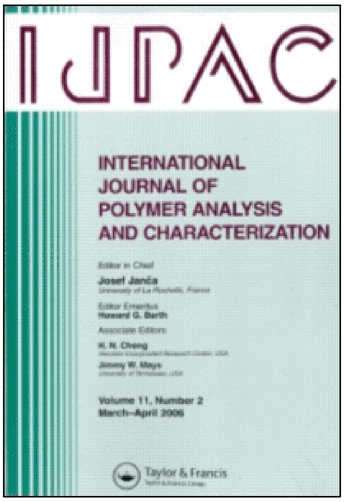

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Molecular Weight Measurements of Star-Shaped Polystyrene-block-Polybutadiene Copolymers Using Gel Permeation Chromatography

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Gel permeation chromatography (GPC) has been used to measure the molecular weight and characterize the number of arms per molecule for star-shaped styrene-butadiene block copolymers (SBS). Conventional GPC method based on polystyrene calibration standards measured a "linear-polystyrene-equivalent" molecular weight that was significantly different from the true molecular weight measured by a GPC hyphenated with a multiangle laser light scattering instrument. The comparison was made on four nearly monodispersed star-shaped copolymers, having a three-arm, four-arm, five-arm, or six-arm molecular structure. In all cases, the "linear-polystyrene-equivalent" molecular weights were higher than the true molecular weights for both the arm and the star molecule. The number of arms as determined based on the "linear-polystyrene-equivalent" molecular weights was consistently smaller than the true number of arms determined based on true molecular weights. The inaccuracy of the conventional GPC method was caused by the use of linear polystyrene calibration standards for characterizing a nonlinear copolymer molecule. The interpolation method developed previously for linear copolymers was unable to produce the accurate molecular weight for star SBS copolymers, and the deviation increases with an increase in the number of arms per molecule.

Keywords: Gel permeation chromatography; Star polymer; Block copolymer; Butadiene; Styrene; Light scattering

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INTRODUCTION

Star-shaped copolymers such as styrene-butadiene block copolymers (SBS) provide compact morphology, reduced solution viscosity, and higher retention of properties under high temperature and high shear applications, and therefore have been extensively used in industrial applications. These star-shaped SBS copolymers are made by a synthesis of living polymeric arms followed by their linking reaction with a multifunctional, electrophilic linking agent[1–8]. The molecular weight and the number of arms per molecule are the two most important parameters of the formed star copolymer that affect its properties. The molecular weight is often measured by a conventional gel permeation chromatography (GPC) method comprising a mass detector and column calibrations, and the ratio of the molecular weight of SBS star copolymer to that of its linear arm determines the number of arms of each molecule. In as much as the conventional GPC method often uses linear polystyrene standards for calibration, the measured molecular weights are actually "linear-polystyrene-equivalent" molecular weights. Knowing that (1) the hydrodynamic volumes of SBS and polystyrene differ[9] and (2) the elution volumes of a star polymer and a linear polymer of an equal molecular weight are not equal[10,11], the measured molecular weights and the determined number of arms of the star polymer are dubious. Whereas this difficulty can be alleviated by using a universal calibration approach, in which the hydrodynamic volume parameter defined as the product of molecular weight and intrinsic viscosity falls on a single calibration curve for various linear and star polymers, the universal calibration method necessitates additional effort for measuring intrinsic viscosity[12]. Therefore, correct molecular weights determination warrants an absolute GPC method that requires no column calibrations.

Since it has been long known that laser light scattering (LS) is an accurate and absolute method for the determination of molecular mass and structure, it seems to be the ideal instrument for analyzing the star-shaped SBS copolymers. However, very little information about the application of LS on SBS copolymers exists in the literature, and comparisons of the accuracy between this absolute method and the conventional GPC method have not been published. Therefore, a GPC hyphenated with a multiangle laser light scattering (MALL) instrument was set up in this current work to measure the absolute molecular weights of the star-shaped SBS copolymers. Four model SBS star polymers were synthesized anionically and had nearly monodispersed three-arm, four-arm, five-arm, and six-arm structures. The conventional GPC method was then compared against the GPC-MALL method in terms of the accuracy of determining the molecular weight and the number of arms of each molecule.

EXPERIMENTAL

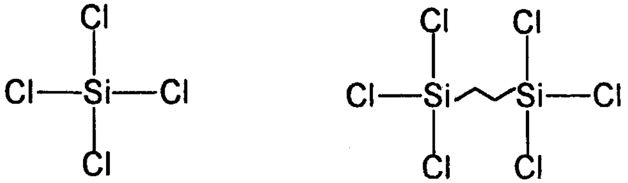
Materials

All materials used in this work were purified prior to their use. Styrene (TSRC, Taiwan) had been treated with activated alumina (Alcoa Co.) to remove the inhibitor. Butadiene (TSRC) had been vaporized, recondensed, and treated with activated alumina to remove any impurities, moisture, and the inhibitor. *n*-butyllithium at 15 wt% concentration was purchased from Merck. Cyclohexane solvent was also obtained from TSRC and dried with activated alumina. Reagent grade tetrahydrofuran (THF) was purchased from Merck and pretreated with activated alumina. Silicon tetrachloride ($SiCl_4$) and 1,2-bis(trichlorosilyl)ethane (BTCE), having four or six functional groups, -Cl, each, (see Scheme 1) were used as the linking agents and purchased from TCI and Aldrich, respectively.

