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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(*n*-hexylisocyanate), PIC), star polymers ($(PSt)_n$ and [poly(α-methylstyrene)]$_4$, $(P\alpha MSt)_4$), linear block copolymers (polystyrene-*block*-polyisoprene, PSt-*block*-PIs) and star block copolymers ($(PSt)_4$-*star*-$(PIs)_7$). For the homopolymers (PSt, PIC, $(PSt)_n$ and $(P\alpha MSt)_4$), the determined $M_n^{\text{GPC-LS}}$ and $M_w^{\text{GPC-LS}}$ values are in good agreement with the M_n^{OSM} and M_w^{LS} values determined by osmometry and light scattering, respectively. For the block copolymers (PSt-*block*-PIs and $(PSt)_4$-*star*-$(PIs)_7$), 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 $M_{n\,\text{BC}}^{\text{GPC-LS}}$ values were in good agreement with the M_n^{OSM} values. GPC-LALLS was found available for determining M_n and M_w of the block copolymers. © 2002 Published by Elsevier Science Ltd.

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.

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2. Experimental

2.1. Polymers

Poly(styrene)s (PSt) were purchased as standard PSts (TSK polystyrenes, Tosoh Co.). Poly(*n*-hexylisocyanate)s (PIC), $-[\mathrm{N(C_6H_{13})-CO}]_n-$, were prepared [15,16] in toluene at −20 °C using a titanium compound ($\mathrm{TiCl_3OCH_2CF_3}$) as the catalyst as reported by Novak [17]. Two star polymers of PSt, ($(\mathrm{PSt})_n$), were, respectively, prepared [18,19] using *n*-BuLi in THF at −78 °C and *s*-BuLi in benzene at room temperature by anionic living polymerization of (4-vinylbenzyl)poly(styrene) macromonomer ($M_n = 4.7_4 \times 10^3$, $M_w/M_n = 1.0_3$). A four-arm star polymer of PSt ($(\mathrm{PSt})_4$) was prepared [20,21] by a coupling reaction of living $\mathrm{PSt^-Li^+}$ ($M_n = 1.4_8 \times 10^5$, $M_w/M_n = 1.0_3$) with 1,2-bis(trichlorosilyl)ethane in benzene at room temperature under high vacuum. A four-arm star polymer of poly(α-methylstyrene) ($(\mathrm{P\alpha MSt})_4$) was prepared [22–25] by reacting (*p*-isopropenylphenethyl)poly(α-methylstyrene) macromonomer ($M_n = 1.8_3 \times 10^3$, $M_w/M_n = 1.0_9$) with a sodium mirror in THF at room temperature under high vacuum. A linear block copolymer of poly(styrene)-*block*-poly(isoprene) (PSt-*block*-PIs) was prepared using *n*-BuLi in THF at −78 °C by a sequential anionic living polymerization of St and Is. A star block copolymer of PSt and PIs ($(\mathrm{PSt})_4$-*star*-$(\mathrm{PIs})_7$) was prepared using *n*-BuLi in THF at −78 °C by a sequential anionic living polymerization of (4-vinylbenzyl)PSt macromonomer ($M_n = 7.1_0 \times 10^3$, $M_w/M_n = 1.0_2$) and (methacryl)poly(isoprene) macromonomer ($M_n = 6.2_5 \times 10^3$, $M_w/M_n = 1.0_2$) [19,26,27].

2.2. Molecular characterization

All polymer samples were tested on gel permeation chromatography (GPC; Model CCPD, 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. × 60 cm; Tosoh Co.) were used for the GPC measurements. Number average molecular weights (M_n^{OSM}) of the samples were determined by osmometry in toluene at 30 °C using a high-speed membrane osmometer (Mechrolab Model 502, Hewlett-Packard Co., New York, USA). Weight-average molecular weights (M_w^{LS}) of the samples were determined by LS in benzene at 30 °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_θ) of a polymer solution is well known as follows:

$$KC/R_\theta = (1/M_w)[1 + (1/3)k^2\langle s^2\rangle + \cdots] + 2A_2C + 3A_3C^2\cdots \qquad (1)$$

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 $1 + (1/3)k^2\langle s^2\rangle + \cdots$, the LALLS instrument used in the present paper has a scattering angle of 5°. In the case of PSt with $M_w = 10^6$ or $M_w = 10^7$, 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_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_w [31]. A simple estimation of $2M_wA_2C$ for PSt was carried out. The sampling volume of the present GPC-LALLS instrument is 100 μl, 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 instrument, about 0.025% of it is eluted at the LALLS detector. Therefore, when a 0.5% PSt solution with $M_w = 10^6$ or $M_w = 10^7$ is injected into the GPC-LALLS, the $2M_wA_2C$ value is 0.15 or 0.9, respectively. When a 0.05% PSt solution with $M_w = 10^6$ or $M_w = 10^7$ is injected into the GPC-LALLS, the $2M_wA_2C$ value is 0.015 or 0.09, respectively. Therefore, when a low polymer concentration of 0.05% is used for the experiments, as a first approximation, the concentration dependence should be neglected in determining M_w which is less than 10^6 within an experimental error of 1.5%.

