Multifunctional Coupling Agents for Living Cationic Polymerization. 7. Synthesis of Amphiphilic Tetraarmed Star Block Polymers with α-Methylstyrene and 2-Hydroxyethyl Vinyl Ether Segments by Coupling Reactions with Tetrafunctional Silyl Enol Ether

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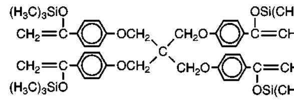
ABSTRACT: By the polymer coupling reaction with a tetrafunctional silyl enol ether [**1**; $C\{CH_2OC_6H_4C(OSiMe_3){=}CH_2\}_4$], amphiphilic tetraarmed star polymers (**6**) with α-methylstyrene−2-hydroxyethyl vinyl ether (αMeSt−HOVE) block arm chains have been synthesized: $C\{CH_2OC_6H_4COCH_2{-}[CH(OCH_2CH_2OH)CH_2]_n{-}[C(CH_3)(C_6H_5)CH_2]_m{-}\}_4$. The synthesis consisted of the following steps: (i) the sequential living cationic polymerization of αMeSt and 2-[(*tert*-butyldimethylsilyl)oxy]ethyl vinyl ether (SiVE) into an αMeSt−SiVE living block copolymer (**4**); (ii) the coupling of four chains of **4** with the quencher **1** into a tetraarmed polymer (**5**); and (iii) the transformation of the poly(SiVE) segment into the poly(HOVE) chain by the fluoride-catalyzed deprotection. In step i the living polymerization was carried out at −78 °C in methylene chloride with a binary initiating system comprising tin tetrabromide and the hydrogen chloride adduct of 2-chloroethyl vinyl ether. After step iii, the tetraarmed amphiphile **6** (αMeSt/HOVE = 27/27 in $\overline{DP}_n$ in each arm) was soluble in ethanol and chloroform, in which its ^{1}H NMR spectra changed dramatically by responding to solvent polarity. For example, in the former polar solvent, the signals of the hydrophobic αMeSt units were hardly detectable, whereas they were clearly observed in chloroform. This responsiveness was attributed to the rigidity of the poly(αMeSt) segment, which contrasts with the more flexible poly(vinyl ether) arm chains in the previously reported tetraarmed amphiphiles.

Introduction

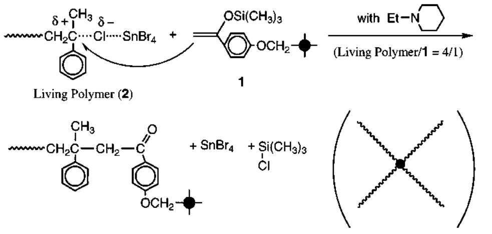
Amphiphilic polymers, which have currently been eliciting interest in both industry and academia,[1] may be synthesized by connecting hydrophilic and hydrophobic (lipophilic) segments by living polymerization. By adopting living cationic polymerizations of pendant-functionalized monomers,[2] we have synthesized a series of primarily nonionic amphiphilic macromolecules including AB- and ABA-block copolymers[3−6] and their “multiarmed” versions often called amphiphilic star polymers.[7−9] The latter appear particularly interesting in view of their unique topology where amphiphilic block polymer chains (arms) spread radially from the center (core), clearly contrasting with their linear analogs.

It has been suggested[10] that the conformation of arm chains in amphiphilic block and multiarmed polymers at interfaces and in micelles may play an important role in determining their properties and performance as amphiphiles, and we have in fact shown[8b,11] that amphiphilic arm chains of multiarmed poly(vinyl ethers) undergo conformational changes responding to solvent polarity. In this regard the segment flexibility or mobility would critically determine the conformational responsiveness of amphiphilic polymers. Though relatively abundant, however, the amphiphilic multiarmed polymers thus far prepared in cationic polymerization are all based on flexible vinyl ether chains.