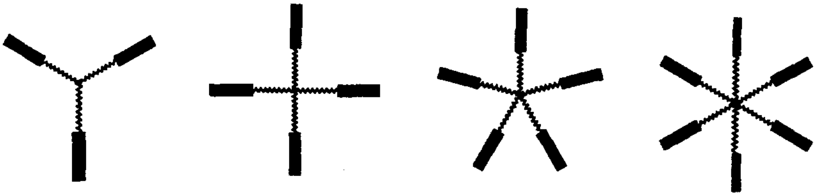
Syntheses of SBS Star-Shaped Copolymers

Star-shaped SBS block copolymers were made via a linking method wherein living diblock precursor arms of the polystyrene-*block*-polybutadiene type were linked by a multifunctional linking agent leading to the formation of the final star copolymer. This synthesized star polymer comprised three, four, five, or six arms extending outwardly from the nucleus formed by the linking agent, such as shown in Scheme 2.

The diblock precursor arm was a block copolymer comprising one block of polystyrene and one block of polybutadiene having a target polystyrene content of 30%. This diblock polymeric arm was a living polymer containing a single lithium atom bonded to a terminal carbon atom, and was readily made via anionic polymerization using *n*-butyllithium as the initiator in cyclohexane solvent. To start our experiments, appropriate amounts of cyclohexane, 0.02 wt% THF, and styrene were put into a 1-L pressure vessel. The vessel content was titrated with *n*-butyllithium until the red color of polystyryllithium anion would not disappear promptly,



SCHEME 1 $SiCl_4$ and BTCE



SCHEME 2 3-arm, 4-arm, 5-arm, and 6-arm SBS star copolymers where ▬ is polystyrene and 〰 is polybutadiene.

thus indicating the complete elimination of impurities. The starting temperature was kept at 40°C prior to the addition of the required weight of *n*-butyllithium. Anionic propagation reaction proceeded quickly with a significant exotherm. Two to 5 min after the vessel temperature reached the maximum, the butadiene monomer was charged into the vessel. The overall diblock precursor arm was synthesized as follows:

$$R\text{Li} \xrightarrow{\text{styrene}} R\text{sss}^-\text{Li}^+ \xrightarrow{\text{butadiene}} \underset{(\text{SB}^-\text{Li}^+)}{R\text{sssbb}^-\text{Li}^+}$$

where $R = n$-butyl.

The diblock arms were then linked using SiCl_4 or BTCE at varying temperatures. Depending on the linking temperature, either complete or incomplete linking occurred. The amount of linking agent was crucial to the number of arms of the formed polymer molecule. Exact amount of linking agent in one-third, one-fourth, one-fifth, or one-sixth molar ratios to the diblock arms was necessary, just sufficient to react with exactly three, four, five, or six chlorine atoms attached to the linking agent:

Case 1:

$$3\text{SB}^-\text{Li}^+ + \text{SiCl}_4 \longrightarrow (\text{SB})_3\text{SiCl} + 3\text{LiCl}$$

Case 2:

$$4\text{SB}^-\text{Li}^+ + \text{SiCl}_4 \longrightarrow \text{Si(SB)}_4 + 4\text{LiCl}$$

Case 3:

$$5\text{SB}^-\text{Li}^+ + \text{BTCE} \longrightarrow (\text{SB})_5\text{SiCl} + 5\text{LiCl}$$

Case 4:

$$6\text{SB}^-\text{Li}^+ + \text{BTCE} \longrightarrow (\text{SB})_6\text{Si} + 6\text{LiCl}$$

In case 1, the amount of $SiCl_4$ charge had to be precise so as to produce monodispersed three-arm molecules respectively. Any undercharge of $SiCl_4$ would provide an insufficient number of linking sites, leading to the formation of four-arm molecules, and any overcharge of $SiCl_4$ would generate too many linking sites, resulting in an increased amount of two-arm and one-arm molecules[7]. However, the amount of $SiCl_4$ charge in case 2 should be that required to react with all linear diblock arms so as to ensure the formation of four-arm molecules in the absence of three-arm, two-arm, and one-arm molecules[7]. Analogously, the syntheses of the 5-arm molecule in case 3 and the 6-arm molecule in case 4 used the same principles. At the completion of the polymerization, the polymer was precipitated in isopropanol. The polymer was later dried and analyzed.

