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Distribution of the number of arms of $(PSt)_{f-n}$-*star*-$(PIs)_n$ hetero-star block copolymers prepared *via* anionic living polymerization of macromonomers

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ABSTRACT

The distributions of the number of arms (DNA) of (polystyrene)$_{6.2}$-*star*-polyisoprene ($(PSt)_{6.2}$-*star*-PIs) and $(PSt)_{7.6}$-*star*-$(PIs)_{6.3}$ hetero-star block copolymers and its precursors prepared *via* anionic living polymerization of macromonomers have been determined by plotting a weight fraction of the number of arms against the number of arms. Three-dimensional molecular weight distributions (3D-M_wD) of the two hetero-star block copolymers and its precursors were also determined by plotting a weight fraction at the *i*th elution volume against the corresponding molecular weight (M_i) and *i*th elution volume using GPC in conjunction with a low-angle laser light-scattering detector, a refractive index detector, and an ultraviolet detector. A non-linear relationship between the *i*th elution volume and M_i of $(PSt)_{6.2}$-*star*-PIs was observed and explained from a g_{star} perspective. The present paper describes the analytical method for determination of the DNA using the M_wD. The DNAs of the six samples were found to be narrow and similar to the M_wDs of the corresponding samples. The synthetic mechanism of the hetero-star block copolymers was discussed from a DNA perspective.

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1. Introduction

We have previously reported the preparation, some physical properties, and morphological behaviors of $(A)_{f-1}$-*star*-B type hetero-star block copolymers *via* anionic living polymerization of (4-vinylbenzyl)polystyrene macromonomer (PStM) and (4-vinylbenzyl)polyisoprene macromonomer (PIsM) [1,2]. When we submitted the manuscript, one of the reviewers pointed out the importance of examining the distribution of the number of arms (DNA) of hetero-star block copolymers, even though the molecular weights of arms (M_n^{arm}) and final hetero-star block copolymers (M_n^{star}) were reported and the average number of arms ($\langle f \rangle$) had been calculated as $\langle f \rangle = M_n^{star}/M_n^{arm}$. The reason for examining the distribution might be that even if the M_n^{arm}, M_n^{star} and $\langle f \rangle$ values of two hetero-star block copolymers are the same as each other, some of their physical properties may differ when their DNAs differ [3,4]. However, the DNA of $(A)_{f-1}$-*star*-B has been difficult to resolve, and this problem has until now remained unresolved.

To our knowledge, there has been no study of the DNA of star polymers and hetero-star block copolymers [5–12]. However, we recently found a special means of analysis to estimate the DNA of the $(PSt)_{f-1}$-*star*-PIs hetero-star block copolymer [13]. In recent years a method has been developed for the preparation of $(PSt)_{f-n}$-*star*-$(PIs)_n$ hetero-star block copolymers [14] *via* anionic living polymerization of PStM and PIsM macromonomers. The present paper describes the analytical method, its results and the synthetic mechanism of the $(PSt)_{f-1}$-*star*-PIs and $(PSt)_{f-n}$-*star*-$(PIs)_n$ hetero-star block copolymers from a DNA perspective.

2. Experimental

2.1. Polymers

PStM and PIsM macromonomers were prepared as described previously [1,2]. The $(PSt)_{6.2}$-*star*-PIs was prepared by sequential anionic living copolymerization of PStM and isoprene by *sec*-BuLi in benzene (Bz) at room temperature. The $(PSt)_{7.6}$-*star*-$(PIs)_{6.3}$ was prepared by sequential anionic living copolymerization of PStM and PIsM by *n*-BuLi in tetrahydrofuran (THF) at −78 °C. Polymerization was carried out in a sealed glass apparatus under a pressure of 10^{-6} mmHg. The polymerization techniques were almost the same as those employed in previous studies [1,2].

2.2. Molecular characterization

The molecular characteristics of two macromonomers and two hetero-star block copolymers of $(PSt)_{f-1}$-*star*-PIs and $(PSt)_{f-n}$-*star*-$(PIs)_n$ are described in Table 1; these characteristics are probably

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Table 1

Molecular characteristics of the $(\mathrm{PSt})_{f-1}$-*star*-PIs[a] and $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_n$[b] hetero-star block copolymers.

Polymers	$10^{-4}\,M_n$		M_w/M_n		Arms[e]	$w^{\mathrm{PIs}}/\%$[f]	
	GPC[c]	LALLS[d]	GPC[c]	LALLS[d]		M_n	$\sum w_i^{\mathrm{PIs}}$
$(\mathrm{PSt})_{4.7}$	1.69	2.58	1.16	1.15	4.7		
$(\mathrm{PSt})_{6.2}$	1.81	3.37	1.10	1.09	6.2		
$(\mathrm{PSt})_{6.2}$-*star*-PIs	4.78	6.49	1.05	1.04	7.2	48	50
$(\mathrm{PSt})_{7.6}$	2.15	4.17	1.16	1.11	7.6		
$(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$	3.38	6.61	1.07	1.06	12.2	37	34
$(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6.3}$	3.41	7.52	1.07	1.06	13.9	45	44

[a] PStM macromonomer ($M_n = 5.45 \times 10^3$, $M_w/M_n = 1.03$) was anionically polymerized by *sec*-BuLi in Bz at room temperature under a pressure of 10^{-6} mmHg and isoprene was sequentially polymerized.

