

# Synthesis and Characterization of Comb-Shaped Ring Polystyrenes

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**ABSTRACT:** A series of comb-shaped ring polystyrene samples, RC, composed of a common ring backbone and multiple linear branches with three different lengths was successfully prepared. Firstly, a highly-purified ring backbone was synthesized by anionic polymerizations followed by multistep size exclusion chromatography (SEC) and interaction chromatography (IC) fractionations. Secondly, this backbone was reacted with excess molar amount of anionic living linear branch chains. Through the coupling reactions, the targeted RC samples were successfully obtained with high grafting efficiency without causing any side reactions. Their chain dimensions in THF were investigated by SEC-MALS measurements and they were evaluated by estimating the shrinking factor  $g^{1/2}$  ( $= R_{g,comb}/R_{g,linear}$ ). All RC samples prepared in this study exhibited smaller  $R_g$  and  $g^{1/2}$  values than those of the corresponding linear combs, LC. Moreover, combs with short branches exhibited an evidently larger  $g^{1/2}$  than the Gaussian chains due to the intramolecular excluded volume effects, being originated from the local high segment density in the vicinity of the branch points. In contrast,  $g^{1/2}$  for combs having long branches agreed reasonably well with the values based on the Gaussian approximation. This result suggests that the intramolecular excluded volume effect is weakened with increasing branch chain length, and consequently the comb behaves like a star polymer. Thus characteristic chain dimensions of comb-shaped ring samples have been clarified, which strongly depend on the branch chain length and the backbone architecture.

## Introduction

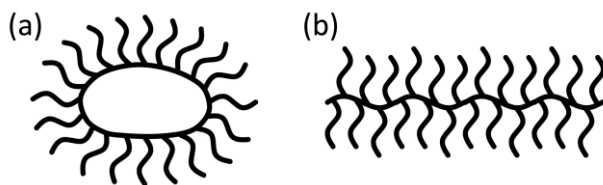
Polymer chain architectures greatly affect various physical properties of polymers. Ring polymers are one of the fascinating model polymers because they have no chain ends. Theoretical studies on the properties of ring polymers have been kept pursuing for more than 70 years.<sup>1-8</sup> Moreover, due to the development of synthesis<sup>9-12</sup> and purification<sup>13,14</sup> techniques of ring polymers, a large number of experimental studies<sup>15-35</sup> has been extensively examined up to date. These studies have revealed some interesting facts as below. In dilute solutions, ring chains have smaller size than the linear ones with the same molecular weights.<sup>15-17,31</sup> Moreover, under the  $\theta$  condition, in which the second virial coefficient  $A_2$  goes zero for linear polymers, rings exhibit positive  $A_2$  due to the topological repulsive interactions.<sup>17,29,34</sup> In bulk, pure rings do not show a rubbery plateau even though they have large molecular weights, and they exhibit much faster terminal relaxation than the linear counterparts.<sup>28,35</sup> This fact strongly suggests that the chain motion as well as the conformation of rings are totally different from those of linear chains.

Physical properties of polymers having featured structures, where linear chains are connected to a ring, are also intriguing. As an example, we recently prepared highly-purified tadpole-shaped polymers, where one or two linear chains are attached on a ring, and investigated their viscoelastic properties.<sup>36,37</sup> They were found to exhibit remarkably slower terminal relaxation than their component ring and linear chains due to characteristic intermolecular ring-linear penetrations. Therefore, introduction of linear chains onto rings might give a new possibility of generating distinctive physical properties.

Comb-shaped ring polymers, sometimes called sun-shaped or jellyfish-shaped polymers, are one of the model branched ring polymers, as schematically illustrated in Figure 1a. To understand their properties, comb polymers with a linear backbone could be a good reference, as shown in Figure 1b. There are several reports on the synthesis of the grafted rings,<sup>38-41</sup> but most of them hold uncertainty in

sample purities mainly due to the difficulty in a primary preparation of highly-purified ring backbones. In fact, Schappacher et al. confirmed that their samples included 50-60 % of ring combs and that the rest was the linear ones or some byproducts by direct observation for single molecules using atomic force microscopy (AFM).<sup>42-43</sup> Hence, to begin with, the preparation of comb-shaped ring samples having definite structures with guaranteed high purity is significant to investigate their physical properties accurately.

In this study, a series of comb-shaped ring polystyrenes having a common ring backbone and multiple linear branch chains with three different lengths was precisely synthesized by anionic polymerizations. The samples obtained were carefully characterized by size exclusion chromatography with a multi-angle light scattering detector, SEC-MALS measurements, where the chain dimensions of comb-shaped rings were evaluated in comparison with those for the corresponding linear combs.



