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Synthesis of Three-Arm Poly(styrene-*arm*-styrene-*arm*-2-vinylpyridine) Star Copolymers

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Development of controlled synthetic strategies for the preparation of architecturally interesting polymers is of considerable importance. This is evidenced by the recent preparation of dendritic polymers,[1-3] ring polymers,[4-6] and star polymers.[7-10] Star and star-block copolymers are normally prepared by anionic living polymerization techniques using either a plurifunctional initiator or a plurifunctional terminating agent.[7,10] In a recent paper, the preparation of a heteroarm star-branch styrene–butadiene thermoplastic elastomer by anionic living polymerization has been reported.[11] While the anionic living polymerization technique is the single most important method for the preparation of star polymers, the technique is not easily amenable to the preparation of three-arm star copolymers where one arm is dissimilar from the two other arms, e.g., poly(styrene-*arm*-styrene-*arm*-2-vinylpyridine). In poly(styrene-*arm*-styrene-*arm*-2-vinylpyridine), the pyridyl group may be quaternized to obtain a three-arm star copolymer with one ionic arm and two nonionic arms. The resulting copolymer is of interest for the formation of reverse micelles and surface micelles.[12,13]

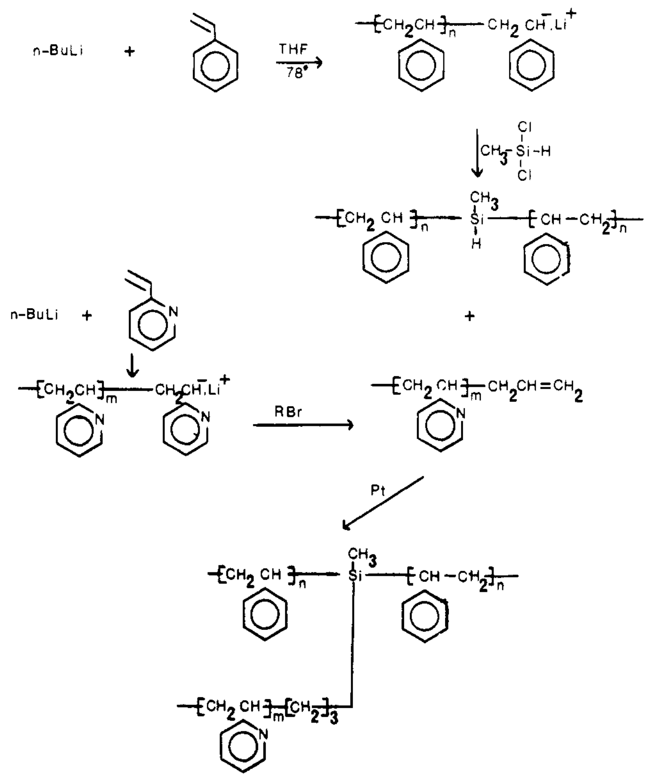
It is well-known that block copolymers, similar to low molecular weight surfactants, associate to form micelles in solvents selective for one of the polymer blocks.[14-16] When a block ionomer is dissolved in an apolar solvent, reverse micelles are formed, with the ionic block located in the center of the aggregates.[12] Most studies on reverse micelles formed by low molecular weight materials have concentrated on surfactants with double or branched aliphatic chains, e.g., sodium bis(2-ethylhexyl)sulfonsuccinate or AOT, because of their superior properties in reverse micelle formation as compared to the single-chain surfactants such as cetyltrimethylammonium bromide.[17,18] Therefore, it is of interest to prepare three-arm star-block ionomers to compare with the micellization process of diblock ionomers.

In this paper, we report on the synthesis of poly(styrene-*arm*-styrene-*arm*-2-vinylpyridine) star copolymers by a combination of anionic living polymerization and hydrosilylation addition chemistry.[19]

Materials: The monomers, 2-vinylpyridine and styrene, were purified by stirring over CaH_2 for 24 h on a vacuum line, distilled, and stored in ampules equipped with break-seals. Dichloromethylsilane and allyl bromide were dried over phosphorus pentoxide, distilled, and stored in a bulb containing phosphorus pentoxide and equipped with a stopcock. Tetrahydrofuran was purified over a sodium/potassium alloy.