[b] PStM macromonomer was anionically polymerized by *n*-BuLi in THF at −78 °C under a pressure of 10^{-6} mmHg and the PIsM macromonomer ($M_n = 5.33 \times 10^3$, $M_w/M_n = 1.04$) was sequentially polymerized.

[c] Determined by GPC using standard PSts.

[d] A special analysis using GPC in conjugation with a low-angle laser light scattering detector [15].

[e] Average number of arms, $\langle f \rangle$ of the star polymers determined by $\langle f \rangle = M_n^{\mathrm{star}}/M_n^{\mathrm{arm}}$, where M_n^{star} and M_n^{arm} are the molecular weights of the final star polymers and the corresponding macromonomers, respectively.

[f] PIs contents determined by $M_n^{\mathrm{PIs}}/M_n^{\mathrm{star}}$ and by GPC using UV and RI detectors.

the same as those reported elsewhere [1]. All polymer samples were tested on gel permeation chromatography (GPC; Model CCPD, Tosoh Co., Tokyo Japan) in conjunction 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.). For the measurements, four high-resolution columns (G2500H, G3000H, G4000, and GMH-M, 7.8 mm i.d. × 60 cm; Tosoh Co.) were connected in a series. A special analysis was required to determine the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the two hetero-star block copolymers using GPC-LALLS. The details have been reported elsewhere [15]. All calculations for determining and drawing the distribution of the number of arms (DNA) were carried out on a personal computer using commercially available software.

3. Results and discussion

3.1. Molecular weight distributions (M_wDs)

The RI intensity (H_i^{RI}) and the LALLS intensity (H_i^{LS}) of the corresponding RI and LALLS chromatograms of $(\mathrm{PSt})_f$, $(\mathrm{PSt})_{f-1}$-*star*-PIs, and $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_n$ at the *i*th elution volume are described as follows:

$$H_i^{\mathrm{RI}} = k_{\mathrm{RI}}(\mathrm{d}n/\mathrm{d}c)_i C_i \tag{1}$$

$$H_i^{\mathrm{LS}} = k_{\mathrm{LS}}\left[(\mathrm{d}n/\mathrm{d}c)_i\right]^2 M_i C_i \tag{2}$$

where $(\mathrm{d}n/\mathrm{d}c)_i$, C_i, and M_i are the refractive index increment, concentration, and molecular weight at the *i*th elution volume, respectively. From the ratio of the square of Eq. (1) to Eq. (2), the $(\mathrm{d}n/\mathrm{d}c)_i$ was eliminated to yield M_i. The resultant M_i is as follows:

$$M_i = \left[\left(H_i^{\mathrm{LS}}/\left(H_i^{\mathrm{RI}}\right)^2\right)\left[k_{\mathrm{LS}}/(k_{\mathrm{RI}})^2\right]^{-1}\right]C_i \tag{3}$$

The instrumental factor of $[k_{\mathrm{LS}}/(k_{\mathrm{RI}})^2]^{-1}$ can be determined for a series of standard PSts with several concentrations.

It has been known that the molecular weight of the block copolymer having composition distribution could not be determined by light scattering. The reason is that the $(\mathrm{d}n/\mathrm{d}c)_i$ of the block copolymers having the composition distribution could not be determined precisely. However, this problem has been resolved using GPC-LALLS [1,15]. Thus the M_i was calculated by considering the composition distribution to become the same equation as Eq. (3). The abstract for deriving Eq. (3) for the block copolymers is described in Appendix A.

The RI intensity of $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_n$ at the *i*th elution volume (H_i^{RI}) is the summation of the RI intensities of the $(\mathrm{PSt})_{f-n}$ block ($H_i^{\mathrm{RI}}{}_{\mathrm{PSt}}$) and the $(\mathrm{PIs})_n$ block ($H_i^{\mathrm{RI}}{}_{\mathrm{PIs}}$). The UV intensities at the *i*th elution volume (H_i^{UV}) are described by the same formula as that of the RI intensities.

$$H_i^{\mathrm{RI}} = H_i^{\mathrm{RI}}{}_{\mathrm{PSt}} + H_i^{\mathrm{RI}}{}_{\mathrm{PIs}} = k'_{\mathrm{PSt}}C_i^{\mathrm{PSt}} + k'_{\mathrm{PIs}}C_i^{\mathrm{PIs}} \tag{4}$$

$$H_i^{\mathrm{UV}} = H_i^{\mathrm{UV}}{}_{\mathrm{PSt}} + H_i^{\mathrm{UV}}{}_{\mathrm{PIs}} = \varepsilon_{\mathrm{PSt}}C_i^{\mathrm{PSt}} + \varepsilon_{\mathrm{PIs}}C_i^{\mathrm{PIs}} \tag{5}$$

