

# Synthesis and Characterization of Well-Defined [Polystyrene-*b*-poly(2-vinylpyridine)]*n* Star-Block Copolymers with Poly(2-vinylpyridine) Corona Blocks

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**ABSTRACT:** This article describes the synthesis and characterization of [polystyrene-*b*-poly(2-vinylpyridine)]*n* star-block copolymers with the poly(2-vinylpyridine) blocks at the periphery. A two-step living anionic polymerization method was used. Firstly, oligo(styryl)lithium grafted poly(divinylbenzene) cores were used as multifunctional initiators to initiate living anionic polymerization of styrene in benzene at room temperature. Secondly, vinylpyridine was polymerized at the periphery of these living (polystyrene)*n* stars in tetrahydrofuran at  $-78$  °C. The resulting copolymers were characterized using size exclusion chromatography, multiangle laser light scattering, <sup>1</sup>H NMR, elemental analysis, and intrinsic viscosity measurements. © 2007 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 45: 3949–3955, 2007

**Keywords:** anionic polymerization; block copolymers; divinylbenzene; polystyrene-*b*-poly(2-vinylpyridine); star polymers

## INTRODUCTION

Immobilizing well-defined polymer chains to a surface is a robust method to control the chemical nature of a surface. Bound polymer chains can al-

ter the wet-ability, adhesion, friction, chemical functionality, biocompatibility, and structural stability of the interface. Controlling the chemistry at the interface is of paramount importance in a number of existing and emerging technologies including adhesives, paints, nano-filled polymers, pharmaceuticals, biomedical implants, and tissue engineering. Beyond the need to understand the properties of tethered polymer chains for specific applications, there is great interest in

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the fundamental physical chemistry of these systems. Polymer chains bound to an interface at one end have been the subject of intense interest in the past 25 years.<sup>1–7</sup> Surprisingly, only very few publications in the literature have addressed systematic studies of the behavior of polymer chains that are bound to an interface at multiple points.<sup>8</sup> In principle, polymer chains that are bound to an interface at multiple points should exhibit improved properties compared to traditional singly bound polymer chains in many circumstances. For example, Dadmun and coworkers observed that tethered polymer “loops” significantly improve the adhesive properties of an interface relative to that of a singly end-tethered polymer chain.<sup>9–12</sup> It is expected that these “loops” will also provide novel and superior properties, such as reduced interpenetration, reduced friction, reduced latent adsorption, and so forth as compared to conventional polymer brushes.<sup>13–16</sup>

A systematic study of structure–property relationships of surfaces covered with multiply bound polymer chains is essential in pursuit of novel materials with improved properties. The ability to reproducibly and controllably create a surface covered by multiply tethered polymer chains with controlled molecular weights, architectures, and binding sites is the key factor in such studies. Living anionic polymerization technique is well-known to be the most promising methodology for the synthesis of macromolecules with well-defined characteristics in terms of controllable molecular weight and chemical compositions with narrow molecular weight distributions and specific complex architectures.<sup>17–20</sup> The purpose of this work is to develop a synthetic strategy leading to well-defined [polystyrene-*b*-poly(2-vinylpyridine)]<sub>*n*</sub> (PS-*b*-P2VP)<sub>*n*</sub> star-block copolymers with the P2VP blocks at the corona. These materials, containing both regular PS and perdeuterated PS segments, will serve as model compounds for use in creation and characterization of well-defined multiply bound polymer chains. P2VP end blocks are used to advantage in such materials because of their adsorption properties, for example P2VP adheres strongly to mica surfaces and it has thus been extensively employed as a component in polymer brushes prepared using block copolymers.<sup>1</sup>

This article describes the anionic synthesis and detailed characterization of two series of such star-block copolymers, one with PS deuterated and the other with no deuteration, varying

only in their PS/P2VP ratios. To our knowledge, these are the first well-defined star-block copolymers of PS and P2VP having the P2VP blocks at the periphery of the star. To make such copolymers, the styrene block must be polymerized first because of the fact that poly(vinylpyridinyl) anions are more stable than poly(styryl) anions. Therefore, a “core-first” approach using multifunctional initiator is preferred. There are several requirements that a multifunctional initiator has to fulfill to produce star polymers with well-controlled characteristics. Difficulties often arise from the insolubility of these initiators because of the strong aggregation effects. This association effect, along with the steric hindrance, may prevent all initiation sites from initiating efficiently.