In conclusion, when a PSt that has a M_w of less than 10^6 and a concentration of 0.05% was subjected to the GPC-LALLS experiments, the determined M_w value has an experimental error of less than 1.5%. We carried out the GPC-LALLS experiments under the above conditions.

3.2. Determination of M_n and M_w for homopolymers

3.2.1. Poly(styrene)s

Assume an unknown sample that has the same RI increment as that of PSt, $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}$, 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:

$$H_i^{\mathrm{RI}} = k_{\mathrm{RI}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}C_i \qquad (2)$$

$$H_i^{\mathrm{LS}} = k_{\mathrm{LS}}[(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^2M_iC_i \qquad (3)$$

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 $M_i^{(\mathrm{d}n/\mathrm{d}c)}$ as follows:

$$M_i^{(\mathrm{d}n/\mathrm{d}c)} = (H_i^{\mathrm{LS}}/H_i^{\mathrm{RI}})[(k_{\mathrm{LS}}/k_{\mathrm{RI}})(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^{-1} \tag{4}$$

The instrumental factor of $[(k_{\mathrm{LS}}/k_{\mathrm{RI}})(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^{-1}$ 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 $A^{\mathrm{RI}} = k_{\mathrm{RI}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}C$. Based on the same procedure, the summation of both sides of Eq. (3) leads to $A^{\mathrm{LS}} = k_{\mathrm{LS}}[(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^2 M_{\mathrm{w}}C$. 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 $k_{\mathrm{RI}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}$ and $k_{\mathrm{LS}}[(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^2$ can be determined independently, and hence the instrumental factor of $[(k_{\mathrm{LS}}/k_{\mathrm{RI}})(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^{-1}$ can also be known. Therefore, the number average molecular weight ($M_{\mathrm{n}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$) and the weight average molecular weight ($M_{\mathrm{w}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$) can be calculated by substitution of $M_i^{(\mathrm{d}n/\mathrm{d}c)}$ in each of the following two equations

$$M_{\mathrm{n}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}} = \sum H_i^{\mathrm{RI}} \Big/ \sum \left(H_i^{\mathrm{RI}}/M_i^{(\mathrm{d}n/\mathrm{d}c)}\right) \tag{5}$$

$$M_{\mathrm{w}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}} = \sum H_i^{\mathrm{RI}} M_i^{(\mathrm{d}n/\mathrm{d}c)} \Big/ \sum H_i^{\mathrm{RI}} \tag{6}$$

As shown in Table 1, the resultant molecular weights of $M_{\mathrm{n}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$ for four PSts in a molecular weight range of 0.91×10^4–35.4×10^4 are in good agreement with the $M_{\mathrm{n}}^{\mathrm{LS}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$ determined by the LS experiments.

3.2.2. *Homopolymers having* $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{unknown}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}$

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

$$H_i^{\mathrm{RI}} = k_{\mathrm{RI}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{unknown}}C_i \tag{7}$$

$$H_i^{\mathrm{LS}} = k_{\mathrm{LS}}[(\mathrm{d}n/\mathrm{d}c)_{\mathrm{unknown}}]^2 M_i C_i \tag{8}$$

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

$$M_i^{\mathrm{C}} = [(H_i^{\mathrm{LS}}/(H_i^{\mathrm{RI}})^2][(k_{\mathrm{LS}}/(k_{\mathrm{RI}})^2]^{-1}C_i \tag{9}$$