From these equations, the concentrations of the $(\mathrm{PSt})_{f-n}$ block (C_i^{PSt}) and the $(\mathrm{PIs})_n$ 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 previously be determined by GPC measurements of the PSt and PIs homopolymers using the RI and UV detectors. Therefore, the concentration of the $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_n$ (C_i) at the *i*th elution volume can be calculated as follows [16]:

$$C_i = C_i^{\mathrm{PSt}} + C_i^{\mathrm{PIs}} = \frac{(\varepsilon_{\mathrm{PSt}} - \varepsilon_{\mathrm{PIs}})H_i^{\mathrm{RI}} + (k_{\mathrm{PIs}} - k_{\mathrm{PSt}})H_i^{\mathrm{UV}}}{k'_{\mathrm{PIs}}\varepsilon_{\mathrm{PSt}} - k'_{\mathrm{PSt}}\varepsilon_{\mathrm{PIs}}} \tag{6}$$

A combination of Eqs. (3) and (6) provides the M_i value by using three detectors of GPC-LALLS measurements.

On the other hand, a weight fraction of $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_n$ hetero-star block copolymers (W_i^{obs}) at the *i*th elution volume can be calculated using Eq. (6) as

$$W_i^{\mathrm{obs}} = C_i/\sum_i C_i \tag{7}$$

3.2. Three-dimensional molecular weight distributions (3D-M_wD)

The three-dimensional M_wDs (3D-M_wD) of $(\mathrm{PSt})_{f-1}$-*star*-PIs (Fig. 1) and $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_n$ (Fig. 2) were determined by plotting W_i^{obs} against M_i and the *i*th elution volume. Plots of W_i^{obs} against M_i are well known as a M_wD and plots of M_i against the *i*th elution

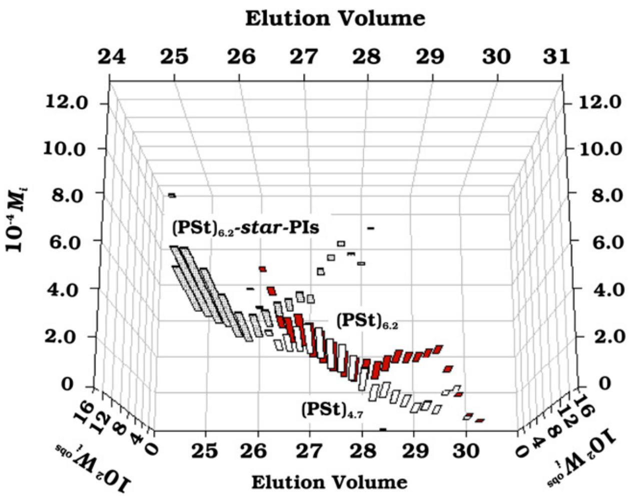

Fig. 1. Three-dimensional molecular weight distributions (3D-M_wDs) of the $(\mathrm{PSt})_{4.7}$, $(\mathrm{PSt})_{6.2}$, and $(\mathrm{PSt})_{6.2}$-*star*-PIs: plots of W_i^{obs} against M_i and the *i*th elution volume.

volume are well known as a calibration curve of GPC measurements. As shown in Fig. 1, during polymerization the 3D-M_wD of $(PSt)_{4.7}$ shifted to that of $(PSt)_{6.2}$ accompanying an increase in M_n and the constancy of the elution volume. Then, the 3D-M_wD of $(PSt)_{6.2}$ shifted to that of $(PSt)_{6.2}$-*star*-PIs accompanying an increase in the M_n and a decrease in the elution volume.

Particular attention should be directed to a non-linear relationship between the *i*th elution volume and M_i observed on the lower M_n sides of $(PSt)_{6.2}$-*star*-PIs: namely, there exist many combinations where the different elution volumes have the same M_n values. This non-linear relationship between the elution volume and M_i has never been observed in common linear polymers. As the number of arms for the star polymers increases, the elution volume does not change significantly. This behavior is known as the g_{star} value, defined as $g_{star} = \langle S^2\rangle_{star}/\langle S^2\rangle_{linear} = (3f-2)/f^2$, where $\langle S^2\rangle$ is the mean-square radius of gyration [17,18]. Let us suppose two $(PSt)_{f-1}$-*star*-PIs hetero-star block copolymers to have the same M_n. One has a higher M_n^{star} of $(PSt)_{f-1}$ and a lower M_n^{PIs} of PIs, while another has a lower M_n^{star} of $(PSt)_{f-1}$ and a higher M_n^{PIs} of PIs. The molecular dimensions of the two $(PSt)_{f-1}$ might be the same, while those of the two PIs differ. Therefore, the two $(PSt)_{f-1}$-*star*-PIs with the same M_n values appear at different elution volumes. Thus, the non-linear relationship between the elution volume and M_i results in the M_n^{PIs} value of the PIs arm being 6 times higher than that of a PSt arm. In contrast, in the case of $(PSt)_{7.6}$-*star*-$(PIs)_{6.3}$ where the M_n values of the PSt arms are probably the same as those of the PIs arms, a relatively linear relationship was observed, as shown in Fig. 2.

