Molecular weight determination of star polymers and star block copolymers using GPC equipped with low-angle laser light-scattering

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Abstract

Gel permeation chromatography equipped with a low-angle laser light-scattering detector (GPC-LALLS) was employed to determine the $M_n$ and $M_w$ of any polymer system such as flexible polymers (polystyrene, PSt), rod-like polymers (poly(o-hexylisocyanate), PIC), star polymers ($\text{PSt}_n$ and $\text{[poly(o-methylstyrene)]_4}$, (POMSt)$_4$), linear block copolymers (polystyrene-block-polyisoprene, PST-block-PIs) and star block copolymers ($\text{PSt}_4$-$\text{[PSt]}$-$\text{[PIs]}_7$). For the homopolymers (PSt, PIC, $\text{PSt}_n$ and $\text{(POMSt)}_4$), the determined $M_n$\textsubscript{GPC-LALLS} and $M_w$\textsubscript{GPC-LALLS} values are in good agreement with the $M_n$\textsubscript{OSM} and $M_w$\textsubscript{LS} values determined by osmometry and light scattering, respectively. For the block copolymers (PSt-block-PIs and $\text{PSt}_4$-$\text{[PSt]}$-$\text{[PIs]}_7$), two composition distributions (CDs) have to be considered: one is a CD among the different molecular weights and the other is a CD among the same molecular weights. Block copolymers are classified into four groups from the viewpoint of a combination of the two CDs. In any group, new analytical equations for determining $M_n$ and $M_w$ were derived by the assumption that the block copolymers, which appear at the same elution volume of the GPC chromatogram, have the same molecular weights. The resultant $M_n$\textsubscript{GPC-LALLS} values were in good agreement with the $M_n$\textsubscript{OSM} values. GPC-LALLS was found available for determining $M_n$ and $M_w$ of the block copolymers.

Keywords: Star block copolymers; Gel permeation chromatography; Low-angle laser light-scattering

1. Introduction

Having prepared new polymers such as star block copolymers [1–4], the molecular weight of the resultant polymers is the most important molecular characteristic for discussing the polymerization mechanism and the physical properties of the polymers. However, it appears difficult to determine number average-molecular weights ($M_n$) by osmometry and weight-average molecular weights ($M_w$) by light scattering (LS) of all polymers prepared. The reason is that we have to carry out the $M_n$ and $M_w$ determination of not only the final product but also a series of precursors that contain a main product, sub-products and monomer for the polymerization experiment. Before performing the absolute $M_n$ and $M_w$ determinations, the main product and sub-products have to be isolated from the mixture of the polymerization solution. Preferably, fractionation should be excluded [5–7]. Thus, $M_n$ and $M_w$ of the resultant polymers can be determined by conventional gel permeation chromatography (GPC) methods [8,9]; namely, using a calibration curve of the log(molecular weight) versus elution volume of standard polystyrenes. However, the determined molecular weights are different from the true molecular weights [10,11].

On the other hand, GPC equipped with a low-angle laser light-scattering detector (GPC-LALLS) has been commonly utilized [12,13]. Although GPC-LALLS is available for determining $M_w$, $M_n$ cannot be determined by conventional methods. In addition, there is a question if it is possible to determine the $M_w$ of block copolymers having a composition distribution (CD) [14] by GPC-LALLS. A systematic study of applying GPC-LALLS to the $M_n$ and $M_w$ determination of any polymer system has not been reported theoretically and experimentally. For any polymer system such as flexible polymers, rod-like polymers, star polymers, linear block copolymers and star block copolymers, a general approach for determining $M_n$ and $M_w$ is described in this paper.
2. Experimental

