



SEC–MALS characterization of cyclization reaction products: Formation of knotted ring polymer

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ABSTRACT

Cyclization reaction products by the end-to-end ring closure of telechelic polystyrenes (PSs) with molecular weight of 47 k and 380 k in THF (good solvent) and also in cyclohexane (poor solvent) were characterized by SEC connected with multi-angle light scattering (MALS). By comparison of the SEC peaks of the monomeric rings from 47 k-PSs in THF and cyclohexane, there is no essential difference both in molecular weight and in molecular weight distribution between the two monomeric rings formed. On the other hand, comparing the data for monomeric rings from 380 k-PSs in THF and cyclohexane by SEC–MALS, it has been found that the ring formed in cyclohexane has the same molecular weight as that of the ring formed in THF, while the former reveals the lower radius of gyration than that of the ring formed in THF. These results clearly indicate the evidence of the formation of knotted ring polymers by experiment for the first time.

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1. Introduction

Over the past several decades, a lot of studies on ring polymers have been extensively pursued theoretically [1–7] and experimentally [8–26], because they are of great interest in investigation of topological effect on their physical properties. Ring polymers are usually prepared by the end-to-end ring closure reactions of bifunctional polymers. Once a ring polymer is formed, its topological state of a polymer chain is permanently fixed. If long and flexible chains are cyclized, the cyclization products formed may possibly contain various topological isomers such as trivial rings, knotted rings, etc. A number of theoretical and simulation studies about knotted ring polymers [27–35] have been reported so far, while little has been performed about experimental works for knotted rings except for the synthesis using ring DNA. Observation of knotted DNA was carried out [36], however DNA is regarded as rigid chain due to inter- or intra-molecular interaction by complementary base pairs. To clarify topological effects on polymer chain behavior without the inter- and/or intra-molecular interactions, knotted ring polymers consisting of flexible chain should be used. In previous results on the synthesis of ring polymers including our studies, possibilities of formation of knotted ring polymers have scarcely been mentioned [13]. It is considered that a knot in a polymer chain is formed by at least three self-

entanglements, therefore, very long precursor polymers have to be cyclized to realize the synthesis of knotted rings, which should be generally very difficult. We have recently succeeded in the preparation of ring polystyrenes with molecular weight over 500 k [26], using the highly skilled synthetic technique where a formation of knotted ring polymer might be possible. In this study, we have tried to synthesize the ring polystyrenes with high molecular weights under good and poor solvent conditions, and the evidence of the formation of knotted ring polymers in the cyclization reaction products obtained was presented using SEC with high resolution connected with multi-angle light scattering (MALS).

2. Experimental section

2.1. Materials

Two telechelic polystyrenes (PSs) having 1,1-diphenylethylene-type vinyl groups at both ends with the molecular weight of 47 k and 380 k were synthesized by anionic polymerization as reported previously [24,26]. The telechelic polymers were diluted with THF as a good solvent and also with cyclohexane as a poor solvent at concentration of ca. 0.1% for 47 k-PS and ca. 0.05% for 380 k-PS. Potassium naphthalene as a cyclization reagent was added into the solutions of the telechelic PSs and stirred for 12 h. The reaction temperature was 25 °C in THF and 30 °C in cyclohexane. The obtained product was precipitated into an excess amount of methanol to remove naphthalene and the other chemical residues, and freeze-dried.

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2.2. Analyses

The SEC system was consisted of a HPLC pump, a DP-8020 of Tosoh Ltd., a RI detector, RI-8020 of Tosoh Ltd., and a Rheodyne 7125 injector equipped with a 100 μ L sample loop. A set of six polystyrene gel columns (G5000H_{HR} \times 3 and G4000H_{HR} \times 3) of Tosoh Ltd. was used for the higher resolution analysis. The eluent used was THF and the flow rate was 1.0 mL/min. The column temperature was kept at 40 $^{\circ}$ C by a column oven, CO-8020 of Tosoh Ltd. Furthermore, MALS detector, DAWN EOS enhanced optical system of Wyatt Technology (Wavelength of the laser light is 690 nm, and temperature of light scattering cell is kept at 25 $^{\circ}$ C) was connected to the SEC system described above for SEC–MALS measurements.