**Figure 1.** Schematic illustrations of comb-shaped (a) ring and (b) linear polymer chains.

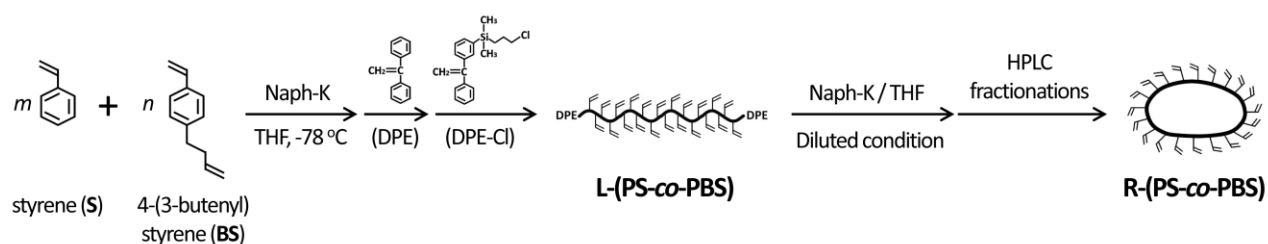
## Experimental Section

**Materials.** A series of comb-shaped ring polystyrene (PS) samples was anionically synthesized by chlorosilane coupling reactions between a ring backbone and multiple linear branches as described below. All operations were conducted in sealed glass apparatuses with breakseals under high-vacuum ( $\sim 1 \times 10^{-3}$  Pa). Styrene, tetrahydrofuran (THF), benzene, potassium naphthalenide (Naph-K), *sec*-butyllithium (*sec*-BuLi), 1,1-diphenylethylene (DPE) and 1-[3-(3-chloropropyl)dimethylsilyl]phenyl-1-phenylethylene] (DPE-Cl) were treated and purified as reported previously.<sup>44</sup> 4-(3-butenyl)styrene (Hokko Chemicals Co.) was dried over calcium hydride under reduced pressure and distilled from a solution of octylbenzophenon sodium. Chlorodimethylsilane (Aldrich, 98%) and dichloro(1,5-cyclooctadiene) platinum (II) ( $C_8H_{12}Cl_2Pt$ ; Aldrich, 98%) were diluted with benzene.

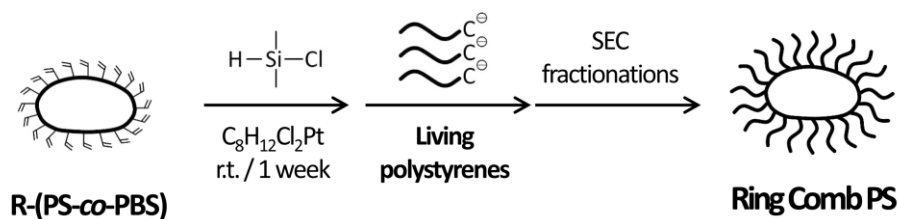
Scheme 1 shows a synthetic route to the ring backbone. A telechelic linear polymer backbone with DPE-type vinyl groups on both ends was synthesized from a mixed monomer of styrene (S) and 4-(3-butenyl)styrene (BS) (ca. 30/1 mol %) with Naph-K as an initiator in THF at  $-78$  °C. To introduce BS units randomly in the backbone, the mixed monomer (28 mL) was added very slowly as droplets little by little into the reactor containing THF solution of Naph-K in more than 10 min. This telechelic polymer, L-(PS-*co*-PBS), was cyclized in dilute solution of THF (ca. 0.1%) and the cyclized product obtained was separated by multi-step size exclusion chromatography (SEC) and interaction chromatography (IC) fractionations to isolate the ring backbone, R-(PS-*co*-PBS), as reported previously.<sup>36</sup> Scheme 2 shows a synthetic route to comb-shaped ring samples. Ruckenstein et al. reported the same method to prepare the comb-shaped polymers with a linear backbone.<sup>45</sup> Firstly, vinyl groups on BS units in the ring backbone were functionalized by the hydrosilylation reaction, i.e., a small amount of benzene solution of chlorodimethylsilane (ca. 1%) and that of  $C_8H_{12}Cl_2Pt$  were successively added to the ring backbone polymer in benzene (ca. 0.2%), and the solution was kept

stirring at a room temperature for one week. This solution was purified by freeze-drying. Secondly, three living linear PSs having different molecular weights were anionically synthesized from *sec*-BuLi as an initiator in benzene at room temperature or in THF at  $-78\text{ }^{\circ}\text{C}$ , and each of them was reacted with the backbone for more than 24 h. To fully introduce the branch chains toward all BS units on the backbone, excess molar amount of branches was added to the solution of the backbone. The coupling products were separated by SEC fractionations to exclude unreacted branch chains and thus to isolate the comb-shaped ring samples. The linear backbone was also reacted with each living linear PS to prepare comb-shaped linear polymers as reference samples. The linear and ring backbones denote LBB and RBB with their molecular weights in the unit of kg/mol, while linear and ring combs denote LC and RC with the molecular weight of a branch chain.

