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The second virial coefficients of highly-purified ring polystyrenes in cyclohexane

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ABSTRACT

The second virial coefficients A_2 of ring polystyrenes with high purity in cyclohexane were measured by light scattering in the temperature range 27.0–34.5 °C. The purity of four samples with M_w of 16k, 42k, 110k and 570k was determined to be all over 96% by HPLC. It has been found that A_2s of all the samples are definitely positive at the theta temperature of linear polystyrene, 34.5 °C, and the measured values for four samples converged to zero at 27.7 °C with decreasing temperature. This value is below the previously reported one, but it is quite consistent with the predicted value based on the topological repulsive interaction among the ring polymer molecules.

1. Introduction

A ring polymer is one of the typical model polymers in investigation of topological effect on their physical properties, such as chain dimensions in solution and in bulk, viscoelastic properties and so on. Various physical properties of ring polymers have been predicted by theoretical studies [1–8], computer simulations [9–17], while they have been examined by experimental studies [17–37]. One of the recent interesting topics for ring polymers is the theta temperature and the relating second virial coefficient (A_2).

Previously Roovers and Toporowski reported on the synthesis of ring polystyrenes and also investigated that the theta temperature of the ring polystyrene (θ_C) was apparently lower than that of the linear polystyrene (θ_L), and A_2s of the ring polystyrenes in cyclohexane are positive at θ_L [23,25]. These experimental results have been discussed thereafter, and the unusual phenomena concerning θ_C and A_2 of ring polymers have been explained by taking a topological repulsive interaction among the ring molecules into consideration by theorists [38–41].

Although many literature for the syntheses of ring polymers have existed so far, almost all the reports have never shown the direct evidence of ring structure, furthermore the purity of the ring molecules has not been determined quantitatively in most of the works. Recently Lee et al. have carefully analyzed the ring polymer samples synthesized by Roovers using a newly-developed HPLC technique, that is, liquid chromatography at the chromatographic critical condition (abbreviated as "LCCC"), and it was confirmed quantitatively that linear molecules were included as much as 10–25% in the ring polymer samples analyzed [42]. To understand the physical properties of ring polymers rigorously, it is essentially important to use well-defined polymer samples with high purity.

In this study therefore, we have prepared four highly-purified ring polystyrenes with molecular weights ranging from 16k to 570k, and the purities of the samples were quantitatively checked using an LCCC technique. Successively the second virial coefficients (A_2s) of the ring polystyrenes in cyclohexane were carefully measured by static light scattering within the temperature range 27.0–34.5 °C.

2. Experimental section

2.1. Sample preparation and characterizations

The details of polymerization procedure of linear telechelic polystyrenes were described previously [34]. The cyclization of the telechelic polymers and isolation of ring polymers using an SEC fractionation were carried out by the same manner as reported [36]. Weight-average molecular weights, M_ws, of the ring polymers were measured by light scattering described below. Molecular weight distribution, M_w/M_n, was determined by SEC with a set of three G4000H$_{HR}$ columns (300 × 7.8 mm I.D., Tosoh Co.) for samples with $M_w < 300$k, while a set of three G5000H$_{HR}$ columns (300 × 7.8 mm I.D., Tosoh Co.) were used for samples with

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$M_w > 300$k. The molecular characteristics of ring samples are summarized in Table 1. Purity of the fractionated ring polymers was determined by LCCC experiment using an HPLC system equipped with two C18 bonded silica gel columns (ODS-80TsQA, 250 mm × 8 mm, 5 μm bead size, 100 Å pore, Tosoh Co.). The mobile phase was a mixture of CH_2Cl_2 and CH_3CN (HPLC grade, Kishida Chemical Co.), the ratio was 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 P2 bath/circulator (HAAKE Co.).

