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Characterization of star-block copolymers having PS-b-PI arms via SEC/RI/RALLS/DV

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Summary
Poly (styrene-b-isoprene) (PS-b-PI) star-block copolymers were studied by triple detector size exclusion chromatography (SEC^3), utilizing a combination of refractive index (RI), right angle light scattering (RALLS), and differential viscosity (DV) detectors. The relationships between the number of arms, the composition, and molecular size of the star polymers were investigated. The effect of the number of arms of the star polymer on elution behavior was established and compared to a linear polystyrene calibration curve. It was found that universal calibration was valid for star polymers having up to 32 arms. The branching parameters (g and g') were calculated from intrinsic viscosity and radius of gyration data. The results indicate that, in addition to molecular weight determinations, much useful conformational information on star-block copolymers can be obtained from SEC^3. The technique is an especially useful tool for characterizing branched copolymers, which are difficult to characterize by conventional SEC.

Key Words: multi-detector SEC, star-block copolymer, dilute solution properties, branching parameters

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Introduction
Star polymers are of great intrinsic scientific and industrial interest (1-5) because of their unique properties in solution and in the solid state, which are a consequence of their molecular architecture. The aim of this work is to characterize the molecular weights and solution properties of star-block copolymers by size exclusion chromatography using a refractive index detector (SEC/RI), on-line with a right angle laser light scattering photometer (RALLS) and a four-capillary bridge design differential viscometer (DV), The enhanced capabilities and reliability of such a system, in comparison to conventional single detector SEC, have been previously reported (6-10).

Experimental Section

Samples
Well-defined star polymers of IS and SI architectures were prepared by anionic polymerization under high vacuum line conditions. The architectures and designations are as follows:

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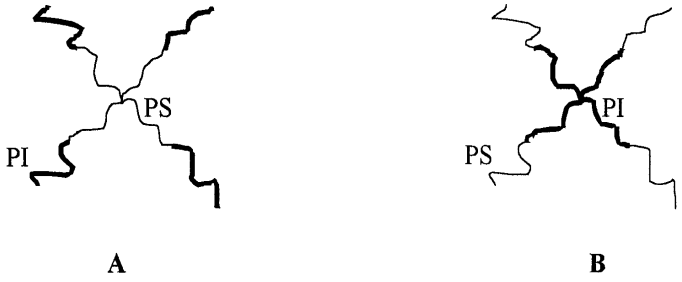
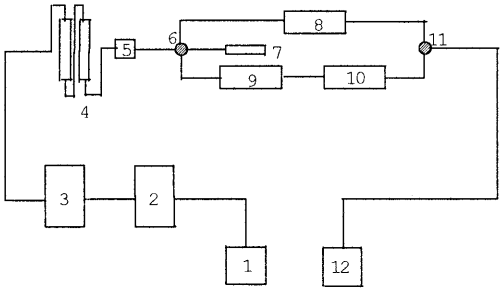


Scheme 1. Models for a 4-arm Star-block Copolymer: (A) IS Star; (B) SI Star.

IS-4 and IS-32 are 4-arm and 32-arm PS/PI star-block copolymers with the PS block as the core. The number-average molecular weight (M_n) of each arm is $6.2x10^4$ and PS content is 76 wt. %. SI-4 is a 4-arm star-block copolymer containing 30 wt. % PS with the PI blocks as the core. Its arm molecular weight is $8.5x10^4$. SI-18 is an 18-arm star-block copolymer containing 36 wt. % PS, with PI blocks as the core and $M_n=2.77x10^4$.

Size Exclusion Chromatography

A dual SEC detector (Model T60, Viscotek Corp.), with RALLS and DV detectors in series, was combined on-line with a differential refractometer (RI, Model 410, Waters Corp.) coupled to a programmable HPLC pump (Model 590, Waters Corp.). Two chromatographic columns (American Polymer Standards Corp., Mentor, Ohio), measuring 30cm in length and packed with 5µm diameter PS gel, were used in series. Tetrahydrofuran (THF) was degassed ultrasonically and used as the mobile phase at a flow rate of 1.0 mL/min. The samples were dissolved in THF at a concentration of 2.000 mg/mL and were filtered through 0.2µm pore size membrane filters. Measurements were performed at 25°C, and injection volumes of the sample solutions were 100µL. TriSEC software (Viscotek) was used to treat the data obtained. Scheme 2 shows the setup of the SEC[3] system.