**Scheme 1. Synthetic scheme of a ring backbone**



**Scheme 2. Synthetic scheme of a comb-shaped ring polystyrene**



**Measurements.** The weight-average molecular weights,  $M_w$ , and the radii of gyration,  $R_g$ , for comb samples prepared in the present study were estimated by SEC with a multi-angle light scattering (MALS) detector, i.e., SEC-MALS measurements. The system was composed of a pump (Agilent 1100 pump; Agilent Technologies), a column oven (A0-30; Shodex), three SEC columns (KF-805L  $\times$  3; Shodex), a MALS detector (DAWN HELEOS II; wavelength  $\lambda = 658$  nm, Wyatt Technology), a UV detector (SPD-20A; Simadzu Co.) and a refractometer (Optilab T-rEX; Wyatt Technology). The eluent used was THF and the operation was carried out at the flow rate of 1.0 mL/min. The column temperature was kept constant at 40 °C. The refractive index increment,  $dn/dc$ , for all samples in THF adopted was 0.185 cm<sup>3</sup>/g from a handbook.<sup>46</sup> The molecular weight distribution,  $M_w/M_n$ , of all samples was determined from SEC measurements in the same manner as reported previously.<sup>36</sup> The purity of the ring backbone was estimated by IC measurements using octadecylsilyl (ODS) silica gel columns and a mixed eluent of dichloromethane and acetonitrile at the ratio of 59/41 in volume. The details of the experimental condition were described previously.<sup>47</sup> The number of 4-(3-butenyl)styrene units in the backbones was estimated from <sup>1</sup>H-NMR measurements with an Ascend 500 NMR spectrometer (Bruker) in CDCl<sub>3</sub>.

## Results and Discussion

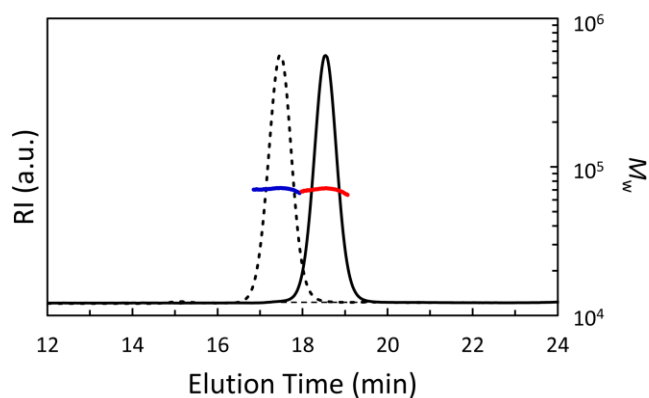
A telechelic linear backbone being randomly composed of styrene (S) and a small fraction of 4-(3-butenyl)styrene (BS) (LBB-70;  $M_w = 70.9$  kg/mol,  $M_w/M_n = 1.01$ ) was anionically synthesized. A ring backbone, RBB-70, was prepared by the cyclization of LBB-70 followed by multi-step SEC and IC fractionations in the same manner as reported previously.<sup>36</sup> The details of the preparation of RBB-70 were described in the Supporting Information, and the final yield of RBB-70 was 0.43 g. Figure 2 shows SEC chromatograms of linear (left) and ring (right) backbones representing simultaneously their weight-average absolute molecular weights,  $M_w$ , displayed by blue and red curves, respectively, which are referred to the right axis. It is evident that the peak for the ring backbone with narrow distribution eluted slower than that for the linear one, while their molecular weights are almost the same. IC chromatograms for the linear and ring backbones are compared in Figure 3. Note that the peaks eluted at 6-8 min are originated from solvents. This figure shows that the peaks for LBB-70 and RBB-70 are separated well. In Figure 3b, a small peak eluted at 8-12 min, which corresponds to the linear contaminations, was detected and the purity of RBB-70 was estimated to be 99.8%. Figure 4a and 4b show  $^1\text{H-NMR}$  spectra of the linear and ring backbones. From the peak area ratio in these spectra and the molecular weights of the backbones, the numbers of functional vinyl groups,  $N_f$ , in the linear and ring backbones were estimated to be approximately 24 and 22, respectively. This difference is consistent with the initial molecular design, i.e., the linear precursor has two extra double bonds originated from DPE on two chain ends. Molecular characteristics of the linear and ring backbones are summarized in Table 1, expressing that a pair of linear and ring backbones with the same molecular weights and the same number of BS units was obtained.