The instrumental factor of $[(k_{\mathrm{LS}}/(k_{\mathrm{RI}})^2]^{-1}$ can be determined by the same procedure as that of $[(k_{\mathrm{LS}}/k_{\mathrm{RI}}) \times (\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}]^{-1}$. C_i can be known as $C_i = C(H_i^{\mathrm{RI}}/\sum H_i^{\mathrm{RI}})$. Hence, $M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$ 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 $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{unknown}}$ values of the homopolymers are not known. Although the $(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}}$ 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 $M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$ values for four PSts are in good agreement with $M_{\mathrm{n}}^{\mathrm{LS}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$ 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} ($M_{\mathrm{n}}^{\mathrm{GPC}}$) and M_{w} ($M_{\mathrm{w}}^{\mathrm{GPC}}$) values of the PIC that were determined by the conventional GPC methods using a calibration curve for standard PSts are also described. The resultant $M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$ values for the five PIC samples having molecular weights in a range of 10×10^3–670×10^3 are in good agreement with the $M_{\mathrm{n}}^{\mathrm{OSM}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$ values determined by osmometry and LS, respectively. As expected for rod-like polymers, the following facts were confirmed, $M_{\mathrm{n}}^{\mathrm{GPC}} > M_{\mathrm{n}}^{\mathrm{OSM}} = M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w}}^{\mathrm{GPC}} > M_{\mathrm{w}}^{\mathrm{LS}} = M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$. The $M_{\mathrm{n}}^{\mathrm{GPC}}/M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ value and $M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ 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 $M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n}}^{\mathrm{GPC}} > M_{\mathrm{w}}^{\mathrm{LS}}/M_{\mathrm{n}}^{\mathrm{OSM}} = M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}/M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$. This gap between the three $M_{\mathrm{w}}/M_{\mathrm{n}}$ values appear to become large with an increase in the $M_{\mathrm{w}}/M_{\mathrm{n}}$ values.

Table 1
Molecular weights of polystyrenes determined by LS and GPC-LALLS using Eqs. (4) and (9)

Polymer	$10^{-3}M_{\mathrm{w}}^{\mathrm{LS}}$ by light scattering[a]			$10^{-3}M_{(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$ using $M_i^{(\mathrm{d}n/\mathrm{d}c)}$ in Eq. (4)			$10^{-3}M_{\mathrm{C}}^{\mathrm{GPC\text{-}LS}}$ using M_i^{C} in Eq. (9)		
	$M_{\mathrm{n}}^{\mathrm{LS\,a}}$	$M_{\mathrm{w}}^{\mathrm{LS}}$	$M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n}}^{\mathrm{GPC\,a}}$	$M_{\mathrm{n}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}/M_{\mathrm{n}\,(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}/M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$
PSt-1	8.9_2	9.1_0	1.0_2	8.8_0	9.0_7	1.0_3	8.8_3	9.1_0	1.0_3
PSt-2	$36_{.8}$	$37_{.2}$	1.0_1	$35_{.3}$	$37_{.1}$	1.0_5	$35_{.8}$	$37_{.6}$	1.0_5
PSt-3	10_4	11_0	1.0_6	10_3	10_9	1.0_6	10_2	10_8	1.0_6
PSt-4	34_7	35_4	1.0_2	33_9	35_7	1.0_5	33_7	35_6	1.0_6

[a] The values were provided by Tosoh Co.; $M_{\mathrm{w}}^{\mathrm{LS}}$ was determined by LS. The $M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n}}^{\mathrm{GPC}}$ value was determined by the conventional GPC methods using a calibration curve of the standard PSts and $M_{\mathrm{n}}^{\mathrm{LS}}$ was calculated by $M_{\mathrm{w}}^{\mathrm{LS}}$ $(M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n}}^{\mathrm{GPC}})^{-1}$.

Table 2
Molecular weights of PIC determined by the conventional GPC methods, osmometry, LS, and GPC-LALLS

Polymer	$10^{-3}M^{\mathrm{GPC}}$ by GPC methods[a]			$10^{-3}M$ by absolute methods[b]			$10^{-3}M_{\mathrm{C}}^{\mathrm{GPC\text{-}LS}}$ using M_i^{C} in Eq. (9)		
	$M_{\mathrm{n}}^{\mathrm{GPC}}$	$M_{\mathrm{w}}^{\mathrm{GPC}}$	$M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n}}^{\mathrm{GPC}}$	$M_{\mathrm{n}}^{\mathrm{OSM}}$	$M_{\mathrm{w}}^{\mathrm{LS}}$	$M_{\mathrm{w}}^{\mathrm{LS}}/M_{\mathrm{n}}^{\mathrm{OSM}}$	$M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}/M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$
PIC-1	$12_{.3}$	$15_{.7}$	1.2_8		$11_{.2}$[c]		8.5_6	$10_{.4}$	1.2_1
PIC-2	$49_{.4}$	$86_{.7}$	1.7_6	$32_{.1}$	$41_{.7}$	1.3_0	$33_{.0}$	$42_{.7}$	1.2_9
PIC-3	12_2	14_0	1.1_5	$48_{.5}$	$50_{.8}$	1.0_5	$47_{.9}$	$50_{.7}$	1.0_6
PIC-4	20_5	23_4	1.1_4	$98_{.4}$	10_6	1.0_8	$97_{.5}$	10_5	1.0_8
PIC-5	54_9	99_9	1.8_2		68_2		47_3	67_9	1.4_4

[a] Determined using a calibration curve of log M versus elution volume for standard PSts.
[b] $M_{\mathrm{n}}^{\mathrm{OSM}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$ were determined by osmometry and LS, respectively.
[c] Determined by a conventional LALLS method using a peak area of the LALLS chromatogram.

