Structural Characterization of Ring Polystyrene by Liquid Chromatography at the Critical Condition and MALDI−TOF Mass Spectrometry

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Introduction

Ring polymers are of interest due to the topological influence of the polymer chains on their physical properties.[1] A number of theoretical[2−7] and experimental studies on ring polymers have been reported.[8−18] Among the various methods used to synthesize ring polymers, anionic polymerization has been the most widely employed method to produce ring polymers with narrow molecular weight distribution, in particular high molecular weight ones. The basic strategy is to form precursor polymers with two carbanion end groups and to have them react intramolecularly with a difunctional electrophile to close the ring.[17−23] However, the cyclization reaction does not go to completion, and side reactions produce linear polymers and dimeric and higher molecular weight polymers. Various fractionation techniques such as fractional precipitation, size exclusion chromatography, and ultracentrifugation have been applied to purify the ring polymers. However, it has been practically impossible to purify the cyclic polymers to a desirable purity.

Recently, two emerging analytical techniques have been applied successfully to characterize ring polymers: liquid chromatography at the chromatographic critical condition (LCCC) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS).[23−25] MALDI−TOF MS employs a soft ionization method and is able to provide absolute molar mass, composition, and functionality of intact polymers.[26,27] The upper limit of molecular weight to be analyzed by MALDI−TOF MS depends on the polymers. For polystyrene (PS), it has been possible to obtain individual oligomer resolution at masses higher than 10 kg/mol.[28] LCCC utilizes the compensation of size exclusion and interaction effect of polymer chains with porous packing materials in chromatographic separation.[23,24,29−32] At the critical condition for a linear polymer species, the retention of linear polymers becomes independent of molecular weight while the retention of ring polymers depends on molecular weight and differs from that of linear polymers.[33,34] In this work, we combined LCCC and MALDI−TOF MS to rigorously characterize a low molecular weight ring PS.

Experimental Section

Low molar mass ring PS (5 kg/mol) was used for this study (R17H in the previous report).[24] It was prepared by anionic polymerization initiated with sodium naphthalenide in tetrahydrofuran (THF) followed by cyclization reaction with $(CH_3)_2SiCl_2$.[22] A small fraction of the PS was directly terminated with methanol prior to the cyclization reaction to obtain linear precursors. The crude cyclization reaction products were fractionally precipitated from benzene−methanol solution to obtain the ring PS.[22] For the LCCC fractionation, a single C18 bonded silica column (Nucleosil C18AB, 100 Å pore, 250 × 4.6 mm) was used. In LCCC experiments, the column was put in a jacket connected with a bath/circulator (Neslab, RTE111), and the column temperature was kept at 33.6 °C. The mobile phase was a mixture of CH_2Cl_2/CH_3CN (58/42, v/v), and the flow rate was 0.5 mL/min. At this critical condition, retention time of linear PS becomes independent of molecular weights.

In MALDI−TOF MS experiments, a Bruker REFLEX III mass spectrometer was used. The spectrometer is equipped with a nitrogen laser ($\lambda = 337$ nm), a pulsed ion extraction, and a reflector. Ions below $m/z = 400$ were removed with pulsed deflection. This instrument operated at an accelerating potential of 20 kV in reflector mode. Dilute polymer solutions (concentration lower than 2 g/L) were prepared in HPLC grade THF (Duksan). The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich), was dissolved in THF at a concentration of 10 g/L. A 5 μL aliquot of the polymer solution was mixed with a 25 μL of the matrix solution and an 1 μL of a silver trifluoroacetate solution (1 g/L in THF), respectively. A 0.5 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature.