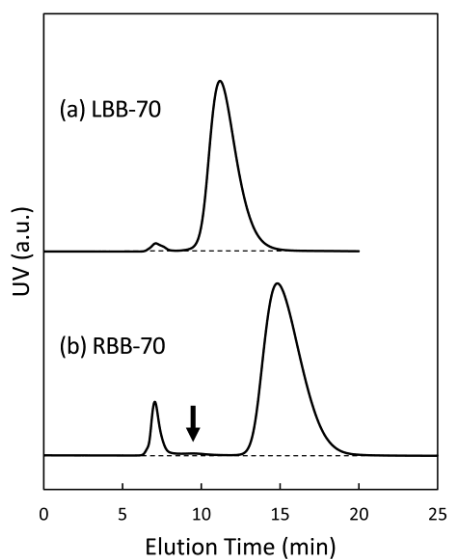
**Table 1. Molecular characteristics of linear and ring backbones**

Sample	$10^{-3}M_w^a$	$M_w/M_n^b$	$N_f^c$	purity <sup>d</sup>
LBB-70	70.9	1.01	24	-
RBB-70	70.5	1.01	22	99.8%

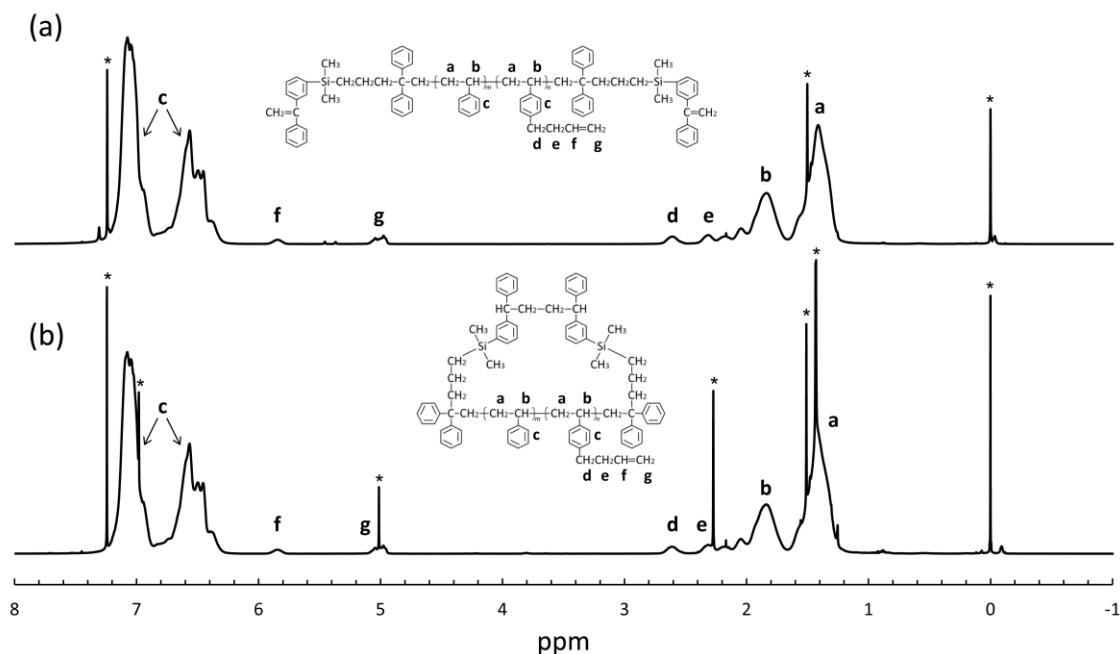
Estimated from <sup>a</sup>SEC-MALS, <sup>b</sup>SEC, <sup>c</sup><sup>1</sup>H-NMR and <sup>d</sup>IC measurements



**Figure 2.** SEC chromatograms of LBB-70 as a dashed curve and RBB-70 as a solid curve showing their absolute molecular weights, displayed by blue and red curves, respectively.



