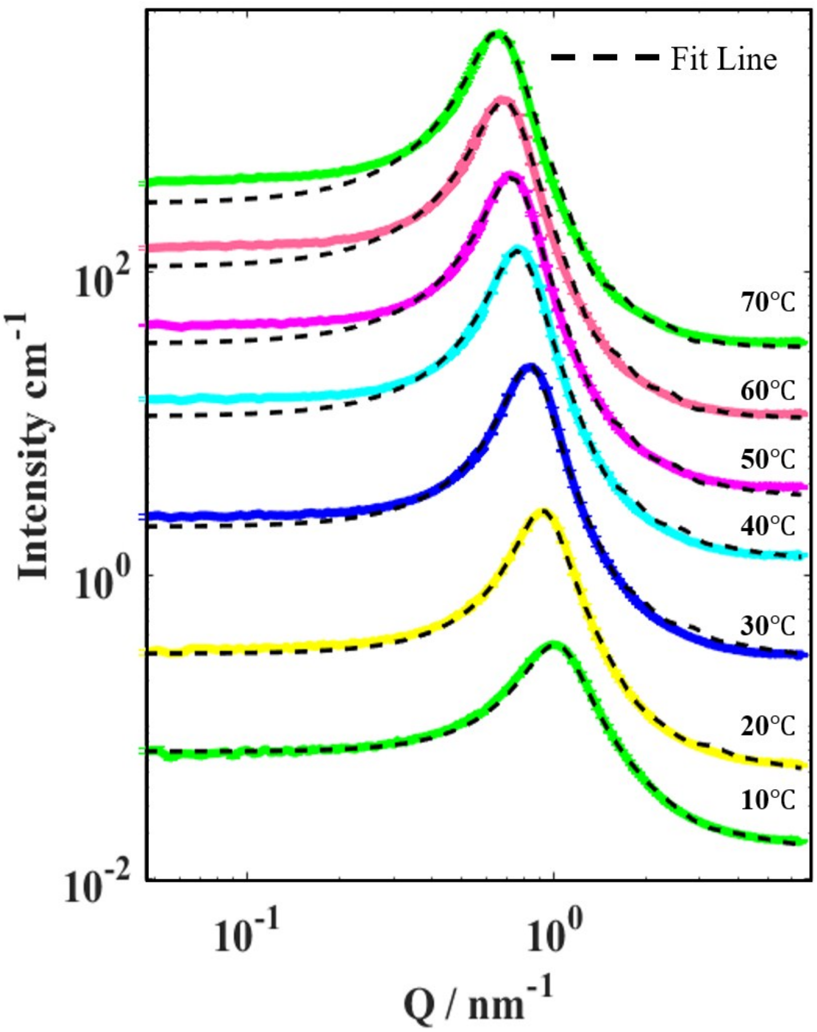

Fig. 4. Scattering intensities of $L62_{0.75}AOT_{0.25}$ solution at 10–70°C. The scattering curves have been shifted vertically for visual clarity.

peak position representing the inter-micellar distance, shifts to the lower q, indicating the expansion of inter-micellar distance. We suspect that the increased charge number per micelle with temperature has caused higher inter-micellar repulsive electrostatic potential. The fitting results are summarized in **Fig. 5**. In **Fig. 5A**, polar radius and equatorial radius of the micelle increase along temperature. Based on the fitting parameters, $R_{\parallel}$ increases from 2.5 nm to 3.9 nm and $R_{\perp}$ increases from 1 nm to 2.4 nm. Charge inside of L62 micelles is measured by applying MPB-RMSA structure factor and the charge amount is denoted by number of electrons. As temperature increasing from 10°C to 70°C, charges contained in each L62 micelle increases from 19e to 27e and fluctuates around $25e$. The increased charge number indicates more AOT monomers are involved as building blocks in forming the L62-rich mixed micelle as the size increasing with temperature, as shown in **Fig. 5B.** However, this deviation from the neighbouring charge values is likely due to the L62 lamellar structure, multiphase nature of the system and the imperfectness of the fitting model, which can describe only the ellipsoid particles and polymer chains. The aspect ratio decreases monotonically with temperature and stabilizes. **(Fig. 7C)** Aspect ratio, $\varepsilon\,(=R_{\parallel}/R_{\perp})$: $\varepsilon < 1$ for a prolate spheroid, ε = 1 for a sphere, and ε > 1 for an oblate spheroid. The initial aspect ratio (ε) is around 2.3 at 10°C and as temperature increases, it drops to around 1.6 and stabilized. Change of aspect ratio indicates that micelles become less oblate and more spherical with (1) increasing temperature and (2) more L62 fraction. The size of the micelle in 30wt.% trail is larger than it of the 5wt.%, while the aspect ratio stabilized at 1.6 for both trails.

