Molecular Shapes of Star-Polystyrenes with Various Arms in Solutions Determined using X-Ray Scattering

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Introduction

Star-shape polymers have gained great attention because of their interesting properties and potential applications.[1-3] Therefore, much effort has been made on their syntheses and characterizations so far. However, these studies were limited to star-shape polymers of low number of arms because their syntheses were not easy. In the present study, we investigated in detail the physical properties of well-defined star-shape polystyrenes with high number of arms (6 to 57 arms) in good and theta solvents using synchrotron X-ray scattering.

Experimental

A series of star-polystyrenes with 6-57 arms were synthesized.[1] 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. 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.

Results and discussion

Figure 1 shown SAXS profiles of the linear and multi-armed polystyrenes in each condition. The F-4 shown that 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. In comparison, the 6-armed polystyrene reveals scattering profiles varying with a power law of q^{-2} in the Debye region, and the 57-armed polystyrene exhibits scattering profiles following a power law of q^{-4} in the Debye region regardless of the good solvent and theta solvent. The other armed polystyrenes show scattering profiles which follow a intermediate power law between those observed for the 6-A and 57-A over the Debye region.

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. From the scattering profiles of the Porod region, it 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 word, the interfaces are presumed to consist of Gaussian chain characteristic of blobs.[5] 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.

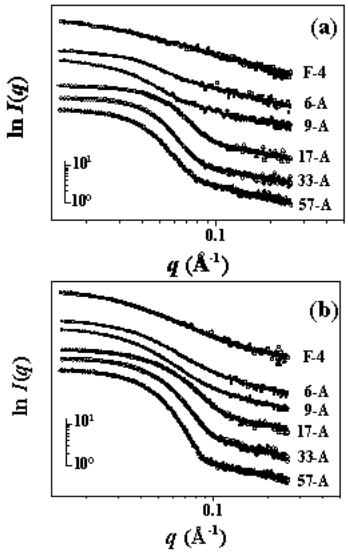

Figure 1. SAXS profiles measured for the linear polystyrene (F-4) and star-polystyrenes of 6-57 arms (6-A to 57-A): (a), measured in THF; (b), measured in cyclohexane at 35°C. The symbols represent the measured data, and the solid lines were obtained by fitting the data with a model-independent approach,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

From the measured scattering profiles, the average radii of gyration (R_g) were determined using the Guinier equation and IFT method. From the determined R_g values, g-factors, which can give information on the relation of between linear and multi-armed polymers,[6] were calculated. Further, theoretical g-factors were calculated using well-established two theories which were proposed by Zimm-Stockmayer (arm number ≤ 17) and Roovers (arm number >17). As a result, it was found that for the 6-armed polystyrene, the determined g value is smaller than the corresponding theoretically calculated g value; however, the other multi-armed polystyrenes show a good agreement between the determined and theoretically calculated g values. In addition, cross-section radii of gyration (R_q) were determined from the scattering profiles. Then, the difference of R_g and R_q (namely, (R_g/R_q)) was estimated, which can give information on molecular shapes of the polystyrenes. The (R_g/R_q) values indicate that the molecular shapes of the 6-A and 57-A are a soft-like ellipsoid and a hard-like sphere, respectively, and the other multi-armed polystyrenes have a molecular shape between soft-like ellipsoid and hard-like sphere depending on the number of arms; here it is noteworthy that the hard-like sphere found in our study still has no sharp interface as discussed above.

From the scattering profiles, both pair distance distribution function $P(r)$ and radial distribution function $\rho(r)$ were calculated; here $P(r)$ and $\rho(r)$ can give information on molecular shapes of the multi-armed polystyrenes. The obtained molecular shape results again confirmed those determined by the (R_g/R_q) values.

Conclusions

The scattering profiles for multi-armed polystyrenes in the good and the theta solvent informed that the molecular shape is changed from soft-ellipsoid to a hard-like sphere with increasing of number of arm. Also, from various parameters, it is concluded that well-defined multi-armed PS can be described as a self-avoiding random walking and excluded volume chain, which consists of blobs, and the molecular shape is change from a fuzzy-ellipsoid for 6-armed PS to a fuzzy-sphere sphere for 57-armed PS according to increasing of number of arm.

References

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