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# Star-Shaped Polymers by Living Cationic Polymerization. 3. Synthesis of Heteroarm Amphiphilic Star-Shaped Polymers of Vinyl Ethers with Hydroxyl or Carboxyl Pendant Groups

**Shokyoku Kanaoka, Takahiro Omura, Mitsuo Sawamoto, and Toshinobu Higashimura***

*Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan*

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ABSTRACT: Amphiphilic star-shaped polymers of vinyl ethers (VEs) (5) where separate sets of hydrophilic and hydrophobic arm chains are independently attached to a single core were prepared on the basis of living cationic polymerization. For example, a living polymer ($\overline{DP}_n$ = 30) of isobutyl VE (IBVE), prepared by the $HI/ZnI_2$ system at −40 °C in toluene, was allowed to react with a small amount of a divinyl ether [1; $CH_2{=}CHOCH_2CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH_2OCH{=}CH_2$] to give a star-shaped poly(IBVE) (3; $\bar{M}_w$ = 50 300, 10 arms). On addition of an ester-containing VE [AcOVE, $CH_2{=}CHOCH_2CH_2OCOCH_3$; VOEM, $CH_2{=}CHOCH_2CH_2CH(COOEt)_2$] to a solution of 3, quantitative polymerization of AcOVE or VOEM immediately ensued from the living active sites on the core and afforded "heteroarm" star polymers (4) with different arms on a single core. The concentration of the living ends, determined by the end-capping with the dibenzyl malonate anion [$^-CH(COOCH_2C_6H_5)_2$], was almost constant and equal to the initial HI concentration throughout the reaction. The product polymers were completely soluble in common organic solvents (toluene, $CHCl_3$, etc.), and the observed $\overline{DP}_n$ of IBVE and AcOVE or VOEM arm chains were in good agreement with the calculated values. Hydrolysis of the ester functions of 4 gave a heteroarm amphiphilic star polymer 5 with hydroxyl or carboxyl pendant groups [$H[-CH_2CH(OiBu)]_m$-(core)-$[-CH_2CH(OCH_2CH_2X)]_n-OCH_3$; **5a** X, OH; **5b** X, $CH(COOH)_2$]. The star polymers **5a** ($m$ = 30, $n$ = 20) and **5b** ($m$ = 30, $n$ = 10) were completely soluble in toluene, chloroform, and methanol. $^1H$ NMR analysis showed that the star polymers 5 changed conformation with solvent polarity.

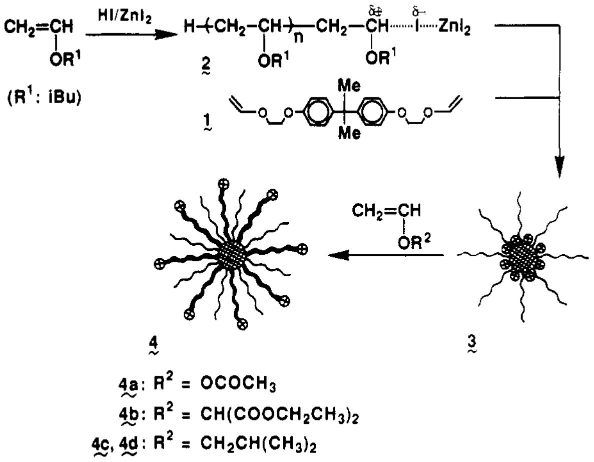
## Introduction

For the last few decades, the synthesis of star-shaped polymers have been performed by living anionic polymerization in several ways,[1] among which the method that is particularly suited to prepare star polymers with many arms involves the linking reaction of linear living polymers with a small amount of a divinyl compound like divinylbenzene.[2] Recently, we have shown that star-shaped polymers of vinyl ethers (VEs) can be prepared in a similar way on the basis of living cationic polymerization (Scheme I),[3] where living poly(VE) chains (2), generated with the $HI/ZnI_2$ system, undergo linking reactions via a bifunctional vinyl ether (1) into a star-shaped polymer (3).

The initially formed star polymer (first star; 3 in Scheme I) may still carry living growing sites within its microgel core. These "core" living sites may be utilized to initiate a second-phase living polymerization to grow new arms from the core to give a "second star" polymer (4) where the number ($f$) of arms per molecule is doubled from the first star. When a second monomer differs from the first polymerized monomer (cf. Scheme I), a "heteroarm" star polymer may be obtained where different arms are attached to a single core. Although such heteroarm star-shaped polymers have been prepared by living anionic polymerization, all of them consist of hydrophobic arms,[4] because of the difficulty in preparing living polymers with pendant polar functional groups.

The living cationic polymerization that we have developed[5,6] is applicable to vinyl ethers with functional pendant groups.[7] Taking this synthetic advantage, we have synthesized a series of amphiphilic star-shaped block polymers, where the arm chain consists of a hydrophilic polyalcohol and a hydrophobic poly(alkyl VE) segment.[8] Such topologically controlled polymers were found to possess properties and functions (like selective host–guest interaction[9]) that differed from those of the corresponding linear block polymers.[8,9] These findings prompted us to synthesize heteroarm amphiphilic star polymers 5 with pendant hydroxyl or carboxyl groups, another type of star-shaped amphiphilic polymers.

### Scheme I



As illustrated in Scheme II, treatment of a linear living polymer 2 of isobutyl vinyl ether (IBVE), prepared by the $HI/ZnI_2$ initiating system, with a small amount of divinyl ether 1 affords "living" star-shaped polymer 3 (first star). From the living sites in its core, an ester-containing VE may be polymerized to give a heteroarm star-shaped polymer 4. Alkaline hydrolysis of the ester pendant groups in 4 then leads to an amphiphilic heteroarm star polymer 5, where separate sets of hydrophobic and hydrophilic arms are independently attached to a single core. The separation of hydrophilic and hydrophobic arms is an important feature of 5; note that for 5, the amphiphilicity stems from these two sets of independent homopolymer arm chains, whereas in the corresponding "star block" versions,[8] each arm is an amphiphilic block polymer.