Scheme 2 A schematic diagram for SEC[3] configuration
1. solvent; 2. pump; 3. injector; 4. columns; 5. filter; 6. valve; 7. pulse dampener; 8. RI; 9. RALLS; 10. DV; 11. valve; 12. waste

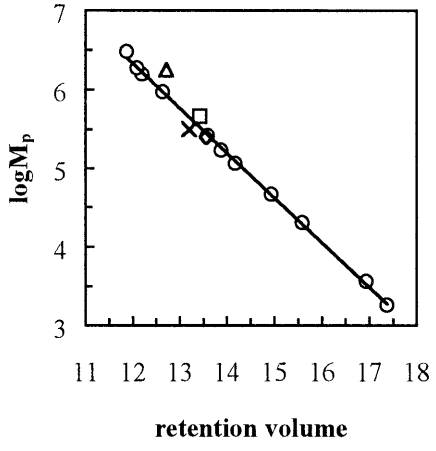


Fig.1 Plot of log M_p vs. retention volume
(○) polystyrene, (◊) IS-4, (Δ) IS-32, (×) SI-4, (□) SI-18

Results and Discussion

Characterization Via SEC/RI (SEC[1]), SEC/RI/DV (SEC[2]), and SEC/RI/RALLS/DV (SEC[3])

The molecular weights (M), intrinsic viscosities ([η]) and radii of gyration (R_g) of the star polymers obtained 1) via conventional with a RI detector (SEC[1]), 2) via SEC with both RI and DV detectors (SEC[2]), and 3) via SEC[3] (RI/DV/RALLS) are presented in Table I. In the case of SEC[2], the R_g values were computed from the intrinsic viscosity and the molecular weight via the Ptitsyn-Eizner modification of the Flory-Fox equation (11). The retention volumes (RV) as a function of [η], Rg and M at peak position of the chromatograms for polystyrene (PS) standards and the star-block copolymers are plotted in Figs. 1, 2, and 3, respectively.

Table I Characterization Data via SEC[1], SEC[2] and SEC[3] for Star Copolymers

Sample	SEC Test	M_n $\times10^{-4}$	M_w $\times10^{-4}$	M_z $\times10^{-4}$	# of Arms	$[\eta]_n$ (dL/g)	$[\eta]_w$ (dL/g)	$[\eta]_z$ (dL/g)	Rg_n (nm)	Rg_w (nm)	Rg_z (nm)
IS-4	SEC[3]	25.3	27.7	30.2	4	0.902	0.919	0.964	20.16	20.52	21.34
	SEC[2]	24.0	27.7	29.9	/	0.918	0.940	0.993	18.50	20.15	21.44
	SEC[1]	21.6	24.0	30.2	/	/	/	/	/	/	/
IS-32	SEC[3]	179	193	209	32	0.844	0.859	0.881	37.81	38.48	39.37
	SEC[2]	176	199	216	/	0.871	0.887	0.906	34.44	36.93	38.83
	SEC[1]	62.2	69.0	66.3	/	/	/	/	/	/	/
SI-4	SEC[3]	32.3	33.8	35.5	4	1.366	1.379	1.394	25.07	25.31	25.58
	SEC[1]	28.4	34.9	34.2	/	/	/	/	/	/	/
SI-18	SEC[3]	47.4	48.9	50.7	18	0.540	0.545	0.549	20.91	21.02	21.15
	SEC[1]	21.7	26.4	27.3	/	/	/	/	/	/	/

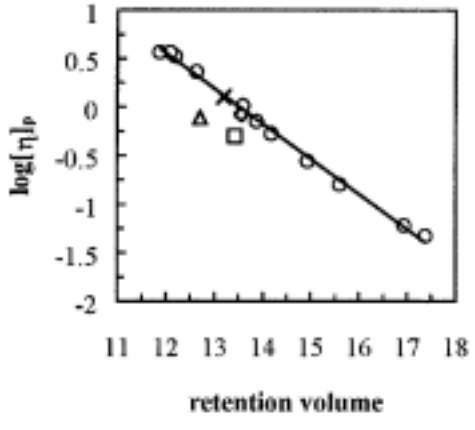


Fig.2 Plot of log $[\eta]_p$ vs. retention volume
(○) polystyrene, (◊) IS-4, (Δ) IS-32, (×) SI-4, (□) SI-18

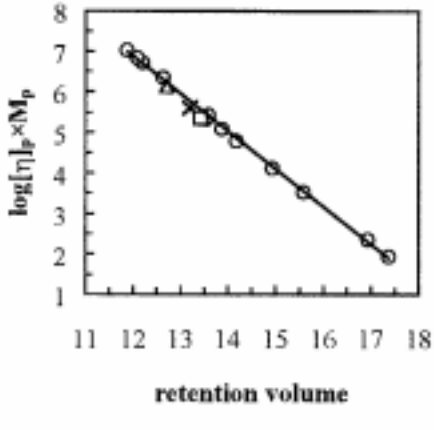


Fig.3 Plot of log $([\eta]_p \times M_p)$ vs. retention volume
(○) polystyrene, (◊) IS-4, (Δ) IS-32, (×) SI-4, (□) SI-18