Noting these circumstances, we synthesized, in this study, tetraarmed amphiphilic polymers in which each arm chain is amphiphilic and comprises the rigid and hydrophobic segment of α-methylstyrene (αMeSt) and the flexible and hydrophilic segment of 2-hydroxyethyl vinyl ether (HOVE). The synthesis is based on our recent two findings, the living cationic polymerization[12] and block copolymerization[13] of αMeSt (eq 1) and the efficient polymer coupling with use of a tetrafunctional silyl enol ether (**1**)[14] that recently proved applicable to not only vinyl ethers[14] but also αMeSt[15].



Tetrafunctional Silyl Enol Ether (**1**)



(1)

More specifically, as illustrated in Scheme 1, this study consists of the following phases: (i) the sequential block copolymerization of 2-[(*tert*-butyldimethylsilyl)oxy]ethyl vinyl ether (SiVE) from the living poly(αMeSt) (**2**) obtained with the vinyl ether−hydrogen chloride adduct (**3**)/tin tetrabromide ($SnBr_4$) initiating system; (ii) the coupling reaction of the resulting αMeSt−SiVE living AB-block copolymer (**4**) with **1** into the corresponding tetraarmed polymer (**5**); (iii) the pendant transformation of the poly(SiVE) segments in **5** into poly(HOVE) to give the target amphiphilic tetraarmed polymers (**6**); and (iv) some characterization of **6** in terms of solubility and arm conformation/mobility in polar and less polar media. As implied in the polymer coupling process, the polymerization sequence from αMeSt to SiVE leads to the tetraarmed architecture

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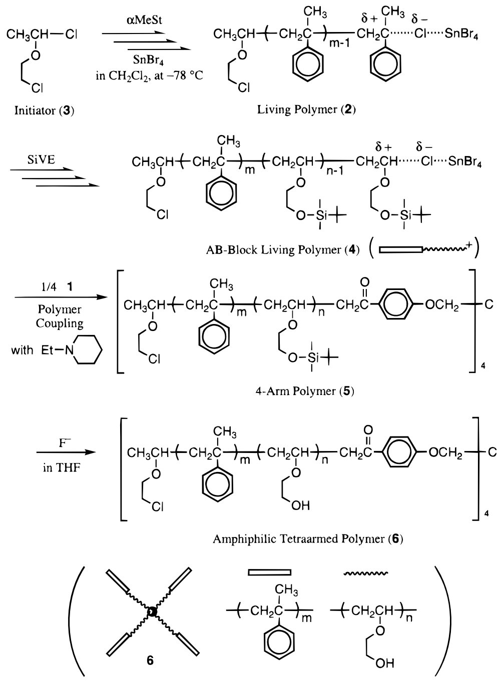
Scheme 1. Synthesis of Amphiphilic Tetraarmed Polymers with AB-Block Arm Chains of α-Methylstyrene and 2-Hydroxyethyl Vinyl Ether



where the hydrophilic HOVE is placed in the inside arm layer. In addition to the successful synthesis of **6**, it was also found herein that the αMeSt-based amphiphilic arms in **6** respond to solvent polarity changes more clearly than the purely vinyl ether-based counterparts.[9]

Results and Discussion

Sequential Block Polymerization of α-Methylstyrene with 2-Hydroxyethyl Vinyl Ether. The sequential living cationic polymerization of αMeSt and SiVE was carried out with the **3**/$SnBr_4$ initiating system in methylene chloride solvent (CH_2Cl_2) at −78 °C (Scheme 1). As initiator, the hydrogen chloride adduct **3** was selected, which has been shown effective for αMeSt and also suitable for the subsequent coupling reaction with **1**.[11,16] Thus, when the conversion of αMeSt reached ca. 95% in 10 min, SiVE was added to a solution of the resultant living polymer **4** ($[\alpha\text{MeSt}]_0 = [\text{SiVE}]_0 = 0.20$ M; $[\mathbf{3}]_0 = 10$ mM). The second-stage polymerization immediately ensued to give ca. 85% SiVE conversion in 15 min. Beside runs to be further treated with silyl enol ether **1** for polymer coupling, the product at each stage of the sequential polymerization was quenched with methanol for structural analysis.