3. Results and discussion

Table 1 lists molecular characteristics of two telechelic PSs. Fig. 1 shows SEC chromatograms of the telechelic PS (black curve) with molecular weight of 47 k, its cyclization reaction products in THF (red curve) and that in cyclohexane (blue curve).

In the chromatograms of two cyclization products, the higher molecular weight polycondensates are produced at the elution volume ranging from 30 mL to 34.4 mL, and the ring polymer appears at the elution volume of 35.6 mL, furthermore linear precursor polymer is remained at 35.0 mL as a small shoulder or a small peak. In Fig. 1, the locations of peak tops in chromatographs are clearly revealed by broken lines, where monomeric linear polymer is named as L1, and dimeric linear condensate is also named as L2, and so on. In the same manner a monomeric ring polymer and dimeric ring condensate are named as R1, R2, as well. Focusing on the monomeric ring polymer formed in the two cyclization products, the peaks are mostly overlapping, and hence have same molecular weight distribution. The result indicates that ring polymers formed in good and poor solvents are consisted of the same polymer species, they could be pure trivial rings. A computer simulation predicted that trivial ring polymer is preferentially formed by cyclization of linear precursor in good solvent condition [29], but the result must be applicable to the one cyclized in the theta solvent condition.

On the other hand Fig. 2 shows SEC chromatograms of the telechelic PS with molecular weight of 380 k, and its cyclization reaction products in THF and cyclohexane, the colors of three curves being the same as those applied for Fig. 1.

Comparing the chromatograms of two cyclization products, the polycondensates are produced at the elution volume ranging from 29 mL to 35 mL, and the ring polymer appears at the elution volume of ca. 36.8 mL, and linear precursor polymer is remained at 35.6 mL. Focusing on the monomeric ring polymer formed in the two cyclization products again, two peaks are not overlapping completely, 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 small hydrodynamic volume. To measure the absolute molecular weights

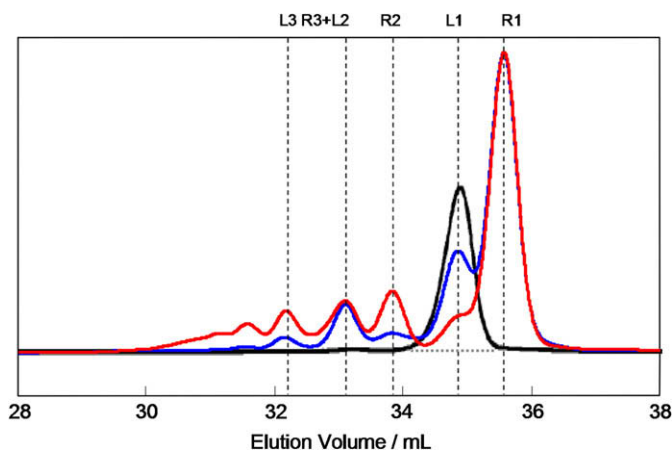


Fig. 1. SEC chromatograms of linear precursor (black line), cyclization reaction products in THF (red line) and that in cyclohexane (blue line) of PS with molecular weight of 47 k (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

(M_w s) and the radii of gyration (R_g s) of the monomeric ring polymers formed in good and poor solvents, SEC–MALS experiments were carried out as shown in Fig. 3.

Fig. 3(a) shows the SEC chromatograms and the corresponding molecular weights of cyclization reaction products prepared in two solvents. Comparing molecular weights between linear precursors appeared at the elution volume of 35.6 mL and those of the rings appeared at 36.8 mL, two ring polymers have exactly the same absolute molecular weight as the linear precursors. Therefore it was confirmed that these ring polymers were formed from linear precursors by successful intramolecular end-to-end ring closure reactions. On the other hand, Fig. 3(b) compares the SEC chromatograms and radii of gyration of cyclization reaction products in two solvents. Comparing radii of gyration between the ring polymer formed in THF (red data) and that formed in cyclohexane (blue data), the ring polymer formed in cyclohexane have definitely smaller R_g than the ring formed in THF particularly at the higher elution volume region around 37 mL. By combining the results obtained from Fig. 3(a) and 3(b), the ring molecule formed in cyclohexane has smaller chain dimension than that in THF, while the molecular weight is exactly the same. In another words, if we compare ring molecules with the same radii of gyration prepared in