Analysis of GPC Chromatograms

The "linear-polystyrene-equivalent" molecular weights and the molecular weight distributions of synthesized polymers were determined by a Waters gel permeation chromatograph (GPC) equipped with Waters M-486 adsorbance (UV) and Waters 410 differential refractive index (RI) detectors. The GPC was operated using three Waters Styragel columns (10^3, 10^4, 10^5 Å) at a norminal flow rate of 1 mL/min with a sample concentration of 0.1% in THF solvent. Monodispersed polystyrene standards were purchased from Polymer Laboratories, UK, for instrument calibration. Conversely, the "true" molecular weights of the star polymers and their corresponding arms were determined by a GPC hyphenated with a multiangle laser light scattering (MALL) instrument (miniDAWN model, Wyatt Technology Corporation) equipped with a 20 mW semiconductor laser. The laser wavelength was 690 nm and the scattered light was detected by three detectors located at 45°, 90°, and 135°. The true molecular weights of the star copolymer and the diblock arm were calculated from the intercepts on the ordinate of the Debye plot based on the following equation[13]:

$$\frac{Kc}{R_\theta} \approx \frac{1}{M_w}\left[1 + \frac{16\pi^2}{3\lambda^2}\langle r_g^2\rangle \sin^2\left(\frac{\theta}{2}\right)\right] \quad \text{at low concentration}$$

where R_θ is the Rayleigh scattering intensity at angle θ, M_w is the molecular weight, c is the concentration of polymer solution, $\langle r_g^2\rangle$ is the mean square radii, λ is the wavelength of the incident light in the solvent, and K is an optical parameter, which is a function of the specific refractive index increment of polymers, *dn*/*dc*. The specific refractive index increment *dn*/*dc* of polymers as required for the calculation was measured using the Wyatt/Optilab DSP Interferometric refractometer.

RESULTS AND DISCUSSION

In case 1, a three-arm polymer having a narrow molecular weight distribution (main-peak polydispersity = 1.03) was observed as depicted in Figure 1 indicating the formation of a nearly monodispersed star polymer. The conventional GPC method indicated the "linear-polystyrene-equivalent" molecular weight of each arm (M_{arm}) was 3.63 × 10^4 and that of the star polymer (M_{star}) was 1.01 × 10^5. The number of arms of each star molecule was determined by their ratio, M_{star}/M_{arm} as 2.78. In contrast, the GPC-MALL method provided the true molecular weights as 2.19 × 10^4 and 6.54 × 10^4 for the arm ($\mathrm{M_{arm}}$) and the star ($\mathrm{M_{star}}$), respectively. (The Debye plots generated by this GPC-MALL instrument for the star copolymer and its constituting diblock arm are shown in Figures 2 and 3.) The good linear curve fit indicated the high accuracy in the GPC-MALL measurements. Their ratio, $\mathrm{M_{star}/M_{arm}}$, was 3.00 showing the correct number of arms of the star molecule. Similarly, the "linear-polystyrene-equivalent" molecular weights and the true molecular weights of the arm and star molecule were measured for the other cases as shown in Figures 4 to 12. All data are summarized in Table I.

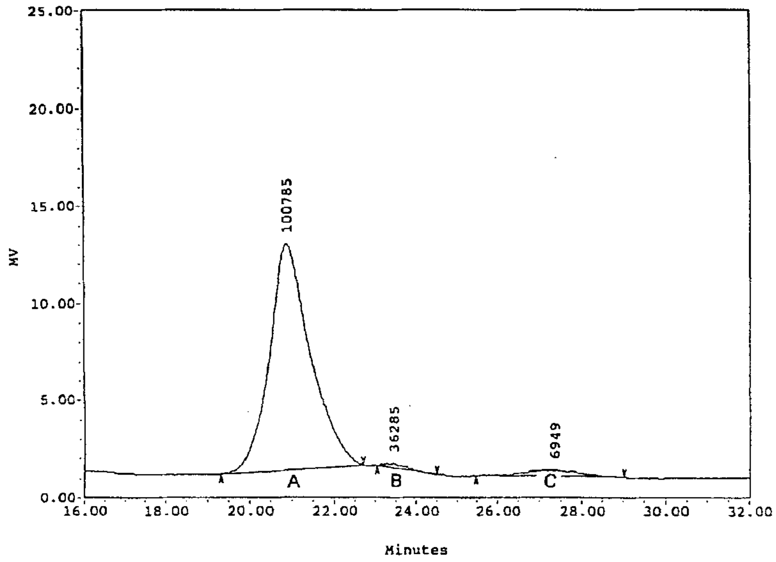


FIGURE 1 Conventional GPC plot for the three-arm star SBS block copolymer synthesized in case 1 (peak A: SBS polymer; peak B: SB arm; peak C: thermal deactivated polystyrene S).