3.3. Distributions of the number of arms (DNA)

A M_wD of the polystyrene macromonomer (PStM) can be determined by GPC measurements using standard polystyrenes. The M_wD is expressed as $[M_{1,i} \sim W_{1,i}]$, where $M_{1,i}$ is the molecular weight at the *i*th elution volume in the GPC measurements and is plotted as the abscissa at 200 g mol^{-1} intervals, and $W_{1,i}$ is the weight fraction at $M_{1,i}$ determined by $W_{f,i} = H_i^{RT}/\sum_i H_i^{RT}$ and is plotted as the ordinate. The M_wD can be described in a (28, 3)-type matrix, where the 28 lines range from $M_{1,1} = 2800$ to $M_{1,28} = 8200$, and 3 rows consist of i, $M_{1,i}$, and $W_{1,i}$. A M_wD of a dimmer of PStM, $[M_{2,i} \sim W_{2,i}]$ can be calculated using $M_{2,i} = \Sigma_{i=j+k}\ (M_{1,j} + M_{1,k})$ and $W_{2,i} = \Sigma_{i=j+k}\ (W_{1,j}\ W_{1,k})$, where $\Sigma_{i=j+k}$ is the summation of the corresponding term for a combination of (j, k) under a condition of $i = j + k$. That is, the probability that the first PStM with M_j and the second PStM with M_k combine directly to produce the dimmer with $M_{i=j+k}$ is assumed to be independent of M_j and M_k of both these PStMs. The resultant M_wD can be described in a (55, 3)-type, matrix, where the 55 lines range from $M_{2,1} = 5600$ to $M_{2,55} = 16400$, and 3 rows consist of i, $M_{2,i}$, and $W_{2,i}$. Thus, a M_wD of a $(PSt)_f$ star polymer, $[M_{f,i} \sim W_{f,i}]$ can be calculated using $M_{f,i} = \Sigma_{i=j+k}\ (M_{f-1,j} + M_{1,k})$ and $W_{f,i} = \Sigma_{i=j+k}\ (W_{f-1,j}\ W_{1,k})$, where f is the number of arms corresponding to a degree of polymerization of PStM. The resultant M_wD of $(PSt)_f$ can be described in a $(28f{-}1, 3)$-type matrix, and each M_wD of $(PSt)_f$ $(f = 1-20)$ is shown in Fig. 3. As shown in Fig. 3, each M_wD of $(PSt)_f$ is narrow and the distribution broadens with increasing f values. This behavior was expected before the calculation.

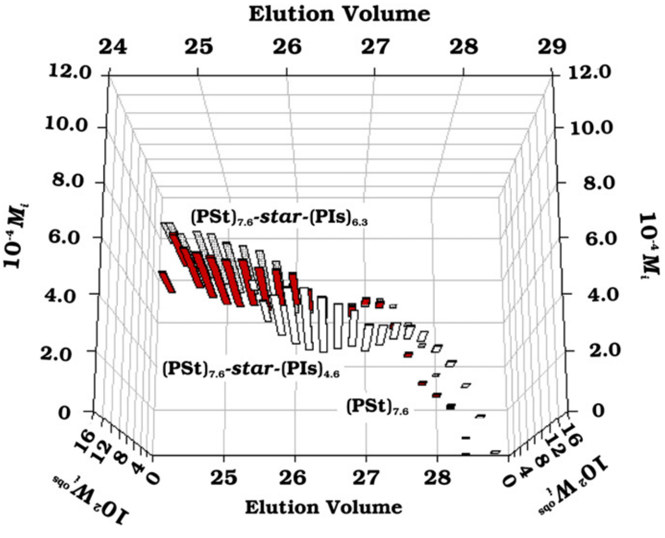

Fig. 2. Three-dimensional molecular weight distributions (3D-M_wDs) of the $(PSt)_{7.6}$, $(PSt)_{7.6}$-*star*-$(PIs)_{4.6}$, and $(PSt)_{7.6}$-*star*-$(PIs)_{6.3}$: plots of W_i^{obs} against M_i and the *i*th elution volume.

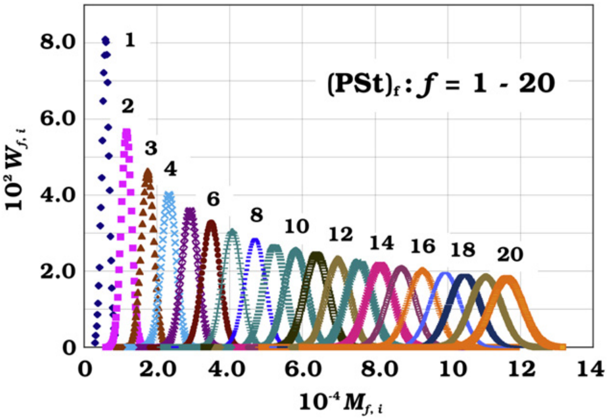

Fig. 3. Each molecular weight distribution of the $(PSt)_f$ star polymers, $[M_{f,i} \sim W_{f,i}]$, where f is a number of arms ranging from 1 to 20.