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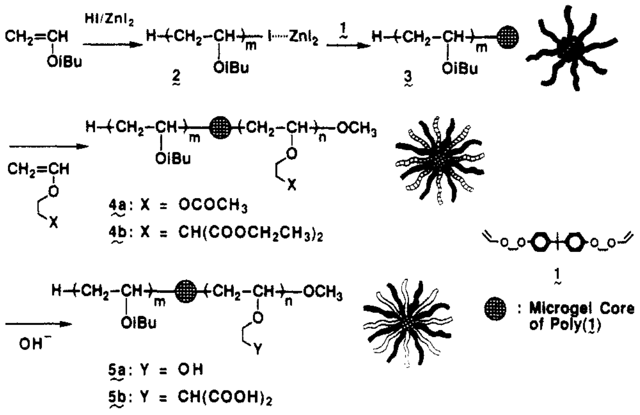
### Scheme II



Therefore, star polymers **5** are expected to possess properties that differ from those of the star block amphiphiles, where outer segments may render inner segments restricted in motion, and govern the properties of the star polymer.

In this study, our first objective was to establish the feasibility of our methodology shown in Schemes I and II, i.e., to polymerize a vinyl ether from the living active sites in the core of the star-shaped poly(vinyl ether). The second and major purpose was to examine (i) the controlled synthesis of heteroarm amphiphilic star polymers **5** and (ii) their solubility characteristics and conformational changes, specifically relative to the corresponding linear AB block polymers and the star-shaped block copolymers.

## Results and Discussion

**1. Synthesis of Double-Arm Star-Shaped Polymers. (a) Polymerization from the Living Active Sites on the Core.** Initially, we studied cationic polymerization of IBVE from the living active sites within the core of the star-shaped polymers **3** prepared by the HI/$ZnI_2$ initiating system (Scheme I). As illustrated in Scheme I, IBVE was polymerized by HI/$ZnI_2$ at -40 °C in toluene into a living polymer (**2**) with a narrow molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n \leq 1.1$; Figure 1A). Without quenching, this polymer was subsequently treated with **1**, 3 equiv to the living ends ($r = [1]_0/[2] = [1]_0/[HI]_0 = 3.0$). After 4 h, **2** and **1** were consumed quantitatively, and the first star polymer **3** (verified by light scattering, see below) was obtained in high yield [$\overline{DP}$(arm) = 19, Figure 1B].[3] On addition of a second feed of IBVE (equimolar to the first feed, $[IBVE]_{add}/[HI]_0 = 19$) to a solution of **3**, a second-stage polymerization ensued and completed in ca. 50 min, and the product polymer was completely soluble in the reaction medium and other common organic solvents at room temperature.

The MWD curve of the product after the second-stage polymerization shifted toward higher molecular weight (Figure 1C). The weight-average molecular weight ($\bar{M}_w$) of the product (by light scattering) was 26 000, clearly higher than that of the first star polymer ($\bar{M}_w$ = 18 300) (Table I). Furthermore, the $\bar{M}_w$ by light scattering is clearly higher than the corresponding value by size-exclusion chromatography. Such a difference provides additional evidence for the formation of a multiarmed structure that is evidently more compact[10] than the linear counterpart with the same molecular weight. The higher the doses of added IBVE (4 equiv to the first feed), the higher the molecular weight of the second star polymer (**4d**; $\bar{M}_w$ = 56 200, Figure 1D), but the MWD curve D shows an additional peak in the lower molecular weight region.[11]

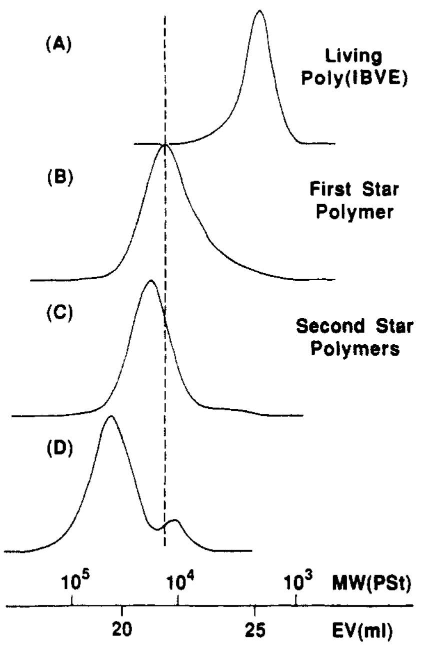


**Figure 1.** MWD of star-shaped poly(IBVE) **3**, **4c**, and **4d** obtained in toluene at -40 °C: (A) living poly(IBVE) **2**, $[IBVE]_0$ = 0.19 M, $[HI]_0$ = 10 mM, $[ZnI_2]_0$ = 0.2 mM, IBVE conversion = 100%; (B) first star polymer **3** obtained from the reaction of **2** and divinyl ether **1**, $\overline{DP}$(arm) = 19, $[3]_0$ = 30 mM, $r = [1]_0/[HI]_0$ = 3.0; (C and D) the products (second star polymers **4c** and **4d**, respectively) obtained by the polymerization of IBVE from the living ends within the core. Molar ratio of a second feed of IBVE to HI (or the living end P*): $[IBVE]_{add}/[HI]_0$: (C) 19; (D) 76.