As the third and fourth samples, three PSt star polymers, $(\mathrm{PSt})_n$ [21,27], and a four-arm star polymer, $(\mathrm{P\alpha MSt})_4$ [23–25], were employed for determining the validity of the present analysis. As shown in Table 3, the resultant $M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$ values for three $(\mathrm{PSt})_n$ and a $(\mathrm{P\alpha MSt})_4$ samples are in good agreement with the $M_{\mathrm{n}}^{\mathrm{OSM}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$ values. As expected for star polymers, the following facts were confirmed, $M_{\mathrm{n}}^{\mathrm{GPC}} < M_{\mathrm{n}}^{\mathrm{OSM}} = M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w}}^{\mathrm{GPC}} < M_{\mathrm{w}}^{\mathrm{LS}} = M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$. These inequalities are opposite those for PIC. These findings are shown in Fig. 1, where the $M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$ (or $M_{\mathrm{n}}^{\mathrm{OSM}}$) and $M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$ (or $M_{\mathrm{w}}^{\mathrm{LS}}$) values are plotted against the $M_{\mathrm{n}}^{\mathrm{GPC}}$ and $M_{\mathrm{w}}^{\mathrm{GPC}}$ values, 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.

In conclusion, the GPC-LALLS experiments using M_i^{C} in Eq. (9) are available for determining the M_{n} and M_{w} of any homopolymer system such as flexible polymers, rod-like polymers and star polymers within an experimental error of 5 %.

3.3. Determination of M_n and M_w for block copolymers

Block copolymers have a CD as well as a molecular weight distribution. The virtual methods for the CD determination of the block copolymers are cross-fractionation [34,35] and thin-layer chromatography [14]. The CD determination by GPC-LALLS is beyond the scope of the present paper. We are trying to determine the M_{n} and M_{w} of block copolymers by GPC-LALLS. When a common LS experiment with a block copolymer is carried out, not a true M_{w} value but an apparent M_{w} one is obtained due to the CD. In order to determine the true M_{w} value, a special LS experiment using more than three solvents must be performed, as described in the textbooks [28–30]. Compared with the LS experiment, the GPC-LALLS experiments have a feature by which the scattering intensity at the ith elution volume can be individually detected. An attempt was made to determine the true M_{n} and M_{w} values of linear block copolymers and star block copolymers by GPC-LALLS in the present study.

It is convenient to imagine a $(\mathrm{PSt})_2$-*star*-$(\mathrm{PIs})_2$ heteroarm star block copolymer that shows a GPC chromatogram having an average PIs composition of 50 wt%, as schematically shown in Fig. 2. The PIs composition at the ith elution volume (w_i^{PIs}) can be determined by the RI and UV signals. The detailed analyses are described in Appendix A. Fig. 2 shows a special case in which w_i^{PIs} of the polymer is independent of the elution volume and is equal to the average PIs composition (w^{PIs}), and the polymer which appears at the same elution volume has a CD among the same molecular weights. In other words, the block copolymers should have two CDs; namely, one is a CD among different molecular weights and the other is a CD

Table 3
Molecular weights of the star polymers for $(\mathrm{PSt})_n$ and $(\mathrm{P\alpha MSt})_4$ determined by the conventional GPC methods, osmometry, LS, and GPC-LALLS

