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# Star-Shaped Polymers by Living Cationic Polymerization. 5. Core-Functionalized Amphiphilic Star-Shaped Polymers of Vinyl Ethers with Hydroxyl Groups: Synthesis and Host–Guest Interaction

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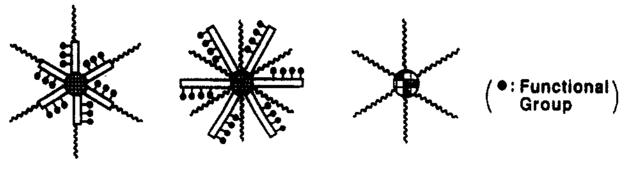
ABSTRACT: Amphiphilic star-shaped polymers of vinyl ethers (5) whose microgel core carries hydroxyl groups were prepared on the basis of living cationic polymerization. Thus, living polymers ($\overline{DP}_n$ = 30–38) of isobutyl vinyl ether (IBVE), prepared with $HI/ZnI_2$ at −15 °C in toluene, were allowed to react simultaneously with a bifunctional vinyl ether [1; $CH_2{=}CHOCH_2CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH_2OCH{=}CH_2$] and an ester-containing vinyl ether (AcOVE; $CH_2{=}CHOCH_2CH_2OCOCH_3$) to give a star-shaped poly(IBVE) [4; $\bar{M}_w$ = (5.9–6.1) × $10^4$, 7–10 arms/molecule] with a microgel core consisting of both 1 and AcOVE units. Hydrolysis of the core's ester functions of 4 gave the "core-functionalized" amphiphilic star polymer 5, where hydrophobic poly(IBVE) arm chains are attached to a hydrophilic microgel core that carries hydroxyl groups. $^1H$ and $^{13}C$ NMR analysis and the solubility characteristics of 5 showed the successful core functionalization. The star polymers 5 (as host) were found to interact specifically with small organic molecules (guests) with polar functional groups such as benzoic acid.

## Introduction

Recently, we have shown that star-shaped polymers of vinyl ethers can be synthesized in cationic polymerization, through the linking reactions of their living polymers with bifunctional vinyl ethers.[1] Analogous syntheses of star-shaped polymers have been performed primarily via living anionic polymerization.[2,3] Most of the anionically prepared star polymers, however, consist of nonpolar arms such as polystyrene, because of the difficulty in preparing living polymers with pendant polar functional groups. It was not until recently that star-shaped polymers with ester groups were synthesized on the basis of living anionic polymerization of *tert*-butyl acrylate.[4]

In cationic polymerization, on the other hand, the hydrogen iodide/Lewis acid ($HI/ZnI_2$, etc.) initiating systems readily induce living polymerizations of vinyl ethers with functional pendant groups.[5] This synthetic advantage enabled us to prepare two types (star block[6] and heteroarm[7]) of amphiphilic star-shaped polymers with hydroxyl groups (see the schematic illustrations A and B).



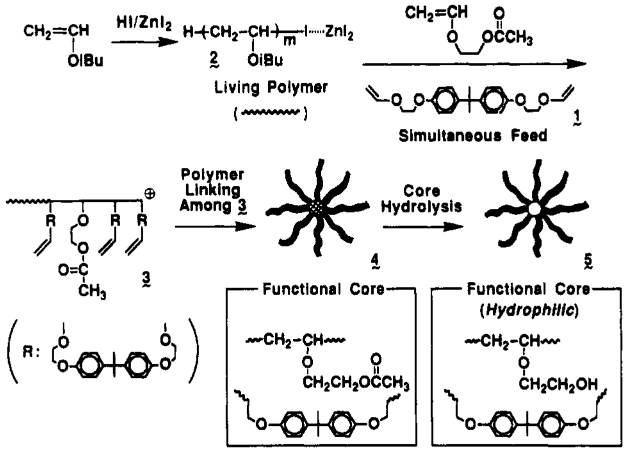
Star Block (A) Hetero-Arm Star (B) Core-Functionalized (C)