Results and Discussion

Figure 1 displays the MALDI−TOF MS spectra of linear precursor PS (a), ring PS (R17H) fractionated by fractional precipitation (b)[22] and ring PS further fractionated by LCCC (c).[24] The molecular weights of the peaks in the mass spectra of the precursor PS and ring PS match well with the corresponding molecular structures of the degree of polymerization n:

$$\text{linear precursor: } 104.15n\ (n \text{ styrene units}) + 1.01 \times 2\ (\text{two hydrogen end groups}) + 107.87\ (\text{Ag}^+)$$

e.g., with $n = 38$ the molar mass of the linear precursor was found to be 4067.0 compared to the calculated mass of 4067.6.

$$\text{ring: } 104.15n\ (n \text{ styrene units}) + 58.16\ (\text{dimethylsilylene group}) + 107.87\ (\text{Ag}^+)$$

e.g., with $n = 38$ the molar mass of the ring was found to be 4124.4, which can be compared to the calculated mass of 4123.7.

However, the ring PS (b, c) shows a lower average molar mass and a narrower molar mass distribution than the linear precursor PS (a). This is likely due to the fractional precipitation process, during which high molecular weight ring polymers were eliminated together with the linear polymers since ring polymer is more soluble than linear polymers in the fractionation condition.[22] Also it would be in part due to the fact that

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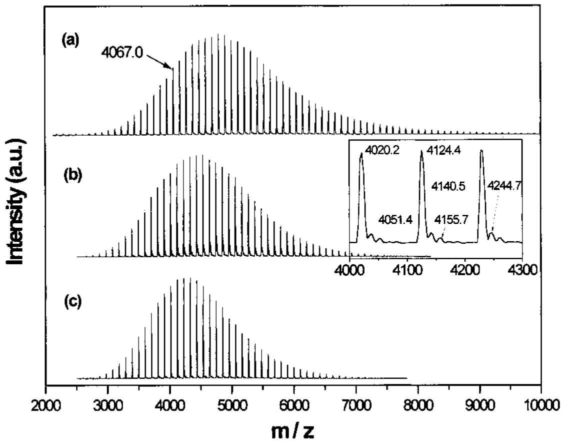

Figure 1. MALDI−TOF MS spectra of linear precursor PS (a) and ring PS fractionated by fractional precipitation (b) and ring PS further fractionated by LCCC (c). In the inset, a magnified spectrum of ring PS (b) is shown.

low molar mass linear polymers are favored in the ring closure step.

In the mass spectrum of ring PS (b), we found two small envelopes other than the major ones of single chain rings. From the magnified spectrum shown in the inset, we confirmed that these two small envelopes correspond to linear PS end-capped with the linking agent at one or both ends. Because of the workup step with methanol, the unreacted chlorosilyl group was converted to methoxysilyl group and the calculated molar mass of the proposed chemical structures of the ring and the linear contaminants PS are in excellent agreement with the experimental results:

$$\text{one end capped: } 104.15n \text{ (}n\text{ styrene units)} + 1.01 \text{ (one end hydrogen)} + 89.19 \text{ (dimethylmethoxysilyl group)} + 107.87 \text{ (Ag}^{+}\text{)}$$

e.g., with $n = 38$ the molar mass of the linear polymer was found to be 4155.7 compared to the calculated mass of 4155.8.

$$\text{both ends capped: } 104.15n \text{ (}n\text{ styrene units)} + 89.19 \times 2 \text{ (two dimethylmethoxysilyl groups)} + 107.87 \text{ (Ag}^{+}\text{)}$$

e.g., with $n = 38$ the molar mass of the linear polymer was found to be 4244.7 compared to the calculated mass of 4244.0.

In the mass spectrum of the LCCC fractionated ring (c), we find that the subsidiary peaks disappeared almost completely to confirm the efficient separation of the ring PS by LCCC from its linear chain contaminants left after the fractional precipitation.

