

## The Ordered Structures of Poly(styrene-*b*-4vinylpyridines)

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### Introduction

Poly(styrene-*b*-vinyl4pyridine) (PS-*b*-P4VP), which is a class of nonionic amphiphilic block copolymers, has been of great interest in study of micellar properties due to its high quality and its relatively easy access to the block copolymers (commercially available). It is also known that PS-*b*-P4VP is in the strongly segregation regime and its critical micelle concentration (cmc) is very low and the size of the micelles remained unchanged in the concentration ranging from  $10^{-3}$  to  $5 \times 10^{-3}$  g/ml. To our knowledge, however, studies regarding the ordered structures of PS-*b*-P4VP have not been reported although it is an important class of block copolymers. In this paper, for the first time, we will report on the structures of the hierarchical ordered mesophases and their subunits (micelles) of poly(styrene-*b*-vinyl4pyridine) (PS-*b*-P4VP) in the toluene solution, which were studied by using small angle X-ray scattering (SAXS), transmission electron microscopy (TEM) and GIFT methods.

### Results and discussion

Figure 1a shows the small angle X-ray scatterings of PS(3.3k)-*b*-P4VP(4.7K) with different concentration levels. The shapes of the scattering curves showed little change until ~ 4 wt %. The intensity levels of the concentrated solutions (higher than 8 wt %) decrease at a low  $q$  due to the structure factor. The large decrease in intensity, at the low  $q$  for the 16 wt % sample, causes a scattering peak at  $q=0.279 \text{ nm}^{-1}$  ( $d=21.5 \text{ nm}$ ). This peak represents the average distance between the micelles in the solution and it shifts to a higher  $q$  ( $q=0.336 \text{ nm}^{-1}$ , 18.7 nm) for the 32 wt % sample. In the case of the 48 wt % sample, several peaks appear and can be indexed by fcc symmetry. The calculated cubic unit cell dimensions ( $a_{fcc}$ ) were 29.1 nm. The closest distance between the micelles for the fcc unit cell is 20.6 nm. As the concentration further increased (64 wt %), the lamellar structure was created with a layer spacing of 13.7 nm. From the SAXS data, we can confirm the existence of spherical micelles (the shape of the micelles will be discussed later in  $p(r)$  analysis), the fcc structure, and the lamellar structure. Figure 1b shows the small angle X-ray scatterings of PS(12K)-*b*-P4VP(11.8K) solutions with different concentration levels. The changes in the shapes of the scattering curves were similar to those of PS(3.3k)-*b*-P4VP(4.7K). The shapes of the scattering curves showed little change until ~ 2 wt %. The intensity started to decrease at a low  $q$  from 4 wt %, due to the structure factor. The large decrease in intensity, at a low  $q$  for the 8 wt % sample, caused a scattering peak at  $q=0.110 \text{ nm}^{-1}$  ( $d=57.1 \text{ nm}$ ). This peak shifted to a higher  $q$  ( $q=0.134 \text{ nm}^{-1}$ ,  $d=46.9 \text{ nm}$ ) for the 16 wt % sample. In the case of the 32 wt % sample, several peaks appeared and could be indexed by fcc symmetry, which is similar with PS(3.3k)-*b*-P4VP(4.7K). The  $a_{fcc}$  and  $R_{mic}$  were 78.8 nm and 55.7 nm, respectively. For a further increase in the concentration level (64 wt %), the bcc symmetry was observed. The  $a_{bcc}$  and  $R_{mbcc}$  values were 57.0 nm and 49.4 nm, respectively. We can confirm the existence of a spherical micelle, the fcc and bcc symmetries from the SAXS data. It is known that steeper, short-range interactions favor fcc, whereas softer, long-range potential favors bcc. The observance of bcc for PS(12K)-*b*-P4VP(11.8K) may be due to the longer shell chains, as compared to PS(3.3k)-*b*-P4VP(4.7K).

