Evaluation of Chain Dimension of Catenated polymer in Dilute Solution

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Since cyclic polymers have no chain end, they have attracted attention as model polymers that differ from linear and branched polymers in terms of solution properties, solid state properties, and viscoelasticity. In addition, cyclic polymers can form topological isomers due to their closed-ring structure, one of the isomers is the catenated polymer, in which multiple cyclic polymers are interlocked between molecules. In this study, we investigated the precise synthesis of catenated polymers and their chain dimension in solution by small-angle neutron scattering (SANS). This year, the radii of gyration of linear and cyclic polymers obtained were measured by SANS in benzene-d_6 (good solvent) as a preliminary work.

Catenated polystyrene was synthesized using anionic polymerization and HPLC separation technique by the synthetic scheme (1) to (4) as shown in Figure 1.

Cyclization reaction of linear telechelic PS ($M_{w,SEC}$=3.49×10^4, $M_{w,LS}$=3.48×10^4, M_w/M_n= 1.02) from scheme (1) yielded multimodal peaks of cyclization reaction products. Various intermolecular products with different molecular weights and molecular structures were identified on the high molecular weight side. In order to remove these products, LCCC /SEC fractionations were carried out to obtain the cyclic PS. Cyclic PS ($M_{w,SEC}$=2.35x10^4, M_w/M_n=1.02) was isolated by the HPLC fractionations, and the purity of the obtained cyclic PS was analyzed by IC as more than 99.7%, and the absolute molecular weight by SEC-MALS was $M_{w,LS}$=3.47×10^4, which is almost equal to that of linear telechelic PS. The radii of gyaration of telechelic PS and cyclic PS in benzene-d_6 were measured by SANS as $R_{g,linear}$=6.10 (nm) and $R_{g,cyclic}$=4.25 (nm), respectively. These values agree well with previous data [1], [2], indicating that SANS measurements provide data of the radius of gyration with high accuracy.

In the future, we plan to synthesize tadpole-shaped polymers, figure-eight polymers, and catenated polymers using scheme (2)-(4) in Figure 1, and compare their chain dimensions in benzene-d_6 (good solvent) and also cyclohexane-d_{12} (theta solvent), and discuss about the relationship between polymer architecture and chain dimension of these model polymers.

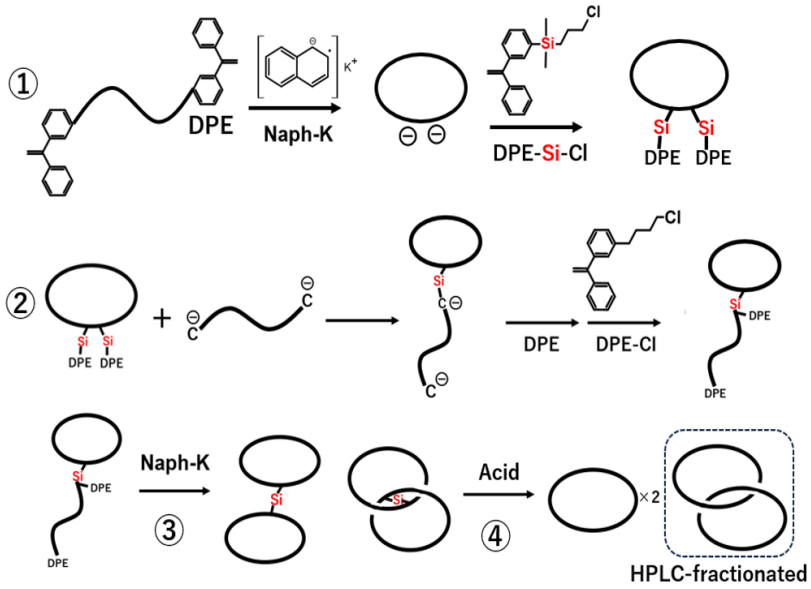

Figure 1. Synthetic scheme for catenated polystyrene.

[1] Y. Miyaki *et al.*, *Macromolecules* **11**, 1180 (1978).

[2] A. Takano *et al.*, *Macromolecules* **45**, 369 (2012).