Multifunctional Coupling Agents for Living Cationic Polymerization. 5. Synthesis of Amphiphilic Tetraarmed Star Poly(vinyl ethers) by Coupling Reactions with Tetrafunctional Silyl Enol Ether

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ABSTRACT: Amphiphilic tetraarmed star poly(vinyl ethers), where each arm carries alkyl (hydrophobic) and alcohol (hydrophilic) pendant groups, have been synthesized by the coupling reaction of AB-block living poly(vinyl ethers) (**4**; arm chain) with a tetrafunctional silyl enol ether **1**, $C[CH_2OC_6H_4\text{-}p\text{-}C(OSiMe_3){=}CH_2]_4$. The living arm chains **4** were prepared by the sequential living cationic polymerization of an alkyl vinyl ether ($CH_2{=}CHOR^1$; $R^1 = i$Bu, CH_2CH_2Cl) and a functionalized vinyl ether ($CH_2{=}CHOCH_2CH_2R^2$; $R^2 = OCOCH_3$, OSi^tBuMe_2) with hydrogen chloride/zinc chloride initiating system in methylene chloride at −15 °C. The treatment of **4** with the silyl enol ether **1** led to tetraarmed block copolymers **5**. The yield of **5** (93−73%) depended on the structure and the polymerization sequence of the monomer pair for the arm chain **4**. The best result (93% yield) was obtained with the AB-block polymer of 2-chloroethyl vinyl ether ($R^1 = CH_2CH_2Cl$; CEVE) and 2-acetoxyethyl vinyl ether ($R^2 = OCOCH_3$; AcOVE) where CEVE was polymerized first. Separate coupling experiments with the homopolymers of these vinyl ethers showed that the coupling yield was higher for monomers with less bulky pendant groups. Subsequent quantitative deprotections of the acetoxy of *tert*-butyldimethylsilyl groups in **5** into hydroxyl groups gave the amphiphilic tetraarmed polymers **6**. By changing the polymerization sequence of the monomer pair, the hydrophilic polyalcohol segments could be placed either inside or outside the tetraarmed structure. For pairs of such inner- and outer-alcohol versions with identical segmental compositions, solubility and arm-chain conformation (by ^{1}H NMR) were compared.

Introduction

Besides their longstanding applications as surfactants, dispersants, etc., amphiphilic polymers have recently been a subject of fundamental research interest in terms of interfacial phenomena, micellization, and other physical and synthetic aspects.[1] In particular, amphiphilic "multiarmed" polymers are of interest. These macromolecules usually carry amphiphilic arm chains, radially spread from a central core, that consist of hydrophilic and hydrophobic segments, and their properties and functions as amphiphiles would considerably differ from those of the linear counterparts.

Among a number of methods for the synthesis of amphiphilic and multiarmed polymers, there are at least three via living polymerizations. In living cationic polymerization, for example, two of them have already been examined by us: the sequential block polymerization with a multifunctional initiating system[2] and the inter- and intramolecular linking of living block polymers via bifunctional monomers (sometimes called the microgel method).[3] The third method, unexamined yet for amphiphilic polymers, is the coupling of living block polymers with a multifunctional coupling or terminating agent. This approach may be considered a hybrid of the first two that inherits their advantages such as the precisely controlled number of arms per polymer as in the multifunctional initiation and the ready characterization of arm chains (precursor living polymers) as in the polymer linking. Its prerequisite is of course the development of efficient coupling agents.

As reported in the previous papers of this series,[4,5] we have shown that certain multifunctional silyl enol ethers (e.g., **1** in Scheme 1) are effective and versatile coupling agents for living poly(vinyl ethers) bearing the chloride counteranion. The silyl enol ethers are able to react with the growing living end without inducing β-proton elimination and other side reactions to give multiarmed polymers (**2**) (4-armed for **1**). We have also shown[6] that the sequential living cationic polymerizations of a pendant-functionalized polar vinyl ether and a nonpolar alkyl vinyl ether lead to linear amphiphilic polymers (after appropriate pendant transformation or deprotection). A typical segmental combination for such linear amphiphiles involves poly(2-hydroxyethyl vinyl ether) [poly(HOVE)] and poly(isobutyl vinyl ether) [poly(IBVE)] as hydrophilic and hydrophobic segments, respectively. As seen in these examples, living cationic polymerization is tolerant against polar functional groups, properly protected in some cases, in monomers.

Based on these backgrounds, this study was to apply the polymer coupling processes with silyl enol ether **1** to AB-block living cationic polymers for the synthesis of amphiphilic multiarmed (4-armed) polymers; Scheme 2 illustrates the possible synthetic pathway. Following this strategy, the work consists of a few phases to establish the synthesis of well-defined, multiarmed, amphiphilic poly(vinyl ethers) by our polymer coupling methods using multifunctional silyl enol ethers: (i) We first demonstrate the clean and efficient coupling of silyl enol ether **1** with living cationic polymers (**3** and **4**) derived from pendant-functionalized vinyl ethers. Herein we employed 2-acetoxyethyl vinyl ether (AcOVE) and 2-(*tert*-butyldimethylsilyl)ethyl vinyl ether (SiVE), which are both precursors for the hydrophilic HOVE segment (see the formula below). The monomers for hydrophobic segments were IBVE and 2-chloroethyl vinyl ether (CEVE). Living cationic polymerizations of these monomers should be initiated with the hydrogen chloride based initiating system (the chloride counteranion),

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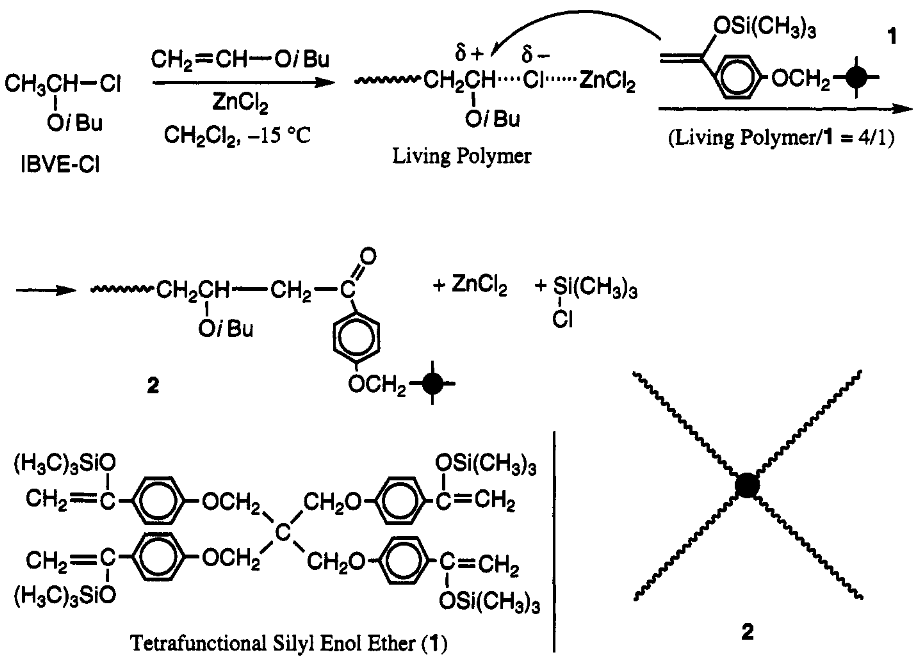
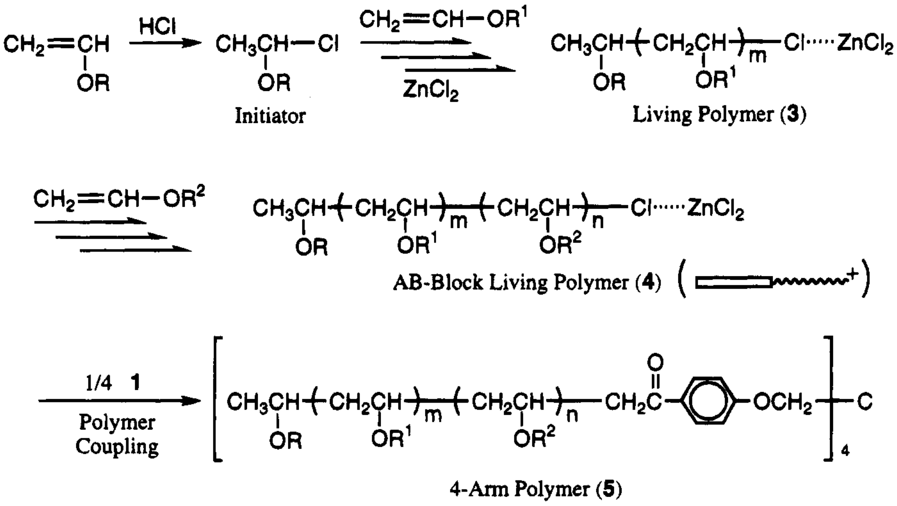
Scheme 1. Synthesis of 4-Arm Poly(IBVE)

