Chain Dimension of Knotted Ring Polymers in solutions

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Ring polymer is usually prepared by end-to-end ring-closure reaction of bifunctional polymer under extremely dilute condition. Since the reaction consists of both intermolecular- and intramolecular coupling reaction, the reaction product is composed of cyclization products and also various kinds of condensates. Furthermore when the cyclization reaction is carried out in poor condition for the prepolymers (where the chains are shrunk), the ring polymers with " knots " may be formed. Using traditional HPLC technique such as size exclusion chromatography (SEC), it is very difficult to characterize the various kind of component polymers in the reaction products precisely. But recent development in HPLC technology has made it possible, that is, " liquid chromatography at the critical condition " (LCCC) and " interaction chromatography " (IC). In this study, the ring polymers synthesized under two cyclization conditions were regorously characterized by the LCCC and IC.

Linear telechelic polystyrenes (Mw=380k, Mw/Mn=1.08) were anionically synthesized and the cyclization reactions were carried out by adding pottasiun naphthalenide under very dilute condition in THF (good solvent) and also in cyclohexane (poor sovent). Figure 1 shows SEC chromatograms of the telechelic PS (black curve), and its cyclization reaction products in THF (red curve) and cyclohexane (blue curve). Focusing on the monomeric ring polymer formed in the two cyclization products (R1), two peaks are not overlapping, and the ring polymer formed in poor solvent has distributed to slightly lower molecular weight and hence has slightly wider molecular weight distribution than the ring formed in a good solvent. This result indicates that the cyclized polymer produced in a poor solvent contains components with smaller hydrodynamic volume. To measure the absolute molecular weights (Mws) and the radii of gyrations (Rgs) of the monomeric rings formed in good and poor solvents, SEC?MALS experiments were carried out. Comparing the molecular weights between linear precursors and two rings, the ring polymers have exactly the same absolute molecular weight as the linear precursors, on the other hand, comparing radii of gyration between the ring polymer formed in THF and that formed in cyclohexane, the ring formed in cyclohexane have definitely smaller Rg than that formed in THF particularly at the higher elution volume region around 37 mL. By combining the results obtained from SEC and SEC-MALS results, the ring molecule formed in cyclohexane has smaller chain dimension than that in THF, while the molecular weight is the same. In another words, if we compare ring molecules with the same radii of gyration prepared in two solvents, their molecular weights are evidently different each other. Hence we can show the direct evidence of the formation of knotted ring polymer with high molecular weight by the intramolecular coupling in poor solvent condition.

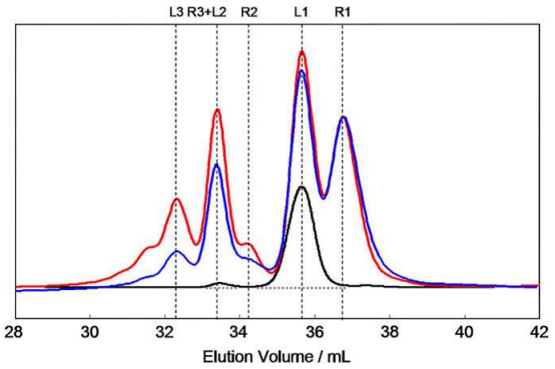

Fig. 1. Figure 1. SEC chromatograms of linear precursor (black line), cyclization reaction products in THF (red line) and that in cyclohexane (blue line) of PS with molecular weight of 380 k.