2.2. Light scattering

Cyclohexane (spectroscopic grade, Kishida Chemical Co.) was used as-received as a solvent for the light-scattering measurement. Solutions were gravimetrically prepared and kept at 50 °C for at least 2 days for the complete dissolution. Under warm atmosphere (ca. 40 °C) the sample solutions were filtered through the PTFE filter (nominal pore diameter 0.2 mm, Advantech Toyo Ltd.) into light scattering cells (inner diameter 22 mm∅) which were modified to be able to seal the solution, followed by dilution with dust-free solvent to produce the solutions of the desired concentration. All the cells containing solutions were subsequently sealed using the hand torch. Static light-scattering experiments were carried out by a DLS-8000 light scattering photometer (Otsuka electronic Co. Ltd.) for ring polystyrenes in cyclohexane. He–Ne laser (wavelength $l = 632.8$ nm) was used as the light source. The compartment of a light scattering cell was thermostated with an RE-206 bath/circulator (Lauda Co. Ltd.), the temperature of the cell was controlled within the accuracy of ±0.02 °C. The specific refractive index increments, dn/dc, of polystyrene in cyclohexane were determined with a Optilab® rEX refractive index detector (Wyatt Technology Corp.) at 25 °C, 30 °C and 35 °C, the dn/dc values obtained at three temperatures were 0.1583, 0.1602 and 0.1625 (mL/g), respectively. From linear plot of the dn/dc values temperature dependence of dn/dc for polystyrene–cyclohexane solution was described as:

$$\mathrm{d}n/\mathrm{d}c = 0.00042t + 0.1477$$

M_w and A_2 were determined on the basis of Zimm's method, and M_ws of four samples were also measured in THF solution at 35 °C by a multiangle laser light scattering, DAWN EOS enhanced optical system of Wyatt Technology, which are shown in Table 1.

3. Results and discussion

Fig. 1 shows examples of the LCCC chromatograms for the ring polystyrene samples with M_w of 110k and 570k. From comparison of peaks for linear polymers and ring polymers in the LCCC chromatograms, it was confirmed that R-110 and R-570 contain 99.0% and 98.0% ring chains, respectively. The purities thus determined are also listed in Table 1.

Table 1
Molecular characteristics of ring polystyrenes.

Sample	10^{-4} M_w[a]	M_w/M_n[b]	Purity[c] (%)
R-16	1.60	1.02	99.0
R-42	4.17	1.02	96.6
R-110	10.9	1.01	99.0
R-570	57.3	1.02	98.0

[a] Determined by light scattering in THF at 35 °C.
[b] Determined by SEC.
[c] Estimated from LCCC.