Parts A and B of Figure 1 compare the molecular weight distributions (MWDs) of the living poly(αMeSt) and the product after the sequential polymerization of SiVE therefrom. The analyses results are also summarized in Table 1. Both samples have narrow MWDs, and there is a clear molecular weight increase after the second-stage polymerization of SiVE. The difference between the M_n values by NMR and by GPC (Table 1) is most likely due to the fact that poly(αMeSt) standard samples were employed for GPC calibration, which is certainly not suitable for determination of average molecular weights of our block copolymers with SiVE. The unquenched sample of polymer B was employed in the subsequent polymer coupling (see below).

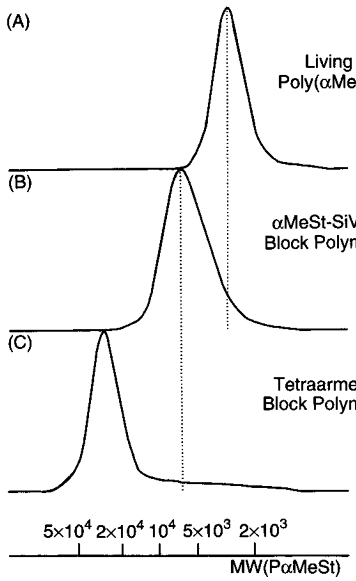


Figure 1. GPC curves of the products in the sequential polymerization of αMeSt and SiVE and the coupling reaction of the resultant AB-block living polymers (Scheme 1): (A) living homopoly(αMeSt) **2** quenched with methanol; (B) AB-block living polymer **4** quenched with methanol; (C) tetraarmed polymer **5** by the coupling reactions of **1** and **4**. Reaction conditions are shown in footnotes *a* and *b*, Table 1.

Table 1. Synthesis of Tetraarmed Polymer 5 by the Coupling Reaction with Tetrafunctional Silyl Enol Ether 1

			$\overline{DP}_n$[e]		$10^{-3}\bar{M}_n$		$\bar{M}_w/\bar{M}_n$
entry	code	yield,[d] %	αMeSt	SiVE	^{1}H NMR[g]	GPC	GPC
1[a]	**2**	~100	21.9[f]			2.7	1.09
2[b]	**4**	~100	21.3	25.4	7.5	5.3	1.20
3[b,c]	**5**	85	27.7	27.3	36.2	27.0	1.14

[a] Living homopolymerization of αMeSt: $[\alpha\text{MeSt}]_0 = 200$ mM; $[\text{initiator } \mathbf{3}]_0 = 10$ mM; $[SnBr_4]_0 = 3.0$ mM; in CH_2Cl_2 at −78 °C for 10 min; αMeSt conversion = 96%. [b] Block copolymerization of SiVE from the living poly(αMeSt) (**2**; entry 1): $[\text{SiVE}]_0 = 200$ mM; in CH_2Cl_2 at −78 °C for 15 min; SiVE conversion ~85%. [c] Polymer coupling with enolate **1**: [living polymer]/[**1**] = 4.0 mole ratio;[15] [*N*-ethylpiperidine] = 0.20 mM; in CH_2Cl_2 at −78 °C for 24 h. [d] Estimated from the MWD of the products shown in Figure 1. [e] $\overline{DP}_n$ shows the degree of polymerization of each segment: $\overline{DP}_n$ = (the pendant functional group in polymer chain)/(α-end group from initiator **3**), by ^{1}H NMR (see text). [f] By GPC with a poly(αMeSt) calibration. [g] $\bar{M}_n(^1\text{H NMR}) = [\overline{DP}_n(\alpha\text{MeSt}) \times (\text{mol wt of } \alpha\text{MeSt}) + \overline{DP}_n(\text{SiVE}) \times (\text{mol wt of SiVE})] \times 4 + (\text{mol wt of the coupling agent})$.

