HPLC Characterization of Cyclization Reaction Product Obtained by End-to-End Ring Closure Reaction of a Telechelic Polystyrene

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ABSTRACT: Cyclization reaction product synthesized by the end-to-end ring closure reaction of a telechelic polystyrene with molecular weight of 38K in extremely dilute conditions was carefully characterized by using two kinds of HPLC techniques, that is, liquid chromatography at the critical condition (LCCC) and size exclusion chromatography (SEC). First, the cyclization reaction product was coarsely separated into linear species and cyclic ones by LCCC; second, each fraction was further separated by high-resolution SEC. It was found from the HPLC analyses that the cyclization reaction product contains both linear and cyclic condensation products. Furthermore, dimeric, trimeric, and more multimeric cyclic molecules with reasonable abundance were identified as well as the monomeric cyclic molecule with high yield, as much as 50%, in the cyclic products.

Introduction

Cyclic polymers are of great interest in investigation of the topological influence on their solution, bulk, and surface properties. Various physical properties of cyclic polymers have been predicted by theoretical studies[1−4] and computer simulations,[5−7] while they have been examined by experimental works.[8−15] Cyclic polymers with narrow molecular weight distribution were synthesized by the linking reaction between bifunctional living polymers and bifunctional coupling agents. For example, polystyrenes,[9,16−21] poly(α-methylstyrene)s,[22] polybutadienes,[23] and poly(2-vinylpyridine)s[24,25] have been synthesized by this method. α,ω-Heterobifunctional polymers have been also used for the synthesis of the cyclic polymers by end-to-end ring closure reactions.[26−28] However, intermolecular linking reactions simultaneously produce dimeric, trimeric, and higher molecular weight polycondensates in addition to the production of linear precursor polymer due to simple termination reaction. In the course of intermolecular reaction, cyclic polycondensates should be produced as well as linear polycondensates. In order to understand the linking reaction quantitatively, it is very important to estimate the fractions of these byproducts; however, there are no reports on the rigorous analysis of cyclization reaction products because usual characterization methods such as SEC are hardly effective for the separation of cyclic analogues from mixtures of linear polymers and cyclic ones.

Recently, two kinds of high-performance liquid chromatography (HPLC) techniques have been developed for rigorous characterization of polymers, i.e., liquid chromatography at the critical condition (LCCC)[29−33] and temperature gradient interaction chromatography (TGIC).[34−37] The former utilizes the compensation of the counterbalanced size exclusion and interaction effects of polymer chains with stationary phase in chromatographic separation. For example, at the critical condition of a linear polymer species, the retention of linear polymers becomes independent of molecular weight, while the retention of cyclic polymers depends on molecular weight and differs from that of linear ones. The latter utilizes the interaction between polymer chains and stationary phase, where the interaction strength can be controlled by varying the column temperature; therefore, it separates polymers based on various parameters, such as molecular weight, chemical composition, etc., with higher resolution.

In this report, we analyzed a cyclization reaction product using SEC and LCCC. First, the raw cyclization reaction product was coarsely separated into linear species and cyclic ones by LCCC. Second, each fraction was further separated by high-resolution SEC, and finally constituent polymers including in the cyclization reaction products were rigorously analyzed.

Experimental Section

Materials. Cyclization was attempted by the end-to-end ring closure reaction of a telechelic polystyrene. The details of polymerization procedure of the telechelic polystyrene were reported previously.[20,21] The telechelic polymer was diluted with purified THF at polymer concentration of 0.2% (w/v). An excess amount of potassium naphthalenide, used as the linking agent, was introduced into the THF solution of the telechelic polymer at room temperature and stirred for 1 day. After being quenched with dried methanol, the obtained polymer was precipitated into an excess amount of methanol.

Weight-average molecular weight (M_w) of the telechelic polystyrene measured by light scattering is 4.17×10^4, and the molecular weight distribution (M_w/M_n) is determined to be 1.02 by SEC measurement using standard polystyrene calibration.

HPLC Measurements. The SEC system consisted of an HPLC pump, a DP-8020, a UV detector, UV-8020 (wavelength 254 nm), and a Rheodyne 7125 injector equipped with a 100 μL sample loop. A set of six polystyrene gel columns ($G4000H_{HR} \times 3$ and $G5000H_{HR} \times 3$) of Tosoh Ltd. were used for the higher resolution analysis; the column temperature was kept at 40 °C by a column oven, CO-8020. The LCCC experiment was carried out on a same HPLC system equipped with two C18 bonded silica gel columns (ODS-80TsQA, 250 mm × 8 mm, 5 μm bead size, 100 Å pore) of Tosoh Ltd. The mobile phase was a mixture of CH_2Cl_2 and CH_3CN (Kishida Chemical, HPLC grade, 57/43 in volume), and the flow rate was 0.5 mL/min. The column temperature was adjusted by circulating a fluid through a column jacket from a programmable bath/circulator (HAAKE, P2, Germany).