Figure 2 shows the  $p(r)$ s for the PS(3.3k)-*b*-P4VP(4.7K) and PS(12K)-*b*-P4VP(11.8K) solutions, up to 16 wt%. The  $p(r)$ s represent a typical sphere and are nearly similar to each other, indicating that the structures of the individual micelles did not change until 16 wt%. The maximum dimensions of the sphere ( $D_{max}$ ) for PS(3.3k)-*b*-P4VP(4.7K) and PS(12K)-*b*-P4VP(11.8K), which are  $r$  values at  $p(r)=0$ , were approximately 18.5 nm and 46 nm, respectively. The radius gyration ( $R_g$ ), which were calculated from the  $p(r)$ s for PS(3.3k)-*b*-P4VP(4.7K) and PS(12K)-*b*-P4VP(11.8K), were 6.74 nm and 14.48 nm, respectively. If the sphere is homogenous, the diameter of the sphere ( $D_{Rg}$ ) for PS(3.3k)-*b*-P4VP(4.7K) and PS(12K)-*b*-P4VP(11.8K) were 17.4 nm and 37.4 nm, respectively,

which are smaller than  $D_{max}$  (18.5 nm and 46 nm). This calculation suggests that the micelle cores are not homogenous. The difference between the  $D_{max}$  and  $D_{Rg}$  of PS(12K)-*b*-P4VP(11.8K) is large compared to that of PS(3.3k)-*b*-P4VP(4.7K).

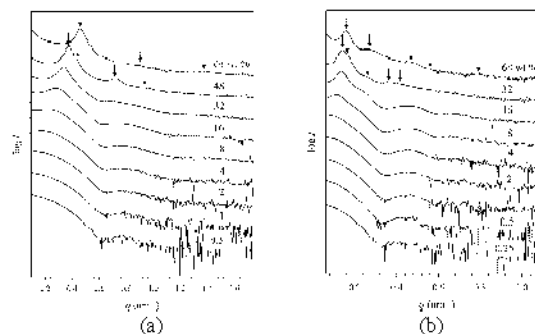


Figure 1. Small angle X-ray scatterings of (a) PS(3.3k)-*b*-P4VP(4.7K) and PS(12K)-*b*-P4VP(11.8K) in a toluene solution of different concentration levels; the arrows represent the reflections mentioned in the text.

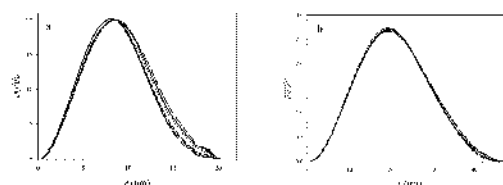


Figure 2. The  $p(r)$ s of (a) PS(3.3k)-*b*-P4VP(4.7K) and (b) PS(12K)-*b*-P4VP(11.8K), with different concentration levels up to 16 wt %.<sup>1-3</sup>

Figure 3 shows the average structure factors ( $S_{avg}(q)$ ) for PS(3.3k)-*b*-P4VP(4.7K) and PS(12K)-*b*-P4VP(11.8K) (up to 16 wt %). The first maximum shifted to a high  $q$  as the concentration increased due to the decrease in the distance between the micelles. The first maximum position is close to the  $D_{max}$  at 16 wt %, indicating that close packing may start around this concentration level. The volume fraction ( $\eta$ ) is nearly proportional to the wt % of the concentration. The  $\eta$  for PS(12K)-*b*-P4VP(11.8K), however, is large compared to that for PS(3.3k)-*b*-P4VP(4.7K) at the same wt %. This result strongly suggests that the core of PS(12K)-*b*-P4VP(11.8K) is less dense than that of PS(3.3k)-*b*-P4VP(4.7K).

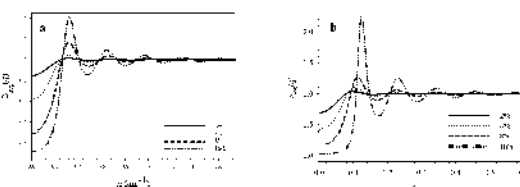


Figure 3. The  $S(q)_{avg}$ s of (a) PS(3.3k)-*b*-P4VP(4.7K) and (b) PS(12K)-*b*-P4VP(11.8K), with different concentration levels up to 16 wt %.<sup>1-3</sup>

### Conclusions

The structures of PS-*b*-P4VP in a toluene solution with different concentration levels were studied by using SAXS and GIFT methods. SAXS showed a good contrast between the core and the solvent. As the concentration increased, fcc symmetry appeared for PS(3.3k)-*b*-P4VP(4.7K), while the fcc and bcc symmetries appeared for PS(12K)-*b*-P4VP(11.8K). A lamellar structure was also identified with a further increase in the concentration for PS(3.3k)-*b*-P4VP(4.7K). These ordered structures of PS-*b*-P4VP, to our knowledge, have not been reported yet. Further studies on fcc/bcc transition and the epitaxial orientation of these ordered structures have been scheduled in order to provide insight regarding their origin.

### References

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