To investigate how LCCC separates the mixture of the linear and ring polymers in more detail, the LCCC eluates were subjected to MALDI−TOF MS analysis. Figure 2 displays the LCCC chromatogram of the ring PS. Among the two elution peaks, the small peak eluted earlier corresponds to the linear contaminants and cyclic PS was eluted later as the major peak.[24] A total of 29 fractions of the LCCC eluates were taken, each of two drops, between retention times of 5.1 and 6.0 min. Since the flow rate was 0.5 mL/min, the volume of each fraction collected was about 30 μL. Each fraction was subjected to the MALDI−TOF MS analysis and the results are shown in Figure 3. The mass spectra of fractions 1−9 show that the major component of the fractions is the linear PS end-capped with dimethylmethoxysilyl groups at both ends. Since the linear PS is in its critical condition, the molecular weight distribution almost does not change among different fractions. In fraction 9, the other envelope starts to show up in the relatively low mass region compared to linear PS and it becomes the major component in fraction 11. This corresponds to the single chain ring PS. The mass spectra of ring PS (fractions 11−29) show a progressive increase of molecular weights since they are in the interaction chromatography region.[35,36] Starting from fraction 27, we notice that another peak envelope starts to appear in the high molar mass region, and it becomes conspicuous in the fraction 29. From the magnified spectrum of fraction 29 shown in the inset of Figure 3, we find that the molecular weights of the new peaks are two times as large as the ring structure in Figure 1 (b, c):

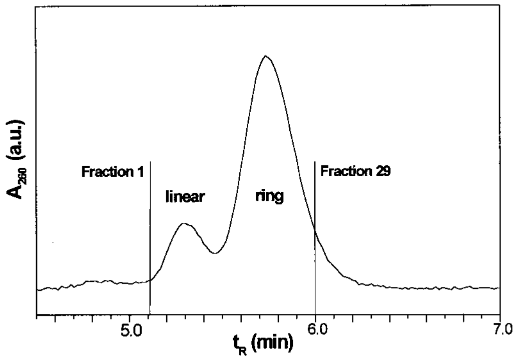

Figure 2. LCCC chromatogram of the ring PS fractionated by fractional precipitation. The eluates between the retention times of 5.1 and 6.0 min are collected into 29 fractions and subjected MALDI−TOF MS analysis as shown in Figure 3.

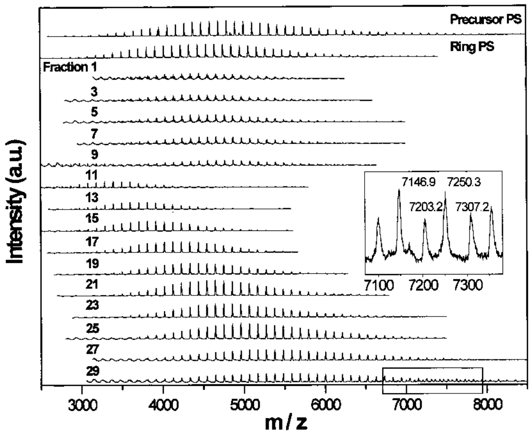

Figure 3. MALDI−TOF MS spectra of the LCCC fractions of the ring PS: In the inset, a magnified spectrum of the high molecular weight region of the fraction 29 is shown.

$$\text{dimeric ring PS: } 104.15n \text{ (}n\text{ styrene units)} + 58.16 \times 2 \text{ (two dimethylsilylene groups)} + 107.87 \text{ (Ag}^{+}\text{)}$$

e.g., with $n = 67$ the molar mass of the dimer ring was found to be 7203.2 compared to the calculated mass of 7202.2.

There are a few possibilities that could be considered to obtain the high molecular weights: two chain single rings, catenated rings, and two ring clusters formed during the MALDI process. We can eliminate the two-ring clusters since they should have been found in other fractions as well, if they are formed in the MALDI process. Although we cannot eliminate the possibility of the formation of catenated rings, it would not constitute a significant fraction, in particular for the low molecular weight polymer. It would be interesting to pursue the identification of the catenated rings from the single rings.

In summary, we combined two powerful techniques, LCCC and MALDI−TOF MS to investigate the side products in a ring PS made by anionic polymerization in detail. LCCC could separate not only the linear PS contaminants from the ring PS but also the dimeric ring PS from the monomeric rings efficiently, and we could identify the chain structures by MALDI−TOF MS.

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