A few studies have reported that well-defined star materials can be obtained from the reaction of living poly(styryl)lithium anions with a small amount of a difunctional monomer, such as divinylbenzene (DVB).<sup>21–23</sup> One feature of this linking chemistry is that the living anions at the core remain active after the reaction. For example, Frater and Mays<sup>21</sup> demonstrated the synthesis of well-defined asymmetric-arm star (A<sub>*n*</sub>A'<sub>*n*</sub>) polymers by polymerizing a set of shorter arms from the star core. Tsitsilianis and Voulgaris<sup>22</sup> reported the synthesis of miktoarm stars (A<sub>*n*</sub>B<sub>*n*</sub>) by conducting the reaction of living polymer A with DVB in tetrahydrofuran (THF) solution at –78 °C followed by initiating a different monomer B from the star core. These authors have also made star-block (AB)<sub>*n*</sub> copolymers by first synthesizing the poly(DVB) living cores in THF at –78 °C then polymerize monomers A and B in sequence under the same conditions.<sup>22</sup>

Since the purpose of this work is to synthesize homologous series of samples for systematic study of structure–property relationships, it is very important that these samples have minimum variation in parameters such as total molecular weight, number of arms, ratios of components, and so forth. In particular, we are interested in making a homologous series of (PS-*b*-P2VP)<sub>*n*</sub> star-block copolymers varying only in their PS/P2VP ratios. Therefore, synthesizing the multifunctional anionic initiator in a nonpolar solvent is advantageous because this will allow us to preserve the activity of the initiator relative longer. In addition, using constriction/break-seal techniques, the initiator can be split into portions and used in different polymerizations. Thus, the functionality of the stars can be kept identical and the molecular weights of the

blocks and the total molecular weights can be precisely controlled.

## EXPERIMENTAL

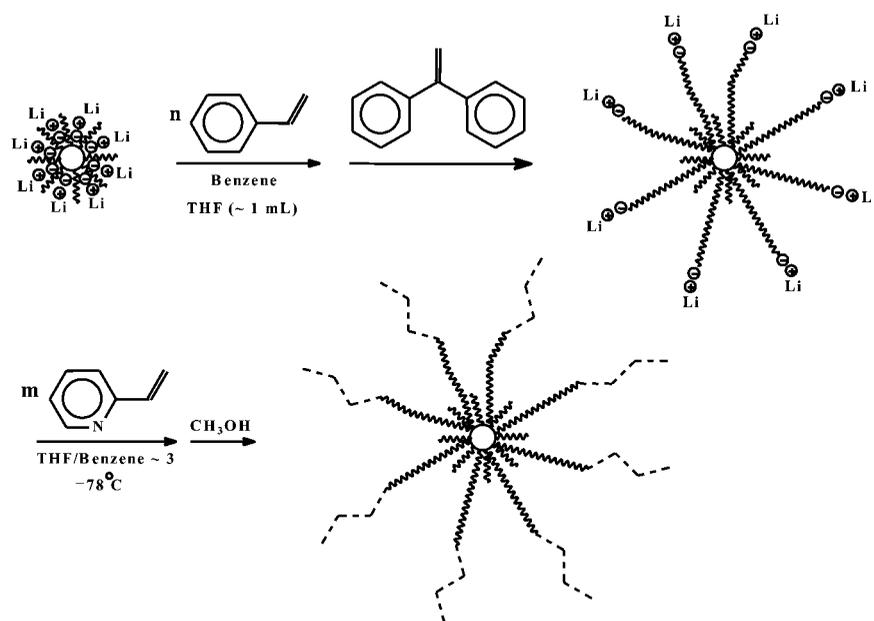
### Multifunctional Anionic Initiator Preparation

Solvents and monomers were purified according to standard published procedures.<sup>20,24,25</sup> A low molecular weight linear poly(styryl)lithium living anion was first prepared in benzene at room temperature using *sec*-butyllithium as initiator. Then the desired amount of purified DVB ([DVB]/[Li]  $\approx$  3) was added to this living PS solution to make the multifunctional anionic initiator. The use of low molecular weight PS here is to increase the solubility of the poly(DVB) microgel nodule in the reaction media. This linking reaction was allowed to proceed for at least 2 days at room temperature. The resulting multifunctional anionic initiator solution was stored at  $-20$  °C until further use.

