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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1021/acs.macromol.7b01511>

Macromolecules, 50, 19, pp. 7770-7776, 2017-09-25

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Intrinsic Viscosity of Cyclic Polystyrene

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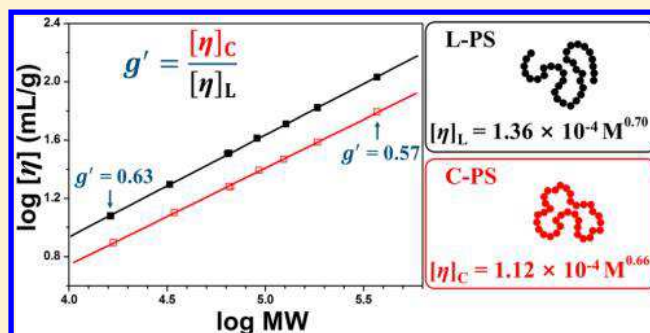
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Supporting Information

ABSTRACT: The intrinsic viscosity of cyclic polystyrenes (C-PS) and linear polystyrenes (L-PS) with molecular weight (MW) ranging from 16K to 370K was measured in THF using size exclusion chromatography coupled with a triple detection system. The C-PS samples were prepared by a ring-closure reaction of telechelic linear precursor synthesized by anionic polymerization. As-synthesized C-PS samples after the ring-closure reaction contain various byproducts, and they were fractionated by liquid chromatography at the critical condition to obtain highly pure C-PS. While the intrinsic viscosity of L-PS agrees well with the literature data, C-PS shows significantly lower value than the literature values. The Mark–Houwink exponent of C-PS is 0.67, somewhat lower than 0.70 for L-PS in the good solvent over the MW range examined. Therefore, the ratio of the intrinsic viscosity of C-PS to L-PS ($g' = [\eta]_C/[\eta]_L$) in THF is not MW independent but decreases as MW increases ($0.63 \geq [\eta]_C/[\eta]_L \geq 0.57$). The trend of intrinsic viscosity agrees well with the computer simulation result. The discrepancy in $[\eta]_C$ from the literature values can largely be attributed to the contamination of linear byproducts in the earlier studies.



INTRODUCTION

Cyclic polymers exhibit many interesting physical properties distinct from linear polymers such as chain dimensions, hydrodynamic properties, viscoelastic properties, etc.^{1,2} One of the properties of cyclic polymers often compared with their linear counterpart is the hydrodynamic property in the dilute solution reflecting their chain dimension. The g' factor (the ratio of the intrinsic viscosity, $[\eta]_C/[\eta]_L$, of a cyclic polymer to the linear polymer at the same molecular weight) in a theta condition was theoretically predicted by Bloomfield and Zimm (0.658)³ and Fukatsu and Kurata (0.645).⁴ Under good solvent conditions, g' was estimated by Douglas and Freed to be 0.673 using the preaveraging approximation⁵ and 0.561 by Schaub et al.⁶ using the renormalization-group theory and perturbative calculations. Although there are many extensive and accurate simulations of other properties, g' was studied considerably less than the ratio of mean-square radius of gyration, $g = (R_g^2)_C/(R_g^2)_L$, and the most advanced estimate of g' for cyclic polymers in a good solvent is perhaps of Rubio et al., $g' = 0.58 \pm 0.01$.⁷

Many experimental studies were also carried out. Geiser and Höcker obtained $g' = 0.65$ for cyclic polystyrenes (C-PS) with molecular weight (MW) from 3K to 24K at the theta condition of linear PS (L-PS, 34.5 °C, cyclohexane).⁸ Roovers reported that Mark–Houwink exponent of C-PS with MW from 7K to 450K was lower than 0.5 ($[\eta]_C \sim M^{0.465}$) at the theta condition of L-PS (35 °C, cyclohexane), and g' value decreases with MW from 0.66–0.68 to 0.58–0.60.⁹ Roovers and Toporowski also reported that the theta temperature (at which the second virial coefficient, A_2 , vanishes) of C-PS (Θ_C) in cyclohexane was 28 °C, about 6 °C lower than the theta temperature of L-PS (Θ_L).¹⁰ Lutz et al. confirmed that $\Theta_C \approx \Theta_L - 6$ °C for C-PS (10K \leq MW \leq 200K) in a few theta solvents (cyclohexane, *d*-cyclohexane, and decalin), but the Mark–Houwink exponent was larger than 0.5 ($[\eta]_C \sim M^{0.53}$) and g' was 0.66 at 34.5 °C in cyclohexane.¹¹ Later, McKenna et al. confirmed the results of

Received: July 17, 2017

Revised: August 22, 2017

Published: September 25, 2017

Lutz et al. with the same C-PS samples presenting $[\eta]_C \sim M^{0.52 \pm 0.03}$ and $g' = 0.65$ at 35 °C in cyclohexane.¹² They suggested that the smaller Mark–Houwink exponent of Roovers might be due to the knots formation in the C-PS sample.