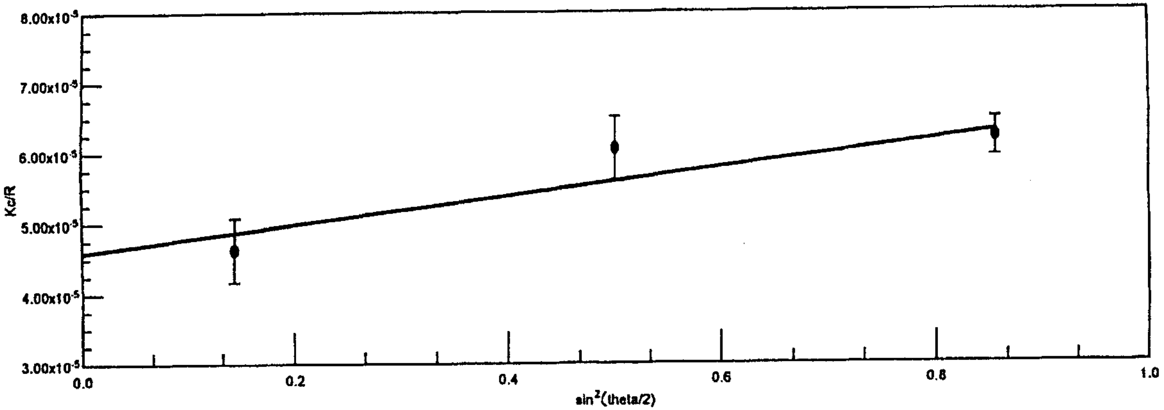


FIGURE 2 Debye plot from the MALL for the linear arm made in case 1.

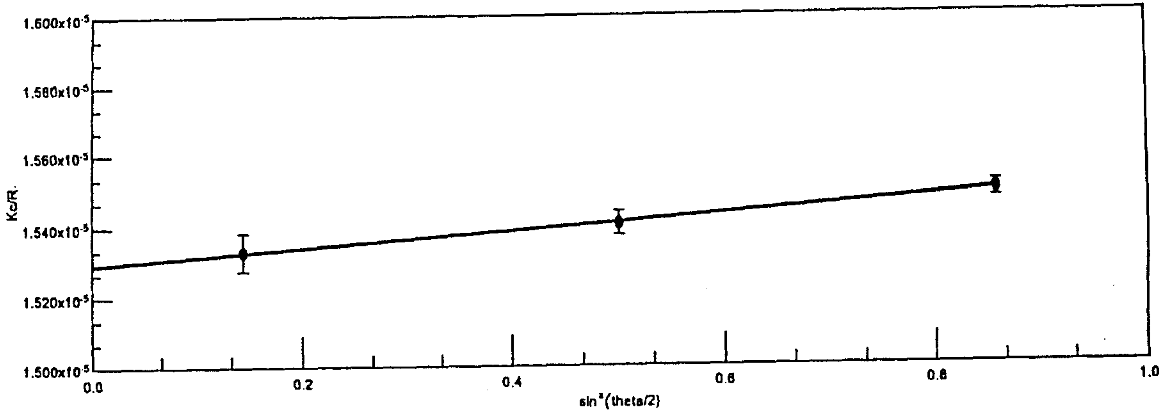


FIGURE 3 Debye plot from the MALL for the three-arm star polymer made in case 1.

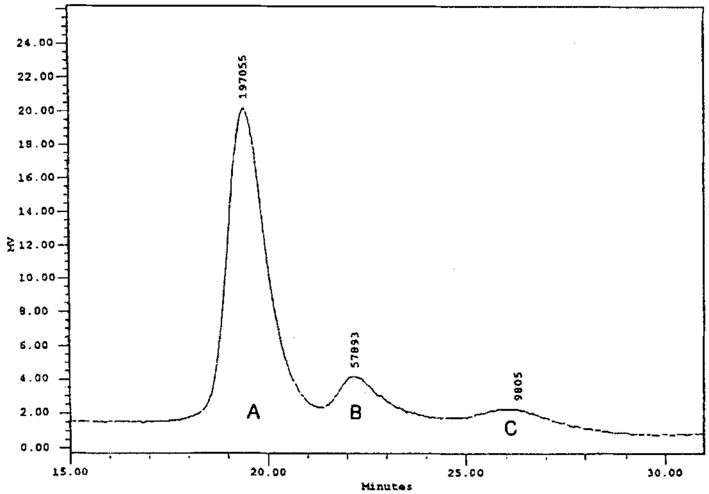


FIGURE 4 Conventional GPC plot for the four-arm star SBS block copolymer synthesized in case 2 (peak A: SBS polymer; peak B: SB arm; peak C: thermal deactivated polystyrene S).