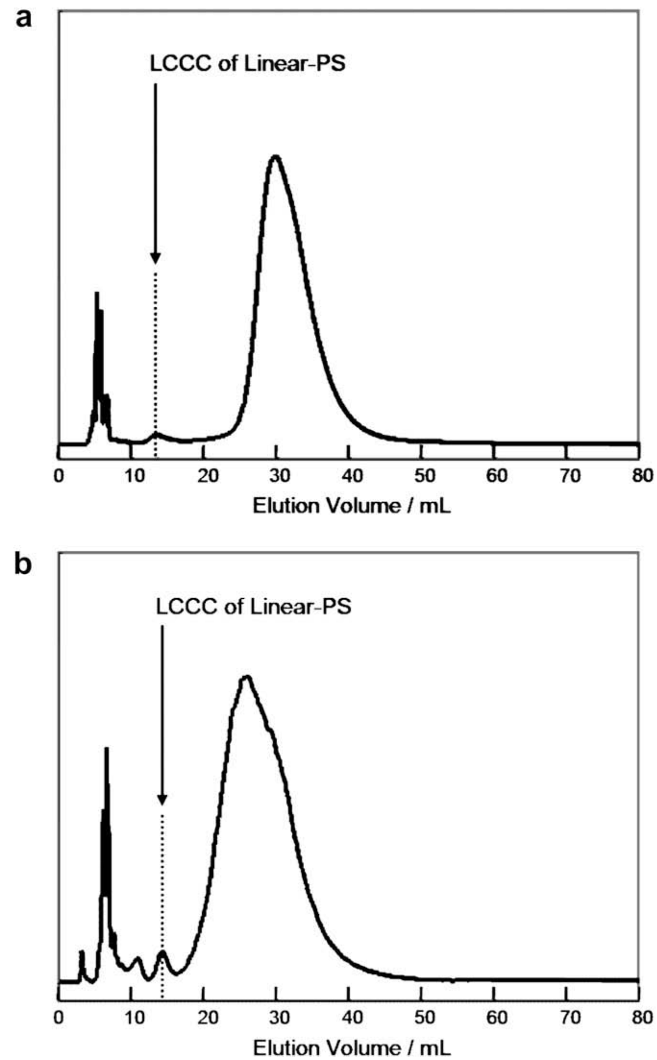

Fig. 1. LCCC chromatogram of the ring polystyrene samples, (a) $M_w = 10.9 \times 10^4$ (R-110) and (b) $M_w = 57.3 \times 10^4$ (R-570).

Fig. 2 shows an example of Zimm's plot for the ring polystyrene sample, R-570 at 34.5 °C. From this data, A_2 of this sample at this temperature was estimated to be 2.5×10^{-5} (cm^3/g^2).

A_2 values for four samples thus obtained at five temperatures, 27.0 °C, 28.0 °C, 30.0 °C, 32.0 °C and 34.5 °C, are listed in Table 2.

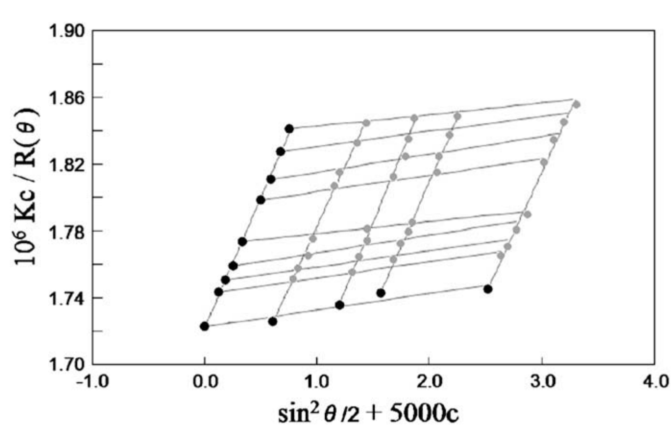

Fig. 2. Zimm's plot for ring polystyrene sample, R-570, at 34.5 °C.

Table 2
Second virial coefficients of the ring polystyrenes.

Sample	$10^5\ A_2$ (cm^3/g^2)				
	27.0 °C	28.0 °C	30.0 °C	32.0 °C	34.5 °C
R-16	−0.71	0.48	2.6	4.3	6.8
R-42	−0.72	0.30	2.3	3.6	6.2
R-110	−0.50	0.26	1.6	3.0	4.4
R-570	–[a]	0.10	0.79	1.7	2.5

[a] Impossible to measure by turbidity.

Fig. 3 shows temperature dependence of A_2 for four ring polymer samples.

From the interporation of the data in Fig. 3, we notice A_2s for four ring polystyrenes in cyclohexane converge to zero at 27.7 °C. This temperature, 27.7 °C, can be called an apparent theta temperature, θ_R, of ring polystyrene in cyclohexane, which is 6.8° lower than the theta temperature of the linear polystyrenes, that is, $\theta_L = 34.5$ °C. This θ_R temperature is fairly close to the reported value by Roovers, $\theta_R = 28.5$ °C, but the temperature lowering is meaningful probably due to the higher purity of the samples used in the present study than the Roovers'. From Fig. 3, we found that all the ring polystyrenes have positive A_2 values at the theta temperature, θ_L, of the linear polystyrenes, 34.5 °C. The temperature lowering and the corresponding A_2 increase of ring polystyrenes at θ_L are consistent with predictions in consideration for topological repulsive interaction among ring polymer molecules by des Cloizeaux [5], Iwata [38,40], Tanaka [39] and Deguchi [41].

