


**Experiment title:**

Effect of the Soluble Block Size on Spherical Diblock Polymer Micelles

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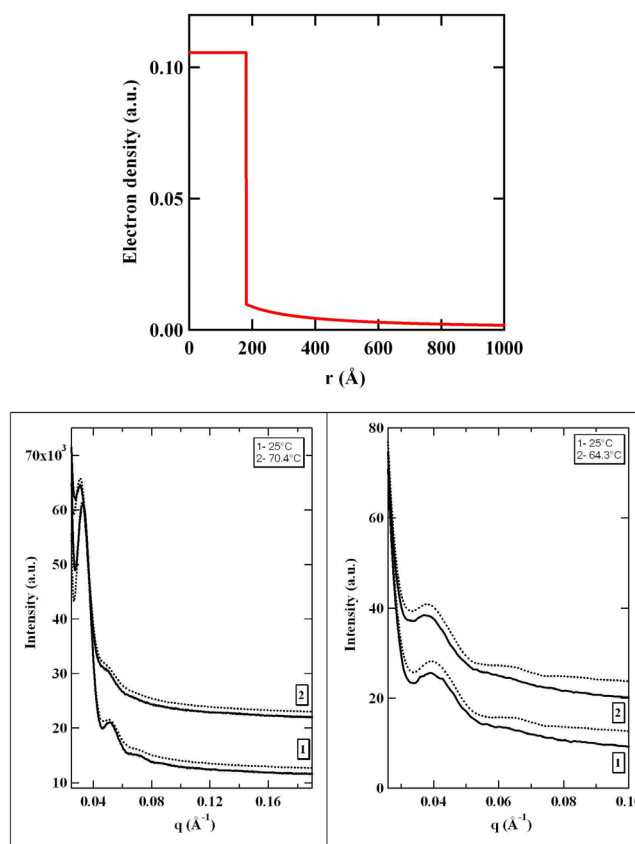
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**Report:**

*Because of the failure of the high-pressure setup, it was impossible to realize the experiments, as initially planned.*

When diblock polymers are dissolved in a selective solvent (good solvent for one block and poor solvent for the other) above a certain concentration, called the critical micelle concentration (CMC), they will associate to form micelles with a core composed of the insoluble block and a corona of the soluble block.<sup>1-2</sup> There has been a significant amount of work on the micelle structure for different types of block copolymer<sup>3-4</sup> and block polyelectrolytes.<sup>5-6</sup> Since the size of the insoluble block has a stronger effect on the micelle properties than does the soluble block, most of these studies have focused on the effect of the insoluble core block size. The few that did investigate the effect of the soluble block used complicated systems containing charged blocks or solvent mixtures both of which are more difficult to compare with currently available theory. To understand the effect of the soluble block, we have done a systematic SAXS study on of the micelle structure two series of PS-*b*-PI with a constant PS block (20 and 40kDa) and PI blocks varying from 10-100kDa.

Using filtered solvent, all diblock solutions were prepared by weighing. After being placed under argon, the samples were equilibrated at 60°C for ~24 hours, and then slowly cooled to room temperature



**Fig.1.** Theoretical electron density profile for the PS-PI micelle of 39k-94k (**top**); SAXS curves corresponding to suspensions of PS-PI 39k-26k (**bottom left**) and 39k-52k (**bottom right**) micelles. The fits with a model of polydisperse spheres are given in dotted lines.

(~0.1°/min). The resulting solution was then equilibrated at room temperature for at least 24 hours prior to measurements. X-ray diffraction experiments were performed using 2D gas detector with sample-detector distance of approximately 1.5 m. The sample temperature was controlled with a Linkam heating stage. The scattering of the pure solvent was subtracted from the curves. The fit of the curves was performed with home-built routines written in IGOR PRO according to the equation:

$$I(s) = \left( \int \langle \Delta\rho(r) \rangle \frac{\sin(sr)}{(sr)} 4\pi r^2 dr \right)^2$$

where  $\langle \Delta\rho(r) \rangle$  –electron density contrast between solvent and micelles (the profile for the PS-PI 39k-94k is shown on Figure 1).