The block polymerization product (B) was characterized by ^{1}H NMR spectroscopy, as shown in Figure 2A. The spectrum exhibits the typical signals of αMeSt and SiVE segments, such as *g* (the αMeSt phenyl) and *k*−*m* (*tert*-butyldimethylsilyl), along with the head (α-end) 2-chloroethyl group from the initiator **3** [$CH_3CH(OCH_2CH_2Cl)$~~~; *a*, methyl; *b*−*d*, methine and methylene] and the ω-end methoxy group {~~~$CH_2CH[OCH_2CH_2OSi(CH_3)_2t\text{Bu}]{-}OCH_3$ (signal *n*)} derived from the quenching with methanol.[17] The ratio of the α- to the ω-end groups [signal ratio $(b + c + d)/n$] was close to unity (observed, 1.0), indicating that almost all of the living ends survived during the two-stage polymerization and were eventually quenched with methanol. The degrees of polymerization for both αMeSt and SiVE segments were also determined from the intensity ratios of the pendant phenyl (*g*) and the *tert*-butyl (*m*) groups to the initiator residue ($b + c + d$): αMeSt, 21; SiVE, 25 (calcd: 20:20). The latter is higher than the calculated value based on the monomer feed ratio (see Table 1, footnote *a*), because the initiation from the initiator

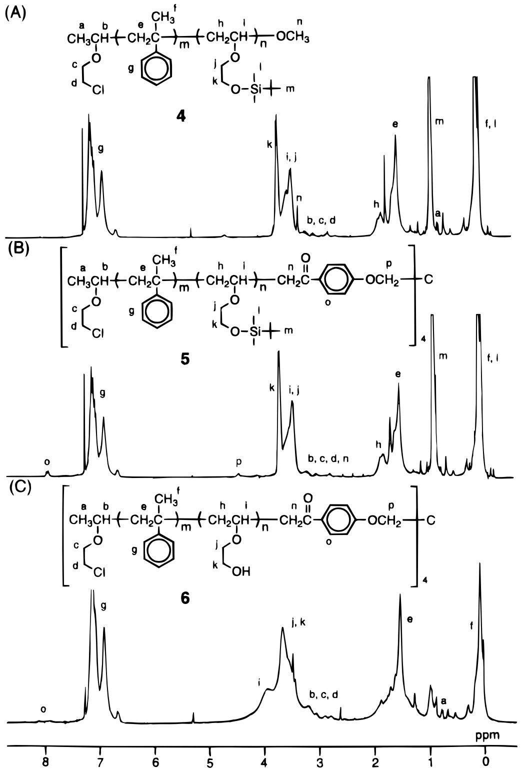


Figure 2. ^{1}H NMR spectra (CDCl$_3$, room temperature) in the synthesis of amphiphilic tetraarmed polymer **6**: (A) αMeSt−SiVE block polymer **4** quenched with methanol (sample B, Figure 1), $m/n = 27/27$ ($\overline{DP}_n$); (B) tetraarmed polymer **5** (sample C, Figure 1); (C) **6** obtained from sample B.

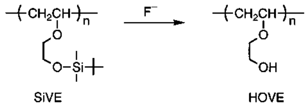
3 is not quantitative (ca. 0.83).[12,15] Therefore, the spectral data show the product is the intended AB-block copolymer (**4**).

Polymer Coupling into Tetraarmed Star Block Polymers (5). Tetrafunctional silyl enol ether **1** was allowed to react with the AB-block living polymer **4** thus obtained. The coupling reaction was carried out in the presence of *N*-ethylpiperidine, a nucleophilic additive that has been shown to enhance the coupling efficiency.[15] After the addition of **1** and the additive into the solution of the unquenched living polymer **4**, the reaction mixture was kept at −78 °C for 24 h with stirring. The quantity of silyl enol ethers in **1**, as required, was identical with that of the living end ([living polymer **4**]/[**1**] = 4). Table 1 and Figures 1 and 2 summarize the results.

The MWD of the coupling product is shown in Figure 1C. It had a narrow MWD and eluted at a higher molecular weight than the original AB-block polymer (Figure 1, C versus B). No appreciable peak of the precursor was found in the region where it should have appeared, though close inspection of the traces indicated the presence of a minor tailing of presumably uncoupled polymer fractions. According to integration of the GPC eluogram under refractive index detection, the overall yield of the coupling product was around 85% (Table 1).