Such topologically controlled polymers were found to possess properties and functions (like selective host–guest interaction[8]) that differed from those of the corresponding linear block polymers.[6,8] These two types of amphiphilic star-shaped polymers, in common, bear functional groups (hydroxyl) in the arm chains. Another type of functionalized star polymer would be "core-functionalized" star polymers, where not arms but the core carries functional groups. To our knowledge, such core-functionalized star polymers have been synthesized in neither anionic nor cationic polymerization. This study now focuses on the synthesis of core-functionalized amphiphilic star polymers (illustration C) of vinyl ethers with core hydroxyl groups, a new type of functionalized star-shaped polymers.

As illustrated in Scheme I, a living polymer (2) of isobutyl vinyl ether (IBVE), prepared with the $HI/ZnI_2$ initiating system, is allowed to react with a mixture of a divinyl ether 1 and 2-acetoxyethyl vinyl ether (AcOVE; $CH_2{=}CHOCH_2CH_2OCOCH_3$). Unlike the previously reported syntheses of star block (A)[6] and heteroarm star (B)[7] polymers, where the polymer-linking agent is 1 alone, herein the simultaneous feeding of 1 and AcOVE permits both monomers (as linking agents) to parallelly react with 2 to undergo a near random copolymerization from the living site of 2, and thereby form a block polymer 3. Subsequent linking reactions among several chains of 3 would lead to a star-shaped precursor polymer 4 whose core consists of a microgel of both 1 and AcOVE units. Alkaline hydrolysis of the ester groups in 4 then leads to the core-functionalized amphiphilic star polymer 5 with hydrophobic poly(IBVE) arms and a hydrophilic microgel core.

The core functionalization in 5 may lead to the higher accumulation of polar hydroxyl groups in a core region which should be smaller in size than the arm moiety of the star-shaped polymers with functionalized arms. Another important feature of 5 is that an outer hydrophobic shell [arm chain layers of poly(IBVE)] of 5 can effectively surround the hydrophilic microgel core with many hydroxyl groups. Therefore, the core-functionalized star polymers are amphiphilic but are expected to possess properties that differ from those of the star block (A) and the heteroarm star (B) amphiphiles. In this study, we examined (i) the controlled synthesis of core-functionalized amphiphilic star polymers 5 and (ii) their solubility characteristics and host–guest interaction with small organic molecules, specifically relative to those of other types of star-shaped polymeric amphiphiles.

Scheme I



### Table I

**Core-Functionalized Star Polymers 4 Obtained by Reaction of Linear Living Poly(IBVE) 2 with Both Divinyl Ether 1 and AcOVE by Living Cationic Polymerization**[a]

| code | polymer structure[b] | unit ratio[c] (obsd) | $\bar{M}_w \times 10^{-4}$ [d] | $f$[e] |
|---|---|---|---|---|
| 4-I | $(IBVE)_{38}$–[$(AcOVE)_{20}$ in the core] | 38/20.4 | 6.14 | 7 |
| 4-II | $(IBVE)_{30}$–[$(AcOVE)_{10}$ in the core] | 30/9.9 | 5.91 | 10 |

[a] Reaction conditions: with $HI/ZnI_2$ in toluene; at −15 °C; conversions of all monomers are 100%; $r = [1]_0/[2] = 5.0$; see Scheme I. [b] The calculated unit ratio of IBVE and AcOVE, shown in the formula, is based on the feed ratio of the monomers to hydrogen iodide. [c] Determined by $^1$H NMR (see text), where the $\overline{DP}_n$ of the poly(IBVE) arm was taken to be 38 or 30 ($=[IBVE]_0/[HI]_0$). [d] Determined by light scattering. [e] The number of arms per molecule; see the Experimental Section.