Typical SAXS curves measured for the micellar systems containing PS block of 39k and PI blocks of 26k and 52k are shown in Figure 1. Data analysis was performed by fitting the curves with a model of polydisperse spheres thereby completely neglecting the contribution from the PI corona.

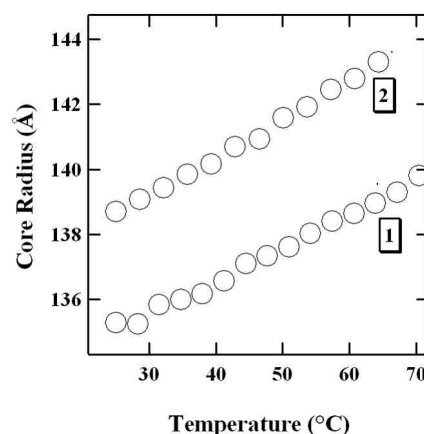
The results of the fits are exemplified in Figure 1. It can be seen that the fits reproduce the main features of the curves such as the ripples due to the scattering from the electron-rich PS core. It was found that the core polydispersity and the account for the solvent scattering is indispensable for the fits. Nevertheless, the fits to the micelle suspension having the shortest PI block are less satisfactory in the low angle region, close to the position of the first ripple. Adding scattering from objects of a different shape (such as cylinders) could in some instances improve the fit of the initial part of the curve but makes it problematic at higher angles. It may be that the spherical shape is not ideal for this particular system.

The temperature dependences of the core-size determined from the temperature-dependent synchrotron SAXS experiments are shown in Figure 2. Note that for both systems the size of the core steadily increases with temperature. The rate of this increase can be characterized by a linear coefficient of thermal expansion of about  $7-9 \cdot 10^{-4} \text{ K}^{-1}$ , which indicates that PS of the micellar core is in the rubbery state.

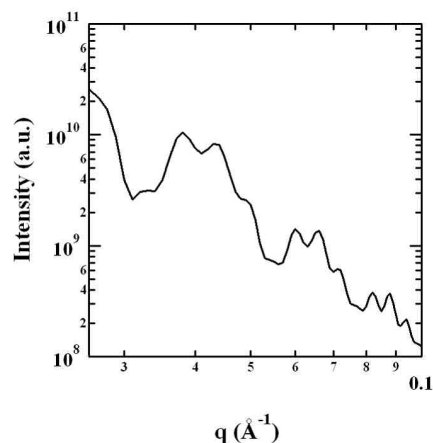
In order to address the question of thermal equilibration of micelles, we analyzed the temperature dependences of the core size with more scrutiny. The thermal expansion of the core for the system 39-94 may be slower at temperatures below 40°C. However, the present data does not allow stating this with certainty. Therefore more experiments are needed to clarify this issue.

As far as the model for the SAXS fits is concerned, it was interesting to check what could be the contribution of the PI shell to the total scattering. Figure 3 shows a simulated scattering profile for the 39-94 system in which the radial distribution of the corona density was added to the model. Note that in this case in addition to ripples due to the core scattering one can observe a fine structure due to the PI corona. In the experiments, we were not able to detect these features in the SAXS curves, which may be due to some non-uniformity of the corona size or differences between the model and real density distributions.

In conclusion, in the frame of the project the SAXS data were used to evaluate the effect of constrained conditions in micellar core on thermal properties (glass transition, thermal expansion) of the PS-PI micelles.



**Fig.2.** Variation of the core size as a function of temperature. The curves 1 and 2 correspond to the micelle suspensions with PS block of 39k and PI block of 94k and 52k, respectively.



**Fig.3.** Theoretical scattering from a dilute micellar suspension corresponding to a system with PS block of 39k and PI block of 94k.

## References

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