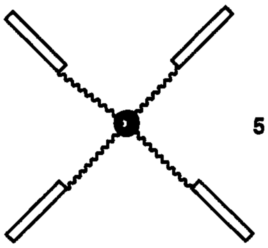


Tetrafunctional Silyl Enol Ether (**1**)

Scheme 2. Synthesis of 4-Arm Poly(vinyl ethers)with AB-Block Arm Chains



code	1st (R^1)	2nd (R^2)
3a–5a	**CEVE**	**AcOVE**
3b–5b	**IBVE**	**AcOVE**
3c–5c	**AcOVE**	**CEVE**
3d–5d	**SIVE**	**IBVE**



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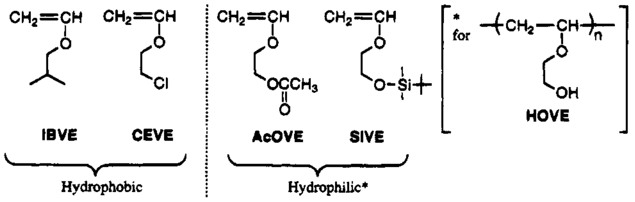
which is mandatory for the efficiency coupling with enol ether **1**.[4,5]



(ii) We next synthesize the 4-armed block polymers (**5**) where the segments of polar monomers are placed in either inside or outside layers of arms. This may be achieved by reversing the polymerization sequence of monomer pairs (e.g., AcOVE and IBVE) in preparing the starting AB-block living chains. (iii) Finally, we transform **5** into target amphiphilic multiarmed polymers (**6**) with polyalcoholic segments by deprotecting the pendant substituent. The products were characterized in terms of structure, composition, solubility characteristics, and other physical characteristics.

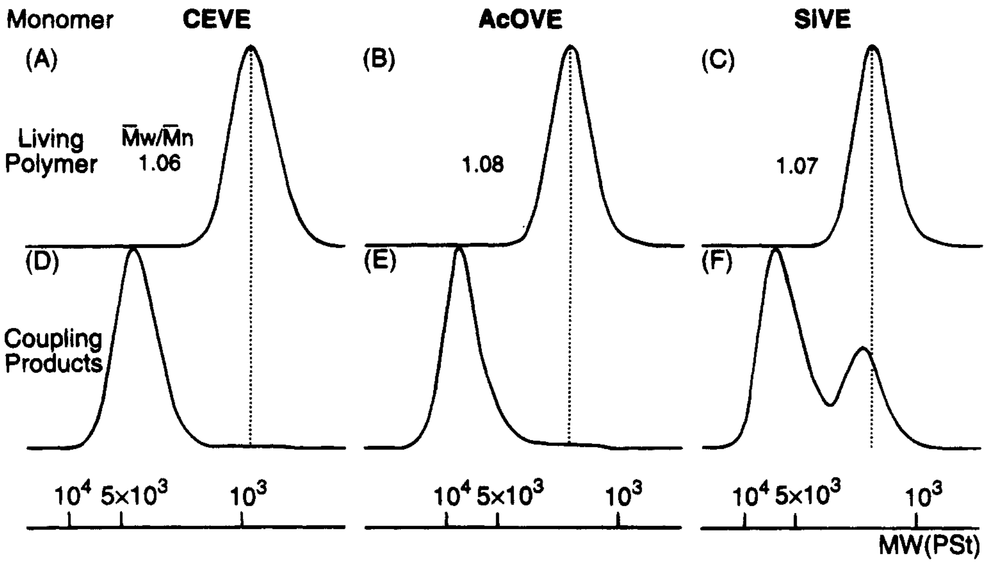


Figure 1. GPC curves of the products obtained by the coupling reactions of the HCl/$ZnCl_2$-initiated living homopolymers of vinyl ethers with tetrafunctional silyl enol ether **1** in CH_2Cl_2 at −15 °C for 24 h: (A−C) linear polymers quenched with methanol; (D−F) coupled products with **1**. Monomers: (A and D) CEVE; (B and E) AcOVE; (C and F) SiVE. [Living polymer]$_0$ = 10 mM; [coupling agent **1**]$_0$ = 2.5 mM. Polymerization conditions are shown in Table 1.

Table 1. Coupling Reactions of Living Homopolymers of Pendant Functionalized Vinyl Ethers with Tetrafunctional Silyl Enol Ether (1)

		polymerization[a]				coupling products[b]						
entry	monomer	initiator	[$ZnCl_2$] (mM)	time (min)	conv (%)	$\bar{F}_n$[c] ^{1}H NMR	$\bar{N}$[d] arm	yield %, GPC	$\overline{DP}_n$(arm)[e] ^{1}H NMR	$\bar{M}_n \times 10^{-3}$ ^{1}H NMR[f]	$\bar{M}_n \times 10^{-3}$ GPC	$\bar{M}_w/\bar{M}_n$ GPC
1	IBVE	IBVE-Cl	0.2	15	80	0.99	3.96	>95	14.9	6.5	6.1	1.09
2	CEVE	CEVE-Cl	3.0	60	90	0.95	3.80	>95	14.5	6.5	3.4	1.09
3	AcOVE	AcOVE-Cl	3.0	90	92	1.02	4.08	>95	16.6	9.4	7.6	1.07
4[h]	SiVE	IBVE-Cl	0.2	120	86	0.90	3.60	68	11.2	9.1	6.0	1.07

[a] Other polymerization conditions: [monomer]$_0$ = 150 mM; [initiator]$_0$ = 10 mM; in CH_2Cl_2 at −15 °C. IBVE-Cl etc. indicate the HCl adducts of IBVE and other corresponding monomers. [b] Coupling reaction conditions: [living polymer]/[**1**] = 4.0; in CH_2Cl_2 at −15 °C for 24 h. [c] $\bar{F}_n$ = (α-end CH_3)/(phenyl groups of coupling agent), by ^{1}H NMR; $\bar{F}_n$(theory) = 1.00; see also ref 9. [d] The number of arms per polymer: $\bar{N}$(arm) = $\bar{F}_n \times 4$ (the number of silyl enol ethers per coupling agent). [e] DP_n shows the degree of polymerization of the arm polymer: $\overline{DP}_n$ = (pendant functional group in the polymer chain)/(α-end CH_3), by ^{1}H NMR. [f] $\bar{M}_n$(^{1}H NMR) = $\bar{N}$(arm) × $\overline{DP}_n$(arm, ^{1}H NMR) × (mol wt of monomer) + (mol wt of the coupling agent). [g] These data are cited from ref 4. [h] For the sample fractionated by preparative GPC from the products shown in Figure 1F.