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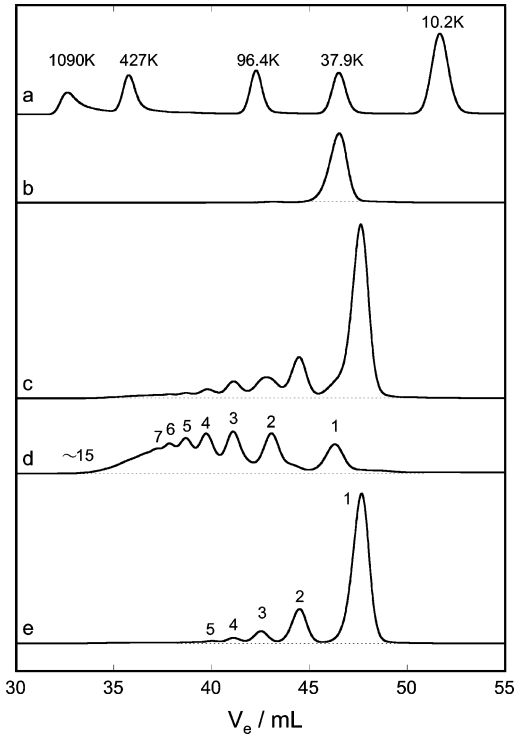

Figure 1. SEC chromatograms of (a) six standard polystyrenes (M_w: 10.2K, 37.9K, 96.4K, 427K, and 1090K), (b) the telechelic polystyrene (M_w: 41.7K), and (c) the cyclization reaction product. Two additional ones are (d) the fraction 1 and (e) the fraction 2 obtained by LCCC fractionation for the cyclization reaction product as shown in Figure 2.

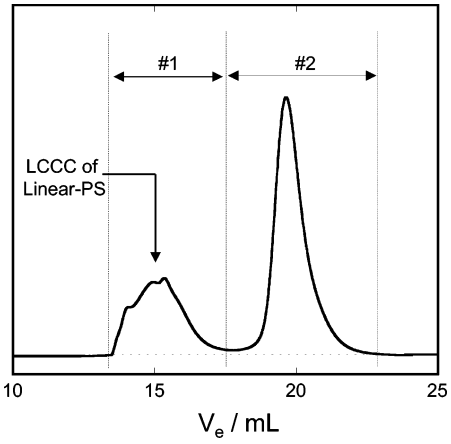

Figure 2. LCCC chromatogram of the cyclization reaction product at the LCCC condition for linear polystyrenes.

Results and Discussion

Figure 1 compares the high-resolution SEC chromatograms of (a) a mixture of five standard polystyrene samples, (b) the telechelic polystyrene with apparent molecular weight of ca. 38K, and (c) the cyclization reaction products. From the comparison of the chromatograms in (b) and (c), the higher molecular weight polycondensates are conceived at the elution volume ranging from 33 to 45 mL, and the cyclic polymer appeares at the elution volume of ca. 47.6 mL; furthermore, a tiny amount of linear precursor polymer is remained at 46.2 mL as a shoulder. It is presumed that the polycondensation products include both linear and cyclic polymer analogues; however, cyclic polymers cannot be distinguished from linear ones by the SEC chromatogram in Figure 1c.

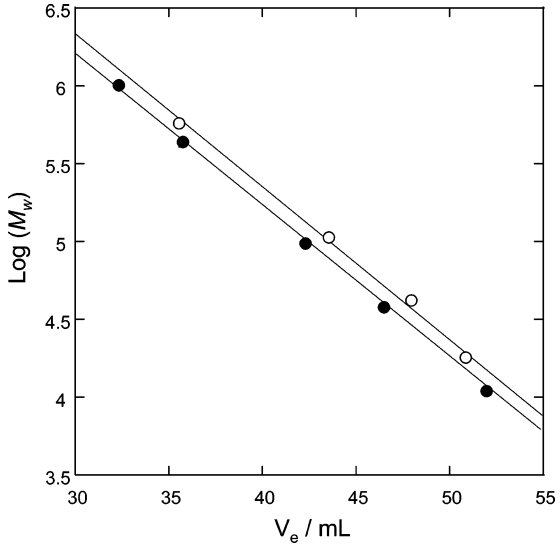

Figure 3. SEC calibration curves based on the data for linear (●) and cyclic (○) polystyrenes.

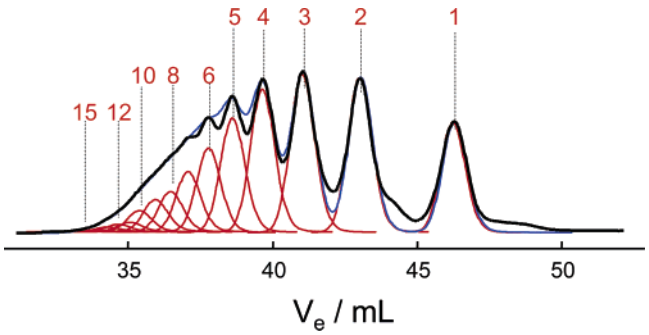

Figure 4. SEC chromatogram of (1) the fraction 1 by LCCC fractionation shown in black, (2) the separated subpeaks for *n*-meric linear condensation polymers applying a curve-fitting method in red, and (3) the integrated curve of all the subpeaks in blue.