Polymer	$10^{-3}M^{\mathrm{GPC}}$ using GPC methods[a]			$10^{-3}M$ by absolute methods[b]			$10^{-3}M_{\mathrm{C}}^{\mathrm{GPC\text{-}LS}}$ using M_i^{C} in Eq. (9)		
	$M_{\mathrm{n}}^{\mathrm{GPC}}$	$M_{\mathrm{w}}^{\mathrm{GPC}}$	$M_{\mathrm{w}}^{\mathrm{GPC}}/M_{\mathrm{n}}^{\mathrm{GPC}}$	$M_{\mathrm{n}}^{\mathrm{OSM}}$	$M_{\mathrm{w}}^{\mathrm{LS}}$	$M_{\mathrm{w}}^{\mathrm{LS}}/M_{\mathrm{n}}^{\mathrm{OSM}}$	$M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}$	$M_{\mathrm{w\,C}}^{\mathrm{GPC\text{-}LS}}/M_{\mathrm{n\,C}}^{\mathrm{GPC\text{-}LS}}$
$(\mathrm{PSt})_{9.6}$	$32_{.4}$	$35_{.0}$	1.0_8	$42_{.7}$	$46_{.5}$	1.0_9	$44_{.5}$	$47_{.3}$	1.0_6
$(\mathrm{PSt})_{10}$	$35_{.6}$	$39_{.5}$	1.1_1	$46_{.1}$	$49_{.5}$	1.0_7	$46_{.5}$	$48_{.8}$	1.0_5
$(\mathrm{PSt})_{4.0}$	44_4	$45_{.5}$	1.0_2		58_0		54_3	57_2	1.0_5
$(\mathrm{P\alpha MSt})_{4.0}$	4.4_0	5.0_6	1.1_5	7.6_3[c]	8.4_7[d]	1.1_0	7.4_2	8.1_3	1.1_0

[a] Determined using a calibration curve of log M versus elution volume for standard PSts.
[b] $M_{\mathrm{n}}^{\mathrm{OSM}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$ 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.

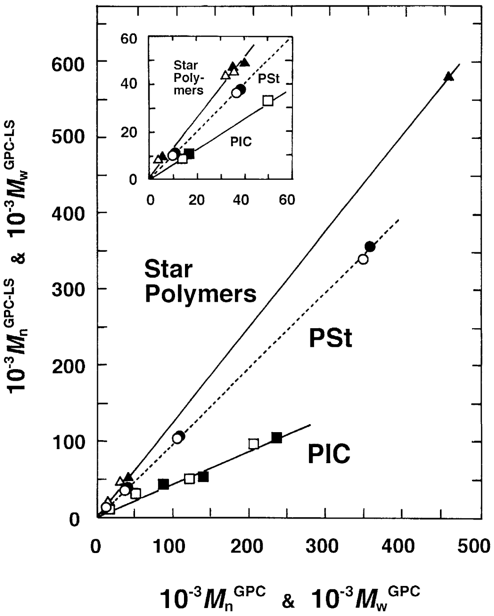

Fig. 1. Plots of M_n^{GPC-LS} *versus* M_n^{GPC} (open symbols), and those of M_w^{GPC-LS} *versus* M_w^{GPC} (closed symbols) for a series of PSt (○, ●), PIC (□, ■), and star polymers (△, ▲). The results observed in the lower molecular weights side are shown in the inserted figure.

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 ith 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 ith elution volume as $M_{i,j}$, $(dn/dc)_{i,j}$, and $C_{i,j}$, 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 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 ($H_{i,j}^{RI}$) and the LALLS signal ($H_{i,j}^{LS}$) of the corresponding RI and LALLS chromatograms of the block copolymers at the ith elution volume are described as follows, in the similar formulas of Eqs. (2) and (3), respectively

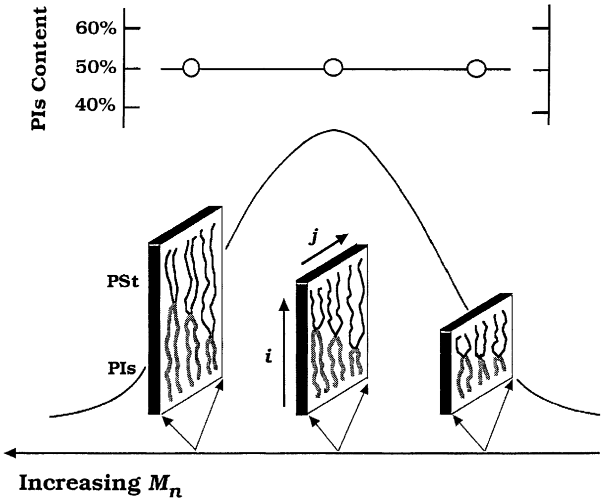

Fig. 2. A schematic GPC chromatogram of a $(PSt)_m$-*star*-$(PIs)_n$ star block copolymer. The $(PSt)_m$-*star*-$(PIs)_n$ molecules appeared at the ith elution volume (having the same molecular weight) should have a CD; namely, this fact is shown in the figure.

$$H_{i,j}^{RI} = k_{RI} \sum_j (dn/dc)_{i,j} C_{i,j} \quad (10)$$

$$H_{i,j}^{LS} = k_{LS} \sum_j [(dn/dc)_{i,j}]^2 M_{i,j} C_{i,j} \quad (11)$$

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, $w_i^{PIs} = w^{PIs}$ and $(dn/dc)_{i,j} = (dn/dc)_i$. (ii) The block copolymer has a CD regarding i and no CD regarding j; namely, $w_i^{PIs} \neq w^{PIs}$ and $(dn/dc)_{i,j} = (dn/dc)_i$. (iii) The block copolymer has no CD regarding i and a CD regarding j; namely, $w_i^{PIs} = w^{PIs}$ and $(dn/dc)_{i,j} \neq (dn/dc)_i$. (iv) The block copolymer has a CD regarding i and a CD regarding j; namely, $w_i^{PIs} \neq w^{PIs}$ and $(dn/dc)_{i,j} \neq (dn/dc)_i$.