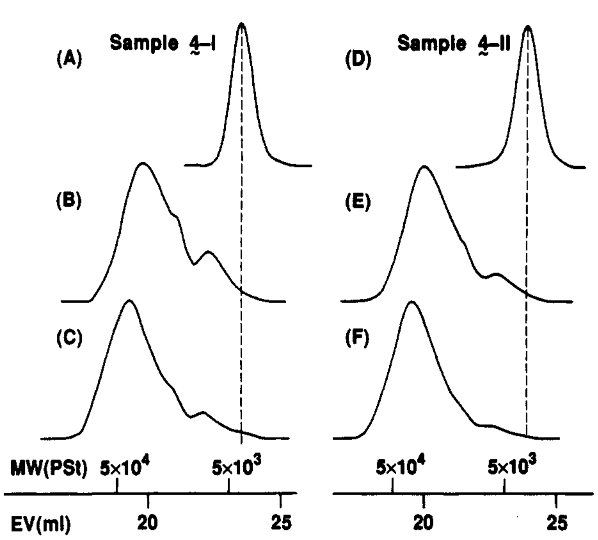


**Figure 1.** MWD of two series of the products obtained in toluene at −15 °C in the synthesis of core-functionalized star-shaped polymers 4 (Scheme I): (A and D) Starting living poly(IBVE) 2, $[HI]_0 = 10$ mM, $[ZnI_2]_0 = 0.20$ mM, IBVE conversion = 100%. $[IBVE]_0$: (A) 0.38 M; (D) 0.30 M. (B and E) Intermediate products obtained from samples A and D, respectively, by the reaction of 2 with a mixture of AcOVE and 1. $[ZnI_2]_{total}$, reaction time after the addition of an AcOVE/1 mixture, and AcOVE conversion: (B) 1.0 mM, 20 min, 50%; (E) 0.50 mM, 30 min, 53%. (C and F) Core-functionalized star polymers 4. IBVE/1/AcOVE unit ratio, reaction time, and AcOVE conversion: (C) 38/5/20, 4 h, 100%; (F) 30/5/10, 6.5 h, 100%.

## Results and Discussion

**Synthesis of Core-Functionalized Amphiphilic Star-Shaped Polymers 5. (a) Core-Functionalized Star-Shaped Precursor Polymers 4.** IBVE was polymerized with $HI/ZnI_2$, and the resultant linear living polymer 2 was allowed to react simultaneously with AcOVE and a small amount of bifunctional vinyl ether 1 to afford precursor star polymer 4 (Scheme I). The core size and the number of hydroxyl groups in 5 would be the factors that affect the properties of the star polymers. Thus, we prepared two samples of 5 with varying amounts of AcOVE; its larger amount may lead to 5 with a larger and more hydrophilic microgel core richer in polar functional groups. The amount of AcOVE was set as follows (Table I): for the larger core, IBVE/1/AcOVE = 38/5/20 mole ratio (sample 4-I); for the smaller core, IBVE/1/AcOVE = 30/5/10 mole ratio (sample 4-II).

To prepare sample 4-I, for example, IBVE was polymerized by $HI/ZnI_2$ at −15 °C in toluene at a low $ZnI_2$ concentration (0.20 mM; $[IBVE]_0 = 0.38$ M; $[HI]_0 = 10$ mM), which led to a living polymer (2) with a narrow molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n \leq 1.1$; Figure 1A). This polymer was subsequently treated with a mixture of 1 and AcOVE (living end 2/1/AcOVE = 1/5/20 mole ratio). As already reported,[9] the living polymerization of AcOVE (less reactive than IBVE) needs a larger amount of $ZnI_2$ than for alkyl vinyl ethers. Accordingly, in the linking reaction of 2 with 1 and AcOVE, an additional dose of $ZnI_2$ (0.80 mM) was added to the reaction mixture.