A M_wD of a $(PSt)_{\langle f\rangle}$ star polymer, $[M_i \sim W_i]^{cal}$ can be calculated using $M_i = \Sigma_f\ w_f M_{f,i}$ and $W_i = \Sigma_f\ w_f W_{f,i}$, where $\langle f\rangle$ is the average number of arms and w_f is the weight fraction of a star polymer having f arms. On the other hand, a M_wD of a $(PSt)_{\langle f\rangle}$ star polymer, $[M_i \sim W_i]^{obs}$ can be determined by the GPC-LALLS measurements. By comparing the resultant $[M_i \sim W_i]^{cal}$ with $[M_i \sim W_i]^{obs}$, DNA, $[f \sim w_f]$ for the $(PSt)_{\langle f\rangle}$ star polymers was determined.

In the case of a $(PSt)_{f-1}$-*star*-PIs hetero-star block copolymer, an additional calculation is necessary to estimate a DNA. The PIs weight fraction of $(PSt)_{f-1}$-*star*-PIs (w_i^{PIs}) at the *i*th elution volume can be determined as

$$\begin{aligned} w_i &= C_i^{PIs}\Big/\left(C_i^{PIs} + C_i^{PSt}\right) \\ &= \left(\varepsilon_{PSt} H_i^{RT} - k'_{PSt} H_i^{UV}\right)\Big/\left[(\varepsilon_{PSt} - \varepsilon_{PIs}) H_i^{RI} + (k'_{PIs} - k'_{PSt}) H_i^{UV}\right] \end{aligned} \tag{8}$$

From Eqs. (3) and (8), the molecular weight of the PIs arm (M_i^{PIs}) of the $(PSt)_{f-1}$-*star*-PIs at the *i*th elution volume can be calculated as $M_i^{PIs} = M_i w_i^{PIs}$. A PIs weight fraction of the PIs arm (W_i^{PIs}) at the *i*th elution volume can also be calculated as $W_i^{PIs} = w_i^{PIs}/\sum_i w_i^{PIs}$. Hence, the M_wD of a PIs arm, $[M_i^{PIs} \sim W_i^{PIs}]$ was estimated. As a M_wD of a $(PSt)_{f-1}$ star polymer, $[M_{f-1,i} \sim W_{f-1,i}]$ has already been calculated, a M_wD of $(PSt)_{f-1}$-*star*-PIs, $[M_{f,i} \sim W_{f,i}]$ can be calculated as follows: $M_{f,i} = \sum_{i=j+k}(M_{f-1,j} + M_k^{PIs})$ and $W_{f,i} = \sum_{i=j+k}(W_{f-1,j} W_k^{PIs})$.

A M_wD of a $(PSt)_{\langle f-1\rangle}$-*star*-PIs hetero-star block copolymer, $[M_i \sim W_i]^{cal}$ can be calculated using $M_i = \Sigma_f\, w_f M_{f,i}$ and $W_i = \Sigma_f\, w_f W_{f,i}$. On the other hand, a M_wD of the $(PSt)_{\langle f-1\rangle}$-*star*-PIs, $[M_i \sim W_i]^{obs}$ can be determined by GPC-LALLS measurements. By comparing the resultant $[M_i \sim W_i]^{\mathrm{cal}}$ with $[M_i \sim W_i]^{\mathrm{obs}}$, a DNA of the $(\mathrm{PSt})_{\langle \mathrm{f}-1\rangle}$-*star*-PIs hetero-star block copolymer was determined. The result is shown in Fig. 4, where a GPC chromatogram and a M_{w}D are also shown.

As shown in Fig. 4, a difference in the elution volume between $(\mathrm{PSt})_{4.7}$ and $(\mathrm{PSt})_{6.2}$ was detected with difficulty, but a difference in the M_{w}D between them was detected with ease. The M_{w}D is better than the GPC chromatogram for discussing the molecular characteristics of the $(\mathrm{PSt})_{\mathrm{f}}$ star polymers. The DNAs of the three samples seem to be similar to the M_{w}Ds of the corresponding samples, even though the abscissas of both M_i and f are different from each other. It should be noted that it is a mistake to convert the abscissa of the M_{w}D into that of the DNA using an equation of $f = M_i/M_{\mathrm{n}}^{\mathrm{arm}}$. The $M_{\mathrm{n}}^{\mathrm{arm}}$ value has a distribution of M_i and is not constant, although the average $M_{\mathrm{n}}^{\mathrm{arm}}$ value is a constant; in other words, the equal of $f = M_i/M_{\mathrm{n}}^{\mathrm{arm}}$ is not correct. If $f = M_i/M_{\mathrm{n}}^{\mathrm{arm}}$ is correct, the f value should not be a natural number and the special calculations performed in the present study would not be necessary to estimate the DNA. In conclusion, it is a new finding and has never been reported that the DNAs of the three samples are similar to the M_{w}Ds of the corresponding samples.