Results and Discussion

Coupling Reactions of Living Homopolymers of Pendant-Functionalized Vinyl Ethers. Polymerizations of AcOVE, SiVE, and CEVE with the hydrogen chloride/zinc chloride (HCl/$ZnCl_2$) initiating system were first examined, because living polymers with chloride counteranion are needed for efficient coupling with silyl enol ethers (cf. Scheme 1).[4,5] Rather surprisingly, the HCl-mediated living polymerizations have thus far been reported only for IBVE[7] and CEVE.[8] As reported for IBVE,[4,5] the HCl/$ZnCl_2$ system is apparently best suited to this end. The polymerizations were carried out in methylene chloride (CH_2Cl_2) at −15 °C, where the actual initiators were the HCl adducts of the monomers to be polymerized (see Experimental Section and Scheme 2), and relatively short polymer chains ($\overline{DP}_n$ ~ 15) were deliberately prepared to facilitate the characterization of them and the coupling products therefrom.

Figures 1A−C show the molecular weight distributions (MWD) of the polymers thus obtained by quenching the reactions with methanol at 80−90% conversions. The MWDs of the homopolymers are invariably narrow ($\bar{M}_w/\bar{M}_n$ < 1.1), and ^{1}H NMR analysis showed the $\bar{M}_n$ to be close to the calculated value assuming the formation of one living chain from each initiator molecule, indicating the living nature of the polymerizations with the HCl/$ZnCl_2$ system for the functionalized vinyl ethers.

These living polymers were then allowed to react with **1** for polymer coupling (Scheme 1). The coupling reactions were carried out for 24 h in CH_2Cl_2 at −15 °C (the same conditions as for the polymerization) where [living polymer]/[**1**] = 4. The results are summarized in Figures 1D−F and Table 1.

The coupling products with poly(CEVE) and poly(AcOVE) (Figures 1D and 1E, respectively) showed MWDs as narrow as those of the precursors (Figures 1A−C), and they shifted clearly to higher molecular weights, as with the corresponding poly(IBVE) (Table 1). There are virtually no peaks in the molecular weight regions where the uncoupled linear polymers would elute, and the coupling yields are estimated to be above 95% from these MWD traces (entries 1−3, Table 1). Thus, despite their polar groups in the pendant substituents, the living polymers of AcOVE and CEVE, as well as IBVE, can be quenched and coupled virtually quantitatively with the silyl enol ether **1**.

When living poly(SiVE) was treated with **1**, as shown in Figure 1F, the products had a bimodal MWD with a secondary minor peak for the uncoupled polymer (the lower fraction), though the coupled product (the higher fraction) had a narrow MWD. The bulkiness of the pendant function may disturb the coupling reaction.

The coupling products (Figures 1D−F) were characterized by ^{1}H NMR, as shown in Figure 2, where Figure

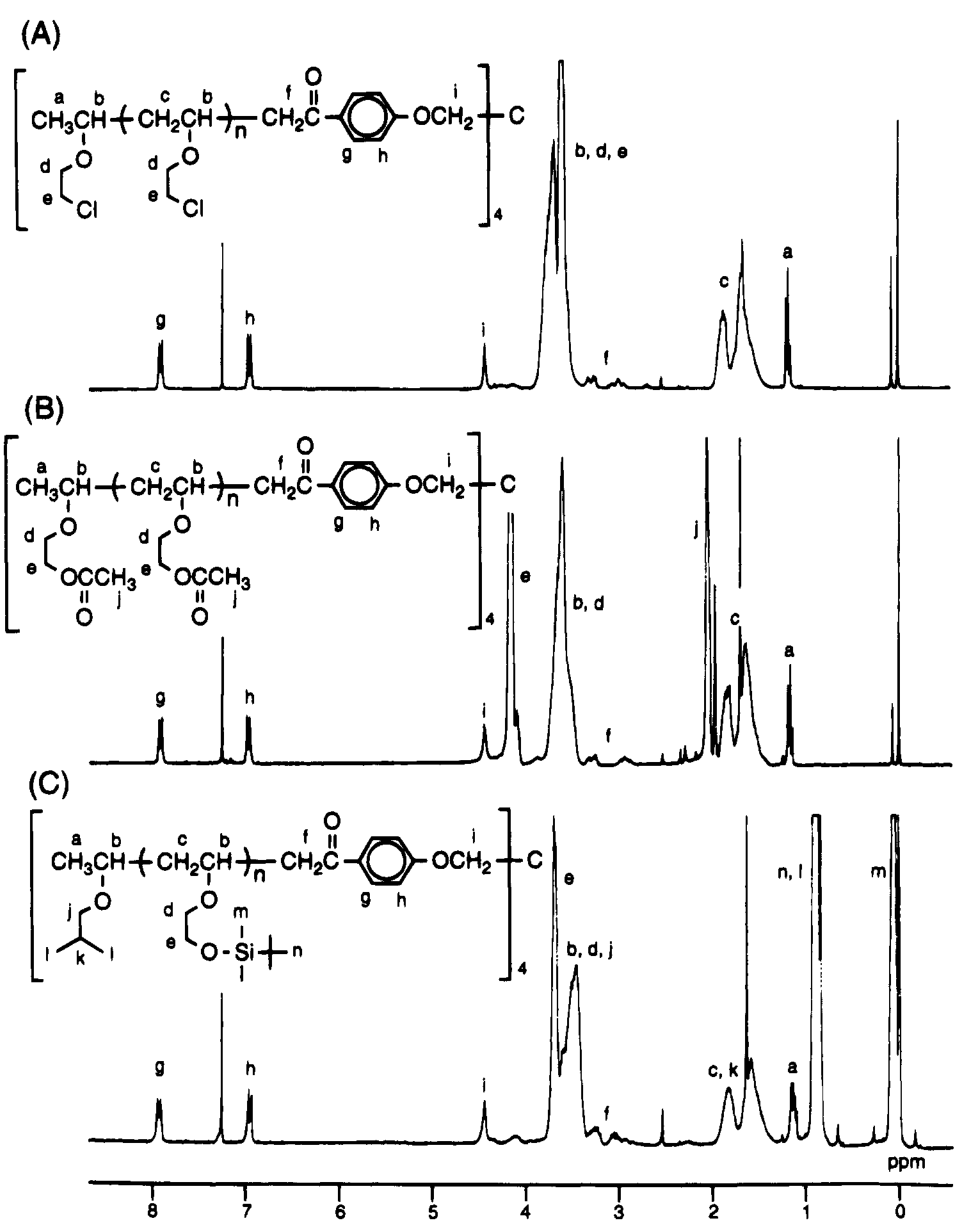


Figure 2. ^{1}H NMR spectra ($CDCl_3$, room temperature) of the tetraarmed polymers of functionalized vinyl ethers. The samples were separated from those shown in Figure 1D–F. Arm chains: (A) CEVE; (B) AcOVE; (C) SiVE.

2C is the spectrum for the sample fractionated by preparative gel permeation chromatography (GPC) from the products shown in Figure 1F. Other samples were subjected to NMR analysis without GPC separation. For the three samples, the α-end methyl group appeared as signal a, which was derived from the initiator (Scheme 1). Signals f–i are assigned to the coupling agent moiety.[4] There are also pendant function signals, (A) d and e (the chloroethyl group), (B) d, e, and j (the acetoxy group), and (C) d, e, m, and n (the *tert*-butyldimethylsilyl ether group). In all cases, no signals indicative of side reactions of silyl enol ether **1** with the pendant functions in the polymers were observed. The number of arms per polymer ($\bar{N}$) of the coupled products were obtained from the intensity ratio of the head methyl group (signal a) to the phenyl group of the coupling agent (signals g and h).[9] Except for poly(SiVE) (entry 4, Table 1), the arm number $\bar{N}$ is close to 4, the functionality of **1** (entries 2 and 3, Table 1); thus the coupled polymers had 4 arms per molecules, as with the living poly(IBVE) (entry 1, Table 1).