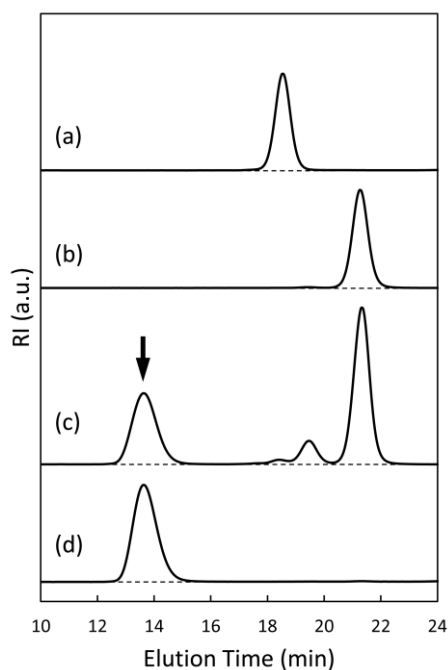
**Figure 3.** IC chromatograms of (a) LBB-70 and (b) RBB-70. The arrow indicates where the peak of linear contaminations is eluted.



**Figure 4.**  $^1\text{H}$ -NMR spectra for (a) LBB-70 and (b) RBB-70 in  $\text{CDCl}_3$ .

By utilizing the linear and ring backbones, three grafting reactions were performed. That is, three living linear PSs with different lengths (designed as 20, 40 and 80 kg/mol, denoting L-20, L-40 and L-80, respectively) were prepared as branch chains, and each of them was reacted with the backbones functionalized by the hydrosilylation reaction. All branch chains are confirmed to possess narrow molecular weight distribution with  $M_w/M_n$  of less than 1.03. As an example, Figure 5 compares SEC chromatograms showing the process of preparation of a comb-shaped ring sample, RC-20, through a grafting reaction between RBB-70 (0.075 g;  $1.1 \times 10^{-6}$  mol) and excess molar amount of L-20 ( $M_w = 19.2$  kg/mol, 1.0 g;  $5.2 \times 10^{-5}$  mol), followed by SEC fractionations. Figure 5a and 5b represent the peaks of RBB-70 and L-20, respectively. After the grafting reaction, a new peak which is considered to be a grafted comb product has appeared at a shorter elution time of 13~15 min in Figure 5c, in addition

to the peaks originated from the excess amount of unreacted linear branch chains appeared at 18~22 min. Since the new peak is a unimodal shape, any side reactions such as a scission of the ring backbone were not convinced to occur. To isolate this grafting product, SEC fractionations were performed. The SEC chromatogram of the purified product was displayed in Figure 5d. It was found that the unreacted branch chains were sufficiently excluded and that the grafting product was isolated. The yield of the isolated product was 0.28 g. The absolute molecular weight of the product in Figure 5d was estimated to be 434 kg/mol from SEC-MALS measurements. The number of branch chains introduced in this comb sample,  $p$ , was calculated to be 18.9 by using the following relation:  $p = (M_{w,\text{total}} - M_{w,\text{bb}})/M_{w,\text{br}}$ , where  $M_{w,\text{total}}$  is the total molecular weight of the comb sample,  $M_{w,\text{bb}}$  and  $M_{w,\text{br}}$  are the molecular weights of the backbone and a branch chain, respectively. This result implies that the grafting reaction proceeds with high efficiency, indicating the targeted comb-shaped ring sample, RC-20, was successfully obtained.



**Figure 5.** SEC chromatograms of RC-20 through a grafting reaction and purification: (a) RBB-70, (b) L-20, (c) a coupling product and (d) the isolated RC-20.

In the same manner, three comb-shaped ring samples with different branch lengths as well as the linear counterparts were prepared. The yield of all comb samples finally obtained was around 0.1 g. Their molecular characteristics were summarized in Table 2. All comb samples except RC-80 were confirmed to possess high purity over 98% by SEC measurements, while RC-80 have slightly lower purity due to a certain fraction of unreacted branches. However, this small amount of contamination is not conceived to affect seriously its dilute solution properties investigated in this study.