Each M_{w}D of the three samples appears to be broad, but the distributions are actually narrow because the corresponding $M_{\mathrm{w}}/M_{\mathrm{n}}$ values are less than 1.09. On the other hand, there is no standard for estimating the sharpness of the DNA. For example, a number-average number of arms (f_n) and a weight-average number of arms (f_{w}) can be calculated as $f_{\mathrm{n}} = \Sigma_f n_f f$ and $f_{\mathrm{w}} = \Sigma_f w_f f$ using the DNA obtained, and these values are similar to M_{n} and M_{w}. However, the f_{w} has no physical meaning and hence the $f_{\mathrm{w}}/f_{\mathrm{n}}$ values, which are calculated to be less than 1.09 also have no physical meaning. So, a measure of the sharpness of the DNA is necessary. A normalized difference between the average number of arms and the actual number of arms (R_{f}) might be proposed as a measure of the DNA.

$$R_f = 100\Sigma_f w_f |f - \langle f\rangle|/\langle f\rangle \qquad (9)$$

The $(100 - R_f)$% value is the probability that the $(\mathrm{PSt})_{\langle \mathrm{f}\rangle}$ and $(\mathrm{PSt})_{\langle \mathrm{f}-1\rangle}$-*star*-PIs star polymers can be, respectively, considered as the homogeneous $(\mathrm{PSt})_{\mathrm{f}}$ and $(\mathrm{PSt})_{\mathrm{f}-\mathrm{n}}$-*star*-PIs star polymers without M_{w}Ds. The $(100 - R_f)$% values of the three samples were found to be more than 80%. The DNAs in Fig. 4 might be concluded to be narrow.

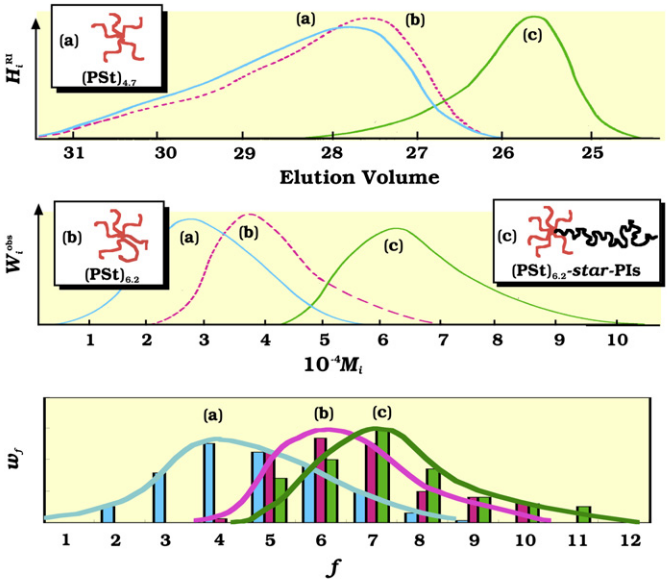

Fig. 4. The GPC chromatograms, the molecular weight distributions (M_{w}Ds), and the distributions of the number of arms (DNAs) for (a) $(\mathrm{PSt})_{4.7}$, (b) $(\mathrm{PSt})_{6.2}$, and (c) $(\mathrm{PSt})_{6.2}$-*star*-PIs.

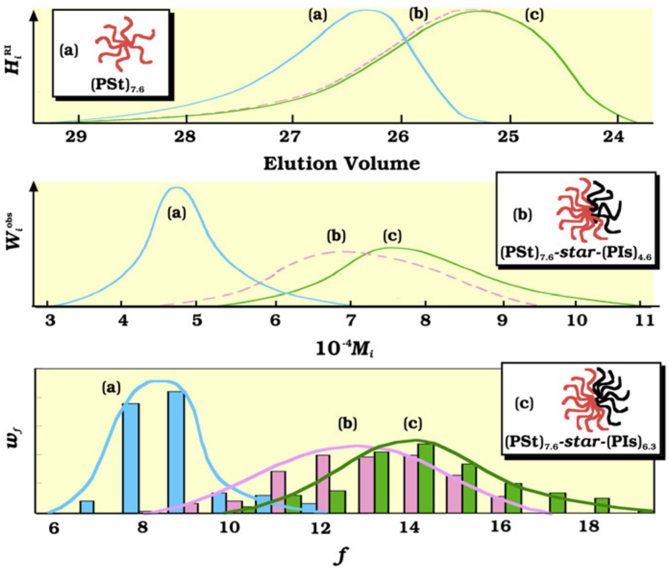

Fig. 5. The GPC chromatograms, the molecular weight distributions (M_{w}Ds), and the distributions of the number of arms (DNAs) for (a) $(\mathrm{PSt})_{7.6}$, (b) $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$, and (c) $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6.3}$.