### Synthesis of (PS-*b*-P2VP)<sub>*n*</sub> Star-block Copolymers

The synthetic route for the making of the (PS-*b*-P2VP)<sub>*n*</sub> star-block copolymers is displayed in Scheme 1. A small amount of *sec*-butyllithium

and  $\sim 1$  mL of THF was added to the multifunctional anionic initiator before it was used to make the star-block copolymers. The use of THF was to promote equal initiation efficiency of all living centers in the multifunctional initiator. A small amount of *sec*-butyllithium was added to obtain a small amount of the arm materials for characterization. The polymerization of the first monomer (styrene) was allowed to proceed for 6 h in benzene (5%, w/v) at room temperature. Then the living PS stars were capped with 1,1-diphenylethylene (DPE). An aliquot of the sample were removed and terminated with purified methanol for characterization. The rest of the living PS stars benzene solution was added into purified THF at  $-78$  °C (THF/benzene = 3, v/v). This solution was used to polymerize the second block (P2VP) at  $-78$  °C. The resulting polymers were collected by precipitation in *n*-heptane. To separate the star from the arm materials as well as the coupled stars, THF/*n*-heptane was used as the solvent/nonsolvent pair to fractionate the raw product. Coupled stars are double or triple star or perhaps structures made up of higher numbers of the original stars presumably formed by the reaction of the living ends in a star with the remaining unreacted double bonds in the DVB units within the core of other stars.



**Scheme 1.** Reaction scheme for the synthesis of (PS-*b*-P2VP)<sub>*n*</sub> star-block copolymers with the poly(2-vinylpyridine) blocks at the corona.

## Characterization Methods

### Elemental Analysis and $^1\text{H}$ NMR

Composition of these star materials were determined by elemental analysis (for the deuterated samples) and  $^1\text{H}$  NMR (for the nondeuterated samples). Elemental analysis services were provided by Galbraith Laboratory Inc. (Knoxville, TN).  $^1\text{H}$  NMR experiments were performed on a Bruker AMX400 spectrometer (Bruker Instruments, Karlsruhe, Germany). A wide bore Oxford/Spectrospin magnet of 9.4T (400.13 MHz) field strength was used for the reported experiment. The experiment temperature was 305 K. Relaxation delay was set to be 30 s to quantitatively measure the aromatic proton. Deuterated chloroform ( $\text{CDCl}_3$ ) was used as the solvent and the sample concentration was 20 mg/mL in all cases. The internal standard was the residual proton chloroform signal of deuterated chloroform (7.24 ppm downfield from tetramethylsilane).

### Multiangle Laser Light Scattering

Multiangle laser light scattering (MALLS) experiments were conducted using a DAWN<sup>®</sup> EOS<sup>™</sup> instrument manufactured by Wyatt Technology Corp. (Santa Barbara, CA). This unit was equipped with a He-Ne source operating at  $\lambda = 695$  nm. THF was used as the solvent and the experiment temperature was 40 °C. The specific refractive index increments ( $dn/dc$ ) were measured using an Optilab DSP Interferometric Refractometer (Wyatt Technology Corp.) at  $\lambda = 695$  nm and all samples have the same  $dn/dc$  value of 0.186 mL/g. ASTRA for Windows software was used to collect and process data.

### Intrinsic Viscosity Measurements

Cannon-Ubbelohde dilution viscometers were used for the intrinsic viscosity  $[\eta]$  measurements. Viscometers were chosen so that all solution flow times ranged between 100 and 200 s. Solutions of polymers were made in freshly distilled toluene (good solvent) and cyclohexane ( $\theta$  solvent) and their relative viscosity values fall between 1.1 and 1.4. Temperature control was maintained at  $35.0 \pm 0.02$  °C for toluene and  $34.5 \pm 0.02$  °C for cyclohexane using thermostated water baths. Solvents and solutions were filtered through a 0.2  $\mu\text{m}$  Teflon membrane filters directly into the viscometer.