2.1. Polymers

Poly(styrene)s (PSt) were purchased as standard PSts (TSK polystyrenes, Tosoh Co.). Poly(n-hexylisocyanate)s (PIC), \(-[\text{N(C}_6\text{H}_{13})_2]-\text{CO}]_n-\), were prepared \([15,16]\) in toluene at \(-20^\circ\text{C}\) using a titanium compound (TiCl\(_3\)) as the catalyst as reported by Novak \([17]\). Two star polymers of PSt, \((\text{PSt})_n\), were, respectively, prepared \([18, 19]\) using n-BuLi in THF at \(-78^\circ\text{C}\) and s-BuLi in benzene at room temperature by anionic living polymerization of (4-vinylbenzyl)poly(styrene) macromonomer \((M_\text{n} = 4.7_1 \times 10^3, M_w/M_\text{n} = 1.0_3)\). A four-arm star polymer of PSt \((\text{PSt})_4\) was prepared \([20,21]\) by a coupling reaction of \(\text{PSt}^-\text{Li}^+\) \((M_\text{n} = 1.4_8 \times 10^3, M_w/M_\text{n} = 1.0_3)\) with 1,2-bis(trichlorosilyl)ethane in benzene at room temperature under high vacuum. A four-arm star polymer of poly(\(\alpha\)-methylstyrene) \((\text{PoMS}t)_4\) was prepared \([22–25]\) by reacting \((p\text{-isopropenylphenethyl})\text{poly}(\alpha\text{-methylstyrene})\) macromonomer \((M_\text{n} = 1.8_3 \times 10^3, M_w/M_\text{n} = 1.0_3)\) with a sodium mirror in THF at room temperature under high vacuum. A linear block copolymer of poly(styrene)-block-poly(isoprene) \((\text{PSt-block-PIs})\) was prepared \([22,23]\) by reacting \((p\text{-(4-methylpent-3-enyl)methyl})\text{poly}(\alpha\text{-methylstyrene})\) macromonomer \((M_\text{n} = 7.1_0 \times 10^3, M_w/M_\text{n} = 1.0_2)\) and \((p\text{-isopropenylphenethyl})\text{poly(isoprene)}\) macromonomer \((M_\text{n} = 6.2_4 \times 10^3, M_w/M_\text{n} = 1.0_2)\) \([19,26,27]\).

2.2. Molecular characterization

All polymer samples were tested on gel permeation chromatography (GPC; Model CCPPD, Tosoh Co., Tokyo, Japan) equipped with a low-angle laser light-scattering (LALLS) detector (Model LS-8000, Tosoh Co.), a refractive index (RI) detector (RI-8010, Tosoh Co.) and an ultraviolet (UV) detector (UV-8011, Tosoh Co.). High-resolution columns (7.8 mm i.d. x 60 cm; Tosoh Co.) were used for the GPC measurements. Number average molecular weights \((M_\text{n}^\text{OSM})\) of the samples were determined by osmometry in toluene at \(30^\circ\text{C}\) using a high-speed membrane osmometer (Mechrolab Model 502, Hewlett-Packard Co., New York, USA). Weight-average molecular weights \((M_\text{w}^\text{LS})\) of the samples were determined by LS in benzene at \(30^\circ\text{C}\) using a LS instrument (DLS-7000, Otsuka Electronics Co., Tokyo, Japan).

3. Results and discussion

3.1. Estimation of appropriate sample concentration in GPC-LALLS experiments

Rayleigh ratio \((R_\theta)\) of a polymer solution is well known as follows:

\[
K\frac{C}{R_\theta} = \frac{1}{M_\text{w}} \left[ 1 + \frac{1}{3}k^2(x^2) + \cdots \right] + 2A_2C + 3A_3C^2 + \cdots
\]

where all symbols are known in a LS experiment \([28–30]\).

When carrying out a LALLS experiment, attention should be called to the two terms, scattering angle dependence and concentration dependence. For the first term as \(1 + (1/3)k^2(x^2) + \cdots\), the LALLS instrument used in the present paper has a scattering angle of \(5^\circ\). In the case of PSt with \(M_\text{w} = 10^6\) or \(M_\text{w} = 10^7\), this term is calculated to 1.000 or 1.009, respectively. Hence, as a first approximation, the scattering angle dependence should be neglected in determining \(M_\text{w}\) which is less than \(10^6\) within an experimental error of 0.1%.

On the other hand, the second term, \(2A_2C + 3A_3C^2\), might play an important role in determining \(M_\text{n}\) \([31]\). A simple estimation of \(2M\text{St}_2A_2C\) for PSt was carried out. The sampling volume of the present GPC-LALLS instrument is 100 \(\mu\text{L}\), and the resultant PSt chromatogram is eluted in the range of about 2 ml of carrier solvent. The original polymer solution is apparently diluted about 20 times. When a PSt solution of 0.5% concentration is injected into the GPC-LALLS, the experimental error of less than 1.5%.

We carried out the GPC-LALLS experiments under the above conditions.

3.2. Determination of \(M_\text{n}\) and \(M_\text{w}\) for homopolymers

3.2.1. Poly(styrene)

Assume an unknown sample that has the same RI increment as that of PSt, \((dn/dc)_{PSt}\), as an example of the PSt star polymers. The signals of the RI detector (\(H_i^{RI}\)) and the LALLS detector (\(H_i^{LS}\)) of the corresponding RI and the LALLS chromatograms at the \(i\)th elution volume are, respectively, described as follows:

\[
H_i^{RI} = k_{RI}(dn/dc)_{PSt}C_i
\]

\[
H_i^{LS} = k_{LS}[(dn/dc)_{PSt}]^2M_iC_i
\]

where \(C_i\) and \(M_i\) are the concentration and molecular weight of the unknown sample at the \(i\)th elution volume,
respectively, and \( k_{RI} \) and \( k_{LS} \) are instrumental constants of the RI and LALLS detectors, respectively. From Eqs. (2) and (3), \( M_i \) can be derived. The resultant \( M_i \) is called \( M_i^{d/n}(dc) \) as follows:

\[
M_i^{d/n}(dc) = \frac{(H_{i,S}^R / H_{i,L}^R) (k_{LS}/k_{RI})(d/n)(dc)_{PSL}}{-1}
\]  