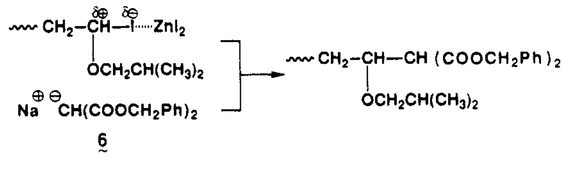
Table I
Star-Shaped Polymers 3, 4c, and 4d Obtained from IBVE and Divinyl Ether 1 by Living Cationic Polymerization (Scheme I)[a]

| code | shape | $[IBVE]_0$, M | $[IBVE]_{add}$,[b] M | $10^{-4}\bar{M}_w$[c] LS | SEC | $f$[d] | $[P^*]/[HI]_0$[e] |
|---|---|---|---|---|---|---|---|
| 2 | linear | 0.19 | | | 0.20 | | 0.98 |
| 3 | first star | 0.19 | | 1.83 | 0.83 | 6 | 0.75 |
| 4c | second star | 0.19 | 0.19 | 2.60 | 1.37 | 11 | 1.04 |
| 4d | second star | 0.19 | 0.76 | 5.62 | 2.76[f] | 11 | 0.99 |

[a] Reaction conditions: with HI/$ZnI_2$ (10/0.20 mM) in toluene at -40 °C; conversions of IBVE and **1** are 100%; $[1]_0$ = 30 mM; $r = [1]_0/[HI]_0$ = 3.0. [b] The concentration of the added IBVE. [c] LS, by light scattering; SEC, by size-exclusion chromatography. [d] The number of arms per molecule; see eq 3. [e] Determined by end-capping with the dibenzyl malonate anion (eq 1; see text). [f] Containing a small amount of a low molecular weight fraction, as seen in Figure 1D.

Such byproducts were virtually absent in curve C, simply because the amount of the second feed of IBVE was small.

**(b) Determination of Living-End Concentration [P*].** To provide evidence for quantitative initiation from the living sites in the core of first star **3**, we measured the living-end concentration, [P*], at each stage of these sequential reactions by an end-capping method with use of the benzyl malonate anion (quencher).[12] As illustrated in eq 1, dibenzyl malonate sodium salt (**6**) reacts quantitatively with the living ends generated by the HI/$ZnI_2$ initiating system (see also the Experimental Section).



$$\sim CH_2-\overset{\delta\oplus}{C}H(OCH_2CH(CH_3)_2)-\overset{\delta\ominus}{I}\cdots ZnI_2 + \overset{\oplus}{Na}\,\overset{\ominus}{C}H(COOCH_2Ph)_2\ (6) \longrightarrow \sim CH_2-CH(OCH_2CH(CH_3)_2)-CH(COOCH_2Ph)_2 \qquad (1)$$

Figure 2 shows $^1H$ NMR spectra of linear poly(IBVE) (**2**), the first star polymer (**3**), and the second star polymers

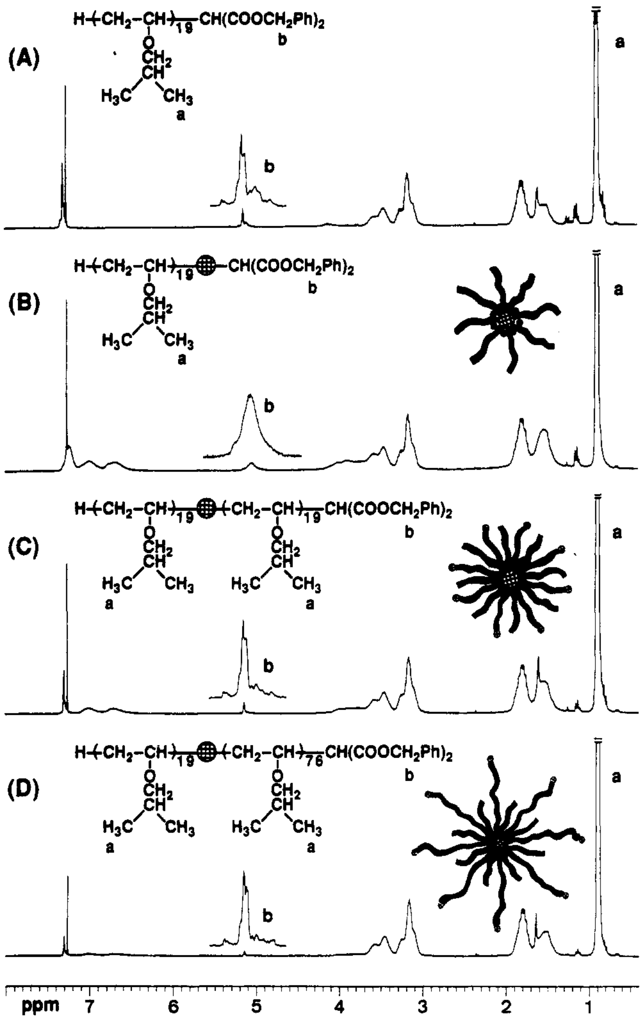


**Figure 2.** $^1$H NMR spectra of the linear (2) and the star-shaped poly(IBVE) (3, 4c, and 4d) end-capped with the benzyl malonate anion 6 in $CDCl_3$ at 25 °C: (A) linear poly(IBVE) 2; (B) first star polymer 3, $\overline{DP}$(arm) = 19; (C and D) second star polymers 4c and 4d, respectively. Degree of polymerization for the secondary arm: (C) 19; (D) 76.

(**4c** and **4d**), each obtained after the termination with **6**. In addition to the signals of linear or star poly(IBVE), the spectra exhibit the absorption assignable to the terminal benzyl malonate group (peak b, 5.1 ppm; Figure 2A–D). This signal is relatively sharp in the spectrum of linear poly(IBVE) (Figure 2A), but it broadened and shifted slightly upfield in that of **3** (Figure 2B), where the terminal groups (the living ends) are within the microgel core. In the spectra of **4c** and **4d** (Figure 2C,D, respectively), peak b became sharp again. These changes show that, in the core, the terminal groups are highly restricted in motion and difficult to observe by $^1$H NMR.