The three-arm poly(styrene-*arm*-styrene-*arm*-2-vinylpyridine), abbreviated as P(SS2VP), copolymers were prepared, according to Scheme I, using break-seal techniques. The α-vinyloligo(2-vinylpyridine), abbreviated as P(2VP)-vinyl, functional oligomers were prepared by slowly distilling 2-vinylpyridine onto a tetrahydrofuran solution of n-BuLi maintained at −78 °C. The living oligopyridyl carbanion solution was terminated with $BrCH_2CH{=}CH_2$ to obtain the vinyl functional oligo(2-vinylpyridine). The functional oligomers were precipitated into hexanes. The central Si–H functional polystyrene, abbreviated as P(S)-SiH, polymers were prepared by adding styrene to an n-BuLi/tetrahydrofuran solution maintained at −78 °C. The resulting living polystyryllithium was coupled by slowly adding under vacuum a very small amount of dichloromethylsilane and allowing the coupling process to take place for 5 min. The process of addition of very small amounts of dichloromethylsilane was repeated several times until the red carbanion color just disappeared. The three-arm star copolymers were prepared by the hydrosilylation addition of the Si–H of the P(S)SiH functional polymers to the vinyl group of the P(2VP)vinyl functional polymers.[19] The hydrosilylations were carried out using 2 drops of platinum/divinyltetramethyldisiloxane, as received from Huls, in refluxing tetrahydrofuran for 4–5 days. The polymers were purified by first precipitating into methanol, followed by a second precipitation into hexanes. The three-arm copolymers were quaternized with methyl iodide in refluxing tetrahydrofuran for 48 h, precipitated into hexanes, and freeze-dried from a benzene/methanol solution. The light scattering measurements were made using the DAWN-F photometer (Wyatt Technology, Santa Barbara, CA) equipped with a flow cell and operating with a He–Ne laser at a wavelength of 632.8 nm. The refractive index increments were determined at the same wavelength using the Optilab 903 (Wyatt Technology) refractometer. The software provided by Wyatt Technology was used to acquire and process data (Dawn-F87 and Skor-F87) and to create Zimm plots (Aurora).

Scheme I



The ^{1}H NMR of P(2VP)vinyl#2 is shown in Figure 1; the vinylic protons appear at 4.7 and 5.3 ppm. The resonances of the aromatic protons are consistent with previously observed values for poly(2-vinylpyridine).[20] The functionality of P(2VP)vinyl#1, determined by comparing the ^{1}H NMR integration of the end methyl group of the

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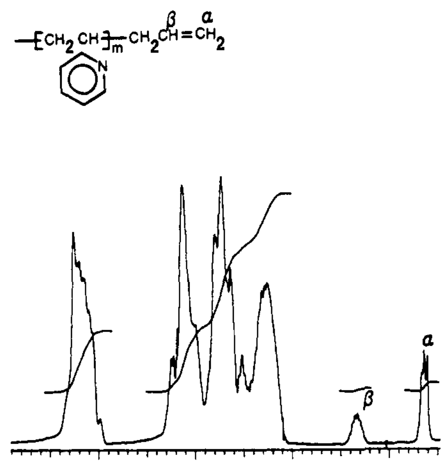

Figure 1. 300-MHz ^{1}H NMR spectrum of P(2VP)vinyl#2 in $CDCl_3$.

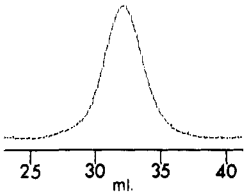

Figure 2. Gel permeation chromatogram of P(SS2VP)#5 in tetrahydrofuran.