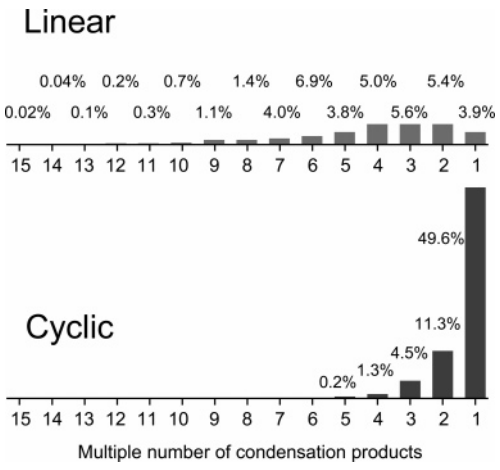

Figure 5. Relative abundance of linear and cyclic constituent polymers included in the cyclization reaction product.

To separate the cyclic polycondensates from linear ones, LCCC for linear polystyrenes was adopted. From the isothermal interaction chromatography experiments using six standard polystyrenes (M_w: 10.2K, 37.9K, 96.4K, 190K, 427K, and 1090K) at different temperatures ranging from 38 to 48 °C, the chromatographic critical temperature for linear polystyrenes was determined to be 40.5 °C, at which the size exclusion contribution and interaction one for the separation mechanism are just canceled out. Figure 2 shows the chromatogram of the cycliza-

tion reaction products at the critical condition for linear polystyrenes. In this figure, linear polymers are eluted around 14−16 mL, while another peak around 20 mL should be for cyclic polymers, separation of two peaks being almost perfect. By comparing two peak areas in Figure 2, it was found that the cyclization reaction products consist of 33% of linear polymers and 67% of cyclic polymers. After separating these two peaks in Figure 2 into two pieces, two fractions were measured by high-resolution SEC again, where LCCC and SEC were operated off-line. Figure 1d shows the SEC chromatogram of the fraction 1, which contains many linear analogues. Using calibration curve for standard linear polystyrenes as shown in Figure 3, it was determined that the molecular weight of the fraction 1 is ranging from 38K to 570K, which correspond to the linear monomeric polymer to the pentadecameric condensation molecule. On the other hand, Figure 1e shows the SEC chromatogram of the fraction 2; it is apparent that they include five independent peaks. Using another SEC calibration curve for cyclic molecules as shown in Figure 3, which was obtained by using the SEC data for four monodisperse cyclic polystyrene samples with high purity (M_w: 17.4K, 41.7K, 109K, and 573K),[21] the apparent molecular weight at the peak top of the cyclic products included in the fraction 2 are determined to be ca. 39K, 81K, 124K, 167K, and 210K. Therefore, these products are conceived to be monomeric, dimeric, trimeric, tertameric, and pentameric cyclic molecules considering the molecular weight, 38K, of the mother telechlic polymer. Cyclic molecules larger than pentamer were not detected in this experiment.

From the comparison of two calibration curves, it appears that the log(M_w) vs V_e lines for linear and cyclic polymers are practically parallel over the investigated molecular weight range, and hence the apparent molecular weight of the cyclic polymers is described by

$$M_{w,cyclic} = 0.73 M_{w,linear}$$

Such a simple relationship between linear and cyclic polymers was previously reported by Roovers et al.,[19] and the reported prefactor, 0.71, which is known as the *g*-factor, is consistent with the present result.

Furthermore, in order to analyze the fraction 1 in Figure 1d rigorously, peak splitting of the multimodal peak into subpeaks was carried out using a curve-fitting method, as shown in Figure 4. For the polycondensate molecules up to the hexameric molecule, peaks having the same fwhm as the monomeric linear molecule are assumed, while for the polycondensates larger than heptamers, the calibration curve for standard linear polystyrenes was used to determine the peak top elution volumes for each molecule, and the same fwhm value was used to generate every peak. The respective peak heights were adjusted in order to match the sum of the subpeaks with the area of the original chromatogram. The integrated curve for all the subpeaks are also shown in a blue line in Figure 4, and it is well fitted with the original chromatogram, while relative fractions of five cyclic molecules can be estimated easily since all peaks are separated completely in Figure 1e. Combining the experimental data obtained from Figures 4, 1e, and 2, percentages of all the constituent reactant molecules including condensation products were evaluated and compared as bar graphs in Figure 5. Surprisingly, it is found that the monomeric cyclic molecule is formed as high as ca. 50% yield, while dimeric and trimeric ones are also formed as much as 11.3% and ca. 4.5%, respectively, under the experimental condition adopted in the present study.

In summary, thanks to the HPLC techniques, not only the linear polycondensation molecules but also the cyclic polycondensates were successfully separated in the present work. From the careful analysis of the chromatograms obtained, it has been clarified that the product obtained from the end-to-end ring closure reaction of a telechelic polystyrene under extremely diluted condition includes relatively high abundance of dimeric and trimeric molecules as well as quite high yield of the monomeric one.

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