A similar discrepancy in the intrinsic viscosity of cyclic polymers also exists in good solvents. Geiser and Höcker reported with C-PS ($3K \leq MW \leq 24K$) that g' decreased from 0.76 to 0.56 with increasing MW in toluene,⁸ while Hild et al. reported an opposite trend for C-PS in THF that $g' = 0.65$ when $MW \leq 60K$ and g' increased to 0.92 when $MW > 100K$.¹³ Roovers reported for C-PS ($7K \leq MW \leq 450K$) that the Mark–Houwink exponent of C-PS (0.67) was substantially smaller than that of L-PS (0.73) in toluene;⁹ thus, g' decreases with MW from 0.67 to 0.57. Lutz et al. reported that the Mark–Houwink exponent for C-PS ($10K \leq MW \leq 200K$) in THF was 0.72 higher than the exponent of L-PS (0.70); thus, g' increases with MW from 0.71 to 0.74.¹¹

The apparent lack of consensus in the intrinsic viscosity of the cyclic polymers is likely due to the low purity of the cyclic polymers considering the good reproducibility for linear polymers. The cyclic polymers were prepared by ring closure of telechelic linear precursors. Because of the imperfect ring closure reaction, contamination of the target cyclic polymers by various byproducts, mostly linear precursors and their adducts, is unavoidable. Therefore, postsynthesis fractionation is necessary to obtain cyclic polymers with high purity. For the fractionation of cyclic polymers from the ring closure reaction mixture, fractional precipitation has been employed most frequently, exploiting the lower theta temperature of cyclic polymer; i.e., cyclic polymer is more soluble than linear polymer near the theta condition.^{10,11,14} Nonetheless, it was not possible to fractionate the byproducts completely from the target cyclic polymers. The purity of cyclic polymers has been examined mostly with size exclusion chromatography (SEC) utilizing the fact that a cyclic polymer has a smaller chain dimension than the linear counterpart at the same MW. However, the SEC retention (related to the hydrodynamic volume of polymer chains) of a cyclic polymer and that of a linear precursor are not sufficiently different to allow complete separation of the elution peaks, and it is not possible to assess the purity of the cyclic polymers by SEC precisely. For example, the C-PS samples prepared and used by Roovers were recharacterized by liquid chromatography at critical condition (LCCC) later, and the samples were found to contain as much as 10–20% linear polymers.¹⁵ Efficiency of the LCCC fractionation of cyclic polymers from their linear counterparts was predicted theoretically and verified experimentally.^{15–18}

It was found that a tiny amount of linear polymer contaminant brought a considerable effect on the melt viscoelastic properties.¹⁹ Although the effect of linear PS contamination on the dilute solution property is expected not as high as the melt property, the effect might be large enough to prevent a reasonable consensus in the intrinsic viscosity of cyclic polymers. Other puzzling reports are from the cyclic polymers prepared by the ring-expansion method using methathesis polymerization. Although the ring expansion mechanism is supposed to produce pure cyclic polymers, the method results in cyclic polymers with a broad MW distribution, and the purity of the cyclic polymers is difficult to be assessed. Interestingly, however, these analysis results of the cyclic polymers commonly show very low g' value, ~ 0.4 .^{20–23}

Therefore, it appears worth to reexamine the intrinsic viscosity of cyclic polymers with high purity samples to shed light on the conflicting situation. In this study, we prepared a set of C-PS of MW ranging from 16K to 370K (including dimeric cycles) by anionic polymerization and LCCC fractionation. The high purity of all samples was confirmed by analytical LCCC. Their intrinsic viscosities were measured in a good solvent (THF) and compared with the existing literature data.