Good agreement is observed between the molecular weights of star-block copolymers obtained via SEC[2] and SEC[3] on examining the data in Table I. Values of [η] and R_g generated by the two methods are also in close agreement. However, differences are

observed between molecular weights obtained for IS and SI star-block copolymers via SEC[2] and SEC[3], and values obtained via conventional SEC[1]. Theoretically, chromatographic column separation in SEC is based on hydrodynamic size. Our conventional SEC[1] was calibrated with polystyrene standards; this technique can only yield molecular weights relative to the molecular weights of the standards. The differences in local chemical structure, and in molecular architecture between star-block copolymers and the linear PS standards, result in large differences in size and retention volume for specimens of the same molecular weight. The differences in the molecular weights obtained by SEC[3] and SEC[1] depend most strongly on the number of arms in the star-block copolymer, as seen by examining the data of Table I. This demonstrates that true molecular weights cannot be measured for the star-block copolymers using conventional SEC[1], since the star polymers exhibit increasingly compact conformations as the number of arms in the star is increased.

Fig. 1 shows that the retention volumes of star polymers are larger than those of polystyrenes with the same molecular weight, and that the deviation away from the standard calibration curve mainly depends on the number of arms in the star copolymer. In addition to the effects of branching on retention volume, it must be noted that the molecular size of PI is larger than that of PS at the same molecular weight in THF at 25°C (12). This means that the retention volume of PI will be smaller than that of PS under these conditions. In other words, at a given molecular weight branching will increase retention volume while increasing PI content will decrease retention volume. The data points for IS-4 and SI-4 samples fall on or below the PS calibration curve, showing that the influence of the branching (4-arm star architecture) on their size is equal to or less than the influence of the PI content. Conversely, the data for the more highly branched IS-32 and SI-18 fall above the linear PS calibration; this means that the effect of branching is more important than PI content for these more highly branched specimens.

The density increases and the intrinsic viscosity decreases as the number of arms of the star polymer increases, as shown in Fig.2. This explains the reasoning that the molecular weights of star polymers obtained via SEC[1] are smaller than the true molecular weights of star polymers obtained via SEC[2] and SEC[3]. Also, the divergence of the molecular weights depends on the number of arms of the star polymer as shown in Table I. All the results above suggest that star polymers exhibit highly compact molecular structure in solution, which reflects the well-known characteristics of branched polymers. Fig.3 shows the plot of $\log[\eta]_p xM_p$ versus retention volume (the subscripts p indicate that peak values are used). It is interesting to note that the data points for IS and SI star-block copolymers fit well on the same calibration curve with data for linear polystyrene standards. These results indicate that the universal calibration concept is applicable to star-block copolymers and suggest that the data obtained by SEC[2] and SEC[3] are reliable.

Fig.4 shows that the concentration responses of SI-4 and SI-18 star-block copolymers are nearly the same. Fig.5 shows that the DV response of the SI-18 star polymer is less than that of SI-4 star polymer. Fig.6 shows that the RALLS response of the SI-18 star polymer is larger than that of the SI-4 star polymer at the same concentration, but the retention volume of SI-18 is slightly larger than that of SI-4. All these results point to the fact that the SI-18 sample exhibits a more compact molecular structure than SI-4 sample, due to its more highly branched architecture. In addition, the results presented in Table I and Figures 1-3 demonstrate that conformational information on macromolecules in solution can be obtained from SEC[3] chromatograms.

