Sol-Gel Transition of Hydrophobically Modified Polyrotaxane

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Recently, we succeeded in preparation of water-soluble polyrotaxanes by introducing hydrophobic groups. In the case of methyl group substitution, i.e., methylated polyrotaxane (Me-PR), Me-PR aqueous solutions exhibited thermosensitivity and underwent a sol-gel transition by increasing temperature. The introduction of methyl groups to PRs leads to thermosensitivity. It is noted here that substitution with larger hydrophobic functional groups, such as ethyl groups and propyl groups, resulted in a macrophase separation even at ambient temperature.

In this report, the sol-gel transition and thermosensitivity of Me-PR aqueous solutions were investigated by means of small-angle neutron scattering (SANS) and dynamic light scattering (DLS). It is known that water-solubility of polyrotaxane (PR), consisting of poly(ethylene glycol) (PEG) and R-cyclodextrin (R-CD), is very low due to stacking of neighboring R-CD molecules on a PEG chain. Methylation of the hydroxyl groups on R-CD molecules resulted in a significant improvement of water-solubility, and Me-PR exhibited a thermoreversible sol-gel transition in water depending on the degree of methylation. For low degrees of methylation (<30%), a Me-PR solution was transparent even up to 80 °C. On the other hand, for high degrees of methylation (>60%), it became opaque with increasing temperature and a gelation took place at high temperature. The temperature dependence of the sliding motion of CD molecules along the PEG chains and the mechanism of sol-gel transition are discussed on the basis of SANS and DLS results.

References

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