EXPERIMENTAL SECTION

Preparation and Characterization of C-PS. Five linear telechelic PS precursors with weight-average MW (M_w) ranging from 16.4K to 185.2K were prepared by anionic polymerization. Cyclization of the telechelic PS precursors was done by the end-to-end radical coupling reaction between the two terminal diphenylethylene moieties. The coupling reactions were carried out in THF to reduce the possibility of the knot formation.²⁴ Details of polymerization procedure and the ring closure reaction of the PS precursors were reported previously.²⁵ All polymers used in this study were characterized by SEC coupled with a triple detector (Malvern, TDA 302). The specific refractive index increment (dn/dc) of PS was measured in THF as 0.185 mL/g. Three PS gel columns (Agilent Polypore 300 × 7.5 mm, Waters Styragel HR4 300 × 7.8 mm, and Jordi mixed bed 300 × 8.0 mm) were used, and the column temperature was controlled at 40 °C by use of a column oven (Fiatron, TC-50). The solvent was THF (Samchun, HPLC grade) at a flow rate of 0.7 mL/min. Polymer samples for the SEC analysis were dissolved in THF at a concentration of ~ 3 mg/mL, and the injection volume was 100 μ L.

LCCC Fractionation. For the preparative fractionation of C-PS from the as-synthesized mixture, two large bore C18 bonded silica columns (Nucleosil C18, 250 × 9.8 mm, 100 Å pore, 5 μ m particle and Nucleosil C18, 250 × 9.8 mm, 300 Å pore, 5 μ m particle) and a mixed eluent of CH_2Cl_2/CH_3CN (58/42, v/v, Samchun, HPLC grade) at a flow rate of 2 mL/min were used. Temperature of the column was controlled at 19 °C by circulating water from a programmable bath/circulator (Thermo-Haake, C25P) through a homemade column jacket. The injection sample solution (~ 10 mg/mL) was prepared by dissolving the polymers in the eluent, and the injection volume was 500 μ L. The chromatograms were recorded by a light scattering detector (Wyatt, miniDAWN) and a UV absorption detector (Younglin, UV7300) operating at a wavelength of 260 nm.

Purity Assessment of Fractionated C-PS. Purity assessment of the C-PS fractionated by preparative LCCC was carried out by analytical LCCC at the critical adsorption point (CAP) of C-PS. Three C18 bonded silica columns (Nucleosil C18, 250 × 4.6 mm, 500 Å pore, 7 μ m particle, Lunasil C18, 250 × 4.6 mm, 300 Å pore, 5 μ m particle, Fuji C18, 150 × 4.6 mm, 100 Å pore, 5 μ m particle) and a mixed eluent of CH_2Cl_2/CH_3CN (58/42, v/v, Samchun, HPLC grade) were used. Column temperature was 21 °C, and 100 μ L sample (2 mg/mL) was injected.

Computer Simulations. There are several approximate simulation methods for calculation of intrinsic viscosity available.²⁶ In this work we use a modified variational lower bound method proposed by Fixman²⁷ and further elaborated by others.^{28,29} A lower bound to the intrinsic viscosity is usually calculated using a fixed approximate diffusion tensor D_a , which is easier to handle in calculations than the original diffusion tensor D , and the computationally expensive matrix inversion of D_a is calculated only once. In our method we set $D_a = D$ and solve the matrix equation $Dx = b$ for vector x using the conjugate gradients method³⁰ for each conformation (no preaveraging was used). As the preconditioner we use the inverse of the nearest circulant matrix to D .³¹ Choosing this form of a preconditioner allows for efficient calculations using the discrete fast Fourier transform and results in a rapid convergence of the conjugate gradients method. For the diffusion tensor we use the usual Rotne–Prager–Yamakawa form.³² The ensemble averaging over polymer conformations is done

using samples generated by a hybrid Monte Carlo simulation for a coarse-grained bead–spring model of the chain in a good solvent. Full details of this simulation method and the polymer model are given elsewhere.³³ The simulation traces of R_g^2 and $[\eta]$ showing efficient Monte Carlo sampling are given in Figures S1 and S2. The combination of these two methods allowed us to run simulations for chains up to 1000 beads with modest computer resources. Simulations of cyclic polymers started from an unknot. Under good solvent conditions the fraction of knots is very small (less than 0.005) for chain lengths considered here.³⁴ The formation of knots in our hybrid Monte Carlo simulations would require crossing of a rather high energy barrier and was not observed. Sample conformations with radii of gyration near the ensemble averages are given in Figures S3 and S4.