These results show that tetrafunctional silyl enol ether **1** was efficient as a multifunctional coupling agent for living polymers of pendant-functionalized vinyl ethers, as well as the alkyl derivatives, to synthesize the tetraarmed polymers near quantitatively. The pendant functions in these polymers did not react with the silyl enol ethers in **1**, though the bulky silyl group in SiVE partly disturbed the coupling reactions

Synthesis of Amphiphilic Tetraarmed Star Polymers. The above basic results were then extended to the synthesis of amphiphilic tetraarmed star poly(vinyl ethers) **6** as shown in Scheme 2. Thus AB-block living polymers **4**, which were prepared by adding the second monomer to the living polymer **3** of the first monomer, were treated with tetrafunctional silyl enol ether **1** to give tetraarmed polymer **5**. Subsequently, the protected groups in **5** were removed completely to yield the amphiphilic tetraarmed star polymers **6**.

(a) Synthesis of AB-Block Living Poly(vinyl ethers). The sequential living cationic polymerizations were examined with $HCl/ZnCl_2$ in CH_2Cl_2 at −15 °C to obtain the AB-block living polymers (**4**) bearing a chloride counteranion, and the results are summarized in Table 2 and Figure 3. Thus, when the conversions of the first monomers were above 90%, the second

Table 2. AB-Block Living Polymerization of Pendant Functionalized Vinyl Ethers with the VE-HCl Adduct/$ZnCl_2$ Initiating System[a]

				first (R^1)			second (R^2)				$\bar{M}_n \times 10^{-3}$		
entry	code	initiator[b]	$[ZnCl_2]_0$ (mM)	monomer	time (min)	conv[d] (%)	monomer	time (min)	conv (%)	$\overline{DP}_n(R^1/R^2)$[e] ^1H NMR	^1H NMR[f]	GPC	$\bar{M}_w/\bar{M}_n$ GPC
1	**4a**	CEVE-Cl	3.0	CEVE	180	95	AcOVE	105	85	19.5/13.1	3.8	3.8	1.07
2	**4b**	IBVE-Cl	0.2 → 3.0[c]	IBVE	20	91	AcOVE	180	89	15.6/12.2	3.2	3.5	1.13
3	**4c**	AcOVE-Cl	3.0	AcOVE	140	97	CEVE	240	88	18.1/14.2	3.9	4.0	1.08
4	**4d**	IBVE-Cl	0.2	SiVE	360	97	IBvE	120	90	15.3/12.7	4.4	3.3	1.10

[a] Other polymerization conditions (cf. Scheme 2): $[\text{1st monomer}]_0 = [\text{2nd monomer}]_0 = 200$ mM; $[\text{initiator}]_0 = 10$ mM; in CH_2Cl_2 at -15 °C. [b] The HCl adducts of the corresponding monomers. [c] After the second monomer was added, an additional amount of zinc chloride was added (see text). [d] Conversion of the first monomer when the second monomer was added to the reaction mixture. [e] $\overline{DP}_n$ shows the degree of polymerization of the respective monomer segment in the AB-block arm polymer: $\overline{DP}_n$ = (pendant functional group in the polymer chain)/(α-end CH_3), by ^1H NMR. [f] $\bar{M}_n(^1H\ \text{NMR}) = \overline{DP}_n(R^1, {}^1H\ \text{NMR}) \times (\text{mol wt of 1st monomer}) + \overline{DP}_n(R^2, {}^1H\ \text{NMR}) \times (\text{mol wt of 2nd monomer}) + (\text{mol wt of methoxy group})$.

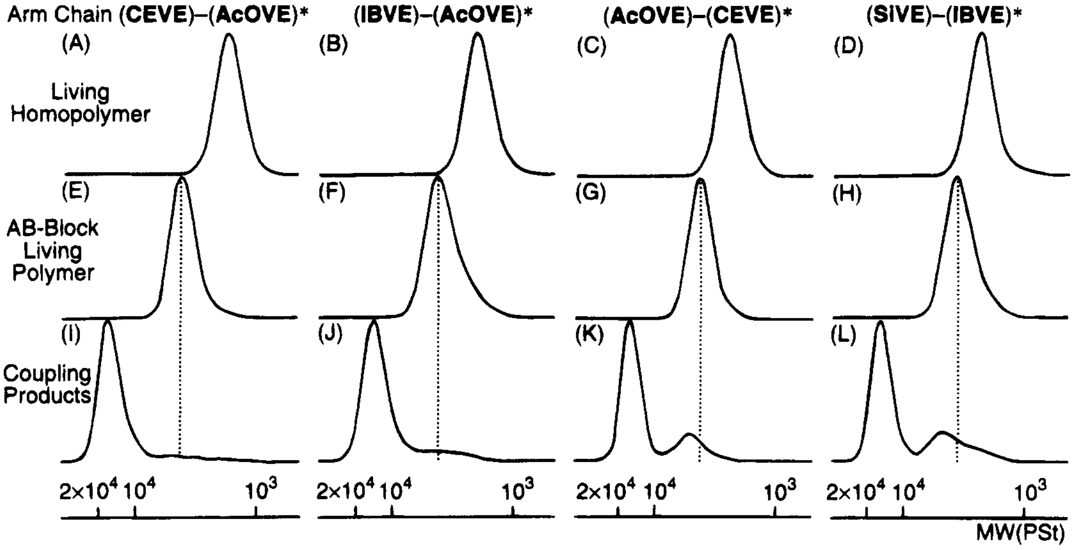


Figure 3. GPC curves of the products obtained by the sequential AB-block polymerization and the coupling reactions of AB-block living polymers: (A–D) living homopolymers **3** quenched with methanol; (E–H) AB-block living polymers **4** quenched with methanol; (I–L) tetraarmed polymers by the coupling reactions of **1** and **4** (cf. Scheme 2). Monomers: (A) CEVE; (B) IBVE; (C) AcOVE; (D) SiVE; (E and I) (CEVE)–(AcOVE)*; (F and J) (IBVE)–(AcOVE)*; (G and K) (AcOVE)–(CEVE)*; (H and L) (SiVE)–(IBVE)*. The asterisk shows the living end. Polymerization and coupling reaction conditions are shown in Tables 2 and 3.

monomers were added to the resultant living polymers **3** (Scheme 2). Four monomer pairs were examined, each of which is a combination of an alkyl vinyl ether (IBVE or CEVE) and a functionalized version (AcOVE or SiVE). For the CEVE–AcOVE pair, two systems were examined (entries 1 and 3, Table 2) where the polymerization sequence of the two monomers was reversed. Besides a run where the living block copolymer was treated with silyl enol ether **1** for polymer coupling, the products in each stage of the sequential polymerization were quenched with methanol and compared in terms of MWD in Figure 3. It should also be noted that, depending on the type of initiator, the $ZnCl_2$ concentration was varied so as to obtain a practically acceptable polymerization rate. Specifically for one of the IBVE–AcOVE systems (entry 2), the zinc concentration was increased on addition of the second monomer, so that two-stage block copolymerizations might proceed smoothly to high conversions.

The MWDs of the AB-block polymers (**4**) quenched with methanol are shown in Figures 3E–H, which are also compared with the living homopolymers in the first-stage polymerization (Figures 3A–D). Polymers E–H have narrow MWDs (see also Table 2) and appeared at higher molecular weight than the corresponding first-stage homopolymers (**3**) (samples (A–D, respectively).

The MWD analysis, shown in Figure 3 (A and E; C and G), also indicates that the block copolymerization of the CEVE–AcOVE pair is "reversible"; i.e., the first monomer may be either CEVE or AcOVE. This is particularly important in the synthesis of the tetraarmed amphiphilic polymers, because the reversibility permits us to prepare two sister samples where the arm segments are identical in compositions (DPs) but different in the placement of the hydrophilic and the hydrophobic parts (e.g., the polyalcoholic part may be inside or outside of the arms).

