

Mechanically Interlocked Structure of Polyrotaxane Investigated by Contrast Variation Small Angle Neutron Scattering

Koichi Mayumi, Hitoshi Endo, Noboru Osaka, Hideaki Yokoyama, Mitsuhiro Shibayama, Kohzo Ito

Graduate School of Frontier Sciences, The University of Tokyo, Institute for Solid State Physics, The University of Tokyo

Advances of supramolecular chemistry has realized novel polymer architectures composed of several components noncovalently bonded [1]. One of the most promising supramolecules is polyrotaxane (PR) in which cyclic molecules are threaded into a linear polymer chain [2]. Covering the axial polymer chain with the cyclic molecules resulted in various applications to nanomaterials such as molecular tubes formed by cross-linking adjacent cyclic molecules in a single polyrotaxane and insulated molecular wires incorporating conductive polymers. The cyclic molecules in polyrotaxane are mechanically interlocked with the axial polymer, and slide and rotate on the chain. This additional kinetic freedom has been utilized to produce functional nanomaterials having novel dynamical properties, examples of which are drug delivery systems, multivalent ligand systems, energy transfer systems, and three-dimensionally cross-linked polyrotaxane networks with movable crosslinks. In particular the mechanically interlocked structure of polyrotaxane leads to various application to nanomaterials.

We performed contrast variation small angle neutron scattering measurements on polyrotaxane composed of polyethylene glycol (PEG) and α -cyclodextrins (CDs) in order to determine the detailed structure of PEG and CD in polyrotaxane. The scattering intensities $I(Q)$'s for PR in mixtures of DMSO-d₆ and DMSO were successfully decomposed into partial scattering functions for the components of polyrotaxane. The CD-PEG cross-term is positive, which corresponds to the mechanically interlocked connection between PEG and CD. In addition, the self-term of CD

showed almost the same Q-dependence as the self-term of PEG. This indicated that the CDs in polyrotaxane are distributed randomly along the PEG chain. Contrast variation SANS is efficient to investigate static structures of components in supramolecular systems such as the conformations of and the correlations between the components in the system.

[1] Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.

[2] Harada, A.; Hashidzume, A.; Takashima, Y. *Adv. Polym. Sci.* 2006, 201, 1.