RESULTS AND DISCUSSION

Intrinsic Viscosity of High Purity C-PS. The results for five PS precursors characterized by SEC with LS detection are summarized in Table 1.

Table 1. Molecular Characteristics of PS Precursors^a

sample	M_w	M_w/M_n
PS 1	16.4K	1.01
PS 2	33.1K	1.01
PS 3	64.6K	<1.01
PS 4	92.2K	<1.01
PS 5	185.2K	<1.01

^aDetermined by SEC/light scattering in THF.

Figure 1 shows the SEC chromatograms of the PS precursors (dotted lines) and the as-synthesized ring-closure products

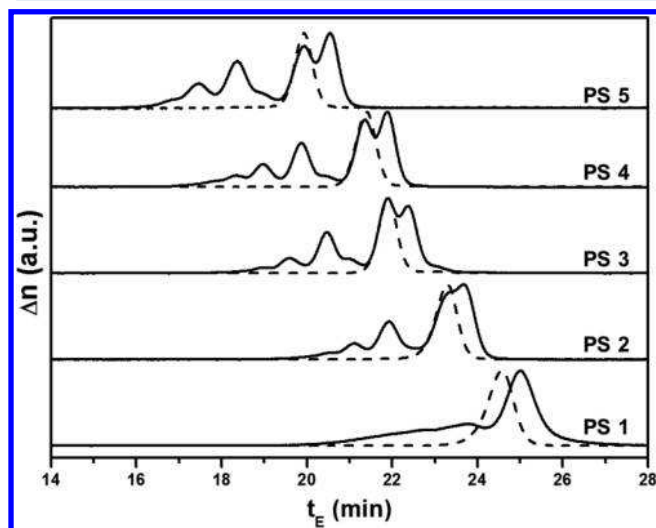


Figure 1. SEC chromatograms of the five as-synthesized C-PSs (solid lines) and the corresponding precursors (dashed lines) recorded by a refractive index detector.

(solid lines). The as-synthesized polymers contain C-PS that elutes later than the precursor PS as well as various high-MW adducts that elute earlier than the precursor PS. The as-synthesized products were fractionated by preparative LCCC.

Figure 2 displays a LCCC chromatogram of as-synthesized C-PS 5 (185.2K) obtained in the LCCC fractionation. The separation condition is between the critical adsorption points (CAP) of L-PS and C-PS.²⁵ Therefore, the C-PS part is separated well from the L-PS part while the individual adducts in both C-PS and L-PS parts are not resolved well. The L-PS

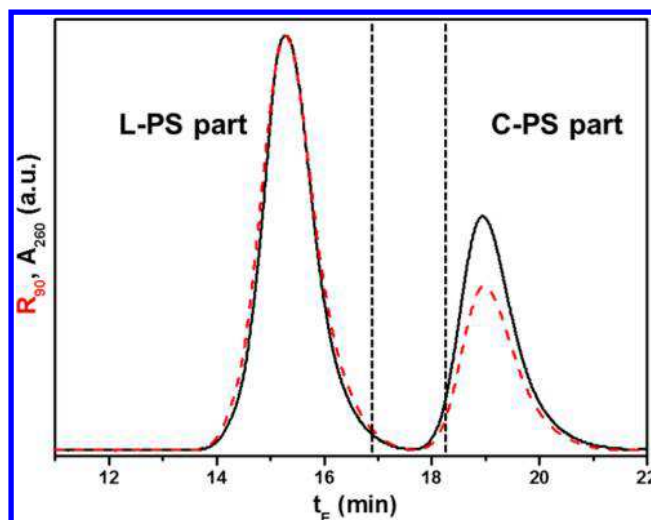


Figure 2. LCCC chromatogram of the as-synthesized C-PS 5 in the preparative LCCC fractionation recorded by a UV absorption (black solid line) and a light scattering (red dashed line) detector.

part appears to have higher MW than C-PS part (from the relatively higher intensity of the LS detector signal than the UV detector signal) since the L-PS part contains more high-MW adducts than the C-PS part. The L-PS part was collected at $t_E = 14$ –16.4 min, and the C-PS part was collected after $t_E = 18.1$ min. The part of $t_E = 16.4$ –18.1 min was discarded to remove the coexisting linear and cyclic PS.