(4)

The instrumental factor of \([k_{LS}/k_{RI}] (d/n)(dc)_{PSL}^{-1} \) can be determined for a series of standard PSTs. That is, the summation from \( i \) equal to the initial value of the RI chromatogram to \( i \) equals the final value of the RI chromatogram of both sides of Eq. (2) leads to \( A_{RI} = k_{RI}(d/n)(dc)_{PSL}C \). Based on the same procedure, the summation of both sides of Eq. (3) leads to \( A_{LS} = k_{LS}(d/n)(dc)_{PSL}C \). In these equations, \( A_{RI} \) and \( A_{LS} \) are the peak-areas of the RI and LALLS chromatograms, respectively, and \( C \) is the concentration of the polymer sample. From each of the two corresponding analyses \( k_{RI}(d/n)(dc)_{PSL} \) and \( k_{LS}(d/n)(dc)_{PSL} \) can be determined independently, and hence the instrumental factor of \([k_{LS}/k_{RI}] (d/n)(dc)_{PSL}^{-1} \) can also be known. Therefore, the number average molecular weight (\( M_{GPC-LS}^{n}(d/n) \)) and the weight average molecular weight (\( M_{GPC-LS}^{w}(d/n) \)) can be calculated by substitution of \( M_i^{d/n}(dc) \) in each of the following two equations

\[
M_{n}(d/n) = \sum H_{RI}^n / \sum (H_{RI}^n / M_i^{d/n}(dc))
\]  

(5)

\[
M_{w}(d/n) = \sum H_{RI}^n M_i^{d/n}(dc) / \sum H_{RI}^n
\]  

(6)

As shown in Table 1, the resultant molecular weights of \( M_{n}(d/n) \) and \( M_{w}(d/n) \) for four PSTs in a molecular weight range of 0.91 \( \times 10^2 \)–35.4 \( \times 10^9 \) are in good agreement with the \( M_{n}^{LS} \) and \( M_{w}^{LS} \) determined by the LS experiments.

3.2.2. Homopolymers having \((d/n)(dc)_{unknown} \)

Assume an unknown sample which has a RI increment different from that of PST, \((d/n)(dc)_{unknown} \). For example, the PIC [15,16] and a four-arm PMS star polymer [23–25]. The RI signal and the LALLS signal of the corresponding RI and LALLS chromatograms at the ith elution volume are as follows:

\[
H_{RI}^i = k_{RI}(d/n)(dc)_{unknown} C_i
\]  

(7)

\[
H_{i,S}^R = k_{LS}(d/n)(dc)_{unknown}^2 M_i C_i
\]  

(8)

The \((d/n)(dc)_{unknown} \) value is not known because of the new polymer. Hence, from the ratio of the square of Eqs. (7) and (8), \((d/n)(dc)_{unknown} \) was eliminated to yield \( M_i \). The resultant \( M_i \) is called \( M_i^{C} \) as follows:

\[
M_i^{C} = [(H_{i,S}^R / H_{i,L}^R)^2] (k_{LS}/k_{RI})^{-1} C_i
\]  

(9)

The instrumental factor of \([k_{LS}/k_{RI}] \) can be determined by the same procedure as that of \([k_{LS}/k_{RI}] (d/n)(dc)_{PSL}^{-1} \). \( C_i \) can be known as \( C_i = C(H_{i,L}^R / \sum H_{i,L}^R) \). Hence, \( M_{n}^{GPC-LS} \) and \( M_{w}^{GPC-LS} \) can be calculated by substitution of \( M_i^{C} \) in Eqs. (5) and (6), respectively.

This analysis can be applied to any homopolymer system even if the \((d/n)(dc)_{unknown} \) values of the homopolymers are not known. Although the \((d/n)(dc)_{PSL} \) of PST is commonly known, a series of PSTs was employed for determining whether this analysis can be applied to determining \( M_n \) and \( M_w \). As shown in Table 1, the resultant \( M_{n}^{GPC-LS} \) and \( M_{w}^{GPC-LS} \) values for four PSTs are in good agreement with \( M_{n}^{LS} \) and \( M_{w}^{LS} \) determined by LS.