The group (i) is the simplest case; namely, $H_{i,j}^{RI}$ in Eq. (10) and $H_{i,j}^{LS}$ 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_n^{GPC-LS} and M_w^{GPC-LS}. Although group (ii) is more complex than group (i), $H_{i,j}^{RI}$ and $H_{i,j}^{LS}$ 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_n^{GPC-LS} and M_w^{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 $M_{i,j} = M_i$ as shown in Fig. 2, because the polymer chains having $M_{i,j}$ appeared at the same ith elution volume. Therefore, $M_{i,j}$ 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 $M_{i\,BC}^{(dn/dc)}$ and $M_{i\,BC}^{C}$ values for the block copolymers, respectively. The results are shown as follows:

$$M_{i\,BC}^{(dn/dc)} = \frac{k_{RI}}{k_{LS}} \frac{H_i^{LS}}{H_i^{RI}} \frac{\sum_j (dn/dc)_{i,j} C_{i,j}}{\sum_j [(dn/dc)_{i,j}]^2 C_{i,j}} \quad (12)$$

$$M_{i\ \mathrm{BC}}^{\mathrm{C}} = \frac{(k_{\mathrm{RI}})^2}{k_{\mathrm{LS}}} \frac{H_i^{\mathrm{LS}}}{(H_i^{\mathrm{RI}})^2} \frac{[\sum_j (\mathrm{d}n/\mathrm{d}c)_{i,j} C_{i,j}]^2}{\sum_j [(\mathrm{d}n/\mathrm{d}c)_{i,j}]^2 C_{i,j}} \tag{13}$$

With the relation of $\sum_j C_{i,j} = C_i$ in mind, the following two average values regarding j could be derived: $\sum_j (\mathrm{d}n/\mathrm{d}c)_{i,j} C_{i,j} = C_i \langle (\mathrm{d}n/\mathrm{d}c)_{i,j} \rangle = C_i (\mathrm{d}n/\mathrm{d}c)_i$ and $\sum_j [(\mathrm{d}n/\mathrm{d}c)_{i,j}]^2 C_{i,j} = C_i \langle [(\mathrm{d}n/\mathrm{d}c)_{i,j}]^2 \rangle = C_i [(\mathrm{d}n/\mathrm{d}c)_i]^2$, where $\langle \ldots \rangle$ means the average of the corresponding RI increments. Therefore, the corresponding equations of $M_{i\ \mathrm{BC}}^{(\mathrm{d}n/\mathrm{d}c)}$ and $M_{i\ \mathrm{BC}}^{\mathrm{C}}$ became as follows:

$$M_{i\ \mathrm{BC}}^{(\mathrm{d}n/\mathrm{d}c)} = (k_{\mathrm{RI}}/k_{\mathrm{LS}})(H_i^{\mathrm{LS}}/H_i^{\mathrm{RI}})[(\mathrm{d}n/\mathrm{d}c)_i]^{-1} \tag{14}$$

$$M_{i\ \mathrm{BC}}^{\mathrm{C}} = [(k_{\mathrm{RI}})^2/k_{\mathrm{LS}})][(H_i^{\mathrm{LS}}/(H_i^{\mathrm{RI}})^2]C_i \tag{15}$$

where the $(\mathrm{d}n/\mathrm{d}c)_i$ can be determined as follows

$$(\mathrm{d}n/\mathrm{d}c)_i = (1 - w_i^{\mathrm{PIs}})(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PSt}} + w_i^{\mathrm{PIs}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{PIs}} \tag{16}$$

The C_i in Eq. (15) and w_i^{PIs} in Eq. (16) are derived from the GPC measurements using RI and UV detectors. These derivations are described in Appendix A. By substituting each of $M_i^{(\mathrm{d}n/\mathrm{d}c)}$ and M_i^{C} in Eqs. (5) and (6), the corresponding two pairs of $M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$ and $M_{\mathrm{w}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$, and $M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$ and $M_{\mathrm{w\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$ were calculated.

