# Sol-gel transition of methylated polyrotaxane

T. Karino, Y. Okumura, M. Shibayama, and K. Ito
*Institute for Solid State Physics, University of Tokyo, Graduate school of Frontier Sciences, University of Tokyo, CREST, JST*

Recently, we prepared successfully a new type of polyrotaxane having hydrophobically modified $\alpha$-cyclodextrin (CD). Methylated polyrotaxanes, which are substituted the hydroxyl groups on CD with methyl groups, showed thermosensitive sol-gel transition. In this experiment, we carried out small-angle neutron scattering (SANS) measurement in order to investigate the structure change as a function of temperature.

Polyrotaxane was prepared from poly(ethylene glycol) (PEG) and CD. The molecular weight of PEG was $3.5\times10^4$. The filling ratio of CD was 27%. The hydroxyl groups on CD molecules were substituted by methyl groups using sodium hydrate and methyl iodide. The degree of methylation was 60% (M60). SANS experiments were carried out at the SANS-U spectrometer. The sample-to-detector distance was 2 and 8m. The temperature was varied from 20 to 80°C. The methylated polyrotaxane was dissolved in $D_2O$.

Fig. 1 shows temperature dependence of SANS intensity function, $I(q)$, for M60. $I(q)$s increase with increasing temperature. In particular, $I(q)$ drastically upturns at 60°C, which agreed well with the macroscopic observation of sol-gel transition. The variation of these scattering profiles is similar to a sol-gel transition of block copolymer solution by temperature-induced microphase separation.

In low temperatures, $I(q)$s decrease monotonically as a function of $q$. This means that the polymer solution was homogeneous. We estimated the correlation length, $\xi$, by using the Ornstein-Zernike function for semi-dilute polymer solutions. The obtained $\xi$ was about 17Å. Above the gelation temperatures, $T_{gel}$, $I(q)$ shows not only a rapid increase of intensity but also a characteristic shoulder about $0.015Å^{-1}$. The inset in Fig.1 shows the so-called Kratky plot ( i.e., $q^2I(q)$ vs $q$) for $T > T_{gel}$. In the gel state, the Kratky plots show a single peak. In order to elucidate the gel structure, we evaluated the characteristic size of inhomogeneities in the gel sate using the following equation,

$$I(q) = I(0)\exp(-R_G^2q^2) \qquad (1)$$

where $R_G$ is the radius of gyration, $I(0)$ is zero-scattering intensity. In this case, $R_G$ means the size of the hydrophobic domains. The obtained $R_G$ was about 160Å.

The following facts were disclosed. CD molecules on PEG are dispersed homogeneously below $T_{gel}$. On the other hand, with increasing temperature, CD molecules are aggregated each other due to hydrophobic interaction of methyl groups on CD. These aggregations play as a role of physical cross-linking points[1, 2].

**References**

[1] T. Karino *et al.*: Macromolecules **39** (2006)9435.
[2] T. Karino *et al.*: Macromolecules **40** (2007) in press.

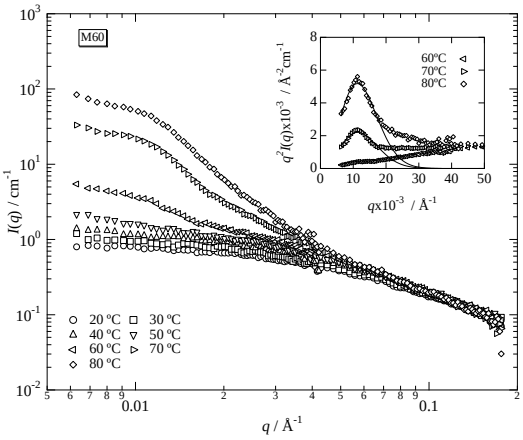


Fig. 1. Temperature dependence of the scattering intensity, $I(q)$ for M60. The inset shows Kratky plots at $T > T_{\mathrm{gel}}$.