From the integrated peak intensities of the terminal malonate (the benzyl protons, peak b) and the IBVE units (the pendant methyls, peak a), [P*] was determined on the basis of the following relation:

$$\frac{(\text{peak area b})/4}{(\text{peak area a})/6} = \frac{[\text{malonate end}]}{[\text{IBVE units}]} = \frac{[\text{P}^*]}{[\text{IBVE consumed}]} \qquad (2)$$

where the brackets [ ] indicate a concentration in moles per liter. The [P*] values thus obtained are listed in Table I, where, for simplicity, they are shown as the ratio ([P*]/$[\text{HI}]_0$) to the initial concentration of hydrogen iodide; note that in the living cationic polymerization with the HI/$ZnI_2$ initiating system [P*] = $[\text{HI}]_0$ throughout the reaction.[6,7,12]

In the first-stage polymerization, the observed [P*] for **2** was equal to the initial HI concentration (Table I, first line). When the terminal end groups are within the core (first star polymer **3**), however, [P*] was smaller than $[\text{HI}]_0$ ([P*]/$[\text{HI}]_0$ = 0.75; Table I, second line). As shown in Table I, the decrease in [P*] is not due to the deactivation of the living growing sites during or after the polymer linking reaction for **3**. For example, with the second star polymers (**4c** and **4d**), the [P*]/$[\text{HI}]_0$ values were then close to 1.0 (Table I, last two lines). If a part of the living site was deactivated in **3**, the [P*] value for **4c** and **4d** would also be smaller than $[\text{HI}]_0$, because those second stars were obtained directly from the particular sample of the first star **3** shown in Table I. These results indicate that no living active sites remain at the central core, where the terminal groups can be hardly seen by $^1$H NMR.[13]

Because the second-stage polymerization is also living, the $\overline{DP}_n$ of the secondary arms is simply determined by the mole ratio of HI ([P*]) and the second feed of IBVE. Thus, on the basis of the $\bar{M}_w$(star) of **4**, the number ($f$) of arms per molecule was calculated from the following relation:[3,14]

$$f = 2(\text{wt fraction of IBVE})\bar{M}_w(\text{star})/(\text{weight of IBVE/moles of HI}) \qquad (3)$$

The results are summarized in Table I. The $f$ values of the second star polymers **4** ($f$ = 11) were nearly doubled from that of the first star polymer **3** ($f$ = 6). These results also support that *all* the living growing sites in the core of **3** polymerize the second feed of IBVE in a living fashion.

**2. Synthesis of Amphiphilic Star-Shaped Polymers 5.** As an extension of the methodology based on the living polymerization from the core living sites, we examined the synthesis of heteroarm amphiphilic star polymers (Scheme II) in the second phase of this study.

**(a) Heteroarm Star-Shaped Copolymers 4.** IBVE was polymerized with HI/$ZnI_2$, and then the resultant linear living polymer **2** was allowed to react with a small amount of bifunctional vinyl ether **1** to afford the first star polymer **3**. The subsequent polymerization of an ester-containing VE from the living active sites in the core of **3** leads to heteroarm star polymer **4** (Scheme II). The ester-containing VEs employed were 2-acetoxyethyl vinyl ether (AcOVE; $CH_2{=}CHOCH_2CH_2OCOCH_3$) and diethyl 2-(vinyloxy)ethylmalonate [VOEM; $CH_2{=}CHOCH_2CH_2CH(COOCH_2CH_3)_2$], whose polymers can be hydrolyzed into a polyalcohol, poly(2-hydroxyethyl vinyl ether) [poly(HOVE)], and a polycarboxylic acid, poly(2-(vinyloxy)ethylmalonic acid) [poly(VOEMA)], respectively. For all these samples, the degree of polymerization for the poly(IBVE) arm chains was invariably 30, while that for the ester-containing counterpart was varied in the range from 10 to 40.

The living polymerization of IBVE was first carried out at −40 °C in toluene at a low $ZnI_2$ concentration (0.20 mM; $[\text{HI}]_0$ = 10 mM), which reached 100% conversion in ca. 40 min to afford a living polymer with a narrow MWD ($\bar{M}_w/\bar{M}_n \leq 1.1$; Figure 3A,D). The linear living polymer **2** was then allowed to react with **1**, 5 equiv to the living ends ($r$ = $[1]_0/[2]$ = 5.0). In 4.5 h, **1** and **2** were quantitatively consumed, and the first star poly(IBVE) **3** was obtained in high yield (Figure 3B,E).[3] The $\bar{M}_w$ of this polymer (by light scattering) and the number ($f$) of arms per molecule were 50 300 and 10, respectively.

As already reported,[6,15] the living polymerization of an ester-containing VE (less reactive than IBVE) needs a larger amount of $ZnI_2$ than that for alkyl vinyl ethers. Accordingly, in the second-phase polymerization of an

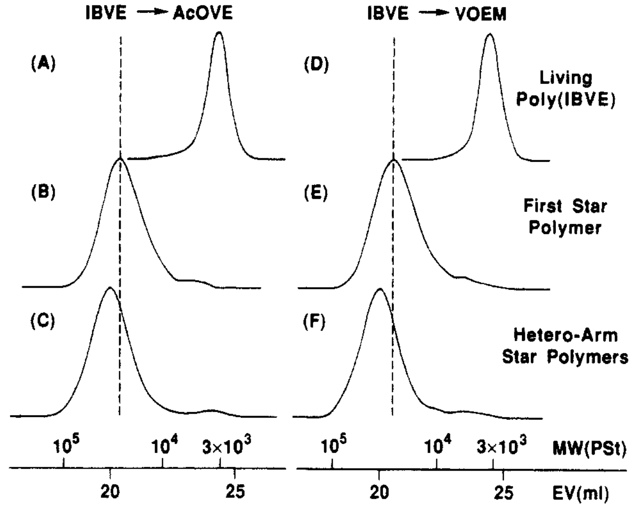


**Figure 3.** MWD of two series of the products obtained in the synthesis of heteroarm star-shaped polymers 4 (**4a**, A–C; **4b**, D–F) (Scheme II): (A and D) starting living poly(IBVE) 2, $[\text{IBVE}]_0 = 0.30$ M, $[\text{HI}]_0 = 10$ mM, $[\text{ZnI}_2]_0 = 0.20$ mM, IBVE conversion = 100%; (B and E) star-shaped poly(IBVE) 3 [$\overline{\text{DP}}$(arm) = 30, $r = [1]_0/[\text{HI}]_0 = 5.0, f = 10$]; (C and F) heteroarm star polymers 4 obtained by the polymerization of (C) AcOVE and (F) VOEM from the living ends within the core of 3. IBVE/AcOVE or VOEM unit ratio ($m/n$) = 30/20. Reaction temperature and $[\text{ZnI}_2]_{\text{total}}$: (A, B, D, and E) −40 °C, 0.20 mM; (C) −15 °C, 1.25 mM; (F) −15 °C, 1.20 mM.