The DNA of the $(\mathrm{PSt})_{4.7}$ shifted to that of the $(\mathrm{PSt})_{6.2}$ in parallel and the DNA of the $(\mathrm{PSt})_{6.2}$ also then shifted to that of the $(\mathrm{PSt})_{6.2}$-*star*-PIs in parallel. These findings suggest that the anionic living polymerization of PStM and Is monomer by $(\mathrm{PSt})_{\mathrm{f}}^{-}$ carbanions proceeded homogeneously. That is, a selective polymerization where PStM and Is are polymerized predominantly by the $(\mathrm{PSt})_{\mathrm{f}}^{-}$ having the lower M_{n} did not occur under the present polymerization conditions.

In the case of the $(\mathrm{PSt})_{\mathrm{f}-\mathrm{n}}$-*star*-$(\mathrm{PIs})_{\mathrm{n}}$ hetero-star block copolymer, the calculation for determining $[M_{f,i} \sim W_{f,i}]$ became too complicated because it is common for both M_{n} and $M_{\mathrm{w}}/M_{\mathrm{n}}$ values of PStM to be different from those of PIsM. However, the M_{n} values of PStM and PIsM are 5.45×10^3 and 5.33×10^3, respectively. The $M_{\mathrm{w}}/M_{\mathrm{n}}$ values of PStM and PIsM are 1.03 and 1.04, respectively. Thus, all arms of the $(\mathrm{PSt})_{\mathrm{f}-\mathrm{n}}$-*star*-$(\mathrm{PIs})_{\mathrm{n}}$ can be considered to be the same as each other when calculating M_{w}D. These conditions had been set to perform the present calculation with ease. Therefore, the M_{w}D of a $(\mathrm{PSt})_{\mathrm{f}-\mathrm{n}}$-*star*-$(\mathrm{PIs})_{\mathrm{n}}$ hetero-star block copolymer, $[M_{f,i} \sim W_{f,i}]$ can be calculated using $M_{f,i} = \Sigma_{i=j+k}\ (M_{f-1,j} + M_{1,k})$ and $W_{f,i} = \Sigma_{i=j+k}\ (W_{f-1,j}\ W_{1,k})$.

The M_{w}D of a $(\mathrm{PSt})_{\langle \mathrm{f}-\mathrm{n}\rangle}$-*star*-$(\mathrm{PIs})_{\langle \mathrm{n}\rangle}$, $[M_{\mathrm{i}} \sim W_{\mathrm{i}}]^{\mathrm{cal}}$ can be calculated using $M_i = \Sigma_f\ w_f M_{f,i}$ and $W_i = \Sigma_f\ w_f W_{f,i}$. By comparing the resultant $[M_i \sim W_i]^{\mathrm{cal}}$ with $[M_i \sim W_i]^{\mathrm{obs}}$ determined by GPC-LALLS measurements, DNA of the $(\mathrm{PSt})_{\langle \mathrm{f}-\mathrm{n}\rangle}$-*star*-$(\mathrm{PIs})_{\langle \mathrm{n}\rangle}$ hetero-star block copolymer was determined. The result is shown in Fig. 5, where a GPC chromatogram and a M_{w}D are also shown.

As shown in Fig. 5, a difference in the elution volume between $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$ and $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6.3}$ was detected with difficulty, but a difference in the M_{w}D between them was detected with ease. The DNAs of the three samples seem to be similar to the corresponding M_{w}Ds. This is a new finding and has never been reported.

Each M_{w}D of the three samples appears to be broad, and the M_{w}D of $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6.3}$ seems especially broad compared to that of $(\mathrm{PSt})_{7.6}$. However, the M_{i} range ratio from 5×10^4 to 11×10^4 of $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6.3}$ is probably the same as that from 3×10^4 to 7×10^4 of $(\mathrm{PSt})_{7.6}$. Actually, the two $M_{\mathrm{w}}/M_{\mathrm{n}}$ values are less than 1.11, and the M_{w}Ds should be narrow. On the other hand, the R_f values of the three samples defined by Eq. (9) were less than 20%. The DNAs in Fig. 5 might be concluded to be narrow.

The DNA of the $(\mathrm{PSt})_{7.6}$ did not appear to shift to that of the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$ in parallel. However, a normalized DNA can be defined as plots of $w_f/w_f^{\max}$ against $f/f_{\max}$, where $w_f^{\max}$ and $f_{\max}$ are, respectively, a maximum of w_f and that of f. The normalized DNA of the $(\mathrm{PSt})_{7.6}$ was found to be the same as that of $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$. In other word, a half width of the normalized DNA of the $(\mathrm{PSt})_{7.6}$ is the same as that of the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$. Hence, the DNA of the $(\mathrm{PSt})_{7.6}$ shifted to that of the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$ in parallel. Then, the DNA of the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{4.6}$ also shifted to that of the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6/3}$ in parallel. These findings suggest that the anionic living polymerization of PIsM by the $(\mathrm{PSt})_{7.6}^{-}$ and the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})^{-}$ carbanions proceeded homogeneously. That is, a selective polymerization where PIsM is polymerized predominantly by the $(\mathrm{PSt})_f^{-}$ and $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})^{-}$ having the lower M_n did not occur under the present polymerization condition. The mechanism of anionic living polymerization of macromonomers for preparing hetero-star block copolymers from a DNA perspective will be discussed in detail elsewhere [14].