As a second sample, PIC that may be obtained as rod-like polymers [16,32] was employed for determining the validity of the present analysis. The results are shown in Table 2, where the PST-reduced \( M_n \) (\( M_{n}^{GPC} \)) and \( M_w \) (\( M_{w}^{GPC} \)) values of the PIC that were determined by the conventional GPC methods using a calibration curve for standard PSTs are also described. The resultant \( M_{n}^{GPC-LS} \) and \( M_{w}^{GPC-LS} \) values for the five PIC samples having molecular weights in a range of 10 \( \times 10^2 \)–670 \( \times 10^9 \) are in good agreement with the \( M_{n}^{OSM} \) and \( M_{w}^{OSM} \) values determined by osmometry and LS, respectively. As expected for rod-like polymers, the following facts were confirmed, \( M_{n}^{GPC} > M_{n}^{OSM} = M_{n}^{GPC-LS} \) and \( M_{w}^{GPC} > M_{w}^{OSM} = M_{w}^{GPC-LS} \). The \( M_{n}^{GPC} / M_{n}^{OSM} \) value and \( M_{w}^{GPC} / M_{w}^{OSM} \) value for PIC-5 appear small, as compared with those for the other PIC samples. This fact suggests that the PIC molecule is rod-like in the lower-molecular-weight range and approaches a spherical random coil as the molecular weight increases [32,33]. As not expected, it was found that \( M_{n}^{GPC} / M_{n}^{GPC-LS} > M_{w}^{GPC} / M_{w}^{GPC-LS} \). This gap between the three \( M_n / M_w \) values appear to become large with an increase in the \( M_n / M_w \) values.

### Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(10^{-3} M_n^{LS} ) by light scattering*</th>
<th>(10^{-3} M_n^{GPC} ) using ( M_n^{d/n}(dc) ) in Eq. (4)</th>
<th>(10^{-3} M_n^{GPC-LS} ) using ( M_n^{C} ) in Eq. (9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PST-1</td>
<td>8.92 ( M_n )</td>
<td>8.80 ( M_n )</td>
<td>8.81 ( M_n )</td>
</tr>
<tr>
<td>PST-2</td>
<td>36.4 ( M_n )</td>
<td>35.3 ( M_n )</td>
<td>35.4 ( M_n )</td>
</tr>
<tr>
<td>PST-3</td>
<td>10.0 ( M_n )</td>
<td>10.0 ( M_n )</td>
<td>10.0 ( M_n )</td>
</tr>
<tr>
<td>PST-4</td>
<td>34.2 ( M_n )</td>
<td>35.0 ( M_n )</td>
<td>35.0 ( M_n )</td>
</tr>
</tbody>
</table>

* The values were provided by Tosoh Co.: \( M_n^{LS} \) was determined by LS. The \( M_n^{GPC} / M_n^{OSM} \) value was determined by the conventional GPC methods using a calibration curve of the standard PSTs and \( M_n^{LS} \) was calculated by \( M_n^{LS} (M_n^{GPC} / M_n^{OSM})^{-1} \).
### Table 2
Molecular weights of PIC determined by the conventional GPC methods, osmometry, LS, and GPC-LALLS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n^\text{GPC}$</th>
<th>$M_w^\text{GPC}$</th>
<th>$M_n^\text{GPC}/M_w^\text{GPC}$</th>
<th>$M_n^\text{OSM}$</th>
<th>$M_w^\text{OSM}$</th>
<th>$M_n^\text{LS}$</th>
<th>$M_w^\text{LS}$</th>
<th>$M_n^\text{GPC}/M_w^\text{GPC}$</th>
<th>$M_n^\text{OSM}/M_w^\text{OSM}$</th>
<th>$M_n^\text{GPC}/M_w^\text{GPC}$</th>
<th>$M_n^\text{OSM}/M_w^\text{OSM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIC-1</td>
<td>123</td>
<td>1572</td>
<td>126</td>
<td>113</td>
<td>136</td>
<td>139</td>
<td>140</td>
<td>1.49</td>
<td>1.51</td>
<td>1.30</td>
<td>1.32</td>
</tr>
<tr>
<td>PIC-2</td>
<td>492</td>
<td>8615</td>
<td>141</td>
<td>326</td>
<td>414</td>
<td>1.03</td>
<td>1.08</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
<td>1.03</td>
</tr>
<tr>
<td>PIC-3</td>
<td>123</td>
<td>1400</td>
<td>1.15</td>
<td>484</td>
<td>500</td>
<td>1.08</td>
<td>1.06</td>
<td>1.08</td>
<td>1.08</td>
<td>1.06</td>
<td>1.06</td>
</tr>
<tr>
<td>PIC-4</td>
<td>205</td>
<td>2348</td>
<td>1.14</td>
<td>100</td>
<td>100</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>PIC-5</td>
<td>548</td>
<td>996</td>
<td>1.82</td>
<td>682</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

$^a$ Determined using a calibration curve of $\log M$ versus elution volume for standard PSTs.
$^b$ $M_n^{\text{OSM}}$ and $M_w^{\text{LS}}$ were determined by osmometry and LS, respectively.
$^c$ Determined by vapor pressure osmometry.
$^d$ Determined by a conventional LALLS method using a peak area of the LALLS chromatogram.