ester-containing VE from the living sites within the core, an additional dose of $\text{ZnI}_2$ was added to the reaction mixture, and the polymerization temperature was raised from −40 to −15 °C as soon as the ester-containing VE was added. In a typical run with AcOVE (IBVE/AcOVE = 30/20 mole ratio, $[\text{ZnI}_2]_{\text{total}} = 1.25$ mM at −15 °C), the polymerization of AcOVE reached ca. 100% conversion in an additional 2 h to give heteroarm precursor **4a** in high yield (Figure 3C). The product was completely soluble in common organic solvents (toluene, chloroform, etc.). The MWD of **4a** shifted toward higher molecular weight relative to that of the first star polymer **3**. The high yield of **4** was also attained with VOEM (Figure 3F, IBVE/VOEM = 30/20 mole ratio). Thus, the heteroarm star polymers **4** of functionalized VEs were obtained by the living polymerization from the living sites within the core of **3** (see below for structural verification).

Parts A and C of Figure 4 show typical $^1$H NMR spectra of the products obtained from the polymerization of AcOVE or VOEM from the core. Spectra A and C exhibit absorptions assignable to the AcOVE and the VOEM units, respectively [AcOVE b, 2.1 ppm; c, 4.2 ppm; (Figure 4A); VOEM e, 1.2 ppm; g, 4.2 ppm (Figure 4C)], in addition to those of the IBVE units and the aromatic protons of **1** (a, 0.9 ppm; d, 6.5–7.2 ppm). These results also support the formation of the heteroarm star polymer **4**, which carries separate poly(IBVE) and poly(AcOVE) or poly(VOEM) homochains on a microgel core of poly(**1**).

Table II summarizes the segment compositions (IBVE/AcOVE or VOEM; by $^1$H NMR) of the heteroarm star polymers **4**. The segment composition was determined from the $^1$H NMR peak intensity ratio of the acetoxy methyl protons (peak b) of the AcOVE units or methylene protons (peak e) of the VOEM units to the methyl protons (peak a) of the IBVE units. As previously reported,[5] the $\overline{\text{DP}}_n$ of the poly(IBVE) arm chain was taken to be 30, which was calculated from the monomer (IBVE)/HI feed ratio. As shown in Table II, the observed segment compositions were in good agreement with the calculated values from the monomer feed ratios.

**(b) Hydrolysis of Pendant Esters.** The pendant ester groups of the AcOVE or VOEM units of **4** were hydrolyzed into hydroxyl or carboxyl functions, respectively, in 1,4-dioxane under basic conditions (Scheme II; see the Experimental Section) to give amphiphilic star-shaped polymers **5**.

Figure 4 compares the $^1$H NMR spectra of the IBVE–AcOVE and the IBVE–VOEM precursor star polymers (**4a** and **4b**) and their hydrolysis products (**5a** and **5b**, respectively). After the hydrolysis, the absorption of the pendant acetoxy groups (b, 2.1 ppm, Figure 4A) completely disappeared; and signal c (4.2 ppm, Figure 4A), due to the methylene protons adjacent to the ester group, shifted upfield and became indistinguishable from that of the methine adjacent to the ether oxygen (Figure 4B). In contrast to these, all other signals of the poly(IBVE) units and the core moiety (a, 0.9 ppm; d, 6.5–7.2 ppm) remained unchanged during the hydrolysis. Similar results were obtained for **4b**, which led to **5b** (Figure 4C,D) with pendant carboxyl groups. After the hydrolysis, for instance, peaks e and g of the malonate ester groups disappeared (Figure 4D).

**3. Characterization of Amphiphilic Heteroarm Star Polymers. (a) Solubility Characteristics.** Table III summarizes the solubility characteristics of six amphiphilic star polymers (**5a** and **5b**); samples **5a**, I–III, carry polyalcohol arm chains, whereas **5b**, I–III, involve hydrophilic arms with carboxyl groups. The ester-containing precursors **4a** and **4b**, irrespective of their segment composition and pendant groups, were soluble in toluene and chloroform but insoluble in methanol and water.

Among the three samples (**5a**, I–III) with the polyalcohol arms, polymer **5a**-I, carrying the shortest hydrophilic arms, is of the same solubility properties as its precursor **4a**, soluble in toluene and chloroform but insoluble in methanol and water. As the hydrophilic arm's chain length is increased, **5a** becomes soluble in methanol (**5a**-II) and then insoluble (but swellable) in toluene (**5a**-III).

A similar trend was observed for the carboxyl counterparts (**5b**, I–III). Polymer **5b**-I with the shortest hydrophilic arms is soluble in toluene, chloroform, and methanol. When the $\overline{\text{DP}}_n$ of the hydrophilic arm is increased from 10 to 20 (**5b**-II), the polymer becomes insoluble and only swells in toluene and chloroform. Polymer **5b**-III with the longest hydrophilic arms is now insoluble even in chloroform and swells in methanol and water.

These trends show that the importance of the hydrophilicity/hydrophobicity balance for the properties of the heteroarm star polymers. When compared with the star block polymers (**7a** and **8a** in Table III), whose solubility depends on the properties of the outer segments,[8] for instance, **5a**-I and **5a**-II are the same in solubility as **7a** and **8a**, respectively.