In all cases, the "linear-polystyrene-equivalent" molecular weight was higher than the corresponding true molecular weight, regardless the arm or the star molecule. The number of arms as determined based on the "linear-polystyrene-equivalent" molecular weights was consistently smaller than the correct number of arms determined based on true molecular weights. Although in case 1 (3-arm star molecule), the correct number of arms per molecule could still be recognized via rounding off the erroneous $M_{\text{star}}/M_{\text{arm}}$ number, for star molecules having larger number of arms as in cases 2 to 4, the differences were too significant for us to determine the correct number using the conventional GPC method. The discrepancy between the molecular weights determined from the conventional GPC method and the GPC-MALL method was attributed to the lack of appropriate calibration standards. Neither SBS standards of copolymer type nor star-shaped polystyrene standards were available. As a consequence, the conventional GPC molecular weight measurements resulted in a $M_{\text{star}}/M_{\text{arm}}$ that was unable to manifest the number of arms of a star-shaped SBS copolymer.

Furthermore, the data collected in the above work provide us information as to the applicability of an interpolation method previously developed for linear copolymers of styrene and butadiene[14]. For linear copolymers, this interpolation method corrects the "linear-polystyrene-

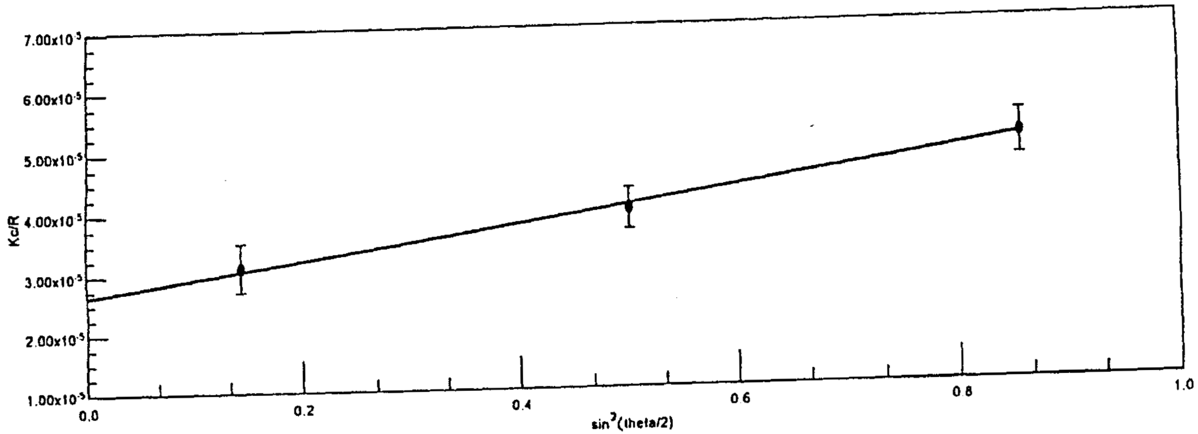


FIGURE 5 Debye plot from the MALL for the linear arm made in case 2.

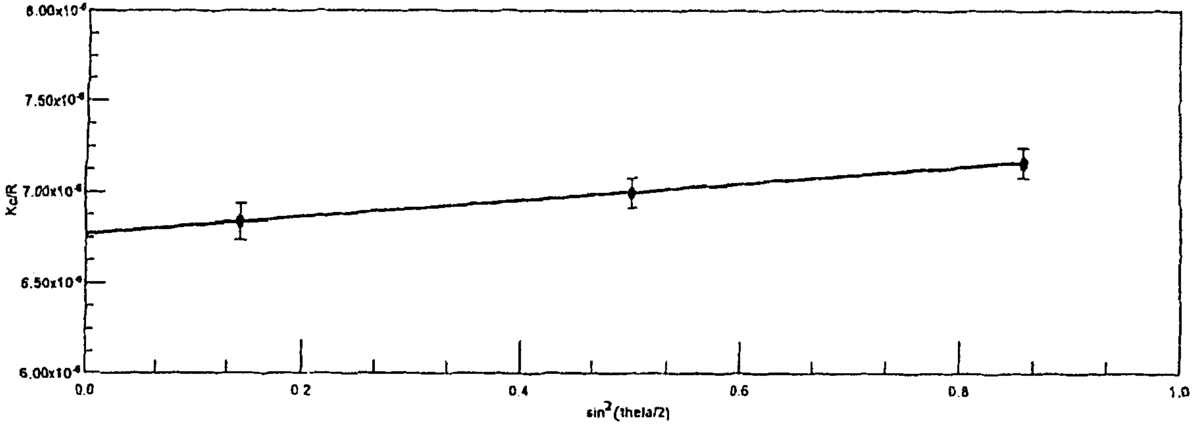


FIGURE 6 Debye plot from the MALL for the four-arm star polymer made in case 2.