As the third and fourth samples, three PST star polymers, (PS)₆, and a four-arm star polymer, (PMSt)₄, were employed for determining the validity of the present analysis. As shown in Table 3, the resultant $M_n^{\text{GPC}}, M_w^{\text{GPC}}, M_n^{\text{GPC}/M_w^{\text{GPC}}}$ values for three PSTs and a (PMSt)₄ sample are in good agreement with $M_n^{\text{OSM}}, M_w^{\text{LS}}, M_n^{\text{LS}}, M_w^{\text{LS}}$ values. As expected for star polymers, the following facts were confirmed, $M_n^{\text{GPC}} < M_n^{\text{OSM}} = M_n^{\text{GPC}/C}$ and $M_w^{\text{GPC}} < M_w^{\text{LS}} = M_w^{\text{GPC}/C}$. These inequalities are opposite those for PIC. These findings are shown in Fig. 1, where the $M_n^{\text{GPC}/C}$ (or $M_n^{\text{OSM}}$) and $M_w^{\text{GPC}/C}$ (or $M_w^{\text{LS}}$) values are plotted against the $M_n^{\text{GPC}}$ and $M_w^{\text{GPC}}$, respectively. This figure corresponds to a general fact that when each of the three polymer systems having the corresponding molecular architecture has the same molecular weight, each has a different molecular dimension; namely, rod-like polymers > flexible polymers > star polymers.

### Table 3
Molecular weights of the star polymers for (PS)₆ and (PMSt)₄ determined by the conventional GPC methods, osmometry, LS, and GPC-LALLS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n^{\text{GPC}}$</th>
<th>$M_w^{\text{GPC}}$</th>
<th>$M_n^{\text{GPC}/M_w^{\text{GPC}}}$</th>
<th>$M_n^{\text{OSM}}$</th>
<th>$M_w^{\text{OSM}}$</th>
<th>$M_n^{\text{LS}}$</th>
<th>$M_w^{\text{LS}}$</th>
<th>$M_n^{\text{GPC}/C}$</th>
<th>$M_w^{\text{GPC}/C}$</th>
<th>$M_n^{\text{GPC}/M_w^{\text{GPC}}}$</th>
<th>$M_n^{\text{OSM}/M_w^{\text{OSM}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS(3.6)</td>
<td>32</td>
<td>35</td>
<td>1.03</td>
<td>42.6</td>
<td>46.6</td>
<td>1.03</td>
<td>1.03</td>
<td>44.4</td>
<td>47.3</td>
<td>1.03</td>
<td>1.03</td>
</tr>
<tr>
<td>PS(1.0)</td>
<td>35</td>
<td>39</td>
<td>1.11</td>
<td>46.1</td>
<td>49.6</td>
<td>1.07</td>
<td>1.07</td>
<td>46.4</td>
<td>48.8</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>PS(3.0)</td>
<td>44</td>
<td>45.5</td>
<td>1.02</td>
<td>58.6</td>
<td></td>
<td></td>
<td></td>
<td>54.3</td>
<td>57.2</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>PMSt(3.0)</td>
<td>4.50</td>
<td>5.00</td>
<td>1.11</td>
<td>7.8</td>
<td>8.4</td>
<td>1.11</td>
<td>1.11</td>
<td>7.42</td>
<td>8.13</td>
<td>1.11</td>
<td>1.11</td>
</tr>
</tbody>
</table>

$^a$ Determined using a calibration curve of $\log M$ versus elution volume for standard PSTs.
$^b$ $M_n^{\text{OSM}}$ and $M_w^{\text{LS}}$ were determined by osmometry and LS, respectively.
$^c$ Determined by vapor pressure osmometry.
$^d$ Determined by a conventional LALLS method using a peak area of the LALLS chromatogram.
among the same molecular weights. When a CD among the same molecular weights was not considered, one has to consider the molecular weight, the RI increment and the concentration of the block copolymer which appears at the i\textit{th} elution volume as \( M_i, (dn/dc)_i, \) and \( C_i \) respectively. When two CDs among the different molecular weights and the same molecular weights have to be considered, we shall consider the molecular weight, the RI increment and the concentration of the block copolymer at the j\textit{th} elution volume as \( M_{ij}, (dn/dc)_{ij}, \) and \( C_{ij} \) respectively. That is, the block copolymer has a molecular weight distribution and two CDs: the former can be represented by the subscript i, and the latter can be represented by a combination of a series of subscript i with subscript j. The combination of a series of the subscript j with a certain subscript i corresponds to a CD among the same molecular weights. In contrast, a combination of a series of the subscript i with a certain subscript j corresponds to a molecular weight distribution of the block copolymer having a certain CD represented by the subscript j. An average composition at a certain subscript i can be experimentally determined, and the resultant composition should be dependent on the subscript j. Therefore, the RI signal (\( H_i^{RI} \)) and the LALLS signal (\( H_i^{LS} \)) of the corresponding RI and LALLS chromatograms of the block copolymers at the i\textit{th} elution volume are described as follows, in the similar formulas of Eqs. (2) and (3), respectively