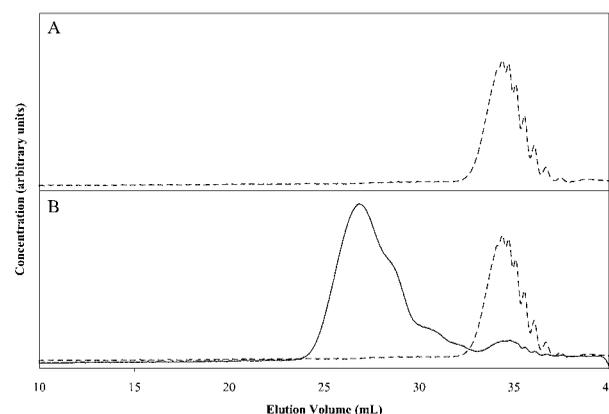
### Size Exclusion Chromatography

Size exclusion chromatography (SEC) was used to determine the average molecular weights and polydispersity ratios,  $M_w/M_n$ , of the polymer samples with respect to polystyrene standards (Polymer Standards Service (PSS), Germany). The instrument was equipped with an isocratic pump (Knauer K-501), an UV detector (Knauer UV-K2501), a RI detector (Knauer RI-K2301), and one LinearS and one 100 Å (8 mm  $\times$  600 mm) linear PSS SDV gel columns. PSS WinGPC software was used to acquire and analyze the chromatograms. Samples of PS and DPS homopolymers were run using THF as the mobile phase. Samples of copolymers containing P2VP component were run using THF with 5% (w/w) triethylamine (TEA) additive as the mobile phase. In all cases, the flow rate was 1 mL/min and the column temperature was 30 °C.

## RESULTS AND DISCUSSION

### Characterization of the Multifunctional Anionic Initiator

Figure 1 shows the SEC chromatograms of the multifunctional anionic initiator made with (A) deuterated styrene (solid line) and its arm material (dashed line) and (B) styrene (solid line) and its arm material (dashed line). In Figure 1(B), the chromatogram of the multifunctional initiator exhibits relative narrow molecular weight distribution. However, when deuterated styrene was used in the place of styrene, while all other



**Figure 1.** SECs of the multifunctional anionic initiator made with (A) deuterated styrene (solid line) and its arm material (dashed line) and (B) styrene (solid line) and its arm material (dashed line).

**Table 1.** Intrinsic Viscosity  $[\eta]$  Results: Determination of the Star Functionality

Sample	$M_w$ , MALLS (g/mol)	$[\eta]_{\theta,1}$ (mL/g)	$[\eta]_{\theta,s}$ (mL/g)	$[\eta]_l$ (mL/g)	$[\eta]_s$ (mL/g)	$g'_\theta$	$g'$	$f$
(PS) <sub><i>n</i></sub> star	$5.6 \times 10^5$	63.9	25.4	153.6	49.1	0.398	0.320	~ 14
(DPS) <sub><i>n</i></sub> star	$2.3 \times 10^6$	130.9	36.9	433.1	59.3	0.282	0.137	~ 26

$[\eta]_{\theta,1}$  is the intrinsic viscosity of the corresponding sample in theta solvent (cyclohexane) of the linear PS having the same  $M_w$  as the star polymer determined by eq 1;  $[\eta]_{\theta,s}$  is the intrinsic viscosity of the corresponding sample in theta solvent (cyclohexane) of the star PS polymer determined experimentally;  $[\eta]_l$  is the intrinsic viscosity in good solvent (toluene) of the linear PS having the same  $M_w$  as the star polymer determined by eq 2;  $[\eta]_s$  is the intrinsic viscosity in good solvent (toluene) of the star PS polymer determined experimentally.

reaction conditions were kept the same, its multifunctional initiator exhibited higher star functionality and polydispersity. In addition, a high mass shoulder is also found in the SEC chromatogram indicating that some coupled stars had formed. Coupled stars are caused by the addition of the living anionic chain ends from one star to the remaining unreacted double bonds in DVB units within the core of another star. Perhaps, some impurity remained in the deuterated styrene monomer after the purification process and this impurity increase the reaction rate of the poly(deuterated styryl)lithium and DVB.

### Characterization of the (PS)<sub>*n*</sub> and (DPS)<sub>*n*</sub> Stars

Intrinsic viscosity  $[\eta]$  measurements of the first block-star were conducted to determine the number of arms in these stars. The  $M_w$  and  $[\eta]$  of the (PS)<sub>*n*</sub> star and (DPS)<sub>*n*</sub> star have been measured. The results are summarized in Table 1. The num-

ber of arms ( $f$ ) in each star was calculated according the following equations:<sup>26,27</sup>

$$[\eta]_\theta = 7.68 \times 10^{-2} M_w^{0.508} \quad (\text{mL/g}) \quad (1)$$