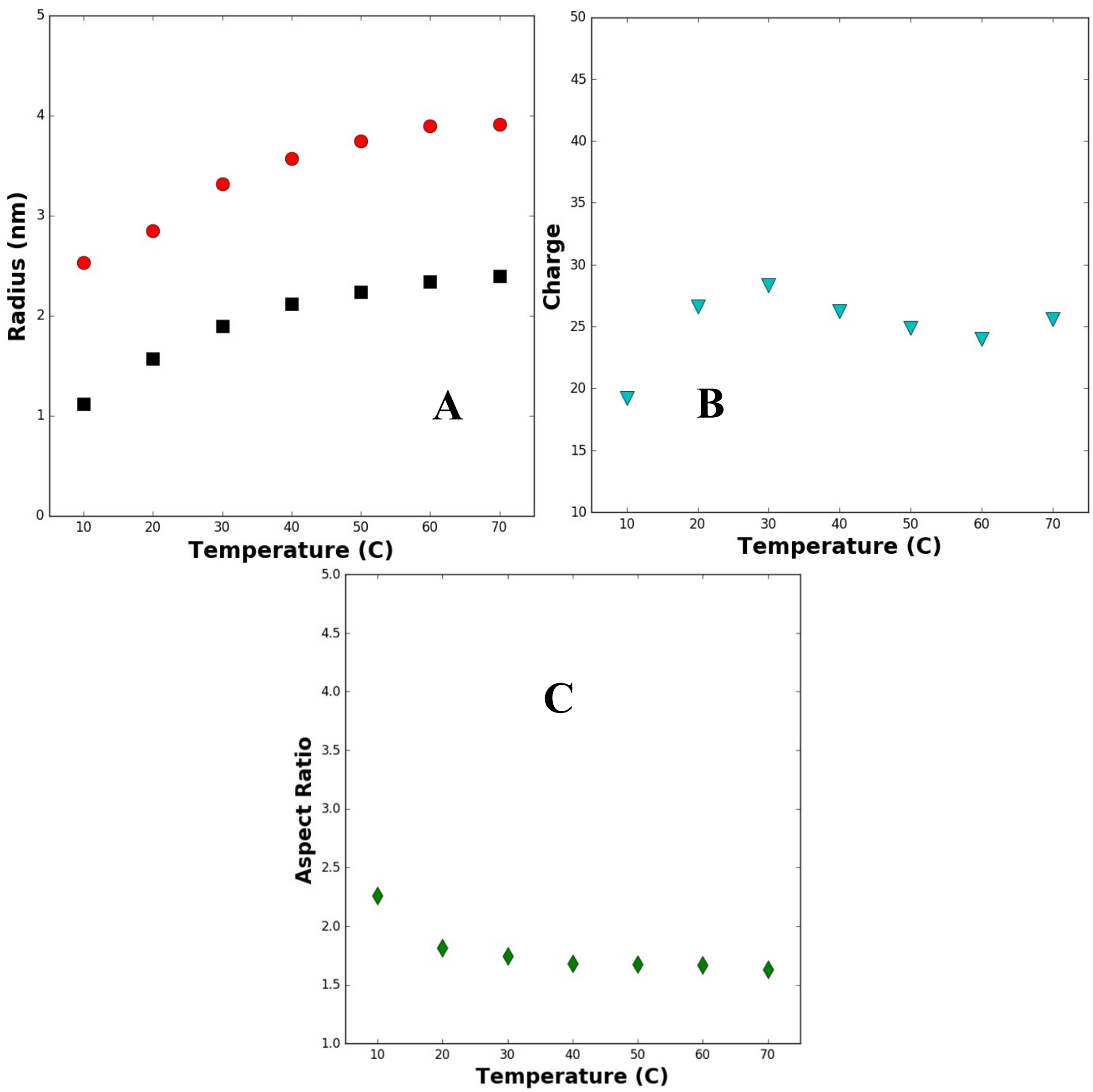

Fig. 5 Various fitted results as a function of temperature for $L62_{0.25}AOT_{0.75}$, (A) Equatorial radius and polar radius. (B) Charge number of micelles. (C) The aspect ratio(ε).