For the AcOVE–IBVE pair, in contrast, such reversibility no longer holds, and the polymerization from IBVE to AcOVE was indeed successful (entry 2, Table 2; Figures 3B and 3F), but the reverse sequence (AcOVE → IBVE) led to a mixture of an apparently block polymer and a homopolymer of AcOVE.[10] The failure is probably due to the large reactivity difference between the two monomers (AcOVE ≪ IBVE), for which the more reactive one should be polymerized first.[10]

Polymer samples E–H were characterized by ^1H NMR. For example, the spectra of the CEVE–AcOVE and the SiVE–IBVE block polymers are shown in Figures 4A and 5A, respectively. Both spectra have typical signals of the segments: (Figure 4A) the chloroethyl group, signals d and e; the acetoxy group, signals

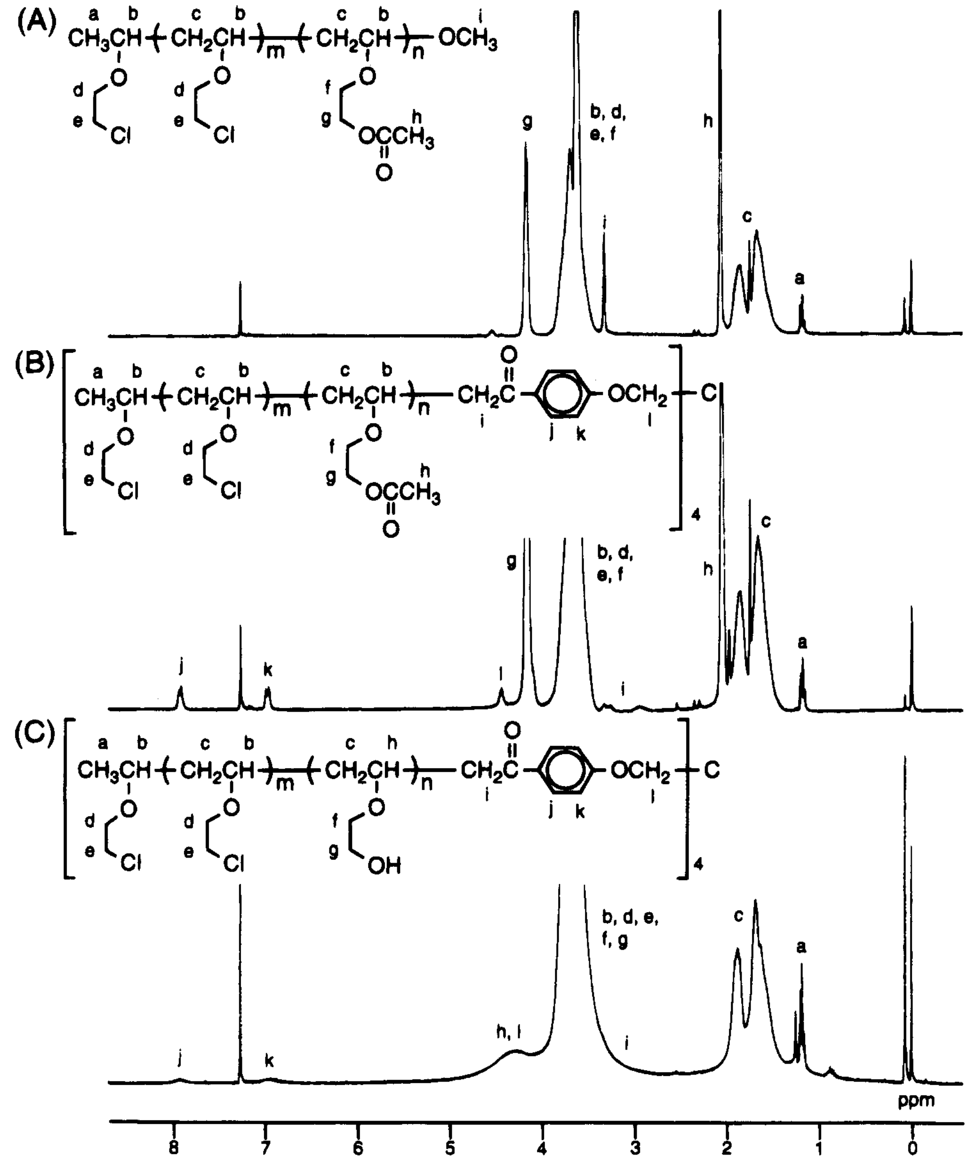


Figure 4. ^1H NMR spectra ($CDCl_3$, room temperature) of the amphiphilic tetraarmed poly(vinyl ethers) by the coupling reaction of CEVE–AcOVE block living polymers **4a** and tetrafunctional silyl enol ether **1** (cf. Scheme 2): (A) block polymer **4a** quenched with methanol; (B) tetraarmed polymer **5a**; (C) amphiphilic tetraarmed poly(vinyl ether) by the deprotection of the acetoxy groups in **5a**.

g and h; (Figure 5A) the *tert*-butyldimethylsilyl groups, signals h–j; the isobutyl group, signal f. Both samples also showed the head methyl group, $CH_3CH(OR)\sim\sim\sim$ (α-end, signal a), and the methoxy acetal group, $\sim\sim\sim CH_2CH(OR^2)OCH_3$ (ω-end, signals i or k), derived from the quenching with methanol.[11] The ratios of the α-end to the ω-end groups were close to unity, as calculated from the NMR peak areas. Other AB-block polymers, AcOVE–CEVE and IBVE–AcOVE (entries 2 and 3, Table 2), were also characterized by ^1H NMR. Therefore, the obtained polymers (Figures 3E–H) were identified as well-defined AB-block living polymers **4** suitable for the coupling with tetrafunctional silyl enol ether **1**.

(b) Coupling Reactions with AB-Block Living Poly(vinyl ethers). Tetrafunctional silyl enol ether **1** was allowed to react with the AB-block living poly(vinyl ethers) **4**. Thus, an enol ether solution in CH_2Cl_2 was added to the unquenched living polymers **4**, and the reaction mixture was kept at −15 °C for 24 h with stirring to accomplish the quantitative coupling reaction as reported previously.[4,5] In the coupling reaction, the quantity of silyl enol ethers in **1** must be identical with that of the living end ([living polymer **4**]/[**1**] = 4). Table 3 and Figure 3 summarize the results.

The MWDs of the coupling products are shown in Figures 3I–L. The products have narrow MWDs ($\bar{M}_w/\bar{M}_n$ < 1.1, Table 3) and eluted at higher molecular weight than the original AB-block living polymers **4** (Figures 3E–H). The $\bar{M}_n$ (^1H NMR) of the products are slightly higher than $\bar{M}_n$(GPC) (polystyrene calibration); the difference supports the multiarmed structure of the products. When the second monomer was AcOVE, the yields of the coupling products were above 90% (entries 1 and 2, Table 3), while the coupling products from the CEVE and IBVE living ends were obtained only in 70–80% yields (entries 3 and 4, Table 3). In these latter cases, despite the long coupling reaction time (24 h), unreacted living polymer **4** is seen in Figures 3K and 3L. Then some of the star may not be the tetraarmed star. This may be due to the effects of the long polymer chain[4] or the mismatching of the polymerization and coupling reaction conditions.