\[
H_i^{RI} = k_{RI} \sum_j (dn/dc)_{ij} C_{ij} \\
H_i^{LS} = k_{LS} \sum_j [(dn/dc)_{ij}]^2 M_{ij} C_{ij}
\]

The block copolymers should be classified into four groups in accordance with the two CDs. (i) The block copolymer has no CD regarding i (among the different molecular weights) and j (among the same molecular weights); namely, \( w_i^{PSt} = w_i^{Pic} \) and \( (dn/dc)_{ij} = (dn/dc)_i \). (ii) The block copolymer has a CD regarding i and no CD regarding j; namely, \( w_i^{PSt} \neq w_i^{Pic} \) and \( (dn/dc)_{ij} = (dn/dc)_i \). (iii) The block copolymer has no CD regarding i and a CD regarding j; namely, \( w_i^{PSt} = w_i^{Pic} \) and \( (dn/dc)_{ij} \neq (dn/dc)_i \). (iv) The block copolymer has a CD regarding i and a CD regarding j; namely, \( w_i^{PSt} \neq w_i^{Pic} \) and \( (dn/dc)_{ij} \neq (dn/dc)_i \). The group (i) is the simplest case; namely, \( H_i^{RI} \) in Eq. (10) and \( H_i^{LS} \) in Eq. (11) coincides with \( H_i^{RI} \) in Eq. (2) and \( H_i^{LS} \) in Eq. (3), respectively. Hence, the same \( M_i^{C} \) as that in Eq. (9) could be derived to determine \( M_i^{GPC-LS} \) and \( M_i^{GPC-LS} \). Although group (ii) is more complex than group (i), \( H_i^{RI} \) and \( H_i^{LS} \) coincide with \( H_i^{RI} \) and \( H_i^{LS} \), respectively. Hence, the same \( M_i^{C} \) as that in Eq. (9) could be derived to determine the corresponding \( M_i^{GPC-LS} \) and \( M_i^{GPC-LS} \).

On the other hand, groups (iii) and (iv) seem to be complicated for calculating \( M_i \). As a first approximation, one can assume that \( M_{ij} = M_i \) as shown in Fig. 2, because the polymer chains having \( M_{ij} \) appeared at the same i\textit{th} elution volume. Therefore, \( M_{ij} \) in Eq. (11) can be moved as \( M_i \) outside of the summation of \( \sum_j \). By this treatment, the same derivation as that of Eqs. (4) and (9) led to the two corresponding \( M_i^{BC} \) and \( M_i^{BC} \) values for the block copolymers, respectively. The results are shown as follows:

\[
M_i^{BC} = \frac{k_{RI_i} \sum_j (dn/dc)_{ij} C_{ij}}{k_{LS_i} \sum_j [(dn/dc)_{ij}]^2 C_{ij}}
\]

![Fig. 1. Plots of \( M_i^{GPC-LS} \) versus \( M_i^{GPC} \) (open symbols), and those of \( M_i^{GPC-LS} \) versus \( M_i^{GPC} \) (closed symbols) for a series of PSt (O, ●), PIC (□, ■), and star polymers (△, ■). The results observed in the lower molecular weights side are shown in the inserted figure.](image1)

![Fig. 2. A schematic GPC chromatogram of a (PSt)\textsubscript{m}-star-(Pls)\textsubscript{n} block copolymer. The (PSt)\textsubscript{m}-star-(Pls)\textsubscript{n} molecules appeared at the i\textit{th} elution volume (having the same molecular weight) should have a CD; namely, this fact is shown in the figure.](image2)
With the relation of \( \sum C_{ij} = C_i \) in mind, the following two average values regarding \( j \) could be derived:

\[
\frac{\sum (dn/dc)_{ij} C_{ij}}{\sum j (dn/dc)_{ij} C_{ij}}
\]

where \( \langle \cdots \rangle \) means the average of the corresponding RI increments. Therefore, the corresponding equations of \( M_{w(\text{BC})} \) and \( M_{n(\text{BC})} \) became as follows:

\[
M_{w(\text{BC})} = \frac{(k_R)^2}{k_L} \frac{H^L}{H^R} \frac{\sum (dn/dc)_{ij} C_{ij}}{\sum j (dn/dc)_{ij} C_{ij}}\]