Figure 3 displays the SEC chromatograms of the LCCC fractions of C-PS and L-PS. Both C-PS and L-PS fractions

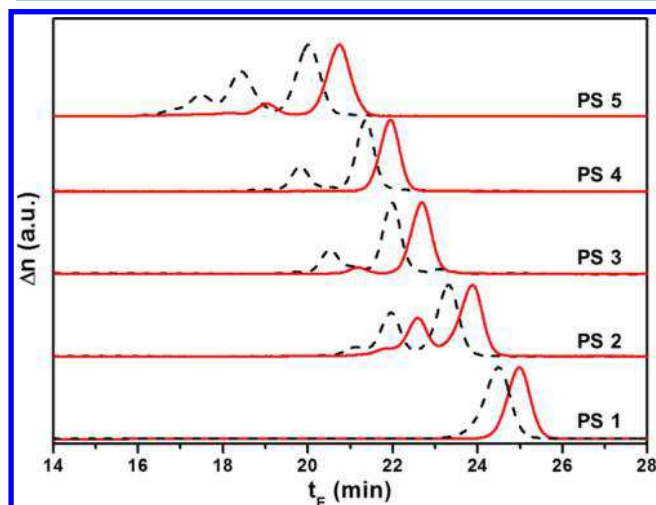


Figure 3. SEC chromatograms of the LCCC-fractionated L-PS parts (black dashed lines) and C-PS parts (red solid lines) recorded by a refractive index detector.

contain high-MW adducts that are identified as the multimers of C-PS and L-PS from the MW of individual peaks determined by LS detection. The enlarged rings were used together with the single ring for the intrinsic viscosity measurement since they are well resolved one another by SEC as shown in Figure 3. The purity assessment of the C-PS was also done without further fractionation of multiple adducts. The elution time of C-PS is longer than L-PS of the same MW to make the apparent MW measured by standard PS calibration smaller than L-PS. We found that $MW_{C,App} = 0.72MW_L$ (see Figure S5) that is

essentially the same as that reported before by Roovers (0.71)¹⁰ and Takano et al. (0.73).¹⁸

Figure 4 shows the analytical LCCC chromatograms at the CAP of C-PS at which different MW C-PS coelute while L-PS

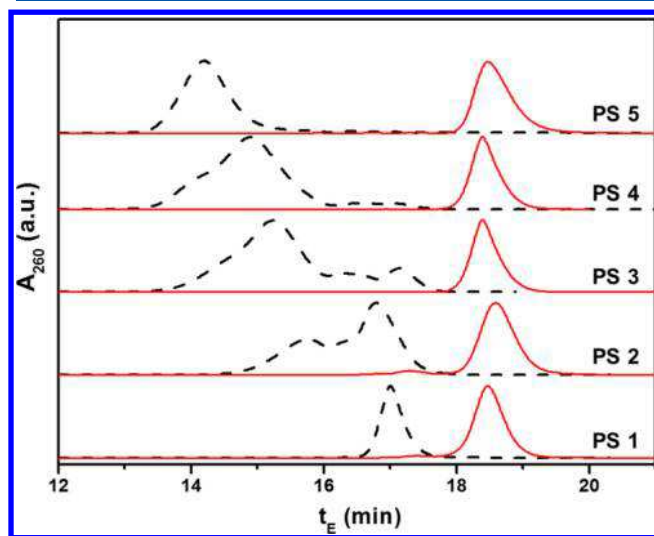


Figure 4. Analytical LCCC chromatograms of the fractionated C-PS parts (red solid lines) and the fractionated L-PS parts (black dashed lines) at the CAP of C-PS recorded by a UV absorption detector.

elute earlier.²² They clearly show that the elution peaks of L-PS and C-PS are completely resolved down to the baseline, indicating the high purity of C-PS.

The intrinsic viscosity of the L-PS and C-PS samples was measured individually by SEC separation coupled with triple detection (a refractive index detector to measure the concentration, a light scattering detector to measure the molecular weight, and a differential viscosity detector to measure the viscosity). While the SEC column temperature was set at 40 °C, absolute M_w and intrinsic viscosity were measured at 25 °C at the detector. Figure 5 shows the SEC chromatograms of the C-PS 5 (red solid line) and the L-PS 5 (black dashed line) recorded by a differential refractive index detector in the triple detection. In addition, MW (top) and intrinsic viscosity ($[\eta]$, bottom) measured by the triple detection are also plotted. Data of the other samples are shown in Figure S6. C-PS and L-PS are easily distinguishable by comparing their relative elution times, MW, or $[\eta]$: C-PS elutes later and has a smaller $[\eta]$ value than the L-PS of the same MW. The LCCC fractionated C-PS part and L-PS part containing multimers are used without further fractionation since SEC resolution is good enough to provide useful information on the dimers in addition to the unimers as shown in Figure 5.