All of the coupling products, separated by preparative GPC when necessary, were identified by ^1H NMR. For example, Figures 4B and 5B show the spectra of the

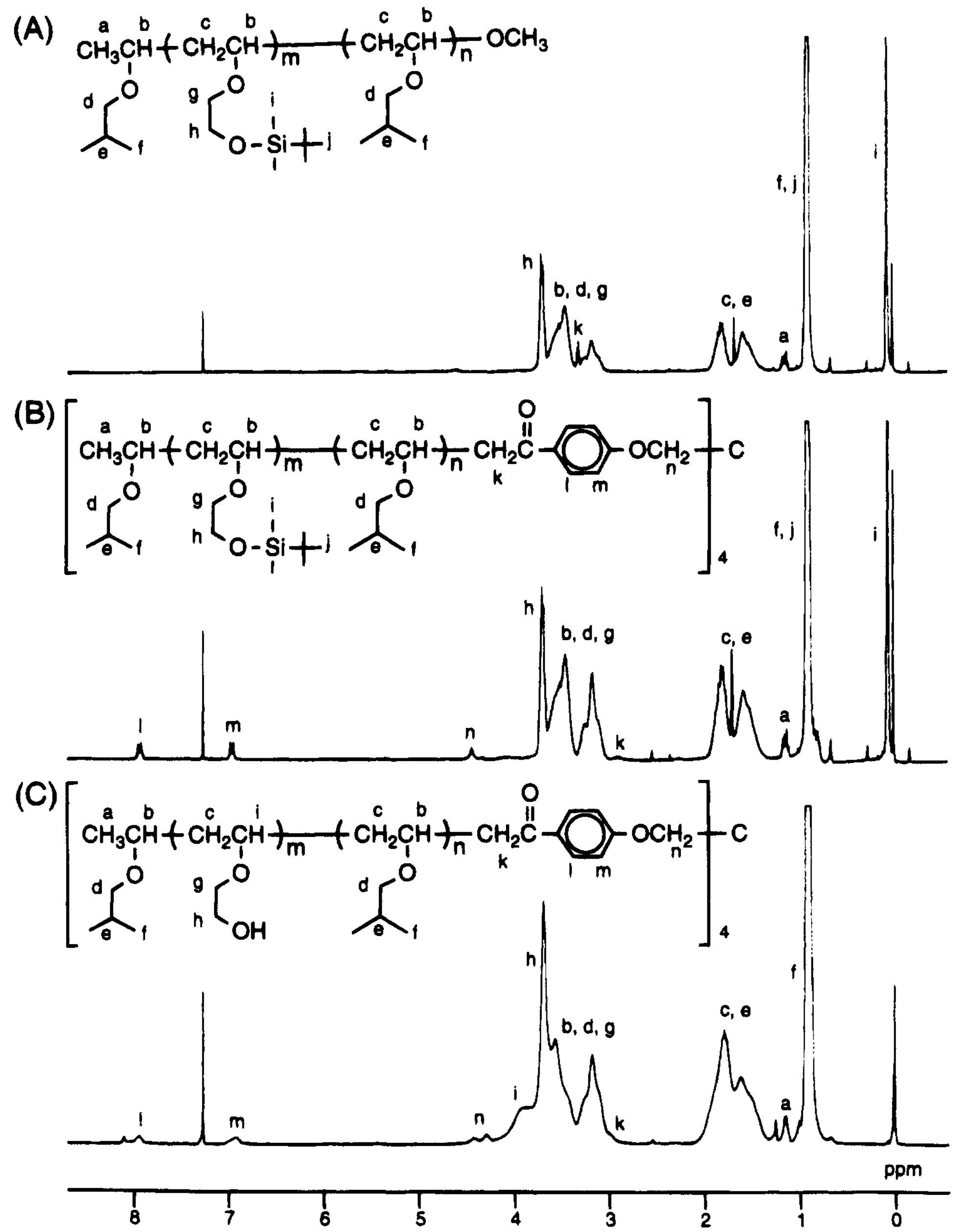


Figure 5. ^{1}H NMR spectra (CDCl$_3$, room temperature) of the amphiphilic tetraarmed poly(vinyl ethers) by the coupling reaction of SiVE–IBVE block living polymers **4d** and tetrafunctional silyl enol ether **1** (cf. Scheme 2): (A) block polymer **4d** quenched with methanol; (B) tetraarmed polymer **5d**; (C) the amphiphilic tetraarmed poly(vinyl ether) by the deprotection of the *tert*-butyldimethylsilyl ether groups in **5d**.

Table 3. Coupling Reactions of AB-Block Living Poly(vinyl ethers) with Tetrafunctional Silyl Enol Ether (1)[a]

		monomer		$\bar{F}_n$[c]	$\bar{N}$[d]	yield	$\overline{\mathrm{DP}}_n(\mathrm{R}^1/\mathrm{R}^2)$[e]	$\bar{M}_n \times 10^{-3}$		$\bar{M}_w/\bar{M}_n$
entry[b]	code	first (R^1)	second (R^2)	^{1}H NMR	arm	%, GPC	^{1}H NMR	^{1}H NMR[f]	GPC	GPC
1	**5a**	CEVE	AcOVE	0.97	3.88	93	19.1/18.8	18.1	15.3	1.06
2	**5b**	IBVE	AcOVE	0.96	3.84	91	16.9/16.7	15.4	13.2	1.07
3	**5c**	AcOVE	CEVE	0.92	3.68	80	17.5/16.0	15.3	15.4	1.04
4	**5d**	SiVE	IBVE	0.89	3.56	73	15.4/19.7	17.2	15.0	1.04

[a] Polymerization conditions are shown in Table 2. Coupling reaction conditions: [living polymer]/[**1**] = 4.0; in CH$_2$Cl$_2$ at −15 °C for 24 h. [b] For the samples fractionated by preparative GPC from the products shown in Figure 3I–L. [c] $\bar{F}_n$ = (α-end CH$_3$)/(phenyl groups of coupling agent), by ^{1}H NMR; $\bar{F}_n$(theory) = 1.00; see also ref 12. [d] The number of arms per polymer: $\bar{N}$(arm) = $\bar{F}_n \times 4$ (the number of silyl enol ethers per coupling agent). [e] $\overline{\mathrm{DP}}_n$ shows the degree of polymerization of the respective monomer segment in the AB-block arm polymer: $\overline{\mathrm{DP}}_n$ = (pendant functional group in the polymer chain)/(α-end CH$_3$), by ^{1}H NMR. [f] $\bar{M}_n$(^{1}H NMR) = $\bar{N}$(arm) × [$\overline{\mathrm{DP}}_n$(R^1, ^{1}H NMR) × (mol wt of 1st monomer) + $\overline{\mathrm{DP}}_n$(R^2, ^{1}H NMR) × (mol wt of 2nd monomer)] + (mol wt of the coupling agent).

coupled products from the CEVE–AcOVE with the SiVE–IBVE pairs (Figures 3I and 3L, respectively). Before and after the coupling reactions with **1** (see Figures 4A and 4B or Figures 5A and 5B), the signals of the AB-block arm chains did not change in both spectra except for the polymer end. After the coupling, the signals of the coupling agent moiety appeared newly as signals i–l in Figure 4B and k–n in Figure 5B. The

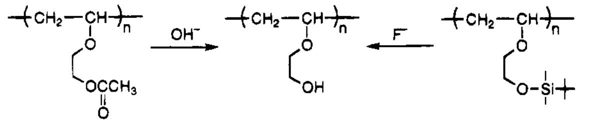
Table 4. Solubility of Amphiphilic 4-Arm Polymers (E–H), Their Precursors (A–D), and Relevant Block Polymers (I and J)

		segment function[a]		solvent[b]					
code	polymer structure	R^1(outer)	R^2(inner)	*n*-hexane	toluene	$CHCl_3$	EtOH	MeOH	H_2O
A	4-arm	CEVE	AcOVE	×	○	○	△	×	×
B	4-arm	AcOVE	CEVE	×	○	○	×	×	×
C	4-arm	IBVE	AcOVE	○	○	○	○	△	×
D	4-arm	SiVE	IBVE	○	○	○	○	△	×
E	4-arm	CEVE	HOVE	×	○	○	×	×	×
F	4-arm	HOVE	CEVE	×	×	△	○	○	○
G	4-arm	IBVE	HOVE	△	○	○	○	△	△
H	4-arm	HOVE	IBVE	×	△	○	○	○	△
I	block	CEVE	HOVE	×	○	○	△	○	×
J	block	IBVE	HOVE	○	○	○	○	○	○

[a] Code **A–H**, $\{[CH_2CH(OR^1)]_n-[CH_2CH(OR^2)]_n\}_4$–(core); code **I** and **J**, $[CH_2CH(OR^1)]_n-[CH_2CH(OR^2)]_n$; $n \sim 20$ (**A–J**). [b] ○, soluble; △, swelling, ×, insoluble; at room temperature, ca. 1 wt %.

ratios of the head methyl group (signal a) to the phenyl group in the coupling agent were calculated by the area ratio of the corresponding signals.[12] The product shown in Figure 4B gave a ratio close to unity (entry 1, Table 3), while the product in Figure 5B gave a ratio less than unity (entry 4) due to the bulkiness of the pendant functions (see above). In the case of other coupling products, the ratios are also close to unity (entries 2 and 3). Therefore, the coupling products shown in Figures 3I–L were identified as tetraarmed polymers **5**.