(13)

The results for the linear and star block copolymers [19, 27] are shown in Table 4. For PSt-block-PIs, the resultant \( M_{w(\text{BC})} \) and \( M_{n(\text{BC})} \) values are in good agreement with each other and with the \( M_{w(\text{OSM})} \) value. For (PSO\(_{12}\)-star-(PIs)\(_7\)), the resultant \( M_{w(\text{BC})} \) and \( M_{n(\text{BC})} \) values are in good agreement with each other and with the \( M_{w(\text{OSM})} \) value. On the other hand, the (PSO\(_{12}\) star polymer could be prepared as a precursor. The number average molecular weight \( (M_{n(\text{PSO})}) \) of (PSO\(_{12}\)) was determined by GPC-LALLS, and the PI composition \( (w_{\text{PIs}}) \) of (PSO\(_{12}\)-star-(PIs)\(_7\)) was determined by NMR. From these values, the number average molecular weight \( (M_{n(\text{PSO-star-PIs})}) \) of (PSO\(_{12}\)-star-(PIs)\(_7\)) was calculated as follows:

\[
M_{n(\text{PSO-star-PIs})} = M_{n(\text{PSO})} / (1 - w_{\text{PIs}})
\]

(17)

The resultant \( M_{n(\text{PSO-star-PIs})} \) value coincides with the \( M_{n(\text{BC})} \) and \( M_{n(\text{BC})} \) values. As mentioned above, it is difficult to determine the \( M_{w} \) of PSt-block-PIs and (PSO\(_{12}\)-star-(PIs)\(_7\)) by LS using more than three solvents. Hence, the comparison of the resultant \( M_{w(\text{BC})} \) and \( M_{n(\text{BC})} \) values with the \( M_{w(\text{OSM})} \) value were not carried out at the present time. It is worth noting that the \( M_{w(\text{BC})}/M_{n(\text{BC})} \) values are in good agreement with the \( M_{w(\text{OSM})}/M_{n(\text{OSM})} \) values determined by the conventional GPC experiment.

The assumption we made in the present analysis is that the polymers which appear at the same elution volume have the same molecular weights; namely, \( M_{ij} = M_i \). Strictly speaking, however, the relation between the molecular dimension in a solution and the molecular weight of PSt should be different from that of PIs, even if THF as a good solvent for PSt and PIs is used as the carrier solvent in the GPC experiment. In other words, the relation \( M_{ij} = M_i \) has to be examined experimentally before calculating \( M_{w(\text{BC})} \) and \( M_{n(\text{BC})} \). On the contrary, the finding that \( M_{w(\text{BC})} = M_{w(\text{OSM})} \) for the two block copolymers suggests that the relation \( M_{ij} = M_i \) was found to hold. That is, the CD among the same molecular weights should be sharp. If the block copolymers which have a broad CD among the same molecular weights are subjected to the present GPC-LALLS experiments, we would observe the fact that \( M_{w(\text{BC})} \neq M_{w(\text{OSM})} \). To determine whether the present expectation is observed, a further study is in progress.

4. Conclusion

For any polymer system such as flexible polymers, rod-like polymers, star polymers, linear block copolymer and star block copolymers, the general equations as \( M_{w(\text{BC})}/M_{n(\text{BC})} \) in Eq. (12) and \( M_{w(\text{BC})}/M_{n(\text{BC})} \) in Eq. (13) have been derived. That is, \( M_{w(\text{BC})}/M_{n(\text{BC})} \) in Eq. (4) and \( M_{w(\text{BC})}/M_{n(\text{BC})} \) in Eq. (9) for homopolymers, and \( M_{w(\text{BC})}/M_{n(\text{BC})} \) in Eq. (14) and \( M_{w(\text{BC})}/M_{n(\text{BC})} \) in Eq. (15) for block copolymers can be employed for determining \( M_{w(\text{OSM})}/M_{n(\text{OSM})} \) in Eq. (14) and \( M_{w(\text{OSM})}/M_{n(\text{OSM})} \) in Eq. (15), respectively.

Attention should be called to the two CDs of the block copolymers. It has been well known that the CDs among different molecular weights could be determined using RI and UV detectors. In contrast, the CDs among the same molecular weights could not be determined by GPC-LALLS using both the RI and UV detectors. This paper also did not present the CD determination among the same molecular weights.