The results of MW (M_p) and $[\eta]$ at each peak position are summarized in Table S1 and plotted in a double logarithmic plot of $\log [\eta]$ vs $\log MW$ in Figure 6. In addition to the data obtained in this study, some representative data of PS in the literature are also plotted together for easy comparison. Our data of C-PS and L-PS show excellent linear relationship between $\log [\eta]$ and $\log MW$. In addition, the universal calibration³⁵ for the SEC data analysis works well for C-PS as shown in Figure S7. The linear least-squares fits yield the following relationships for L-PS and C-PS,

$$[\eta]_L = 1.363 \times 10^{-4} M^{0.700 \pm 0.005}$$

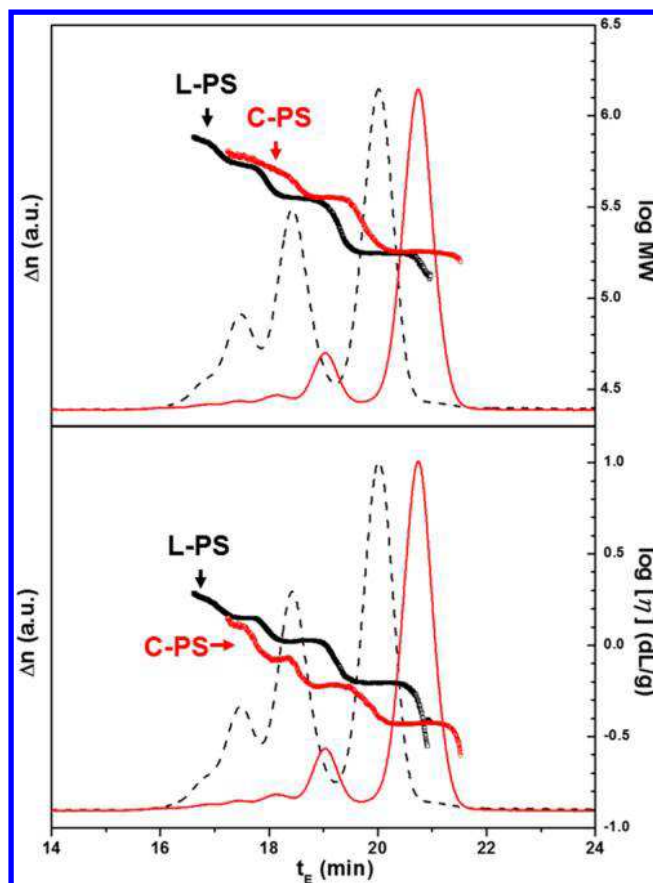


Figure 5. SEC chromatograms of the C-PS 5 part (red solid line) and the L-PS 5 part (black dashed line) recorded by a RI detector. The M_w obtained from the light scattering detection (top) and the intrinsic viscosity obtained from the viscosity detection (bottom) are shown in the plot.

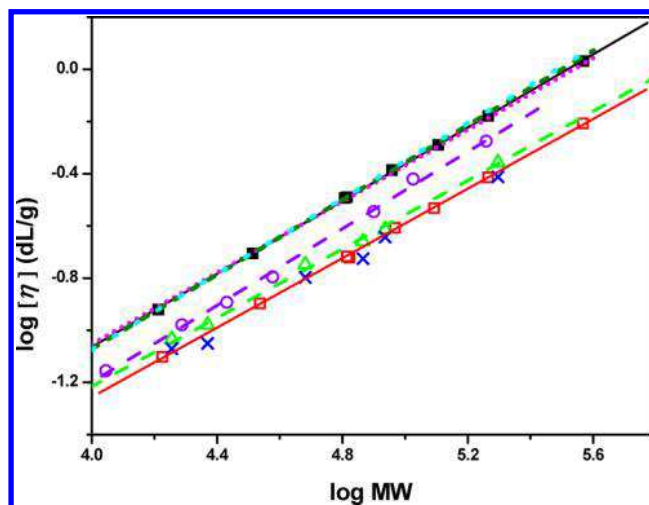


Figure 6. Comparison of Mark–Houwink plots of C-PS and L-PS. This work: L-PS (black filled square and solid line), C-PS (red open square and solid line). Literature data: L-PS in THF at 25 °C (pink dotted line),³⁶ L-PS in toluene at 35 °C (dark green dashed line),³⁷ L-PS in THF at 25 °C (light blue dotted line),³⁸ C-PS in THF at 25 °C (violet open circle and dashed line),¹¹ C-PS in toluene at 35 °C (light green open triangle and dashed line),⁹ and the C-PS data of Roovers⁹ corrected for linear contaminants (blue cross).

