Structural Analysis of Well-Defined Star-Shape Polystyrenes in Solutions Using Synchrotron 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.

Methods and Materials

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 & 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 of $q^{-5/3}$ in the Porod region, and the 57-armed polystyrene 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. 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. 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 word, the interfaces are presumed to consist of Gaussian chain characteristic of blobs.[5]

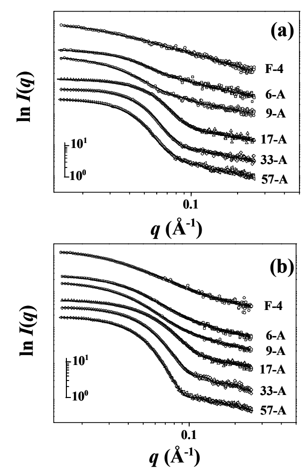

Fig.1. SAXS profiles measured for the linear polystyrene F-4 and star-polystyrenes of 6-57 arms (6-A to 57-A): (a), measured in THF; (b), measured in cyclohexane at 35°C. The symbols represent the measured data, and the solid lines were obtained by fitting the data with a model-independent approach,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

From the measured scattering profiles, many parameters were calculated. The average radii of gyration (R_g), g-factors, and cross-section radii of gyration (R_q) were determined from the scattering profiles. In additional, from the scattering profiles, both pair distance distribution function $P(r)$ and radial distribution function $\rho(r)$ were calculated. From these parameters, the solution behaviors were analysis for multi-armed polystyrenes in more detail.

References
[1] A. Hirao, Y. Tokuda, Macromolecules 36, 6081 (2003),.
[2] J. F. G. A. Jansen, et al. Angew. Chem. 34, 1206 (1995).
[3] D.-L. Jiang, T. Aida, Nature 388, 454 (1997).
[4] O. J. Glatter, Appl. Crystallogr. 13, 577 (1980).
[5] S. Rathgeber, et al. J. Chem. Phys. 117, 4047 (2002).