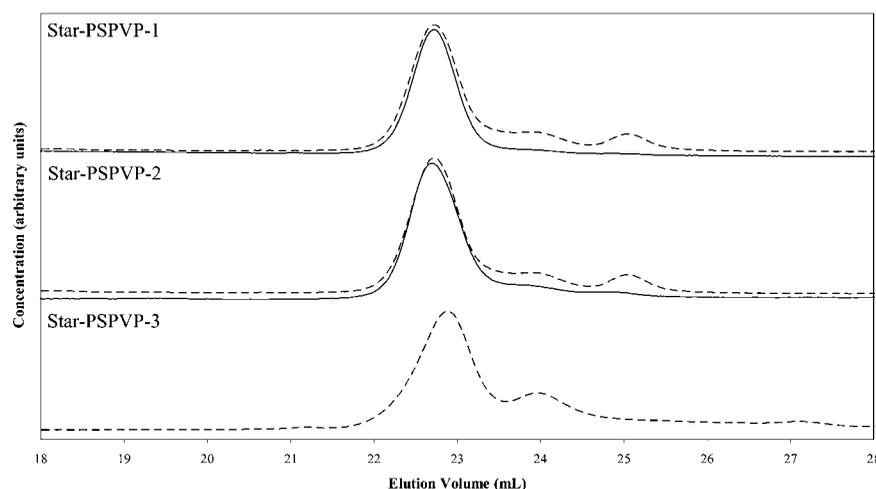
$$[\eta] = 9.27 \times 10^{-3} M^{0.734} \quad (\text{mL/g}) \quad (2)$$

$$g' = \left( \frac{[\eta]_s}{[\eta]_l} \right)_M \quad (3)$$

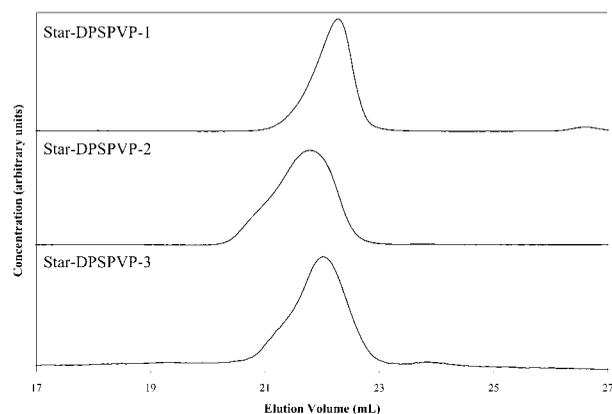
$$g'_\theta = \left( \frac{[\eta]_{\theta,s}}{[\eta]_{\theta,1}} \right)_M \quad (4)$$

$$g'_\theta = \left( \frac{3f - 2}{f^2} \right)^{0.58} \quad (5)$$

Here, the subscript  $M$  denotes that the values are taken for the same molecular weight; the



**Figure 2.** SECs of three (PS-*b*-P2VP)<sub>*n*</sub> star-block copolymers (AB)<sub>*n*</sub> synthesized by living anionic polymerization using polystyrene grafted poly(DVB) as multifunctional initiator. In all three cases, dashed lines represent raw products and solid lines represent the corresponding products after solvent/nonsolvent fractionation.



**Figure 3.** SECs of three [poly(deuterated styrene)-*b*-poly(2-vinylpyridine)]<sub>n</sub> star-block copolymers synthesized by living anionic polymerization using poly(deuterated styrene) grafted poly(DVB) as multifunctional initiator. These chromatograms were taken after fractionation.

subscripts *s* and *l* denote the values for the star and linear polymers; the subscript *θ* denotes that experiments were done in cyclohexane (*θ*-solvent for PS); otherwise experiments were done in toluene (good solvent for PS). Using eqs 1 and 2, the intrinsic viscosity values of linear polymers having the same *M<sub>w</sub>* as the star polymers were calculated. The *g'* and *g'<sub>θ</sub>* of the star polymers were calculated using eqs 3 and 4 from the intrinsic viscosity values experimentally determined. Then the functionality values of the stars (*f*, number of arms) can be found from eq 5. The *g'* values obtained in our work are in good agreement with the published data,<sup>27</sup> which were obtained from PS star polymers with similar number of arms.

### Characterization of the Star-Block Copolymers

SEC chromatograms of three (PS-*b*-P2VP)<sub>n</sub> star-block copolymers are displayed in Figure 2. The dashed lines are the chromatograms of the raw products and solid lines are those of the corresponding products after solvent/nonsolvent fractionation. Polydispersity indices of these polymers are all below 1.2. Figure 3 shows the SEC curves of three (DPS-*b*-P2VP)<sub>n</sub> stars after fractionation. The polydispersity of these polymers are relatively high and the arm numbers are less controllable. This might be caused by an unknown impurity that was not removed during our purification procedure.