initiator fragment to the α-CH_2 of the vinyl group, is around 95%. In Table I, the molecular weight data for the functional polymers and star copolymers are listed. The data indicate that the vinyl functional oligo(2-vinylpyridine)s show narrow molecular weight distributions. The central silicon hydride (Si–H) functional polystyrenes prepared by coupling living polystyryllithium display somewhat broad (polydispersity of 1.4–1.5) molecular weight distributions. The coupling of the living polystyrene with dichloromethylsilane results in an approximate doubling of the peak molecular weights. For example, the peak molecular weight of the coupled product P(S)SiH#3 is 9500 while that of the precursor polystyrene is 5800. The molecular weight data seem to indicate that the product contains both coupled chains and some uncoupled chains. The uncoupled chains should result in the formation of end (Si–H) functional polystyrene. However, gel permeation chromatography shows that the final product, the three-arm star copolymer, is obtained in relatively pure form. The gel permeation chromatogram of P(SS2VP)#5 is shown in Figure 2. It is interesting to note that the M_p of P(SS2VP)#5, gel permeation chromatogram shown in Figure 2, is 14 000, while the M_p of the precursor functional polymers P(2VP)vinyl#2 and P(S)-SiH#3 are 1200 and 9500, respectively. This reflects different hydrodynamic behavior of the three-arm star copolymer as compared to linear polymers. In other words, if the three-arm star copolymer behaved as linear polymers, the M_p should have been around 10 700 instead of the observed value of 14 000. The star copolymer P(SS2VP)-#2 displays similar behavior. This overestimation of the molecular weight of the three-arm star copolymers is in contrast to the general observation that the hydrodynamic volumes of the star copolymers are smaller than those of their linear counterparts of the same M_w.[7] This is because star copolymers have a compact structure compared to their linear counterpart. The overestimation of the molecular weight in our case may be explained if the core region of the three-arm polymers is relatively extended or expanded because of the incompatibility between poly(2-vinylpyridine) and polystyrene. The M_w value of 24 000 obtained by light scattering for P(SS2VP)#2 is lower than the gel permeation chromatography value of 28 000, supporting our explanation for a larger hydrodynamic volume relative to a linear polymer. The fact that the hydrodynamic behavior results in an overestimation of the molecular weight makes it easier to conclude that the star copolymers are essentially free from the precursor functional polymers and diblock copolymers that may form because of the presence of any uncoupled end (Si–H) functional polymer. The experimental yield of the purified star copolymers is between 65 and 75%. The FT-IR and NMR spectra of star copolymers are consistent with the structure. The FT-IR spectrum of P(SS2VP)#2 (Figure 3) shows peaks due to both polystyrene and poly(2-vinylpyridine); the peaks at 1585, 1515, 1475, and 1435 cm^{-1}, marked by arrows, are absorptions of poly(2-vinylpyridine). These peaks are also observed in the P(2VP)vinyl functional precursor polymers. The bands due to polystyrene in this region appear at 1600, 1580, 1495, and 1450 cm^{-1}. The ^{1}H NMR spectrum shows the H-4 resonance of the pyridine ring at 8.3 ppm; the remaining resonances are overlapping with the polystyrene resonances. The elemental analysis of P(SS2VP)#2 (C_{found} = 91, C_{calc} = 91; H_{found} = 7.8, H_{calc} = 7.5; N_{found} = 1.1, N_{calc} = 1.6) is in reasonable agreement with the NMR data.[21]