(c) Amphiphilic Tetraarmed Star Poly(vinyl ethers). To obtain the amphiphilic arm segments as shown in eq 1, the acetoxy or the silyl pendant groups in **5** were deprotected by alkaline hydrolysis[13] and the desilylation with n-$Bu_4N^+F^-$,[14] respectively (see Experimental Section).



(1)

In the alkaline hydrolysis of the acetoxy groups, for example, the CEVE–AcOVE polymer (**5a**) was treated with aqueous NaOH solution (5 equiv with respect to the ester function) in 1,4-dioxane at room temperature. As can be seen in the ^{1}H NMR spectra before and after deprotection (Figures 4B and 4C), the methyl group (signal h, Figure 4B) of the acetyl moiety in **5a** disappeared, and the signal of the methylene protons neighboring the acetoxy group was shifted to higher magnetic field. Other AcOVE-based polymers (**5b** and **5c**) were also deprotected completely. The chloroethyl, isobutyl, and phenyl groups of **5** remained unchanged during the deprotection.

The *tert*-butyldimethylsilyl ether groups of the SiVE–IBVE arms in **5d** were removed with F^- anion. Thus, **5d** was allowed to react with n-$Bu_4N^+F^-$ (5 equiv with respect to the silyl ether function) in THF at room temperature. The ^{1}H NMR spectra (Figures 5B and 5C) show that the signals of the methyl group and the *tert*-butyl group disappeared completely (signals i and j, Figure 5B), but the isobutyl groups and the coupling agent moiety survived.

These data demonstrate that the silyl enol ether coupling of living AB-block copolymers (Scheme 2) provided a series of amphiphilic tetraarmed poly(vinyl ethers) (**6**) with controlled and uniform arm length and compositions. In these polymers, equally important, the hydrophilic poly(HOVE) segments may be placed either inside or outside of the arm moieties.

Characteristics of the Amphiphilic Tetraarmed Polymers. The combination of the tetraarmed star structure and the amphiphilicity of the arms in the tetraarmed poly(vinyl ethers) (**6**) would lead to interesting characteristics, and this point was examined in relation to the precursor tetraarmed polymers (**5**) and the corresponding amphiphilic linear AB-block copolymers (**4**).

(a) Solubility Characteristics. Table 4 shows the solubility of a series of the tetraarmed star polymers and the AB-block polymers. Samples A–D are the tetraarmed polymers (**5**) before deprotection, E–H are their amphiphilic forms (**6**) (e.g., E from A, F from B, etc.), and I and J are the corresponding amphiphilic linear AB-block polymers. In all these samples, the hydrophobic and the hydrophilic segments (or their protected forms) are nearly the same in length ($\overline{DP}_n$ ca. 20 each). Comparison may be made on a pair of polymers (e.g., B and F) before and after the deprotection or on another pair (e.g., E and F) where the placement of two segments in the arm chains is reversed.

As seen for samples B and F, for example, the deprotection of the ester pendant groups (B) into the hydrophilic alcohol functions (F) transforms the originally lipophilic polymer (B, soluble in toluene and chloroform) into a hydrophilic polymer (F, soluble in alcohols and water). However, this expected change is true only for the tetraarmed polymers with outer alcoholic segments (samples F and H). For the inner-alcohol version, such as E and G, their solubility characteristics are very similar to those of their protected, less hydrophilic forms (A and C, respectively), and the corresponding linear block polymers (I and J) are also similar in solubility to those inner-alcohol polymers.

Thus, comparison of samples E and F clearly shows that reversing the placement of hydrophilic segments in the arms completely alters the solubility of these polymers, and the overall solubility is primarily determined by the nature of the outer segments; namely, E with inner alcohols is soluble in less polar organic solvents, but F with outer alcohols is soluble in alcohols and water. These trends appear general, as has been observed for the multiarmed amphiphilic poly(vinyl ethers) prepared by the multifunctional initiation[2] and by the polymer linking methods.[3]

(b) Solvent Effects on ^{1}H NMR Spectra. The solubility analysis (Table 4) shows that samples G and H are indeed amphiphilic, soluble both in polar and nonpolar solvents (ethanol and chloroform, respectively). In these solvents the two samples gave ^{1}H NMR spectra