$$[\eta]_C = 1.198 \times 10^{-4} M^{0.666 \pm 0.005}$$

Although the SEC-TD method is widely used to measure intrinsic viscosity of polymers, the accuracy of the method needs to be examined vis-à-vis the data obtained by the traditional method using capillary viscometers and extrapolation to the zero concentration. For the purpose, we compare the L-PS data measured by the SEC-TD method in this study with three sets of literature data that are most frequently cited as references: Meyerhoff and Appelt ($[\eta]_L = 1.363 \times 10^{-4} M^{0.714}$ in THF, 25 °C),³⁸ Strazielle and Herz ($[\eta]_L = 1.4 \times 10^{-4} M^{0.7}$ in THF, 25 °C),³⁶ and Roovers ($[\eta]_L = 1.02 \times 10^{-4} M^{0.73}$ in toluene, 35 °C).³⁷ Although they do not match perfectly one another due to the experimental uncertainty and different MW range of the studies, they are remarkably similar. Our SEC-TD data are consistent with the literature data that verifies the accuracy of our SEC-TD measurements.

On the other hand, we found that the literature data of C-PS deviate one another seriously: Lutz et al. ($[\eta]_C = 7.88 \times 10^{-5} M^{0.73}$ in THF, 25 °C)¹¹ and Roovers ($[\eta]_C = 1.413 \times 10^{-5} M^{0.658}$ in toluene, 35 °C).⁹ Our $[\eta]_C$ values are significantly lower than the others. We speculate that the disparity of the C-PS data can be attributed to the low purity of the C-PS used in the earlier studies. According to the later LCCC characterization result of the C-PS samples used in the study of Roovers,⁹ the contamination of L-PS was not negligible, amounting 10–20% despite the extensive purifications by fractional precipitation.¹⁵ We do not know the purity of the samples of Lutz et al., but it would not be an unreasonable speculation that their samples also would have contained a significant amount of L-PS contaminants since no purification method better than fractional precipitation was available at that time.

In his earlier work, Roovers suspected the purity of his C-PS and suggested a correction method for the experimentally observed $[\eta]$ as follows:⁹

$$[\eta] = x[\eta]_L + (1 - x)[\eta]_C$$

where the $[\eta]$, $[\eta]_L$, and $[\eta]_C$ are the intrinsic viscosity of the impure sample, pure linear polymer, and pure cyclic polymer, respectively, and x is the weight fraction of the linear polymer in the sample. The C-PS samples used by Roovers in his study⁹ was examined by LCCC earlier.¹⁵ The fraction of the L-PS contaminant in the samples was estimated from the LCCC chromatogram (Figure 2 in ref 15), and the results are shown in Table 2.

Table 2. Weight Fraction of L-PS Contaminants in the C-PS Samples in Ref 15

M_w	weight fraction of L-PS	M_w	weight fraction of L-PS
6.9K	0.23	73.3K	0.21
18K	0.19	86.9K	0.11
23.4K	0.26	198K	0.18
48K	0.22		

Using the L-PS fractions listed in Table 2, the intrinsic viscosities of pure C-PS are calculated and plotted with blue crosses in Figure 6. They are in good agreement with the $[\eta]_C$ values measured in this study. It strongly supports the speculation that the disparate $[\eta]_C$ data found in the literature are due to the imperfect purity of the cyclic polymers in the earlier studies.