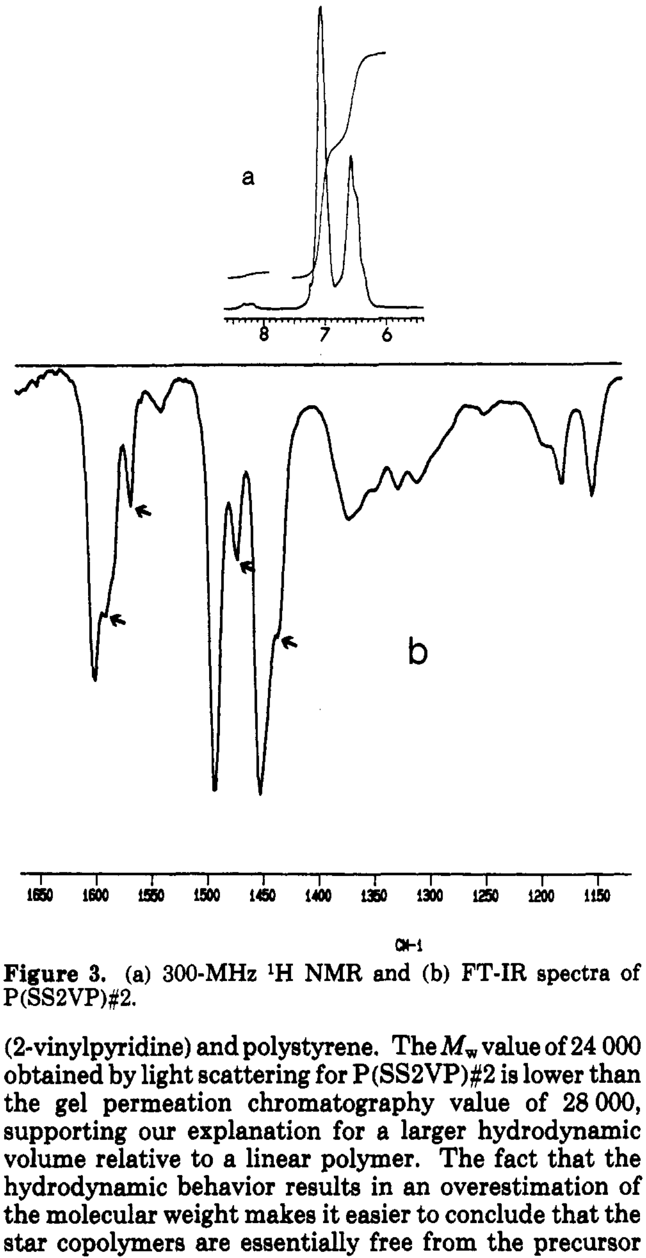

Figure 3. (a) 300-MHz ^{1}H NMR and (b) FT-IR spectra of P(SS2VP)#2.

Gel permeation, FT-IR, and NMR studies indicate that using the synthetic strategy, shown in Scheme I, it is possible to prepare successfully three-arm poly(styrene-*arm*-styrene-*arm*-2-vinylpyridine) star copolymers. The star copolymers are obtained essentially in the pure form. In particular, we have demonstrated that hydrosilylation

Table I
Molecular Weight Data for Functional Polymers and Star Copolymers[a]

polymer	M_w	M_n	M_p	M_w/M_n
P(2VP)vinyl#1	3 200	2 800	3 500	1.14
P(2VP)vinyl#2	1 200	1 100	1 200	1.09
P(S)SiH#1	16 000	11 000	13 000	1.46
P(S)SiH#2	12 600	8 500	10 700	1.48
P(S)SiH#3	10 600	7 000	9 500	1.51
P(S)#3a[b]	7 500	4 900	5 800	1.53
P(SS2VP)#2[c]	28 000	21 000	23 000	1.33
P(SS2VP)#5[d]	18 000	12 000	14 000	1.50

[a] Gel permeation chromatography carried out in tetrahydrofuran using 10^5-, 10^4-, 10^3-, 500-, and 100-Å Ultrastyragel columns. Molecular weights are relative to polystyrene standards. [b] Precursor polystyrene to P(S)SiH#3. [c] Star copolymer from P(S)SiH#1 and P(2VP)vinyl#1. [d] Star copolymer from P(S)SiH#3 and P(2VP)vinyl#2.

is a relatively easy method for coupling the functional polymers P(S)SiH and P(2VP)vinyl to prepare star copolymers. We are currently in the process of extending this synthetic strategy for preparing other star copolymers and also diblock copolymers by hydrosilylation of end functional polymers.[22] Previously, multiblock copolymers of polystyrene and poly(dimethylsiloxane) have been prepared by the hydrosilylation reaction between α,ω-dihydrogenopoly(dimethylsiloxane) and α,ω-bis(vinylsilane)-polystyrene.[23] Our interest in these materials is to obtain more information about the micellization process of block ionomers. Preliminary light scattering studies indicate that P(SS2VP)#5, quaternized with methyl iodide, form aggregates of molecular weight 4×10^5 in toluene.

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