The alcoholic star polymers **5a** are similar in solubility to the corresponding linear block polymers. In contrast, the solubility characteristics of the carboxylic versions **5b**-II and **5b**-III differ from those of the corresponding linear block polymers, being insoluble in methanol and water. The solubility characteristics of these heteroarm star amphiphiles also differ from those of hydrophobic poly(IBVE) and hydrophilic homochains.

**(b) Conformational Changes with Solvents.** As described above, for a particular composition and functional group, the amphiphilic heteroarm star polymers **5** are soluble in various solvents; the hydrophilic arms may extend in a polar solvent, whereas the hydrophobic arms

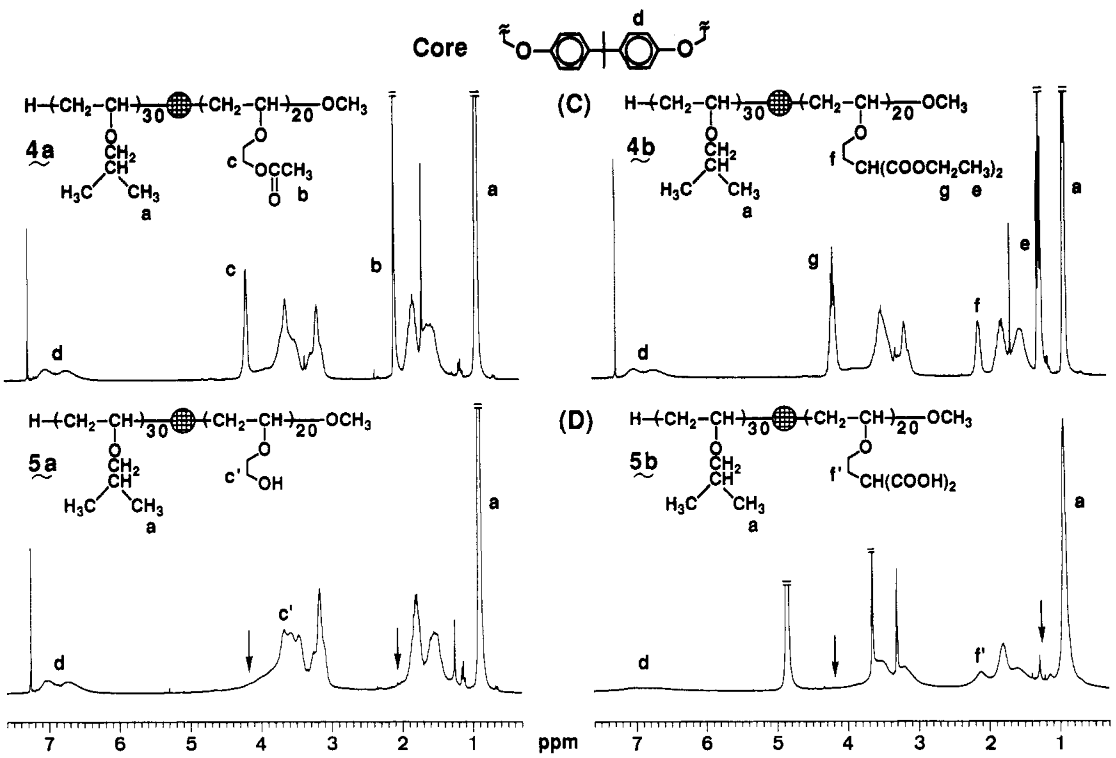


**Figure 4.** $^1$H NMR spectra in $CDCl_3$ (A–C) and in $CD_3OD$ (D) at 25 °C: (A) IBVE–AcOVE heteroarm star polymer **4a**; (B) amphiphilic star polymer **5a** from sample A after hydrolysis; (C) IBVE–VOEM heteroarm star polymer **4b**; (D) amphiphilic star polymer **5b** from sample C after hydrolysis. $\overline{DP}_n$ of arm chains is as indicated.

**Table II**
**Heteroarm Star Polymers 4 Obtained by Living Cationic Polymerization of AcOVE or VOEM from Living Active Sites on the Core of Star-Shaped Poly(IBVE) 3**[a]

| code | added monomer | polymer structure[b] | $\overline{DP}_n$(obsd)[c] |
|---|---|---|---|
| **4a** | AcOVE | $(IBVE)_{30}$-(core)-$(AcOVE)_{10}$ | 30/10.7 |
| **4a** | AcOVE | $(IBVE)_{30}$-(core)-$(AcOVE)_{20}$ | 30/20.6 |
| **4a** | AcOVE | $(IBVE)_{30}$-(core)-$(AcOVE)_{40}$ | 30/39.7 |
| **4b** | VOEM | $(IBVE)_{30}$-(core)-$(VOEM)_{10}$ | 30/10.6 |
| **4b** | VOEM | $(IBVE)_{30}$-(core)-$(VOEM)_{20}$ | 30/21.6 |
| **4b** | VOEM | $(IBVE)_{30}$-(core)-$(VOEM)_{40}$ | 30/41.0 |

[a] Reaction conditions: with $HI/ZnI_2$ in toluene; at −40 °C for the first-phase polymerization of IBVE; at −15 °C for the subsequent polymerizations of AcOVE and VOEM; conversions of all monomers are 100%; $r = [1]_0/[P^*] = 5.0$; see Scheme II. AcOVE: $CH_2{=}CHOCH_2CH_2OCOCH_3$; VOEM: $CH_2{=}CHOCH_2CH_2CH(COOC_2H_5)_2$. [b] The $\overline{DP}_n$(calcd) of arms, shown in the formula, is based on the feed ratio of the monomers to hydrogen iodide. [c] The observed $\overline{DP}_n$ of arms, determined by $^1$H NMR (see text), where the $\overline{DP}_n$ of the poly(IBVE) arms were taken to be 30 ($=[IBVE]_0/[HI]_0$).