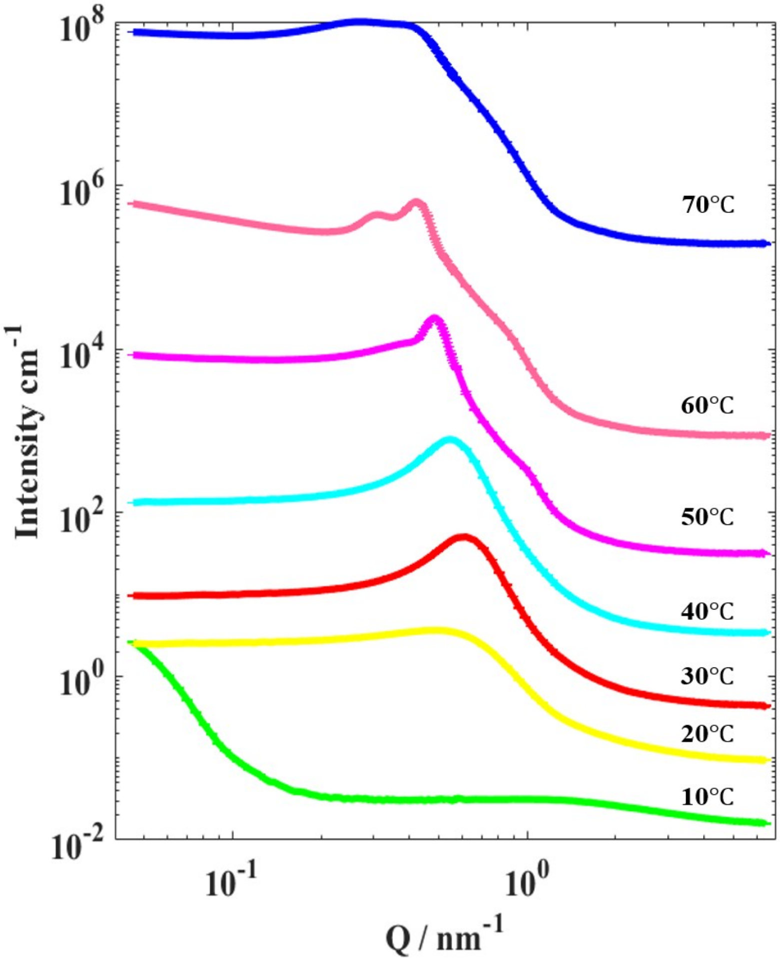

Fig. 6. Scattering intensities of 5wt% **(**L62/D_2O**)** solution at 10 – 70°C. The scattering curves have been shifted vertically for visual clarity.

Result of L62:D_2O = 30wt.%

In pure L62 solution (L62: AOT=100:0), Pluronic L62 copolymer remains as Gaussian chains below the room temperature and no micelle structure is observed. (**Fig. 6)** Intensity data from 20℃ resembles the feature of the isotropic micelle phase and at 30℃, the scattering intensity shows clear deviation from other curves; a broad scattering peak is developed, which indicates there is interaction among micelles. From 50℃ to 60℃, the L62 solution exhibit mixed features of micellar and lamellar phase, representing the micellar and lamellar phase coexist. At 70℃, the lamellar/micelle mixed phase changes into multi-phase region. The phase behaviours extracted from this intensity data are consistent with the reported results from previous study.[2]

Reference

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2 P. Alexandridis, D. Zhou and A. Khan, Lyotropic Liquid Crystallinity in Amphiphilic Block Copolymers: Temperature Effects on Phase Behavior and Structure for Poly(ethylene oxide)- *b* -poly(propylene oxide)- *b* -poly(ethylene oxide) Copolymers of Different Composition, *Langmuir*, 1996, **12**, 2690–2700.