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Synthesis, separation and characterization of knotted ring polymers

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ABSTRACT

Knotted ring polystyrene (PS) with molecular weight of 380 k was successfully synthesized by intramolecular cyclization reaction in cyclohexane under extremely diluted condition. Crude product was confirmed to include linear precursor molecule, single ring molecules, and various intermolecular-reacted byproducts by SEC and interaction chromatography characterizations. The crude product was fractionated repeatedly several times by high performance interaction chromatography and finally highly-purified knotted ring molecules were obtained. It has been found by SEC-MALS that the chain dimension of the knotted ring polymers is evidently smaller than those of linear and the trivial ring polymer, while knotted polymer molecules have the same absolute molecular weight as the corresponding counterparts.

1. Introduction

Ring polymers show specific structures with no chain ends and they have been attracting many researchers. In addition to theoretical [1–8] and simulational researches [9–13], experimental investigations on ring polymers were conducted in accordance with the progress of synthetic methods for several decades [8,14–43]. A ring polymer has topological isomers, e.g., a concatenated ring and knotted ring polymers and they themselves are also interesting targets in polymer science. However, experimental trials to prepare these polymers have hardly been proceeded because of the difficulty in synthesizing these complicated molecules by regular synthetic approaches.

The methods of preparing ring polymers can be divided into several types. For example, ring expansion reaction of small cyclic molecule [14–17], intermolecular coupling reaction between a polymer with two carbanion end groups and a bifunctional coupling reagent [8,18–24] and simpler intramolecular coupling reaction [25–31] were developed in several decades. Thanks to such progress in synthetic methods, fundamental properties such as solution and viscoelastic properties of ring polymers can be elucidated in recent years. Additionally, these synthetic methods for ring polymers lead to the simultaneous syntheses of their topological isomers. In short, topological isomers of a ring polymer can be also produced by bimolecular coupling or intramolecular end-to-end coupling reactions taken place statistically. Synthesis of a catenated polymer with relatively high molecular weight is conducted by an intramolecular ring closure reaction naturally hooked on a ring polymer under diluted condition [44,45], while knotted ring molecules can be possibly prepared by an end-to-end intramolecular reaction occurred under the condition that the molecule possesses self-entanglement. Little has been reported for knotted ring polymers except for the ring DNAs and oligomers. Knotted ring DNAs have been synthesized and observed by TEM by Liu et al. [46,47] and Krasnow et al. [48]. However DNA is regarded as a rigid chain due to inter- and/or intramolecular interaction by complementary base pairs. To elucidate the topological effects on polymer chain behavior free from the inter- and/or intramolecular interactions, knotted ring polymers consisting of flexible chains are required. Formation of knotted oligomers using metal template syntheses have been reported by many researchers [49–58], but they cannot be used for the investigation of topological effects on polymer chain as well. Recently Ohta et al. reported the formation of knotted ring polystyrenes in cyclization reaction product of telechelic polystyrene with high molecular weight (M_w = 380k) synthesized in cyclohexane, which is a theta solvent of polystyrene [59]. Direct observation of knotted ring polymers by an atomic force microscopy was reported by Schappacher et al. [60], however, the separation (isolation) and characterization of these polymers are not achieved successfully even today, so that several properties are not known yet so far.

Recently a novel liquid chromatography technique called “liquid chromatography at critical condition” (LCCC) was developed and this method enables to analyze and separate the polymers with

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different molecular architectures [24,32–34]. Moreover, interaction chromatography (IC) is useful for analysis and separation of ring polymers with high molecular weight [30]. By applying these methods to the preparation of ring chains, we can prepare ring polymers and can even determine their purity quantitatively. Here we report on the synthesis and separation of knotted ring polymers by using these high-performance liquid chromatography methods coupled with light scattering techniques.

2. Experimental

2.1. Materials and sample preparation

Industrial grade of tetrahydrofuran (THF) for SEC analysis and SEC fractionation was purchased from Daishin Chemical Co. Ltd. and used as received. Acetonitrile and dichloromethane were also purchased from Kishida Chemical Co. Ltd. and used as received for LCCC and IC analyses. For polymer syntheses, GR grade of THF were purchased from Hayashi Pure Chemical Inc., Ltd. and purified using anthracene soduim in glass apparatus in vacuo, being used for both polymerization and cyclization reactions. EP grade of cyclohexane was purchased from Kishida Chemical Co. Ltd. and distilled with n-butyl lithium and then sealed in a glass apparatus. The purification of styrene and 1,1-diphenylethylene (DPE) were conducted as the same manner reported previously [61].

The telechelic polystyrene (PS) with the molecular weight of 3.8×10^5 having a DPE type double bond on both ends was synthesized by an anionic polymerization and followed by end capping reaction [29]. The telechelic polymers were diluted with THF as a good solvent and also with cyclohexane as a poor solvent at concentration of ca. 0.05%. Potassium naphthalenide as a cyclization reagent in THF was added into the solutions of the telechelic PSs and stirred for 12 h, and the reaction temperatures were 25 °C in THF and 34 °C in cyclohexane, respectively. Latter condition is near the θ-temperature of the solvent for PS. The products thus obtained were precipitated into an excess amount of methanol to remove naphthalene and the other chemical residues, followed by freeze-drying from dioxane solutions. The details of experimental procedures were reported previously [59].