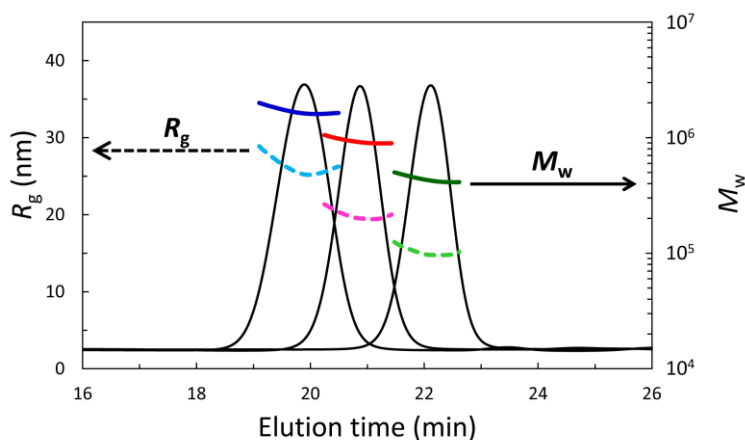
**Table 2. Molecular characteristics of a series of LC and RC samples**

Sample	$10^{-3}M_{w,\text{total}}^a$	$M_w/M_n^b$	$10^{-3}M_{w,\text{br}}^a$	$p^c$	Purity <sup>d</sup>
LC-20	491	1.02	20.2	21	99.6
RC-20	434	1.03	19.2	19	99.7
LC-40	1070	1.05	41.5	24	99.7
RC-40	929	1.04	41.5	21	98.8
LC-80	1630	1.08	75.9	21	99.1
RC-80	1690	1.13	84.5	19	96.4

Estimated from the main peak of final products by <sup>a</sup>SEC-MALS and <sup>b</sup>SEC measurements. <sup>c</sup> $p$ : the average number of branch chains calculated from  $p = (M_{w,\text{total}} - M_{w,\text{bb}})/M_{w,\text{br}}$ . <sup>d</sup>Estimated from the peak area ratio between the main peak and the peaks of unreacted branches by SEC measurements.

Chain dimensions of the comb-shaped ring samples in a diluted THF solution were also evaluated by SEC-MALS measurements. Figure 6 shows SEC chromatograms for three RC samples, RC-20, RC-40 and RC-80, with their weight-average molecular weights,  $M_w$ , and radii of gyration,  $R_g$ , and all values estimated were summarized in Table 3. Note that errors for these values are convinced to be relatively small, i.e., the errors for  $M_w$  are within  $\pm 0.2\%$  and those for  $R_g$  are within  $\pm 1\%$  when  $R_g$  are larger than

20nm, while they are within  $\pm 3\%$  when  $R_g$  are smaller than 20 nm. The  $M_w$  and  $R_g$  values for linear PSs in THF measured under the same experimental conditions are summarized in Table S1 in the Supporting Information. The  $R_g$  values for the linear and ring backbones are thought to be smaller than 10 nm, and hence it is difficult to estimate their size accurately by using MALS detector. Therefore we cannot discuss this issue in this study.



**Figure 6.** SEC chromatograms of RC-80, RC-40 and RC-20 (from left to right) showing their absolute molecular weights as solid curves and radii of gyration as dashed curves in THF.

**Table 3. Dilute solution properties of LC and RC samples in THF**

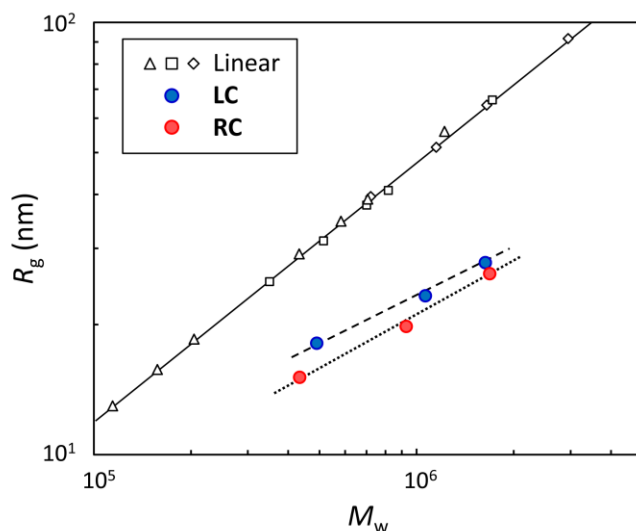
Sample	$10^{-3} M_w$	$R_g$ (nm)	$R_{g,\text{linear}}$ (nm) <sup>a</sup>	$g_{\text{exp}}^{1/2}$ <sup>b</sup>	$g_{\text{cal}}^{1/2}$ <sup>c</sup>
LC-20	491	18.1	30.9	0.58 <sub>5</sub>	0.49 <sub>5</sub>
RC-20	434	15.1	28.7	0.52 <sub>6</sub>	0.43 <sub>2</sub>
LC-40	1070	23.3	49.2	0.47 <sub>4</sub>	0.41 <sub>5</sub>
RC-40	929	19.8	45.3	0.43 <sub>7</sub>	0.39 <sub>6</sub>
LC-80	1630	27.8	63.6	0.43 <sub>7</sub>	0.41 <sub>5</sub>
RC-80	1690	26.2	64.8	0.40 <sub>4</sub>	0.40 <sub>0</sub>

<sup>a</sup>Calculated from the relationship,  $R_g = 0.0119 \times M_w^{0.60}$  (nm) in THF. <sup>b</sup>Shrinking factor  $g^{1/2} = R_{g,\text{comb}}/R_{g,\text{linear}}$  with the same  $M_w$ . <sup>c</sup>Calculated from eq. 3, which follow the Gaussian chain distribution.