The product, separated by preparative GPC, gave the ^{1}H NMR spectrum (Figure 2B) that is consistent with the tetraarmed polymer **5**. For example, while the signals (*a*−*m*) of the AB-block chains did not change from those for the linear precursor (Figure 2A), the *ω*-end methoxy peak (*n*) is now absent, and the signals of the coupling agent moiety such as *n*−*p* newly appeared. The mole ratio of the α-end group from initiator **3** (signal *b*−*d*) and the core (signal *p*)[18] was close to unity (observed, 1.2), indicating the average number of arms per polymer is 4.8. The segment DP's, as determined by ^{1}H NMR (see above), were αMeSt/SiVE = 27/27, nearly the same as those in the precursor block copolymer (Table 1). Therefore, the coupling product was identified as the tetraarmed polymer **5**. As also seen in Table 1, the total molecular weight ($\bar{M}_n$) of **5** by gel permeation chromatography (GPC; see the Experimental Section) is considerably smaller than that by ^{1}H NMR, further supporting the multiarmed structure of the product.

Synthesis of Amphiphilic Tetraarmed Star Polymer (6). In order to obtain the αMeSt−HOVE amphiphilic arm segments, the *tert*-butyldimethylsilyl ether moieties of the SiVE segments in **5** were converted into the hydroxyl groups with the fluoride anion (eq 2).[19]



(2)

The reaction was performed in the presence of tetra-*n*-butylammonium fluoride (n-Bu$_4$N$^+$F$^-$; 5 equiv to the silyl ether) in tetrahydrofuran at room temperature (see the Experimental Section) to give the product whose ^{1}H NMR spectrum is shown in Figure 2C. Comparison between spectra B and C demonstrates that the signals (*i* and *j*, Figure 2B) of the methyl and *tert*-butyl groups of the silyl ether part disappeared completely (Figure 2C), but those of the αMeSt segments (e.g., *g*) and the coupling agent moiety (*n*−*p*) remain unchanged, indicating the absence of undesirable side reactions during the pendant deprotection.

These data demonstrate that the silyl enol ether coupling of the αMeSt−SiVE living block copolymer (Scheme 1) provided new amphiphilic tetraarmed polymer **6**, the arms of which comprise the αMeSt (hard, hydrophobic) and HOVE (soft, hydrophilic) segments with controlled compositions and uniform arm lengths. Note that therein the hydrophilic arm segments are placed inside the molecule.

Characteristics of the Amphiphilic Tetraarmed Polymers. Structurally, polymer **6** may be characterized by its radially tetraarmed star architecture, the amphiphilicity of the AB-block arms of uniform lengths, and controlled segmental compositions, where the relatively rigid poly(αMeSt) segment is connected to the flexible poly(HOVE) segment, and all of these would develop interesting physical properties in **6** as macromolecular amphiphiles. Thus, some physical characteristics were examined for **6** in relation to the precursor tetraarmed polymers (**5**) and the linear AB-block copolymers (**4**) that were incorporated into **5** and **6** as arm chains. In addition, comparison was also made with the corresponding purely vinyl ether-based versions with block polymer arms of isobutyl vinyl ether (IBVE) and HOVE.[9]

(a) Solubility Characteristics. Table 2 shows the solubility of the tetraarmed star polymers and the AB-block polymers. Samples A and B, respectively, are the tetraarmed polymers (**5**) before deprotection and the corresponding amphiphilic form therefrom (**6**); D and E are the corresponding linear AB-block polymers (**4**), also before and after the deprotection, respectively. In all four samples, the αMeSt and the SiVE or HOVE segments had the same $\overline{DP}_n$ (=27). Samples C and F, on the other hand, are the purely vinyl ether-based