The results for the linear and star block copolymers [19, 27] are shown in Table 4. For PSt-*block*-PIs, the resultant $M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$ and $M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$ values are in good agreement with each other and with the $M_{\mathrm{n}}^{\mathrm{OSM}}$ value. For (PSt)$_4$-*star*-(PIs)$_7$, the resultant $M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$ and $M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$ values are in good agreement with each other and with the $M_{\mathrm{n}}^{\mathrm{OSM}}$ value. On the other hand, the (PSt)$_4$ star polymer could be prepared as a precursor. The number average molecular weight ($M_{\mathrm{n\ PSt}}^{\mathrm{GPC\text{-}LS}}$) of (PSt)$_4$ was determined by GPC-LALLS, and the PIs composition ($w_{\mathrm{PIs}}^{\mathrm{NMR}}$) of (PSt)$_4$-*star*-(PIs)$_7$ was determined by NMR. From these values, the number average molecular weight ($M_{\mathrm{n\ PSt}\text{-}star\text{-}\mathrm{PIs}}^{\mathrm{NMR}}$) of (PSt)$_4$-*star*-(PIs)$_7$ was calculated as follows:

$$M_{\mathrm{n\ PSt}\text{-}star\text{-}\mathrm{PIs}}^{\mathrm{NMR}} = M_{\mathrm{n\ PSt}}^{\mathrm{GPC\text{-}LS}}/(1 - w_{\mathrm{PIs}}^{\mathrm{NMR}}) \tag{17}$$

The resultant $M_{\mathrm{n\ PSt}\text{-}star\text{-}\mathrm{PIs}}^{\mathrm{NMR}}$ value coincides with the $M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$ and $M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$ values. As mentioned before, it is difficult to determine the $M_{\mathrm{w}}^{\mathrm{LS}}$ of PSt-*block*-PIs and (PSt)$_4$-*star*-(PIs)$_7$ by LS using more than three solvents. Hence, the comparison of the resultant $M_{\mathrm{w}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$ and $M_{\mathrm{w\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$ values with the $M_{\mathrm{w}}^{\mathrm{LS}}$ value were not carried out at the present time. It is worth noting that the $M_{\mathrm{w\ BC}}^{\mathrm{GPC\text{-}LS}}/M_{\mathrm{n\ BC}}^{\mathrm{GPC\text{-}LS}}$ values are in good agreement with the $M_{\mathrm{w\ BC}}^{\mathrm{GPC}}/M_{\mathrm{n\ BC}}^{\mathrm{GPC}}$ 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, $M_{i,j} = M_i$. 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 $M_{i,j} = M_i$ has to be examined experimentally before calculating $M_{\mathrm{n\ BC}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w\ BC}}^{\mathrm{GPC\text{-}LS}}$. On the contrary, the finding that $M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}} = M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}} = M_{\mathrm{n}}^{\mathrm{OSM}}$ for the two block copolymers suggests that the relation $M_{i,j} = M_i$ 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 $M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}} \neq M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}} \neq M_{\mathrm{n}}^{\mathrm{OSM}}$. 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 copolymers and star block copolymers, the general equations as $M_{i\ \mathrm{BC}}^{(\mathrm{d}n/\mathrm{d}c)}$ in Eq. (12) and $M_{i\ \mathrm{BC}}^{\mathrm{C}}$ in Eq. (13) have been derived. That is, $M_i^{(\mathrm{d}n/\mathrm{d}c)}$ in Eq. (4) and M_i^{C} in Eq. (9) for homopolymers, and $M_{i\ \mathrm{BC}}^{(\mathrm{d}n/\mathrm{d}c)}$ in Eq. (14) and $M_{i\ \mathrm{BC}}^{\mathrm{C}}$ in Eq. (15) for block copolymers can be employed for determining $M_{\mathrm{n}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w}}^{\mathrm{GPC\text{-}LS}}$ that are in good agreement with $M_{\mathrm{n}}^{\mathrm{OSM}}$ and $M_{\mathrm{w}}^{\mathrm{LS}}$, 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

Table 4
Molecular weights of a linear block copolymer, PSt-*block*-PIs and a star block copolymer, (PSt)$_4$-*star*-(PIs)$_7$ determined by osmometry and GPC-LALLS