Figure 7 compares the molecular weight dependence of the radii of gyration for LC and RC samples. The data for linear PSs including ours and those reported by Nakamura et al.<sup>48</sup> and Park et al.<sup>49</sup> are also plotted in the figure. All data for linear PSs are placed on a straight line, which corresponds to the following equation:

$$R_g = 0.0119 \times M_w^{0.60} \text{ (nm)} \quad \text{for linear PS in THF} \quad (1)$$

In contrast, both LC and RC samples exhibit clearly much smaller  $R_g$  values than the linear PSs, which must be originated from their branching structures. In particular,  $R_g$  for RC are even slightly smaller than those for the corresponding LC due to the difference in the backbone chain architecture. Moreover, the molecular weight dependence of  $R_g$  for RC seems weaker than that for linear PSs. However, since the number of data points for both LC and RC is limited, it is not appropriate to discuss their dependence qualitatively here.



**Figure 7.** Molecular weight dependence of  $R_g$  for LC (blue) and RC (red) samples, compared with linear PSs ( $\Delta$ : this work,  $\square$ : Nakamura et al.,<sup>48</sup>  $\diamond$ : Park et al.<sup>49</sup>) in THF. The dashed and dotted lines are simply guide for eyes.

Instead, the data obtained were discussed by estimating the comb/linear  $R_g$  ratio for PS with the same molecular weights, i.e., the shrinking factor,  $g^{1/2}$ , defined as

$$g^{1/2} = R_{g,\text{comb}}/R_{g,\text{linear}} \quad (2)$$

Note that  $R_{g,\text{linear}}$  for linear chains with the same molecular weights as combs were calculated from eq.1 and the values obtained are summarized at the fourth column in Table 3, successively,  $g^{1/2}_{\text{exp}}$  for the comb samples were estimated and summarized at the fifth column in Table 3. It has been found that  $g^{1/2}_{\text{exp}}$  decrease as branch chains become longer and that  $g^{1/2}_{\text{exp}}$  values for RC are smaller than those for the corresponding LC.

To discuss their chain dimension quantitatively,  $g^{1/2}$  for combs were calculated, where both the backbone and branches are assumed to follow the Gaussian chain distribution. Now we assume a comb polymer, whose  $p$  branch chains with the number of segments,  $N_{\text{br}}$ , are regularly attached on a linear backbone with  $N_{\text{bb}}$ , the total number of segments for one comb chain,  $N_{\text{total}}$ , being defined as  $N_{\text{total}} = N_{\text{bb}} + pN_{\text{br}}$ . The ideal mean square radius of gyration  $\langle S^2 \rangle = R_g^2$  for the comb is expressed by the Orofino equation:<sup>50</sup>

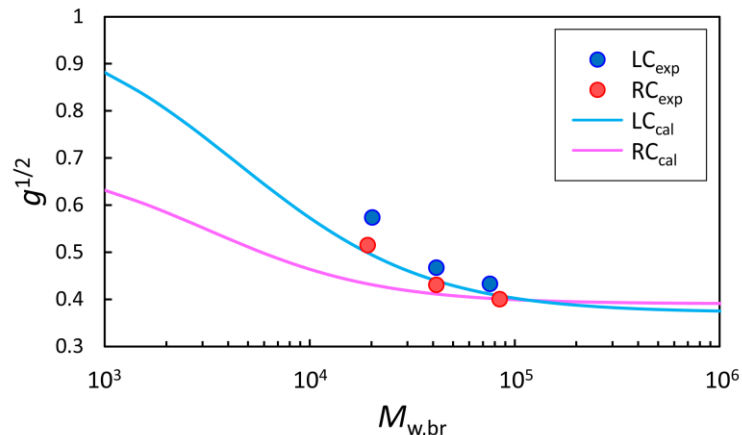
$$R_{g,\text{comb}}^2 = R_{g,\text{bb}}^2 (1 + \Phi_{\text{br}}/p^2) + R_{g,\text{br}}^2 (3 - 2/p) \Phi_{\text{br}} \quad (3)$$