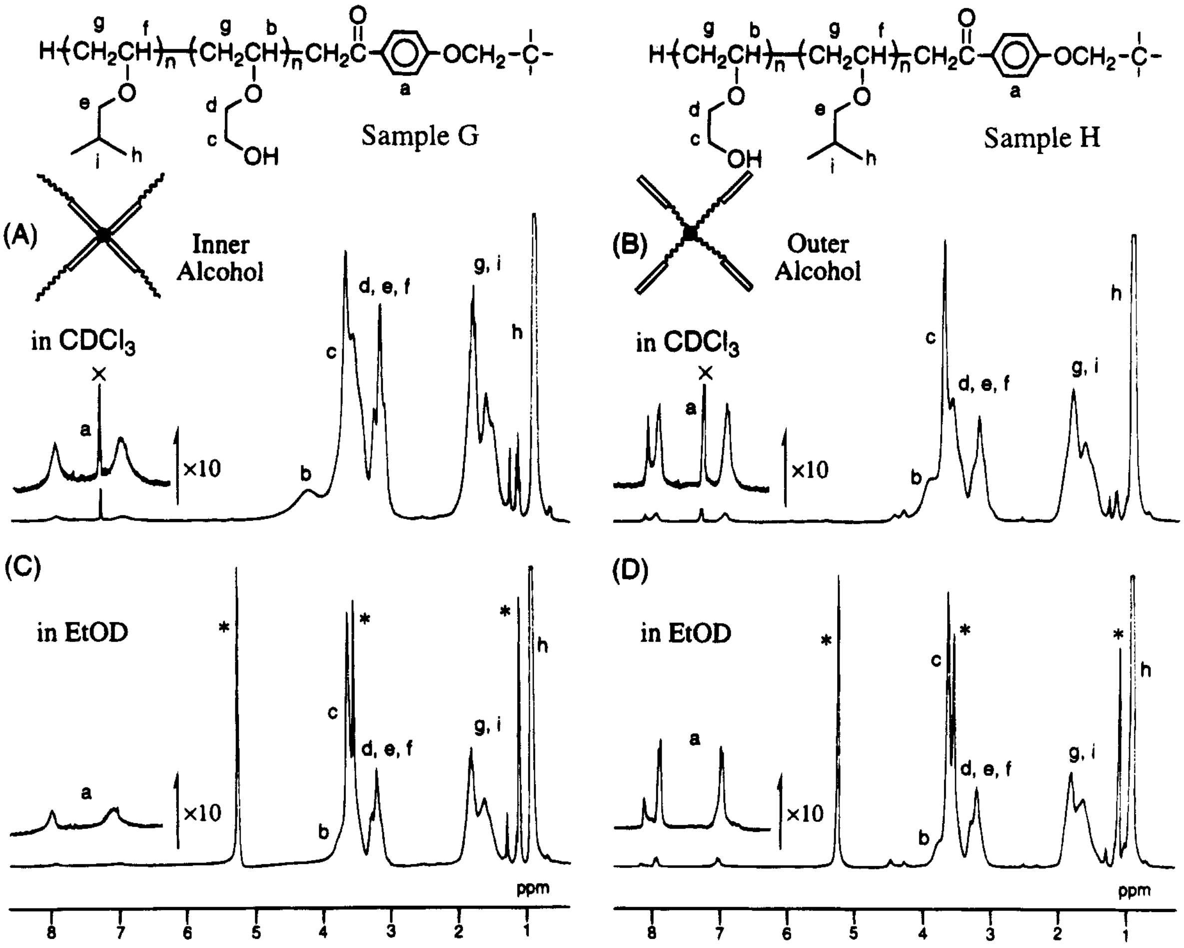


Figure 6. ^{1}H NMR spectra (room temperature) of the amphiphilic tetraarmed poly(vinyl ethers): (A and C) sample **G** in Table 4; (B and D) sample **H**. Solvents: (A and B) chloroform-*d*; (C and D) ethanol-d_6. × and * in the spectra show the protons of chloroform and ethanol, respectively.

that clearly depended on solvent polarity and on the location of the hydrophilic poly(HOVE) segments in the arms, which is the only structural difference between them. Figure 6 summarizes the results.

For example, the peaks due to the poly(HOVE) segments (b and c for both G and H) are clearly sharper in ethanol than in chloroform (Figures 6A and 6B), and in the latter medium, they are sharper with the outer-alcohol version H than with the inner counterpart G (Figure 6B vs 6A). These spectral changes indicate that the hydrophilic poly(HOVE) segments assume a more extended conformation in ethanol and also that the extension is enhanced for sample H, because its hydrophilic arm segments would be solvated more readily.

The signals of the core phenyl groups (a) are also affected by solvent polarity and arm structure. In ethanol, a polar solvent, the aromatic signals of polymer H are sharp (Figure 6D), whereas those of polymer G are broad and weak (Figure 6C), probably because the nonpolar poly(IBVE) segments shrink more in sample G than in H, rendering the core less mobile in the former. A similar trend can be seen in the spectra in chloroform (Figures 6A and 6B), but signal a with sample G is stronger than in methanol, because of a more extended form of the outer poly(IBVE) segments.

Overall, the NMR signal shape and strength, or the relative mobility of the core and arms, appear to depend on the nature of the outer arm segments in relation to the solvent.

Conclusion. The coupling reactions of AB-block living poly(vinyl ethers) **4** with tetrafunctional silyl enol ether **1** provided tetraarmed poly(vinyl ethers) **5** with AB-block arm chains in high yield (Scheme 2). The deprotections of the acetoxy or the silyl ether groups in **5** led to amphiphilic tetraarmed star poly(vinyl ethers) (**6**) having well-defined arm chains, which showed the interesting behavior in solution.

Experimental Section

Materials. The following reagents were washed by the usual methods[15] and distilled over calcium hydride (CaH_2) at least twice before use: polymerization solvents (*n*-hexane and CH_2Cl_2), monomers (IBVE, CEVE, AcOVE, and SiVE), and internal standards for GC (CCl_4 for IBVE, *n*-octane for CEVE, phenyl chloride for AcOVE, and 1,2,3,4-tetrahydronaphthalene for SiVE). AcOVE[13] and SiVE[14] were prepared as reported. Diethyl ether (Dojin, anhydrous) as the solvent for $ZnCl_2$ was distilled over lithium aluminum hydride before use. Zinc chloride (Aldrich, 1.0 M in diethyl ether) was used as received and diluted with the distilled diethyl ether to a given concentration. The HCl adducts of IBVE,[7] CEVE,[16] and AcOVE[17] (as initiators; 1.0 M stock solutions in *n*-hexane) and tetrafunctional silyl enol ether **1** (coupling agent, CH_2Cl_2 solution)[4] were prepared as reported. Tetra-*n*-butylammonium fluoride (Aldrich, 1.0 M THF solution) was used as received.

Procedures. (a) Polymerization and Coupling Reactions. Synthesis of AB-block living cationic polymers **4** was carried out under dry nitrogen in a 50-mL baked flask equipped with a three-way stopcock with magnetic stirring.[4,6] For example (see Scheme 2), a mixture of CEVE (0.2 mL), *n*-octane (0.2 mL, internal standard for GC analysis), and CH_2Cl_2 (7.6 mL) was cooled to −15 °C, and solutions of the CEVE-HCl adduct (1.0 mL; 0.10 M in *n*-hexane) and $ZnCl_2$ (1.0 mL; 30 mM in diethyl ether) were added in order. Living polymer

3a ($\overline{\mathrm{DP}}_n \sim 15$; [living end] = 10 mM) was formed in nearly quantitative yield after 180 min. To the as-prepared solution of **3a** was quickly added a mixture (1.0 mL) of AcOVE (1.3 mL), phenyl chloride (0.7 mL, internal standard for GC analysis), and CH_2Cl_2 (3.0 mL). AB-block living polymer **4a** was formed in nearly quantitative yield after 105 min. Other AB-block living polymers (**4b–d**, [living end] = 10 mM) were prepared similarly under the conditions shown in Table 2.

To these solutions of AB-block living polymers **4** (10 mL) kept at −15 °C, the CH_2Cl_2 solution of the coupling agent was quickly added at room temperature with vigorous stirring. The amount of the coupling agent (**1**, 0.60 mL of a 41.4 mM solution) was determined so as to maintain the stoichiometry ([living end] = [silyl enol ether group]) as closely as possible. The mixture was stirred at −15 °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. The samples for ^{1}H NMR analysis and the deprotection were separated by preparative gel permeation chromatography (Shodex K2003; exclusion limit = 7×10^4; 2.5 cm i.d. × 30 cm).

(b) Deprotection. The acetoxy groups in **5a–c** were removed by alkaline hydrolysis at room temperature.[13] For example, an aqueous solution of sodium hydroxide (0.68 mL, 2 N; 5 equiv with respect to the ester functions) was added to a mixture of **5a** (78 mg; entry 1, Table 3) and 1,4-dioxane (6.0 mL) with stirring. After 7 h, during which period the solution became cloudy, water (3.0 mL) was added to obtain a transparent solution. The mixture was stirred further for an additional 2 days.

The *tert*-butyldimethylsilyl ether groups in **5d** were removed by the F^- anion at room temperature.[14] Thus, $n\text{-}Bu_4N^+F^-$ (2.9 mL, 1.0 M THF solution; 5 equiv with respect to the silyl group) was added to the mixture of **5d** (110 mg; entry 4, Table 3) and THF (7.0 mL) with stirring. The mixture was stirred for 5 h.

After the deprotection, the solvents were removed under reduced pressure. The residues were dissolved in water or a water/1,4-dioxane 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.[6] The amphiphilic tetraarmed poly(vinyl ethers) were finally obtained by evaporating the water and 1,4-dioxane.

(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 polystyrene standard samples. ^{1}H NMR spectra (270 MHz) were recorded on a JEOL GSX-270 spectrometer at room temperature.

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(10) When IBVE was added to living poly(AcOVE) ($\bar{M}_n = 2500$, $\bar{M}_w/\bar{M}_n = 1.08$) under conditions similar to those for entry 3, Table 2, IBVE was completely consumed, but a small amount of homopoly(AcOVE) was seen in the GPC trace. The product had a broader MWD than the prepolymer ($\bar{M}_n = 4100$, $\bar{M}_w/\bar{M}_n = 1.22$). See: Kojima, K.; Sawamoto, M.; Higashimura, T. *Polym. Bull.* **1990**, *23*, 149.

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