Deguchi has theoretically estimated the molecular weight dependence of A_2 of "trivial" ring polymers [41] at θ_L by numerical simulation using random polygons, in which the topological effect and knotting probability were taken into consideration. The scaling A_2–M_w relationship was represented as $A_2 \sim M_w^{-0.34}$, when the molecular weight is high.

Fig. 4 represents double logarithmic plots of molecular weights of ring polystyrenes and the A_2 at θ_L obtained in this study. It is apparent that the data are on a straight line when the molecular weight is high and the A_2–M_w relationship for ring polymers at θ_L with relatively high molecular weight range ($M_w > 40$k) is described as

$$A_2 = 2.3_4 \times 10^{-3} M_w^{-0.34}$$

Comparing the experimental results with the simulation, the molecular weight dependence of A_2 in experiments is quite consistent with the prediction by simulation [41]. Here we can assume that the ring polymer samples used in this study are "trivial" ring polymers because they were synthesized in a good solvent under extremely dilute condition, that is, the synthesized ring polymers hardly contain concatenated molecules and also knotted ring molecules. Therefore it could be considered that the topological interaction among ring molecules is substantially effective and important at θ_L for ring polymers.

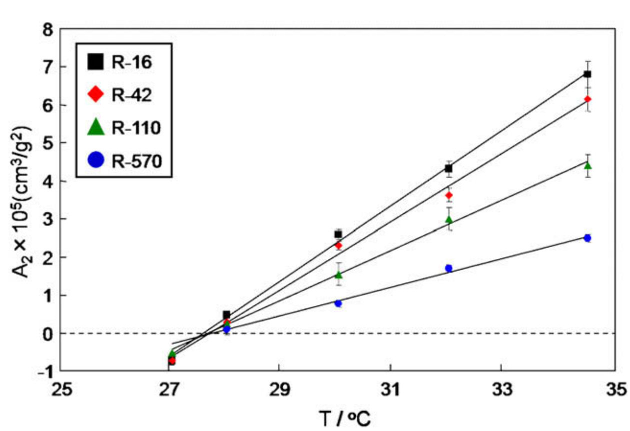

Fig. 3. Relationship between temperature and A_2 for four ring polymer samples. (■) R-16, (◆) R-42, (▲) R-110, (●) R-570.

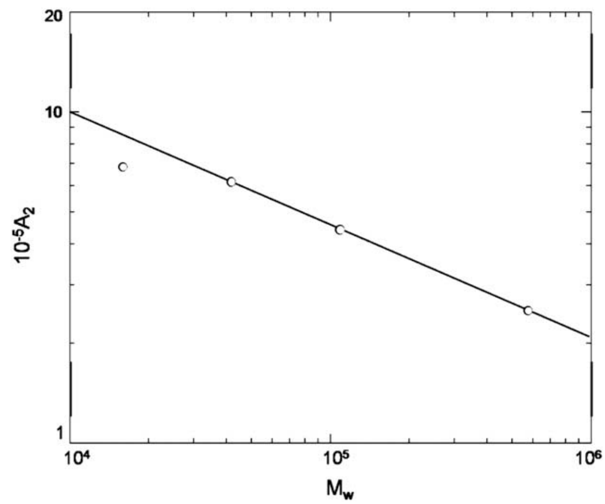

Fig. 4. Double logarithmic plots of M_w and A_2 for four ring polymers at θ_L, the slope of the solid line is −0.342.

In conclusion, from the precise measurements of light scattering intensities for a series of ring polystyrenes with high purity in cyclohexane, it was confirmed that A_2 increase and the corresponding theta temperature lowering were obviously observed. Experimentally obtained A_2–M_w relationship agrees quantitatively well with theoretically predicted one based on the simulation by consideration of topological repulsive interaction among ring polymer molecules.

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