4. Conclusion

We have previously prepared $(\mathrm{PSt})_{6.2}$-*star*-PIs and $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})_{6.3}$ hetero-star block copolymers *via* anionic living polymerization of PStM and PIsM macromonomers. By considering the composition distribution of the hetero-star block copolymers, the M_i was precisely calculated to become the same equation as Eq. (3) using GPC-LALLS. Thus three-dimensional molecular weight distributions (3D-M_wD) of the two $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_\mathrm{n}$ and its four precursors were determined by plotting a weight fraction (W_i^{obs}) at the ith elution volume against the corresponding molecular weight (M_i) and ith elution volume. A non-linear relationship between the ith elution volume and M_i of $(\mathrm{PSt})_{6.2}$-*star*-PIs was first observed and explained from a g_{star} perspective.

The distributions of the number of arms (DNAs) of the two $(\mathrm{PSt})_{f-n}$-*star*-$(\mathrm{PIs})_\mathrm{n}$ and its four precursors were determined. The analysis for determining the DNA was evaluated as a reliability factor (R) as defined as

$$R = 100\sum_i |W_i^{\mathrm{obs}} - W_i^{\mathrm{cal}}| / \sum_i W_i^{\mathrm{obs}} \tag{10}$$

The R values for the six samples were found to be less than 6%. Hence, the DNAs shown in Figs. 4 and 5 might be concluded to be valid. The DNAs seems to be similar to the corresponding M_wDs. Anionic living polymerization of PIsM by the $(\mathrm{PSt})_{7.6}^{-}$ and the $(\mathrm{PSt})_{7.6}$-*star*-$(\mathrm{PIs})^{-}$ carbanions was found to proceed homogeneously from a DNA perspective.

Appendix A

The star block copolymers have a molecular weight distribution and a composition distribution (CD) among the different molecular weight and the same molecular weights. For this reason, we will consider the molecular weight, the refractive index increment and the concentration of the star block copolymer at the ith elution volume as $M_{i,j}$, $(\mathrm{d}n/\mathrm{d}c)_{i,j}$, and $C_{i,j}$, respectively. That is, a molecular weight distribution can be represented by the subscript i, and the CD can be represented by the subscript j. Thus the refractive index (RI) intensity (H_i^{RI}) and the LALLS intensity (H_i^{LS}) of the corresponding RI and LALLS chromatograms of the star block copolymers at the ith elution volume can be described as follows.

$$H_i^{\mathrm{RI}} = k_{\mathrm{RI}}\sum_j (\mathrm{d}n/\mathrm{d}c)_{i,j} C_{i,j} \tag{A1}$$

$$H_i^{\mathrm{LS}} = k_{\mathrm{LS}}\sum_j \left[(\mathrm{d}n/\mathrm{d}c)_{i,j}\right]^2 M_{i,j} C_{i,j} \tag{A2}$$

As a first approximation, one can assume that $M_{i,j} = M_i$, because the polymer chains having $M_{i,j}$ appeared at the same ith elution volume. As reported by the present authors elsewhere [15], the $M_\mathrm{n}^{\mathrm{LALLS}}$ values determined using $M_{i,j} = M_i$ were found to be equal to the $M_\mathrm{n}^{\mathrm{OSM}}$ values determined by membrane osmometry for linear and star block copolymers. The relation of $M_{i,j} = M_i$ is an assumption but was found to be used for determining $M_\mathrm{n}^{\mathrm{LALLS}}$ of the star block copolymers having sharp composition distributions in THF as a good solvent for PSt and PIs. Therefore, $M_{i,j}$ in Eq. (A2) can be changed to M_i and moved outside of the summation of Σ_j. By this treatment, Eq. (A3) can be derived as follows:

$$M_i = \frac{(k_{\mathrm{RI}})^2}{k_{\mathrm{LS}}}\frac{H_i^{\mathrm{LS}}}{\left(H_i^{\mathrm{RI}}\right)^2}\frac{\left[\sum_j (\mathrm{d}n/\mathrm{d}c)_{i,j} C_{i,j}\right]^2}{\sum_j (\mathrm{d}n/\mathrm{d}c)_{i,j} C_{i,j}} \tag{A3}$$

With the relation of $\Sigma_j C_{i,j} = C_i$ in mind, the two summations in Eq. (A3) can be changed as follows: $\Sigma_j\, (\mathrm{d}n/\mathrm{d}c)_{i,j}\, C_{i,j} = C_i\, \langle(\mathrm{d}n/\mathrm{d}c)_{i,j}\rangle = C_i\, (\mathrm{d}n/\mathrm{d}c)_i$ and $\Sigma_j\, [(\mathrm{d}n/\mathrm{d}c)_{i,j}]^2\, C_{i,j} = C_i \langle[(\mathrm{d}n/\mathrm{d}c)_{i,j}]^2\rangle = C_i\, [(\mathrm{d}n/\mathrm{d}c)_i]^2$, where $\langle\ \ldots\ \rangle$ means the average of the corresponding refractive index increments. The corresponding equations of M_i thus became Eq. (3) in the text.

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