**Table III**
**Solubility of Amphiphilic Star-Shaped Polymers**[a]

| code | polymer structure[b] | solvent<br>toluene | <br>$CHCl_3$ | <br>$CH_3OH$ | <br>$H_2O$ |
|---|---|---|---|---|---|
| **5a-I** | $(IBVE)_{30}$-(core)-$(HOVE)_{10}$ | ○ | ○ | × | × |
| **5a-II** | $(IBVE)_{30}$-(core)-$(HOVE)_{20}$ | ○ | ○ | ○ | × |
| **5a-III** | $(IBVE)_{30}$-(core)-$(HOVE)_{40}$ | △ | ○ | ○ | × |
| **5b-I** | $(IBVE)_{30}$-(core)-$(VOEMA)_{10}$ | ○ | ○ | ○ | × |
| **5b-II** | $(IBVE)_{30}$-(core)-$(VOEMA)_{20}$ | △ | △ | ○ | × |
| **5b-III** | $(IBVE)_{30}$-(core)-$(VOEMA)_{40}$ | × | × | △ | △ |
| **7a** | $(IBVE)_{30}$-$(HOVE)_{10}$-(core) | ○ | ○ | × | × |
| **8a** | $(HOVE)_{10}$-$(IBVE)_{30}$-(core) | ○ | ○ | ○ | × |

[a] ○, soluble; △, swelling; ×, insoluble; at room temperature, ca. 3 wt %. [b] The segment compositions ($\overline{DP}_n$) are the calculated values before hydrolysis; see Table II. HOVE unit, $-CH_2CH(OCH_2CH_2OH)-$; VOEMA unit, $-CH_2CH[OCH_2CH_2CH(COOH)_2]-$.

may extend in a less polar medium, and hence **5** are indeed soluble in both polar and nonpolar solvents (Table III). By $^1$H NMR analysis, we thus examined the conformational changes of the amphiphiles **5a** and **5b** according to solvent polarity (chloroform vs methanol); the samples were polymers **5a-III** (with hydroxyl pendants) and **5b-I** (with carboxyl pendants), both soluble in the two solvents. Figure 5 shows a series of their $^1$H NMR spectra taken in $CDCl_3$ and $CD_3OD$.

In $CDCl_3$ (a less polar solvent; Figure 5A,C), the methyl absorption (a, 0.9 ppm) of the IBVE units was strong and sharp, whereas the signals of the hydrophilic arms (peak b) were weak and indistinguishable from the signals of the other protons. Upon an increase in solvent polarity (Figure 5B,D; in $CD_3OD$), the signal a of the hydrophobic IBVE units broadened and, in turn, the signals b of the hydrophilic arms are now strong and sharp. This indicates that, in polar solvent, hydrophilic arm chains extend in conformation, whereas hydrophobic counterparts shrink. These solubility characteristics (Table III) and conformational changes (Figure 5) also support the formation of the heteroarm amphiphilic star polymers **5**, where hydrophilic and hydrophobic arms attach to the core independently of each other.

In conclusion, we demonstrated that on the basis of the living cationic polymerization the amphiphilic heteroarm star-shaped polymers (**5a** and **5b**) of vinyl ethers can be synthesized, where separate hydrophilic and hydrophobic arm chains are independently attached to a single core. These polymers differ in solubility from the corresponding hydrophilic or hydrophobic linear homopolymers and change their conformation with solvent polarity.

## Experimental Section

**Materials.** AcOVE[16] and VOEM[17] were prepared by the reactions of 2-chloroethyl vinyl ether with sodium acetate and sodio malonic ester, respectively. These monomers and commercial IBVE were purified by double distillation over calcium hydride before use. Bifunctional vinyl ether **1** was prepared according to the literature method[18] and doubly recrystallized