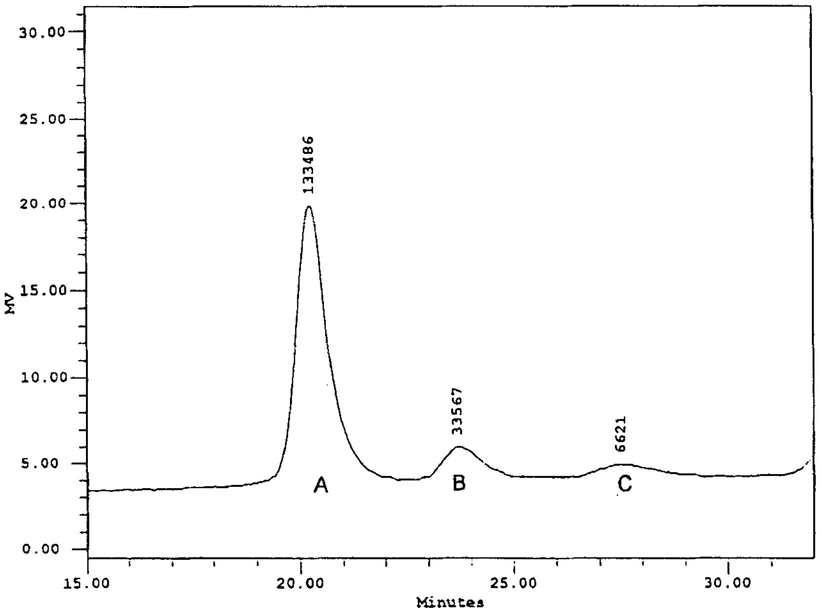


FIGURE 7 Conventional GPC plot for the five-arm star SBS block copolymer synthesized in case 3 (peak A: SBS polymer; peak B: SB arm; peak C: thermal deactivated polystyrene S).

equivalent" molecular weights (*M*) based on the overall composition of the copolymers

$$M_{\text{corrected}} = F^{x}M$$

where F is the factor for the polybutadiene of the copolymer, and x is the weight fraction of the polybutadiene portion of the copolymer. The value of the term F^{x} goes to the value F at pure polybutadiene and to 1 at pure polystyrene. The value of F was previously determined as 0.548 ~ 0.571[14]. Using an average value of 0.560, the corrected molecular weights are tabulated and compared with the true molecular weight determined from GPC-MALL in Table II. As shown, the interpolation method provides a correction with acceptable accuracy (3%) for the three-arm copolymer but tends to underestimate the molecular weight for star molecules having higher degree of branching. The relative error increases with an increase in the number of arms per molecule, and up to 15% error was observed for the six-arm copolymer. This deviation thus ascertains the inapplicability of the interpolation method for linear copolymers to the star-shaped SBS copolymers.

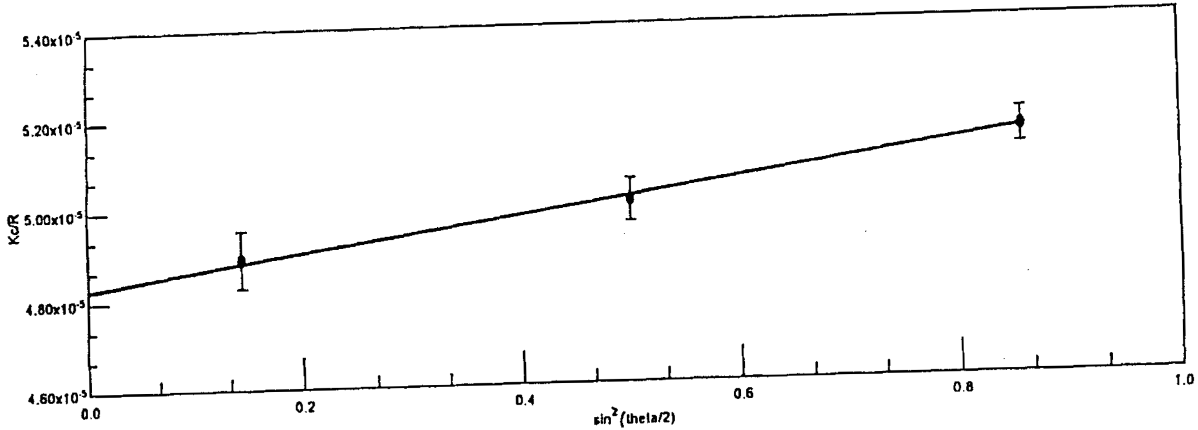


FIGURE 8 Debye plot from the MALL for the linear arm made in case 3.