Computer Simulations. The main results of our computer simulations are the ratios $g = (R_g^2)_C / (R_g^2)_L$ and $g' = [\eta]_C / [\eta]_L$ given in Figure 7. The estimated value of $g = 0.538 \pm 0.006$ for

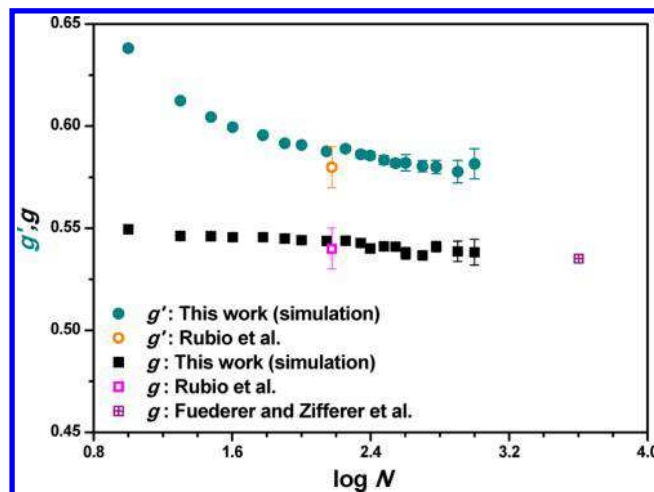


Figure 7. Ratios $g = (R_g^2)_C / (R_g^2)_L$ and $g' = [\eta]_C / [\eta]_L$ as a function of the number of beads N .

the longest chains agrees perfectly with the results of extensive lattice simulation of Fueederer and Zifferer (0.535) for about 4 times longer chains³⁴ and with the extrapolation of Rubio et al. (0.54 ± 0.01) for shorter chain as well.⁷ The dependence of R_g^2 on the number of beads N is given in Figure S8. As usual, there is a certain curvature at low values of N due to the corrections to scaling. For simplicity, we fitted the relationship $R_g^2 \sim N^{2\nu}$ for highest values of N only. The determined exponents of $\nu = 0.60 \pm 0.01$ are not very accurate, but within the statistical uncertainty they are the same as the more accurate values obtained by Fueederer and Zifferer³⁷ and by the renormalization group theory calculations (0.588 ± 0.0015).³⁹ We did not find any statistically significant difference of the exponents ν between cyclic unknot and linear chains.

Similarly, the dependence of $[\eta]$ on the number of beads N is given in Figure S9. The fitted Mark–Houwink exponents at high N are again approximately the same but showed a more pronounced curvature than R_g toward low N . Therefore, as shown in Figure 7, the ratio g' is more dependent on the chain length than the ratio g . The value of g' decrease from 0.637 for the shortest chains to 0.577 ± 0.007 for the longest chains. These values agree well with the extrapolation of Rubio et al. (0.58 ± 0.01). Furthermore, they are in excellent agreement with the present experimental results with the values of g' decreasing from 0.63 for the shortest chains to 0.57 for the longest chains. A different dependence of g and g' of cyclic polymers on molecular weight was observed also in a previous simulation study,⁴⁰ suggesting a nontrivial relationship between chain architecture, excluded volume, and hydrodynamic interactions. The calculated values of g' may be also affected by a slower convergence of dynamical properties with the chain length.⁴¹

CONCLUSION

In this study, C-PS with MW ranging from 16K to 370K were prepared and fractionated to high purity and their intrinsic viscosity was measured in THF, a good solvent for PS, together with the precursor L-PS. While the intrinsic viscosity of L-PS agrees well with the literature data, that of C-PS is significantly

lower than the literature values. The Mark–Houwink exponent of C-PS is found 0.67, somewhat lower than 0.70 for L-PS in the good solvent over the MW range examined. Therefore, the ratio of the intrinsic viscosity of C-PS to L-PS ($g' = [\eta]_C/[\eta]_L$) in THF is not MW independent but decreases as MW increases ($0.63 \geq [\eta]_C/[\eta]_L \geq 0.57$). The trend of intrinsic viscosity change with MW agrees well with the computer simulation result. The discrepancy in $[\eta]_C$ from the literature values can largely be attributed to the contamination of linear byproducts in the earlier studies.

The g' value has been used often as an “indicator” to justify the successful preparation of cyclic polymers. But the experimental g' values in the literature are scattered and did not reach a reasonable consensus. We hope that the results of this study draw attention from the research community of cyclic polymers for a better assessment of the purity of cyclic polymers.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01511.

Figures S1–S9 and Table S1 (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

T.C. acknowledges support from NRF-Korea (2015R1A2A2A01004974). F.U. acknowledges support from the Operational Programme Research, Development and Education (CZ.02.1.01/0.0/0.0/15_003/0000417) and access to the CERIT-SC computing facilities (LM2015085).

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