Table 2. Solubility of Amphiphilic 4-Arm Polymer 6, the Precursor 5, and Relevant Block Polymers (C and D)

code	polymer structure	segment units[a] outer/inner ($\overline{DP}_n$)	solvent[b]					
			n-hexane	toluene	$CHCl_3$	EtOH	MeOH	H_2O
A	4-arm (**5**)	αMeSt/SiVE (27/27)	○	○	○	×	×	×
B	4-arm (**6**)	αMeSt/HOVE (27/27)	×	○	○	○	×	×
C[c]	4-arm	IBVE/HOVE (20/20)	△	○	○	○	△	△
D	block (**4**)	αMeSt/SiVE (27/27)	○	○	○	×	×	×
E	block	αMeSt/HOVE (27/27)	×	○	○	×	×	×
E-1	block	αMeSt/HOVE (27/66)	×	×	○	○	○	×
F[c]	block	IBVE/HOVE (20/20)	○	○	○	○	○	○

[a] See Scheme 1 for polymer structures. [b] (○) soluble; (△) swelling; (×) insoluble; at room temperature, ca. 1 wt %. [c] The data from ref 12. IBVE shows the isobutyl vinyl ether segment: $-CH_2CH[OCH_2CH(CH_3)_2]-$.

versions of IBVE−SiVE (C) or −HOVE (F) combinations with nearly the same segmental $\overline{DP}_n$ (=20) as samples A, B, D, and F. Recall that both series of the αMeSt- and vinyl ether-based tetraarmed polymers involve the same segmental arrangement where the hydrophilic HOVE (and SiVE) parts are placed in the inner arm layers.

Interesting comparison may be made on a pair of polymers (A and B) before and after the deprotection or on another pair (B and C) where the outer hydrophobic segments are hard (αMeSt) and soft (IBVE), respectively. When the silyl ether pendant groups (A; **5**) were transformed into the hydrophilic alcohol functions (B; **6**), solubility characteristics of the polymer changed very little; both polymers were soluble in nonpolar solvents (toluene and $CHCl_3$) and insoluble in highly polar solvents (water and methanol). However, interestingly, sample B with polyalcoholic inner segments became soluble in another polar solvent, ethanol, but insoluble in *n*-hexane; the opposite is the case for its precursor (A). Thus, **6** proved in fact to be amphiphilic, being both soluble in both less polar (toluene and $CHCl_3$) and polar protonic solvents (ethanol). Such amphiphilicity was absent for the corresponding linear block (sample E), whose solubility characteristics are almost the same as those of the protected version (sample D), and both are soluble only in less polar organic solvents. For the AB-block polymers to be amphiphilic, as seen for another sample E-1, the hydrophilic HOVE segment must be longer [segmental $\overline{DP}_n$: 27 (E) versus 66 (E-1)]; also, E-1 turned out to be soluble in methanol but insoluble in toluene, completely opposite to its sister sample E.

Comparison between samples B and C, as well as E and F, shows that the αMeSt-based polymers (B and E) are more sensitive to solvent polarity and nature than the purely vinyl ether counterparts (C and F). The latter dissolve in a wider range of solvents; in particular, the linear block F dissolves in all the solvents examined herein, either polar or nonpolar.

(b) Solvent Effects on ^{1}H NMR Spectra. The higher sensitivity of solubility to solvent polarity with the αMeSt-based tetraarmed (**6**) and the linear block version (**4**) most likely stems from the rigidity of the styrene segments relative to the vinyl ether segment. Noting this and also the amphiphilic nature of these polymers, we analyzed the ^{1}H NMR spectra of the tetraarmed (sample B; **6**) and the linear block (sample E-1) in both polar (ethanol) and less polar (chloroform) solvents in terms of peak shape and intensity (Figure 3).

In the spectrum of the tetraarmed polymer B in chloroform (Figure 3A), the peaks due to both poly(αMeSt) (*a*−*c*) and poly(HOVE) (*e*−*g*) segments are relatively sharp, with a weak signal (*h*) from the core, as previously observed for homopolymers of both monomers.[9] In ethanol (Figure 3B), in contrast, the αMeSt signals (especially *a* and *b*) become considerably broader and weaker, whereas those of the poly(HOVE) segments (*d*−*g*) and the coupling agent core (*h*) become sharper than in chloroform.