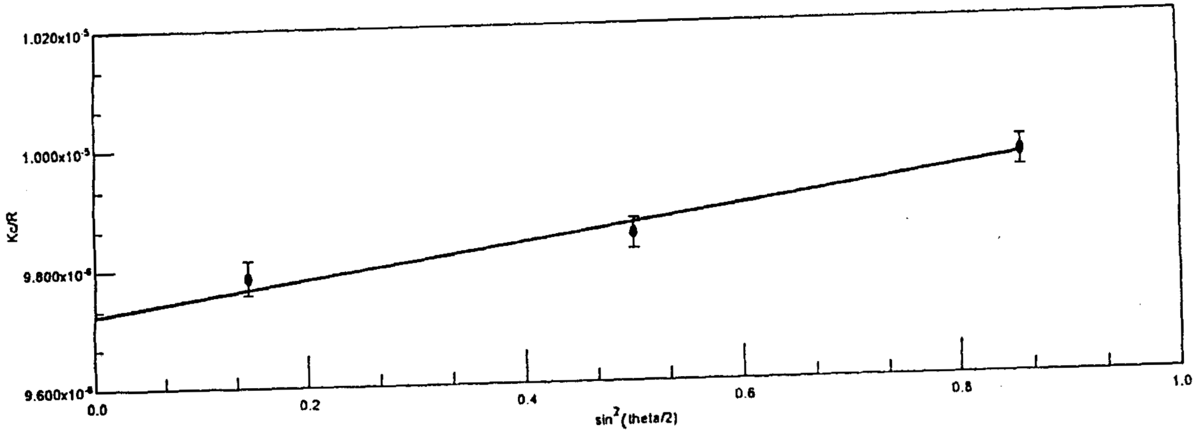


FIGURE 9 Debye plot from the MALL for the five-arm star polymer made in case 3.

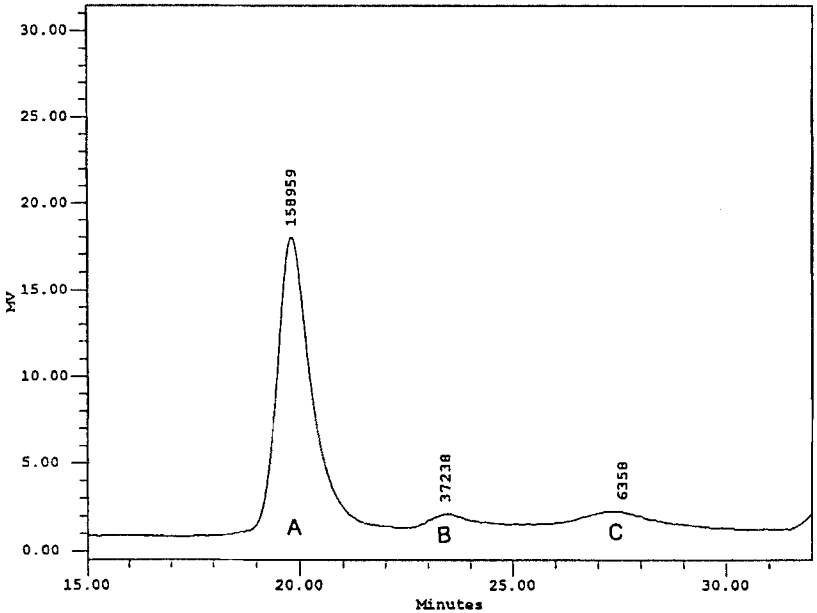


FIGURE 10 Conventional GPC plot for the six-arm star SBS block copolymer synthesized in case 4 (peak A: SBS polymer; peak B: SB arm; peak C: thermal deactivated polystyrene S).

CONCLUSIONS

Molecular weight measurements were made on four nearly monodispersed star-shaped copolymers having a three-arm, four-arm, five-arm, or six-arm molecular structure. For both the arm and the star molecule, the conventional GPC method based on polystyrene calibration standards measured a "linear-polystyrene-equivalent" molecular weight that was significantly higher than the true molecular weight measured by a GPC hyphenated with a multiangle laser light scattering instrument. Consequently, the number of arms as determined based on the "linear-polystyrene-equivalent" molecular weights was consistently smaller than the true number of arms determined based on true molecular weights. The inaccuracy of the conventional GPC method was attributed to the use of inappropriate calibration standards (because neither SBS standards of copolymer type nor star-shaped polystyrene standards were available). The interpolation method developed previously for linear copolymers was unable to produce the accurate molecular weight for star SBS copolymers, and the deviation increases with an increase in the number of arms per molecule.