Table 4. Molecular weights of a linear block copolymer, PSt-block-PIs, and a star block copolymer, (PSO\(_{12}\)-star-(PIs)\(_7\)), determined by osmometry and GPC-LALLS

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( 10^{-3} M_{w(\text{OSM})} )</th>
<th>( 10^{-3} M_{n(\text{BC})} ) using ( M_{w(\text{BC})} ) in Eq. (14)</th>
<th>( 10^{-3} M_{w(\text{BC})} ) using ( M_{n(\text{BC})} ) in Eq. (15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSt-block-PIs</td>
<td>( 19.4 )( ^a )</td>
<td>( 20.4 )</td>
<td>( 22.1 )</td>
</tr>
<tr>
<td>(PSO(_{12})-star-(PIs)(_7))</td>
<td>( 71.2 ) (72.0)(^a)</td>
<td>( 70.6 )</td>
<td>( 73.3 )</td>
</tr>
</tbody>
</table>

\(^a\) Determined by NMR: \( M_{n(\text{PSO-star-PIs})} = M_{w(\text{PSO})} / (1 - w_{\text{PIs}}) \), where \( w_{\text{PIs}} \) was determined by NMR.
weights. However, even if the CD among the same molecular weights is not known; namely, the both values of \((dn/dc)_{i,j}\) and \(C_{i,j}\) are not known at the present time, the summation of \(\sum_{j_i}(dn/dc)_{i,j}C_{i,j}\) and \(\sum_{j_i}[(dn/dc)_{i,j}]^2C_{i,j}\) could be determined by GPC-LALLS using the assumption of \(M_{i,j} = M_i\). Hence, the \(M^*_i\text{GPC-LS}\) and \(M^*_w\text{GPC-LS}\) values were determined.

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Appendix A

The RI signal of PST-block-PIs at the \(i\)th elution volume \(H_{i}^{\text{RI}}\) is the summation of the RI signals of the PST block \(H_{i}^{\text{RI PST}}\) and the PIs block \(H_{i}^{\text{RI PIs}}\). The UV signals at the \(i\)th elution volume \(H_{i}^{\text{UV}}\) are described by the same formula as that of the RI signals.

\[
H_{i}^{\text{RI}} = H_{i}^{\text{RI PST}} + H_{i}^{\text{RI PIs}} = k_{\text{PIS}}^{i}C_{i}^{\text{PST}} + k_{\text{PIs}}^{i}C_{i}^{\text{PIs}}
\]

\[
H_{i}^{\text{UV}} = H_{i}^{\text{UV PST}} + H_{i}^{\text{UV PIs}} = \epsilon_{\text{PST}}^{i}C_{i}^{\text{PST}} + \epsilon_{\text{PIs}}^{i}C_{i}^{\text{PIs}}.
\]

From these equations, the concentrations of the PST block \(C_{i}^{\text{PST}}\) and the PIs block \(C_{i}^{\text{PIs}}\) at the \(i\)th elution volume can be determined using the \(k_{\text{PIS}}^{i}, k_{\text{PIs}}^{i}, \epsilon_{\text{PST}}^{i}, \) and \(\epsilon_{\text{PIs}}^{i}\) values: these four instrumental constants could be previously determined by the GPC measurements of the PST and PIs homopolymers using the RI and the UV detectors. Therefore, the PIs composition of PST-block-PIs at the \(i\)th elution volume \(w_{i}^{\text{PIS}}\) can be calculated as follows:

\[
w_{i}^{\text{PIS}} = \frac{C_{i}^{\text{PIS}}}{C_{i}^{\text{PST}} + C_{i}^{\text{PIS}}} = \frac{\epsilon_{\text{PSt}}^{i}H_{i}^{\text{RI PST}} - k_{\text{PIS}}^{i}H_{i}^{\text{UV PST}}}{(\epsilon_{\text{PST}}^{i} - \epsilon_{\text{PIS}}^{i})H_{i}^{\text{RI PST}} + (k_{\text{PIS}}^{i}k_{\text{PSt}}^{i} - k_{\text{PIs}}^{i})H_{i}^{\text{UV PST}}}.
\]

The concentration of the PST-block-PIs at the \(i\)th elution volume can be calculated as the summation of the concentrations of the PST block \(C_{i}^{\text{PST}}\) and the PIs block \(C_{i}^{\text{PIs}}\). The result is described as follows:

\[
C_{i} = C_{i}^{\text{PST}} + C_{i}^{\text{PIS}} = \frac{(\epsilon_{\text{PST}}^{i} - \epsilon_{\text{PIS}}^{i})H_{i}^{\text{RI PST}} + (k_{\text{PIS}}^{i}k_{\text{PSt}}^{i} - k_{\text{PIs}}^{i})H_{i}^{\text{UV PST}}}{k_{\text{PIs}}^{i}\epsilon_{\text{PSt}}^{i} - k_{\text{PIS}}^{i}\epsilon_{\text{PIS}}^{i}}.
\]

References