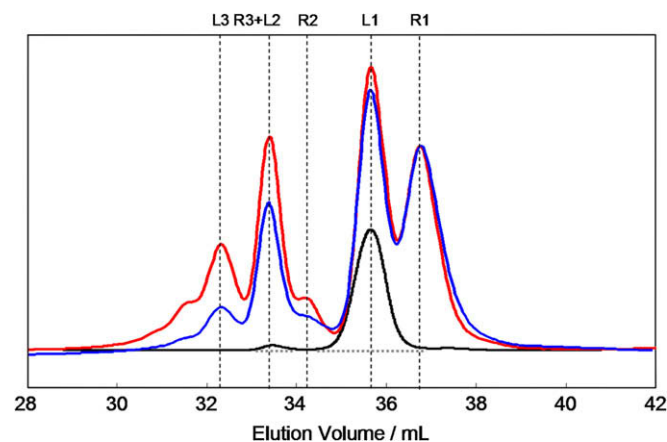


Fig. 2. SEC chromatograms of linear precursor (black line), cyclization reaction products in THF (red line) and that in cyclohexane (blue line) of PS with molecular weight of 380 k (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 1
Molecular characteristics of telechelic polymers.

Sample code	$10^{-3} M_w^a$	M_w/M_n^b
PS-47 k	47	1.02
PS-380 k	380	1.08

^a Determined by light scattering.

^b Determined by SEC.

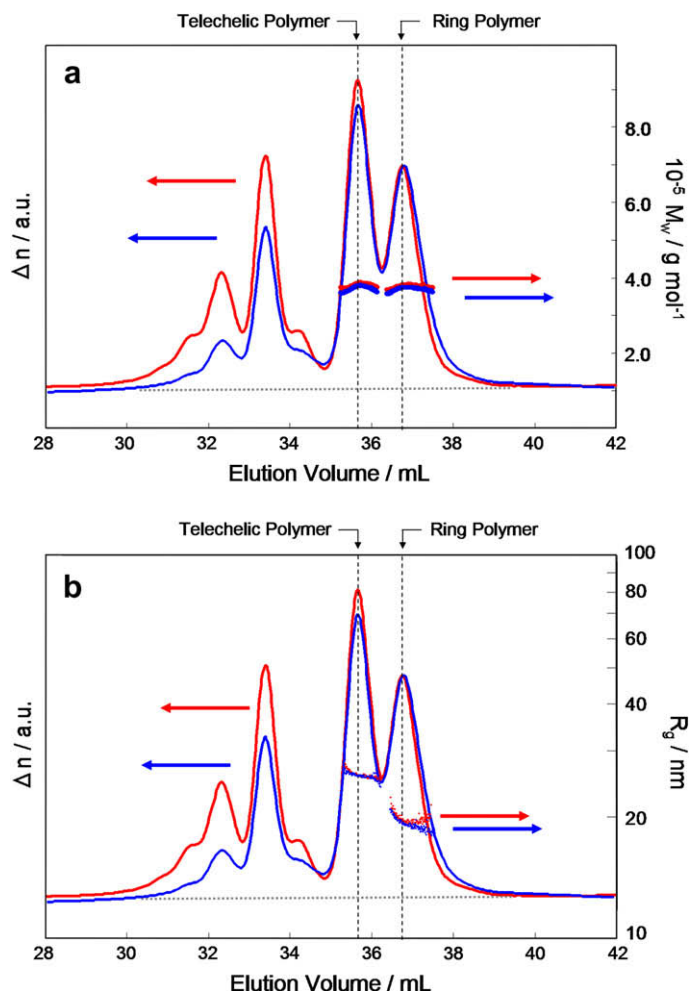


Fig. 3. SEC chromatograms of cyclization reaction products and (a) absolute molecular weight (M_w s) and (b) radii of gyration (R_g s) of linear/ring products in THF (red) and cyclohexane (blue) determined by SEC–MALS (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

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.

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