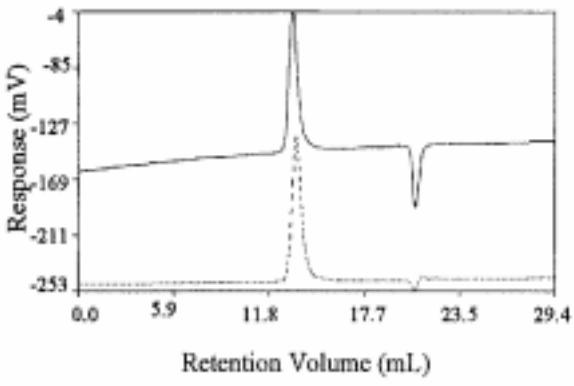


Fig.4 RI traces of SI star-block copolymers
SI-4 ————; SI-18 ……

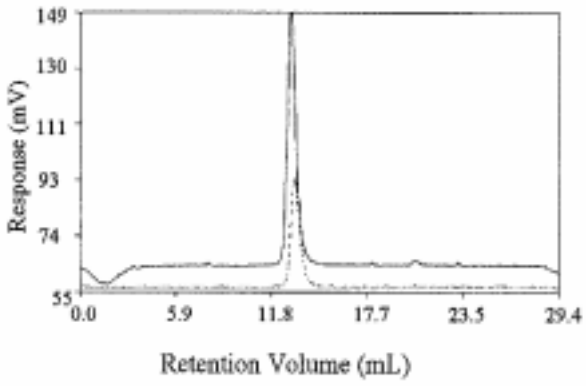


Fig.5 DV traces of SI star-block copolymers
SI-4 ————; SI-18 ……

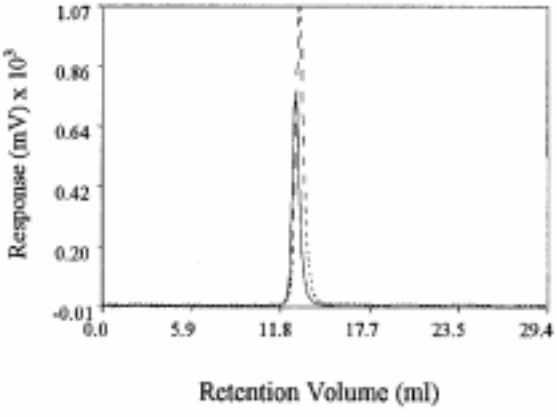


Fig.6 LS traces of SI star copolymers
SI-4 ————; SI-18 ……

Long Chain Branching Parameters g and g'

For the same molecular weight and composition of star polymers, the radius of gyration and the intrinsic viscosity decrease as the number of arms increases. This reflects an increase in polymer chain segment density as the degree of branching is increased. The branching parameters g and g' compare, respectively, the squared radii of gyration and the intrinsic viscosities of branched polymers to those values for their linear counterparts having equivalent molecular weights:

$$g = (R_g^2{}_{br}/R_g^2{}_l)_M \qquad (1)$$

and

$$g' = ([\eta]_{br}/[\eta]_l)_M \qquad (2)$$

The relationship between the number of arms (f) of the star polymers and g has been calculated theoretically (13) using random flight statistics for a star model under unperturbed (theta) conditions. However, it is also common to employ these branching parameters, as measured under good solvent conditions, to obtain insight into the extent

of branching (14). In general, the smaller the values of g and g', the more highly branched is the polymer.

To obtain linear PS/PI copolymer data on R_g and [η] corresponding to the same compositions of the star-block copolymers studied in this work, we utilized data on linear PS and PI published by Jackson et al. (15) in THF, which are,

$$R_g \text{ (PS in nm)} = 1.11\text{x}10^{-2}\, M^{0.60} \quad (3)$$

$$R_g \text{ (PI in nm)} = 1.30\text{x}10^{-2}\, M^{0.60} \quad (4)$$

$$[\eta] \text{ (PS in dL/g)} = 0.90\text{x}10^{-4}\, M^{0.73} \quad (5)$$

$$[\eta] \text{ (PI in dL/g)} = 1.57\text{x}10^{-4}\, M^{0.73} \quad (6)$$

By interpolation based on the known compositions of the star-block copolymers studied, approximate power laws for linear block copolymers can be calculated. Molecular weights, radii, and intrinsic viscosities used for the star-blocks are the weight-average values from Table I, with values from SEC[2] and SEC[3], averaged whenever possible. The calculated g and g' values are given in Table II. The g and g' values show the expected trend of smaller values as the number of arms in the star is increased. A more detailed analysis of these data does not appear prudent in light of the approximate method used to generate the data for the linear block copolymers.

Table II Branching Parameters for Star-block Copolymers

Sample	f	g	g'
IS-32	32	0.30	0.21
IS-4	4	0.90	0.93
SI-18	18	0.43	0.29
SI-4	4	0.94	0.92

Conclusions

In summary, SEC[3] has been shown to be a powerful and time saving technique for the characterization of star-block copolymers. With a limited amount of sample, the technique can be used to generate much meaningful information on branched block copolymers, such as various average molecular weights, polydispersity, radius of gyration, intrinsic viscosity, and branching parameters g and g'. Complex polymers, such as the branched block copolymers of this work, cannot usually be effectively characterized using conventional SEC.

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