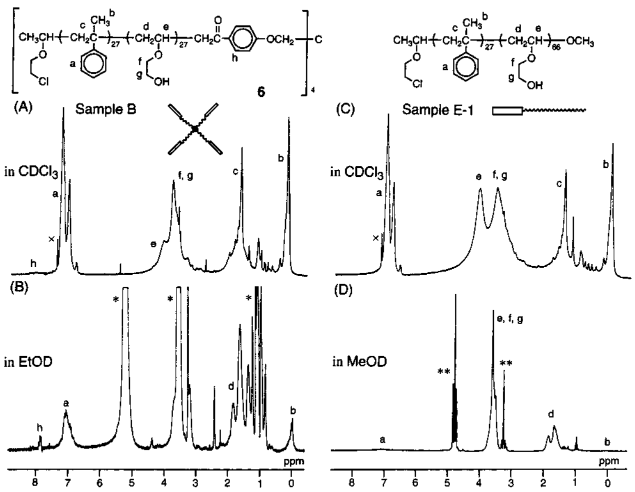


Figure 3. ^{1}H NMR spectra (room temperature) of the amphiphilic tetraarmed polymer (**6**) and the corresponding αMeSt−HOVE block polymer: (A and B) sample B (**6**) in Table 2; (C and D) sample E-1. Solvents as indicated. The symbols ×, *, and ** in the spectra show the protons of nondeuterated chloroform, ethanol, and methanol, respectively.

For the corresponding linear block copolymers (E-1) (Figure 3C,D), the spectral changes are similar but clearer. Namely, all protons of the αMeSt units (*a*−*c*), appearing sharp in chloroform (Figure 3C), are hardly detectable in ethanol (Figure 3D), suggesting that the styrene segments are highly restricted in motion in the latter polar solvent.

These observations indicate that, in polar ethanol solvent, the hydrophilic poly(HOVE) segments, both in the tetraarmed (**6**) and the linear block (**4**) polymers, extend and are freer to move, while the hydrophobic poly(αMeSt) chains shrink or aggregate intramolecularly and are highly restricted in thermal motion. From comparison with our previous results for the purely vinyl ether-based counterparts,[9] the spectral changes with solvent polarity are far more dramatic with the αMeSt-based polymers, which certainly results from the rigidity and higher hydrophobicity of the styrene hydrocarbon segments. It is also interesting that such clear responsiveness to solvent polarity is observed for **6**, where the hydrophilic polyalcohol segments are located in the inner layer of the arms.

Conclusions. The coupling reaction of the αMeSt−SiVE block polymer **4** with silyl enol ether **1** has led to tetraarmed “star block” polymer **5** in high yield, which has been further converted into the amphiphilic star block polymers **6** carrying four αMeSt−HOVE block arm chains with uniform lengths (Scheme 1). With the rigid styrene segments, the amphiphile exhibited clear and considerable responsiveness to solvent polarity in both solubility and ^{1}H NMR spectral patterns, which contrast with those of the vinyl ether-based polymers with flexible arm chains.

Experimental Section

Materials. αMeSt, *n*-hexane, and CH_2Cl_2 (solvents) and 1,2,3,4-tetrahydronaphthalene (tetralin; GC standard) were from commercial sources and purified as already reported.[9] SiVE was prepared from 2-hydroxyethyl vinyl ether[19b] and distilled over calcium hydride at least twice before use. Commercial $SnBr_4$ (Aldrich, 1.0 M in CH_2Cl_2) was used as received and diluted with the dry CH_2Cl_2 at a given concentration. The hydrogen chloride adduct of 2-chloroethyl vinyl ether (**3**; 1.0 M stock solution in *n*-hexane)[12] and the tetrafunctional silyl enol ether **1** (37.7 mM solution in CH_2Cl_2)[14] were prepared as reported. *N*-Ethylpiperidine, predried with molecular sieves 3 Å, was distilled twice over calcium hydride just before use. Tetra-*n*-butylammonium fluoride ($n\mathrm{Bu_4N^+F^-}$; Aldrich, 1.0 M THF solution) was used as received.