We deliberately added a small amount of mono-functional initiator, *sec*-butyllithium, to the multifunctional initiator during the synthesis of the stars. This excess mono-functional initiator will produce linear polymer chains that have the same mass as the arms in the stars. The weight-average molecular weights, *M<sub>w</sub>*, of these arm materials were measured by SEC with RI detection. Two batches of (PS)<sub>n</sub> stars and two batches of (DPS)<sub>n</sub> stars were synthesized. The *M<sub>w</sub>* of arm materials of the two (PS)<sub>n</sub> stars are  $2.5 \times 10^4$  g/mol and  $4.0 \times 10^4$  g/mol, respectively. Combining with the PS/PVP ratios determined by <sup>1</sup>H NMR, the *M<sub>w</sub>* of the diblock arms can be calculated. For example, the (PS)<sub>n</sub>-1 star with arm molecular weight equals to  $4.0 \times 10^4$  g/mol was used to make (PSPVP)<sub>n</sub>-1. The PS/PVP ratio of this sample was determined by <sup>1</sup>H NMR to be 7. So the *M<sub>w</sub>* of the diblock arm can be calculated as  $4.0 \times 10^4$  g/mol  $\div$  [7/8] =  $4.6 \times 10^4$  g/mol. Similarly, the *M<sub>w</sub>* of arm materials of the two (PS)<sub>n</sub> stars are  $4.5 \times 10^4$  g/mol and  $9.0 \times 10^4$  g/mol, respectively. These calculations are based on the

**Table 2.** Molecular Characteristics of Star-Block Copolymers

Sample ID	<i>M<sub>w</sub></i> (Star), MALLS (g/mol)	<i>M<sub>w</sub></i> (Arm), RI (g/mol) <sup>a</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>b</sup>	PS/PVP	<i>f</i> <sup>c</sup>
(PSPVP) <sub>n</sub> -1	$6.4 \times 10^5$	$4.6 \times 10^4$	1.15	7 <sup>d</sup>	14
(PSPVP) <sub>n</sub> -2	$7.6 \times 10^5$	$6.0 \times 10^4$	1.16	2 <sup>d</sup>	13
(PSPVP) <sub>n</sub> -3	$6.0 \times 10^5$	$5.0 \times 10^4$	1.18	1 <sup>d</sup>	12
(DPSPVP) <sub>n</sub> -1	$2.6 \times 10^6$	$1.0 \times 10^5$	1.23	1 <sup>e</sup>	26
(DPSPVP) <sub>n</sub> -2	$3.2 \times 10^6$	$1.1 \times 10^5$	1.45	5 <sup>e</sup>	29
(DPSPVP) <sub>n</sub> -3	$3.0 \times 10^6$	$1.0 \times 10^5$	1.36	9 <sup>e</sup>	30

<sup>a</sup> Calculated from SEC measurements with RI detector of the arm materials combined with the PS/PVP molar ratios obtained from <sup>1</sup>H NMR measurements.

<sup>b</sup> Obtained from SEC measurements with RI detector. Measurements are taken after fractionation.

<sup>c</sup> Calculated from the *M<sub>w</sub>* values of the stars and their arm materials.

<sup>d</sup> Calculated from <sup>1</sup>H NMR.

<sup>e</sup> Calculated from elemental analysis.

assumption that all the living arms in the (PS)<sub>*n*</sub> stars and (DPS)<sub>*n*</sub> stars initiated the polymerization of the second monomer. Table 2 summarizes the molecular characteristics of all diblock-stars synthesized in this work. The functionality (*f*) obtained from intrinsic viscosity measurements and weight-average molecular weight measurements agree quite well.

## CONCLUSIONS

We have demonstrated the synthesis of low polydispersity star-block copolymers of poly(styrene-*b*-poly(2-vinylpyridine)) where the poly(2-vinylpyridine) blocks are at the corona using all-glass high vacuum living anionic polymerization techniques. A set of short polystyrene chains were grafted to the poly(DVB) core to increase the solubility of the multifunctional anionic initiator. The resulting star-block copolymers exhibit well-defined characteristics. The properties of the surfaces/interfaces fabricated using these materials are currently under investigation.

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