

# Synchrotron X-Ray Scattering Studies of Star-Shape Polymers

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## ABSTRACT

Shapes and structures of star-polystyrenes bearing 6 to 57-arms were in detail investigated in good and theta solvents by small-angle X-ray scattering with synchrotron radiation sources.

**Keywords:** small angle X-ray scattering, multi-arms star-polystyrene, good and theta solvent condition

## 1 INTRODUCTION

Star-shape polymers have gained great attention because of their interesting properties and potential applications [1-12]. Therefore, much effort has been made on their syntheses and characterizations so far [1-13]. In particular, star-shape polymers' molecular structures and properties have been extensively studied in good and/or theta solvents for last three decades [13]. However, the physical properties studies for highly star-polymers are not enough as yet. In particular, information of inner structure and shapes for highly star-polymers are not enough because of the synthesis of highly star-polymer is not easy, and methods for internal structure analysis were only a few and various approach for data analysis were insufficient.

To obtain more information about inner structure and shape of star-polymer, X-ray scattering method is very useful. In the present study, we used powerful method which is small angle X-ray scattering (SAXS) to obtain the physical properties and shapes of highly star-polystyrenes, and various model simulations were used. The molecular shapes and structures of well-defined star-polystyrenes which has highly multi-arms (6-, 9-, 17-, 33-, and 57-arms) are observed from SAXS measurements in good and theta solvent condition. SAXS experiment from the high flux of a synchrotron light source provides data of sufficient quality to make a more detailed description of the intramolecular organization for star-polystyrene.

## 2 EXPERIMENTAL

A series of star-polystyrenes with 6-57 arms were synthesized as described elsewhere [1,2]: 6-, 9-, 17-, 33-, and 57-arms. A Linear polystyrene was purchased from Varian: F-4 ( $\overline{M}_w = 43,900$ ; PDI= 1.01). Solutions of each

polystyrene sample were prepared at a concentration of 1-4 wt% in tetrahydrofuran (THF), a good solvent and cyclohexane at 35°C, a theta solvent. Small-angle X-ray scattering (SAXS) measurements were conducted at the 4C1 beamline (BL) of the Pohang Accelerator Laboratory [14]. The wavelength and size of the monochromatized X-ray beam were 1.608 Å and 0.6 x 0.6 mm respectively; a two-dimensional charge-coupled device (2D CCD) detector, an evacuated scattering path with Kapton windows, and a sample-to-detector distance (SDD) of 1-2 m were used. Sample solution cells used in this study had a gap of 1 mm with thin Kapton windows. SAXS data were corrected from the dark run and solvent run (THF or cyclohexane at 35°C) as well as the empty cell run.

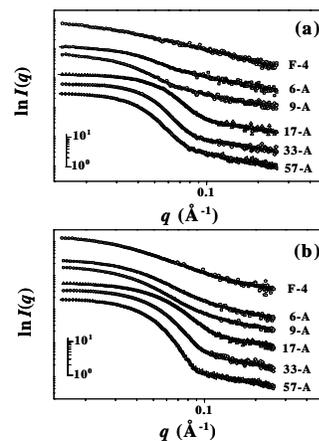


Figure 1: SAXS profiles measured for the linear polystyrene F-4 and star-polystyrenes of 6-57 arms (6-A to 57-A): (a), measured in THF; (b), measured in cyclohexane at 35°C. The symbols represent the measured data, and the solid lines were obtained by fitting the data with a model-independent approach, indirect Fourier transform (IFT) method [13].

## 3 RESULTS AND DISCUSSION

Figure 1 shows SAXS profiles of the linear and multi-armed polystyrenes measured in THF, a good solvent, as well as in cyclohexane at 35°C, a theta solvent. As can be seen in Figure 1a, the linear polystyrene F-4 reveals a

scattering profile which follows a power law of  $q^{-5/3}$  in the intermediate  $q$  region (namely, the Debye region) as well as in the high  $q$  region (Porod region). In the theta condition, the F-4 exhibits a scattering profile varying with  $q^{-2}$  over the intermediate and high  $q$  regions (Figure 1b). These scattering profiles are characteristics of a Gaussian coil, which has a Gaussian sphere behaving self-avoiding random walk in the solvent but excluded volume effect in the theta solvent. These results are consistent with those reported in the literature [14].

In comparison, the 6-armed polystyrene 6-A reveals scattering profiles varying with a power law of  $q^{-2}$  in the Debye region and of  $q^{-5/3}$  in the Porod region regardless of the good solvent and theta solvent (Figure 1). Namely, the 6-A shows a characteristic similar to that of the F-4 in the theta solvent over the Debye region but resembles that of the F-4 in the good solvent over the Porod region. The 57-armed polystyrene 57-A exhibits scattering profiles following a power law of  $q^{-4}$  in the Debye region and of  $q^{-5/3}$  in the Porod region regardless of the good solvent and theta solvent (Figure 1). The other armed polystyrenes show scattering profiles which follow an intermediate power law between those observed for the 6-A and 57-A over the Debye region; however, in the Porod region they all also reveal scattering profiles varying with  $q^{-5/3}$  as observed for both the 6-A and 57-A. Further no solvent effect was found for all the multi-armed polystyrenes over the Debye region as well as over the Porod region.

As described above, in the Porod region the scattering profiles of all the multi-armed polystyrenes in the good solvent follow a power law of  $q^{-5/3}$ , regardless of the number of arms. In fact, the form factor  $P(q)$  of a multi-armed polystyrene in the Porod region is dominated with a power-law dependence originating from the density fluctuations on length scales smaller than its dimension. Taking this fact into account, the observed power law indicates that the multi-armed polymer molecules have no sharp interface in the good solvent, regardless of the number of arms. The observed power law is the characteristic of a Gaussian chain behaving self-avoiding random walk. Therefore, the scattering profiles of the Porod region suggest that all the multi-armed polystyrenes own an interface composed of Gaussian characteristic of polymer chain parts, which behave self-avoiding random walk; in other words, the interfaces are presumed to consist of Gaussian chain characteristic of blobs. However, the interfaces of the multi-armed polystyrenes are somewhat different each other in the depth, depending on the number of arms; polystyrene of higher number of arms might have thinner interfacial layer.

In the theta solvent condition, the scattering profiles of all the multi-armed polystyrenes vary with  $q^{-5/3}$  over the Porod region as observed in the good solvent. The results are quite different from that of the linear polystyrene F-4. These results might come from two reasons as follows. The first one is the theta temperature in which the scattering profiles of the multi-armed polystyrenes were measured. In

fact, the theta condition in our study is for the linear polystyrene rather than the multi-armed polystyrenes; in general, an increase in the number of arms causes a decrease in the theta temperature. The second reason is related to structures of the multi-armed polystyrenes in solvent, which are different from the Gaussian sphere of linear polymer.

Further detailed data interpretations and discussions will be given for the scattering data analysis results.

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