Procedures. (a) Polymerization and Coupling Reactions. The synthesis of the AB-block living polymer **4** was carried out under dry nitrogen in a 50-mL baked flask equipped with a three-way stopcock with magnetic stirring bar.[12,15] Thus, a mixture of αMeSt (0.26 mL), tetralin (0.24 mL, internal standard for GC analysis), and CH_2Cl_2 (7.5 mL) was cooled to −78 °C, and solutions of the initiator **3** (1.0 mL; 0.10 M in *n*-hexane) and $SnBr_4$ (1.0 mL; 30 mM in CH_2Cl_2) were added in order with vigorous stirring. Under these conditions, αMeSt conversion exceeded 90% in 10 min. To the resultant living polymer (**2**; $\overline{\mathrm{DP}}_n \sim 20$; [living end] = 8.2 mM) was quickly added a solution of SiVE (0.48 mL) in CH_2Cl_2 (1.52 mL) to form the AB-block living polymer **4** almost quantitatively within 15 min (see footnotes *a* and *b* in Table 1 for the reagent concentrations and other details).

To this solution of the living polymer **4** (10 mL) kept at −78 °C were quickly added the CH_2Cl_2 solutions of the coupling agent **1** (0.55 mL of a 37.7 mM solution) and *N*-ethylpiperidine (0.02 mL of a 100 mM solution), in this order, with vigorous stirring. The amount of the coupling agent was determined so as to maintain the stoichiometry ([living end] = [silyl enol ether group]) as closely as possible.[9,15] The mixture was stirred at −78 °C for an additional 24 h, washed three times with water (30 mL), evaporated to dryness under reduced pressure, and finally vacuum dried to give the coupled polymer **5**. The samples for ^{1}H NMR analysis and the deprotection (see below) were separated by preparative gel permeation chromatography (Shodex K2003; exclusion limit = 7×10^4; 2.5 cm i.d. × 30 cm).

The IBVE−HOVE block copolymer[4a] and its tetraarmed version[9] (cf. Table 2) were prepared as reported previously.

(b) Deprotection. The *tert*-butyldimethylsilyl ether groups in **5** were converted into hydroxyl by treatment with the fluoride anion at room temperature.[19] Namely, in a 50-mL round-bottomed flask equipped with a magnetic stirrer bar, a mixture of **5** (67.2 mg) and tetrahydrofuran (10 mL) was prepared, and $n\mathrm{Bu_4N^+F^-}$ (1.5 mL, 1.0 M THF solution; 5 equiv to the silyl group) was added. The mixture was stirred for 5 h, during which period the deprotection was completed, and the solvent was removed under reduced pressure. The residue was dissolved in a water/THF mixture (1:1 v/v), and the salts were removed by dialysis (Spectra/Por 7, molecular weight cutoff ca. 1000) for 3 days at room temperature.[4a,9] The amphiphilic tetraarmed polymer (**6**) was finally obtained by evaporating the water and THF and subsequent vacuum drying.

(c) Polymer Characterization. Gel permeation chromatography was carried out in chloroform on a JASCO Trirotar-II chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803, and K-804; exclusion limit = 4×10^5; 8.0 mm i.d. × 30 cm each) and refractive index/ultraviolet dual-mode detectors. The number-average molecular weight ($\bar{M}_n$) and the MWD of the polymers were determined on the basis of poly(αMeSt) standard samples.[12] ^{1}H NMR spectra (270 MHz) were recorded on a JEOL GSX-270 spectrometer at room temperature. Solubility characteristics (Table 2) were determined on 1 wt % mixtures of polymers at room temperature.

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(18) As seen in Figure 2B, the α-end signals *b*−*d* overlap with the signal *n* of the coupling agent. However, the latter should have the same area as signal *p*. Thus, the α-end/core mole ratio was estimated from $[(b + c + d + n - p)/5]/(p/2)$.

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