Polymer	$10^{-3}M_{\mathrm{n}}^{\mathrm{OSM}}$	$10^{-3}M_{(\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$ using $M_{i\ \mathrm{BC}}^{(\mathrm{d}n/\mathrm{d}c)}$ in Eq. (14)			$10^{-3}M_{\mathrm{C}}^{\mathrm{GPC\text{-}LS\ BC}}$ using $M_{i\ \mathrm{BC}}^{\mathrm{C}}$ in Eq. (15)		
		$M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$	$M_{\mathrm{w}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$	$M_{\mathrm{w}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}/M_{\mathrm{n}\ (\mathrm{d}n/\mathrm{d}c)}^{\mathrm{GPC\text{-}LS\ BC}}$	$M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$	$M_{\mathrm{w\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$	$M_{\mathrm{w\ C}}^{\mathrm{GPC\text{-}LS\ BC}}/M_{\mathrm{n\ C}}^{\mathrm{GPC\text{-}LS\ BC}}$
PSt-*block*-PIs	19_4	20_4	23_1	1.1_3	20_1	22_7	1.1_3
(PSt)$_4$-*star*-(PIs)$_7$	$71_{.2}$ $(72_{.0})^9$	$70_{.6}$	$73_{.4}$	$1.0_{.4}$	$70_{.3}$	$72_{.5}$	1.0_3

[a] Determined by NMR: $M_{\mathrm{n\ PSt}\text{-}star\text{-}\mathrm{Pls}}^{\mathrm{NMR}} = M_{\mathrm{n\ PSt}}^{\mathrm{GPC\text{-}LS}}/1 - w_{\mathrm{Pls}}^{\mathrm{NMR}})$, where $w_{\mathrm{Pls}}^{\mathrm{NMR}}$ was determined by NMR.

weights. However, even if the CD among the same molecular weights is not known; namely, the both values of $(\mathrm{d}n/\mathrm{d}c)_{i,j}$ and $C_{i,j}$ are not known at the present time, the summation of $\sum_j (\mathrm{d}n/\mathrm{d}c)_{i,j} C_{i,j}$ and $\sum_j [(\mathrm{d}n/\mathrm{d}c)_{i,j}]^2 C_{i,j}$ could be determined by GPC-LALLS using the assumption of $M_{i,j} = M_i$. Hence, the $M_{\mathrm{n\,BC}}^{\mathrm{GPC\text{-}LS}}$ and $M_{\mathrm{w\,BC}}^{\mathrm{GPC\text{-}LS}}$ values were determined.

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Appendix A

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

$$H_i^{\mathrm{RI}} = H_{i\,\mathrm{PSt}}^{\mathrm{RI}} + H_{i\,\mathrm{PIs}}^{\mathrm{RI}} = k'_{\mathrm{PSt}} C_i^{\mathrm{PSt}} + k'_{\mathrm{PIs}} C_i^{\mathrm{PIs}} \tag{A1}$$

$$H_i^{\mathrm{UV}} = H_{i\,\mathrm{PSt}}^{\mathrm{UV}} + H_{i\,\mathrm{PIs}}^{\mathrm{UV}} = \varepsilon_{\mathrm{PSt}} C_i^{\mathrm{PSt}} + \varepsilon_{\mathrm{PIs}} C_i^{\mathrm{PIs}} \tag{A2}$$

From these equations, the concentrations of the PSt block (C_i^{PSt}) and the PIs block (C_i^{PIs}) at the *i*th elution volume can be determined using the k'_{PSt}, k'_{PIs}, $\varepsilon_{\mathrm{PSt}}$, and $\varepsilon_{\mathrm{PIs}}$ 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^{PIs}) can be calculated as follows:

$$w_i^{\mathrm{PIs}} = \frac{C_i^{\mathrm{PIs}}}{C_i^{\mathrm{PIs}} + C_i^{\mathrm{PSt}}} = \frac{\varepsilon_{\mathrm{PSt}} H_i^{\mathrm{RI}} - k'_{\mathrm{PSt}} H_i^{\mathrm{UV}}}{(\varepsilon_{\mathrm{PSt}} - \varepsilon_{\mathrm{PIs}}) H_i^{\mathrm{RI}} + (k'_{\mathrm{PIs}} - k'_{\mathrm{PSt}}) H_i^{\mathrm{UV}}} \tag{A3}$$

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^{PSt}) and the PIs block (C_i^{PIs}). The result is described as follows:

$$C_i = C_i^{\mathrm{PSt}} + C_i^{\mathrm{PIs}} = \frac{(\varepsilon_{\mathrm{PSt}} - \varepsilon_{\mathrm{PIs}}) H_i^{\mathrm{RI}} + (k'_{\mathrm{PIs}} - k'_{\mathrm{PSt}}) H_i^{\mathrm{UV}}}{k'_{\mathrm{PIs}} \varepsilon_{\mathrm{PSt}} - k'_{\mathrm{PSt}} \varepsilon_{\mathrm{PIs}}} \tag{A4}$$

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