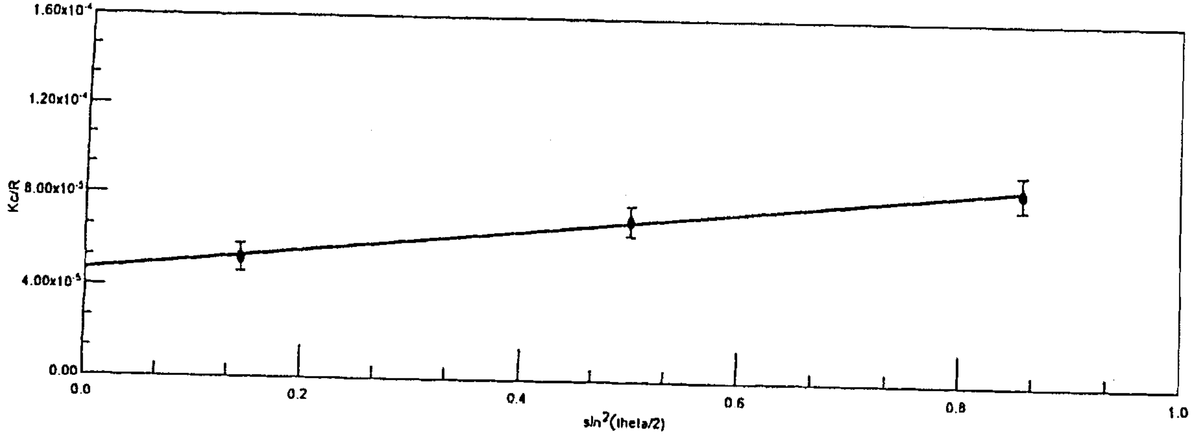


FIGURE 11 Debye plot from the MALL for the linear arm made in case 4.

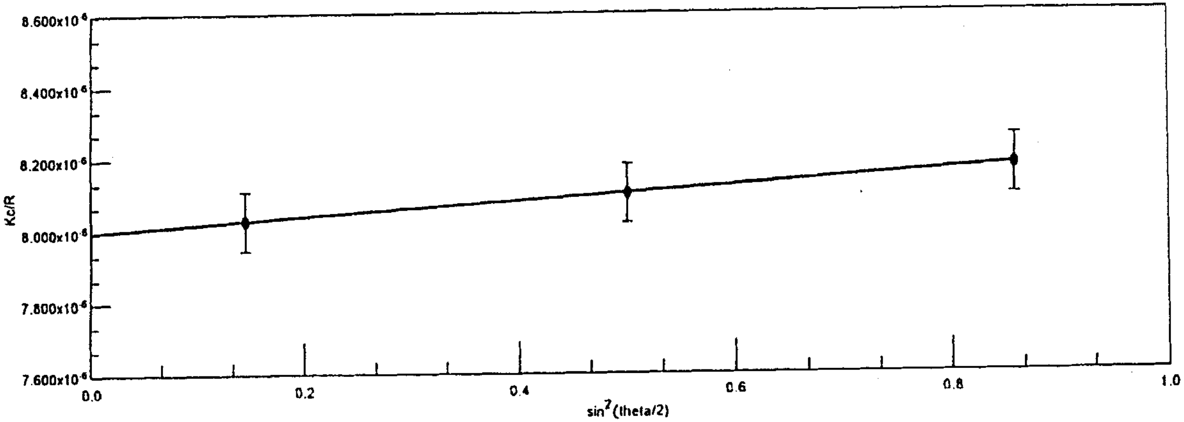


FIGURE 12 Debye plot from the MALL for the six-arm star polymer made in case 4.

TABLE I Molecular Weights of the Synthesized Polymers

	GPC-MALL measurements			Conventional GPC method		
	$\mathrm{M}_{\mathrm{arm}}$	$\mathrm{M}_{\mathrm{star}}$	$\frac{\mathrm{M}_{\mathrm{star}}}{\mathrm{M}_{\mathrm{arm}}}$	M_{arm}	M_{star}	$\frac{M_{\mathrm{star}}}{M_{\mathrm{arm}}}$
Case 1	2.19×10^4	6.54×10^4	3.00	3.63×10^4	1.01×10^5	2.78
Case 2	3.79×10^4	1.48×10^5	3.90	5.79×10^4	1.97×10^5	3.40
Case 3	2.07×10^4	1.03×10^5	4.96	3.36×10^4	1.33×10^5	3.98
Case 4	2.12×10^4	1.25×10^5	5.89	3.72×10^4	1.59×10^5	4.27

*M: true molecular weight.

M: linear-polystyrene-equivalent molecular weight.

TABLE II Relative Errors in the Application of Linear Interpolating Method for Estimating Molecular Weights of Star-Shaped Copolymers

	GPC-MALL $\mathrm{M}_{\mathrm{star}}$	Linear interpolation $\mathrm{M}_{\mathrm{corrected}}$	Ratio $\mathrm{M}_{\mathrm{corrected}}/\mathrm{M}_{\mathrm{star}}$	Relative error %
Case 1	6.54×10^4	6.73×10^4	1.03	3
Case 2	1.48×10^5	1.31×10^5	0.89	11
Case 3	1.03×10^5	8.86×10^4	0.86	14
Case 4	1.25×10^5	1.06×10^5	0.85	15

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