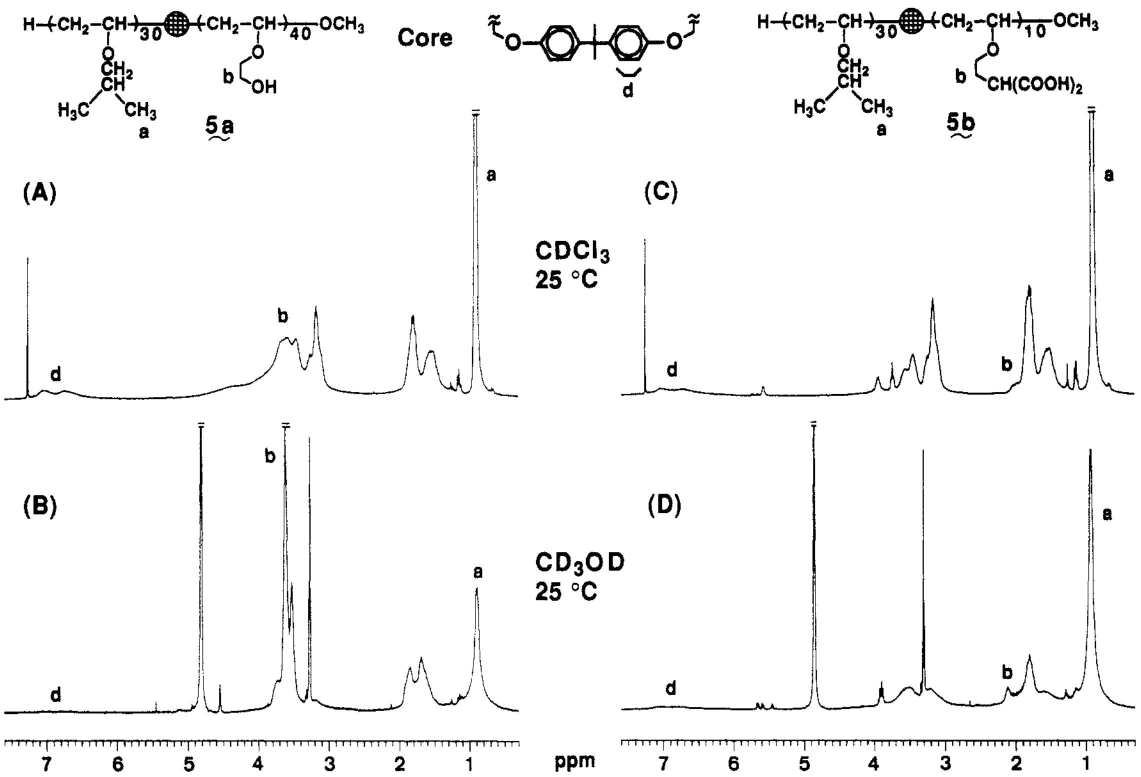


**Figure 5.** $^1$H NMR spectra in $CDCl_3$ (A and C) and $CD_3OD$ (B and D) at 25 °C: (A and B) amphiphilic heteroarm star polymer **5a**; (C and D) amphiphilic heteroarm star polymer **5b**. $\overline{DP}_n$ of arm chains is as indicated. In spectra B and D, the sharp peaks at 3.3 and 4.8–4.9 ppm are due to $CH_3OH$ and water, respectively, in the $CD_3OD$ solvent.

from ethanol. Dibenzyl malonate sodium salt **6** (ca. 200 mM in 1,4-dioxane) was prepared from dibenzyl malonate and sodium hydride as reported previously.[17a] The purity of all these materials exceeded 99%.

Anhydrous hydrogen iodide was obtained as an *n*-hexane solution by the dehydration of commercial hydroiodic acid (57 wt %) using phosphorus pentoxide.[5] The solution was sealed in brown ampules under dry nitrogen and stored in a freezer. Zinc iodide (Aldrich; purity > 99.99%) was used as received; it was vacuum dried overnight in the dark, transferred to a flask in a nitrogen-filled drybox, and dissolved in diethyl ether just before use. Toluene (polymerization solvent) was washed by the usual methods[6] and distilled over calcium hydride at least twice before use. Diethyl ether (anhydrous, Wako Chemicals) was distilled over $LiAlH_4$ before use.

**Polymerization Procedures.** The living polymerization of IBVE with $HI/ZnI_2$ (10/0.20 mM) and the reaction of **2** with divinyl ether **1** were carried out at −40 °C under dry nitrogen in a baked flask equipped with a three-way stopcock.[5,6] After the first star polymer (**3**) was thus obtained, a solution of AcOVE or VOEM was added. Immediately after the monomer addition, an ether solution of $ZnI_2$ was added to increase its concentration to 1.2–2.0 mM, the solution temperature was raised to −15 °C, and the mixture was magnetically stirred until quenched with prechilled methanol containing a small amount of ammonia. The reaction mixture was washed with 10% aqueous sodium thiosulfate solution and then with water, evaporated to dryness under reduced pressure at room temperature, and vacuum dried overnight to give the product polymers.

**End-Capping Analysis.** For some runs for the determination of the living-end concentration, the living polymerization of IBVE was terminated with the dibenzyl malonate anion **6** (8-fold molar excess over hydrogen iodide; ca. 2 mL of a ca. 200 mM solution). The product polymers were recovered from the quenched reaction mixtures as mentioned in the previous section.

**Hydrolysis of Heteroarm Star Polymers 4a and 4b.** A sample of polymer **4a** or **4b** (300–450 mg) was dissolved in 1,4-dioxane (ca. 15 mL), and an aqueous solution of sodium hydroxide (5 equiv to the ester units in the polymer) was added. The mixture was magnetically stirred at room temperature for 2 or 3 days, and the solvent was removed by evaporation. The hydrolyzed polymers were dissolved in tetrahydrofuran and poured into 200 mL of water. The precipitated polymers were separated by filtration. These purified samples were finally vacuum dried overnight to give polymer **5**.

**Polymer Characterization.** The weight-average molecular weight ($\bar{M}_w$) of the polymers was determined by small-angle laser light scattering in ethyl acetate at 25 °C on a Chromatix KMX-6 photometer ($\lambda$ = 633 nm; five-point measurements; $c = 5 \times 10^{-4}$–$2.5 \times 10^{-3}$ g/mL). The refractive index increment (d*n*/d*c*) was measured in ethyl acetate at 20 °C on an Otsuka Electronics DRM-1020 double-beam differential refractometer ($\lambda$ = 633 nm; three-point measurements; $c = 2 \times 10^{-3}$–$8 \times 10^{-3}$ g/mL). The d*n*/d*c* values of second star poly(IBVE) **4** depended on the length of the secondary arm [$\overline{DP}$(secondary arm)] [0.109 mL/g for $\overline{DP}$(secondary arm) = 19, $9.79 \times 10^{-2}$ mL/g for $\overline{DP}$(secondary arm) = 76], and they were slightly smaller than that (0.115 mL/g) of the first star poly(IBVE) **3** [$\overline{DP}$(arm) = 19, $r$ = 3, $f$ = 6].[3]

The $\bar{M}_w$ was also measured, relative to standard polystyrene samples, by size-exclusion chromatography in chloroform on a Jasco 880-PU chromatograph equipped with polystyrene gel columns (Shodex K-802, K-803, K-804) and ultraviolet/refractive index dual detectors. The same chromatograph was employed to determine the MWD and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) of the polymers on the basis of a polystyrene calibration. $^1$H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer at 25 °C.

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(14) In eq 3, the presence of the factor 2 is valid for not only **4c** but also **4d**. The ratio (weight of IBVE)/(moles of HI) leads to the total molecular weight of the first and the second sets of poly(IBVE) arm chains [MW(total arm)], which are ca. 3800 and 9500 for **4c** and **4d**, respectively. Thus, dividing (wt fraction of IBVE)$\bar{M}_w$(star) by MW(total arm) gives the number ($f$) of arms, assuming that the first and the second arms are regarded as a single linear poly(IBVE), which are half the actual $f$ values.

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