2.2. Characterization

The SEC analyses and SEC fractionation experiments were conducted by using an HPLC pump, DP-8020 of Tosoh Ltd., a UV detector, UV-8020 of Tosoh Ltd., and a Rheodyne 7125 injector equipped with a 100 μL sample loop. A set of three polystyrene gel columns (TSK-gel G5000H_{HR}, 7.8 mm(I.D.) × 300 mm, particle size is 5 μm and pore size is 65 nm) of Tosoh Co. Ltd. was used for the higher resolution analyses. The eluent used was THF and the flow rate was 1.0 mL/min. The column temperature was kept at 40 °C by a column oven, CO-8020 of Tosoh Co. Ltd.

The IC analyses and IC fractionation experiments were carried out by using the same apparatuses, i.e. a pump, a UV detector and an injector as for SEC. A set of two ODS gel columns (Inertsil WP300 C18, 4.6 mm(I.D.) × 25 mm, particle size is 5 μm and pore size is 30 nm) of GL Science Inc. was used for the separation of each component. The eluent used was the mixture of acetonitrile and dichloromethane (42/58, v/v) and the flow rate was 0.5 mL/min. The column temperature was precisely controlled at 27.5 °C by a hand-made column jacket and a cooling circulator, HAAKE Phoenix II C25P. In this condition LCCC for linear polystyrenes was observed at 30.5 °C.

The SEC-MALS system was also consisted of an HPLC pump (DP-8020), a column oven (CO-8020) and three polystyrene gel columns (TSK-gel G5000H_{HR}) of Tosoh Co. Ltd. The eluent used was THF and the flow rate was 1.0 mL/min. The column temperature was kept at 40 °C. A MALS detector, DAWN HELEOS-II of Wyatt Technology, was used to measure scattering intensities, where wavelength of the laser light adopted is 658 nm, and temperature of light scattering cell was kept at 40 °C. Optilab rEX differential refractometer was connected to the SEC system described above for SEC-MALS measurements.

3. Results and discussion

The samples used and compared were two cyclization products from a telechelic PS with molecular weight of 380k in a good solvent (THF) and in a poor solvent (cyclohexane). Our main interest is in separation of unknotted ring polymer chains, which is defined as “trivial” ring here, and “knotted “ones included in the cyclization products.

Fig. 1(a) compares SEC chromatograms of linear precursor (black curve), cyclized product in THF (red curve) and that in cyclohexane (blue curve). From these curves, we clearly notice that the dimerized linear and ring components (L2, R2), trimerized components (L3, R3), and also multicoupling components were produced by cyclization reactions in two solvents in addition to an intramolecular cyclic component (R1). These intermolecular byproducts were fractionated out from the crude product by preparative SEC fractionation. Fig. 1(b) shows the chromatograms of a fractionated product cyclized in THF (red) and that in cyclohexane (blue) after SEC fractionation. Referring two chromatograms in Fig. 1(a), it is clear that intermolecular byproducts were thoroughly removed from both cyclization products by successful fractionation. In

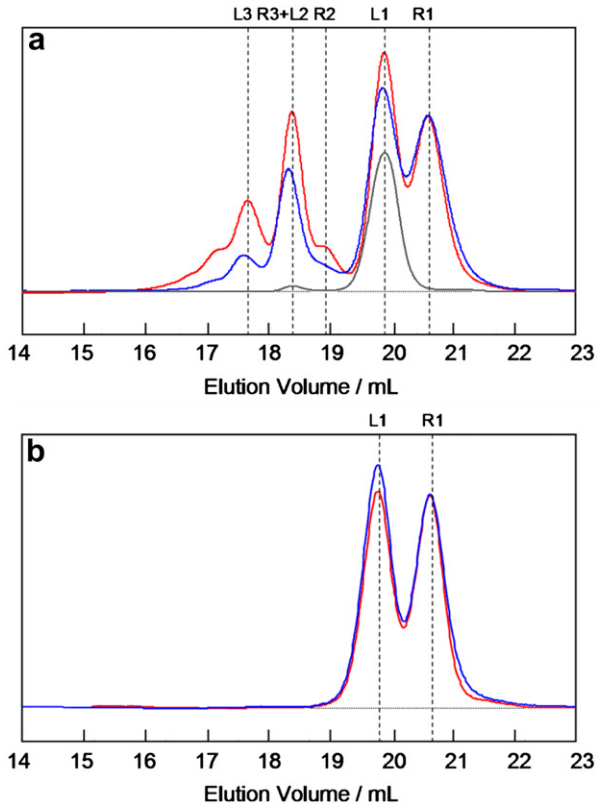

Fig. 1. SEC chromatograms of linear precursor (black curve), cyclized products in THF (red curves) and that in cyclohexane (blue curves) of (a) Crude products and (b) SEC-fractionated products. L1 denotes non-reacted linear precursor, R1 does intramolecular coupling ring polymer, while LX and RX mean intermolecular-coupled linear or ring X-mers.