Conformation and Dynamics of Polyrotaxane in Solution

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

Polyrotaxane (PR) is a typical supramolecule, in which cyclic molecules are threaded onto a linear polymer chain [1]. The cyclic molecules in PR can slide and rotate on the polymer chain, and the degree of freedom of movement within a chain is the most unique feature of PR. This additional kinetic freedom has been utilized to produce functional nanomaterials having novel dynamical properties [2]. For example, PR, composed of polyethylene glycol (PEG) and α-cyclodextrins (CDs), was applied to a novel kind of polymer network, called " slide-ring gel " [3], which was prepared by cross-linking CDs belonging to different PR. The cross-linking point of slide-ring gels can slide along the polymer chain, and this unique structure causes the high extensibility and huge degree of swelling ratio in slide-ring gels. These remarkable physical properties were derived from nanoscale sliding motion of cyclic molecules.

We investigated the conformation and dynamics of polyrotaxane (PR) composed of polyethylene glycol (PEG) and α-cyclodextrins (CDs) by means of small angle neutron scattering (SANS) and neutron spin echo (NSE) technique, respectively. We analyzed the scattering functions for polyrotaxane in DMSO using a form factor based on the wormlike chain model, and it was found that the persistence length for PR dissolved in DMSO was approximately 30 , which is three times as large as that of PEG dissolved in DMSO [4]. Furthermore, the monomer dynamics of PR observed by NSE measurements was slower than that of PEG [5]. These findings indicate that threading CDs into PEG stretched the PEG chain and suppressed the local dynamics.

[1] A. Harada, J. Li, M. Kamachi, Nature (London) 356, 325 (1992)..
[2] J. Araki, K. Ito, Soft matter 3, 1456 (2007).
[3] Y. Okumura, and K. Ito, Adv. Mater. 13, 485 (2001).
[4] K. Mayumi, N. Osaka, H. Endo, H. Yokoyama, Y. Sakai, M. Shibayama, K. Ito, Macromolecules, 41, 6480 (2008).
[5] K. Mayumi, N. Nagao, H. Endo, N. Osaka, M. Shibayama, K. Ito, Physica B, in press.