where  $R_{g,\text{bb}}^2$  and  $R_{g,\text{br}}^2$  denote the mean square radii of gyration for the backbone and branch, respectively, and  $\Phi_{\text{br}}$  indicates the fraction of the branches, i.e.,  $\Phi_{\text{br}} = pN_{\text{br}}/N_{\text{total}}$ . By calculating the square root of the ratio of  $R_{g,\text{comb}}^2$  and  $R_{g,\text{linear}}^2 (= N_{\text{total}}b^2/6)$  at the same  $N_{\text{total}}$ , the shrinking factors,  $g^{1/2}_{\text{cal}}$ , were estimated and summarized at the sixth column in Table 3. Specifically, eq.3 is also available for comb-shaped ring polymers when  $R_{g,\text{bb}}^2$  is substituted for  $R_{g,\text{ring}}^2 = N_{\text{bb}}b^2/12$ ,<sup>2</sup> since the

contribution of the backbone and branches are conceived to be independent of each other in eq. 3. Since all the measurements carried out in this study were performed in a good solvent, a comparison of the present data with the calculated unperturbed Gaussian chains might not be appropriate. However,  $g^{1/2}$  values in good solvents are known to be close to those in  $\theta$  solvents for branched polymers with relatively simple branching structures such as star polymers.<sup>51</sup> Hence, in this study, the calculated  $g^{1/2}_{\text{cal}}$  for combs with the Gaussian chain distribution are compared with the values experimentally obtained in good solvents.

Figure 8 compares the branch chain length dependence of  $g^{1/2}$  for LC and RC samples. Two curves, a light blue and a light red ones, indicate the dependence for LC and RC calculated from eq.3, following the Gaussian chain distribution. Note that in this calculation the numbers of branch chains  $p$  for LC and RC were assumed to be constant as 21 and 19, respectively, to match with the actual molecular characteristics. It is evident from this figure that the present comb chains exhibit clearly larger  $g^{1/2}$  values than those for the Gaussian prediction when the branch chains are short. These results indicate that the branch and backbone chains are rather expanded due to the intramolecular excluded volume effect, which must be due to the local high segment density in the vicinity of the multiple branch points. In contrast, the experimental  $g^{1/2}_{\text{exp}}$  for combs with long branches, 80 kg/mol, are in good agreement with the calculated  $g^{1/2}_{\text{cal}}$  values. These facts suggest that the intramolecular excluded volume effect can be nearly neglected as simple star polymers for combs with long branches. Moreover, all RC samples used in this study exhibit smaller  $g^{1/2}$  values than the corresponding LC, suggesting that the difference in the backbone chain architecture definitely affects their chain dimensions within the molecular weight range adopted in this study.





**Figure 8.** Branch chain length dependences of experimental  $g^{1/2}_{\text{exp}}$  for LC (blue) and RC (red) samples, compared with those calculated from the Orofino equation (eq. 3) with Gaussian chain distribution.

In this paper, chain dimensions of a series of RC samples consisting of only one ring backbone were investigated. However, the number of branch chains as well as the length of backbone chains might affect their chain dimension in solution. Therefore, we are planning to examine these effects by preparing the other series of RC samples with different backbones.

## Conclusion

In this study, a series of comb-shaped ring polystyrene samples, RC, composed of a common ring backbone and multiple linear branches with three different lengths was prepared. Firstly, a ring backbone with high purity was synthesized by anionic polymerizations followed by multi-step SEC and IC fractionations. Secondly, this backbone was treated by a chlorosilane coupling agent and subsequently reacted with excess molar amount of living linear branch chains. Through the coupling reactions, the targeted RC samples were successfully obtained with high grafting efficiency without causing any side reactions. The chain dimensions of RC samples in THF were investigated by

SEC-MALS measurements. All RC samples used in this study exhibited smaller  $R_g$  and  $g^{1/2}$  values than the corresponding linear combs, LC. Moreover, combs with short branches exhibited evidently larger  $g^{1/2}$  values than the Gaussian chains due to the intramolecular excluded volume effects, being originated from the local high segment density in the vicinity of the branch points. In contrast,  $g^{1/2}$  for combs having long branches are close to the values based on the Gaussian approximation. This is probably because the intramolecular excluded volume effect is weakened with increasing the branch chain lengths, and consequently the comb behaves like a star polymer. Thus, characteristic chain dimensions of comb-shaped ring samples have been clarified that they evidently depend on the branch chain length and the backbone architecture.

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# Synthesis and Characterization of Comb-Shaped Ring

## Polystyrenes

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