Under these conditions, 20 min after the addition of 1 and AcOVE, a polymer was obtained, whose molecular weight was clearly higher than that of 2 (Figure 1B). At this point, a small amount of 1, 50% of AcOVE, and low molecular weight polymers remained unreacted. In 4 h, both 1 and AcOVE were consumed quantitatively, and a polymer of a clearly higher molecular weight was obtained in high yield (Figure 1C).[10] The product was completely soluble in common organic solvents (toluene, chloroform, etc.). The weight-average molecular weight ($\bar{M}_w$) of the product (by light scattering) was 61 400, clearly higher than that of the poly(IBVE) arm chain ($\bar{M}_w = 3800$). The high yield of 4 was also attained with IBVE/1/AcOVE = 30/5/10 (sample 4-II; Figure 1D–F).[10] The conversion data for 1 and AcOVE, given above, show that both monomers in fact reacted simultaneously with living polymer 2, which in turn indicates the formation of the star-shaped polymer 4 with a microgel of both 1 and AcOVE.

**(b) Product Characterization.** Figure 2A shows a typical $^1$H NMR spectrum of the product (sample 4-I) obtained from the reactions of the living poly(IBVE) 2 with both 1 and AcOVE. Spectrum A exhibits absorptions assignable to the AcOVE units (b, 2.1 ppm; c, 4.2 ppm), in addition to those of the IBVE units and the aromatic protons of 1 (a, 0.9 ppm; d and e, 6.5–7.2 ppm). These results also support the incorporation of both 1 and AcOVE units in the star polymer 4.

Table I summarizes the $\bar{M}_w$ values (by light scattering), the arm numbers ($f$) per molecule (see the Experimental Section), and the unit ratios (IBVE/AcOVE; by $^1$H NMR) of the two samples of the core-functionalized star-shaped polymers 4. The unit ratio of the arm was determined from the $^1$H NMR peak intensity ratio of the acetoxy methyl protons (peak b) of the AcOVE units to the methyl protons (peak a) of the IBVE units. The $\overline{DP}_n$ of the poly(IBVE) arm chain was taken to be 38 or 30, which was calculated from the IBVE/HI feed ratio.[9] As shown in Table I, the observed unit ratios were in good agreement with the calculated values; the two samples bear 7 and 10 poly(IBVE) arms/molecule.

**(c) Evidence for Core Functionalization.** The key to the successful core functionalization according to the route given in Scheme I is evidently the simultaneous incorporation of 1 and AcOVE repeat units into the poly(IBVE) chain ends (2), and for such a near random

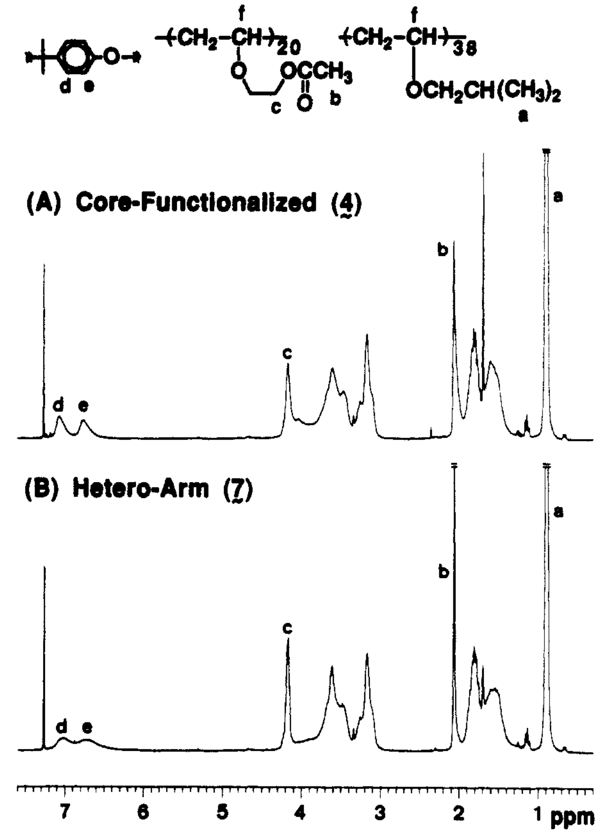
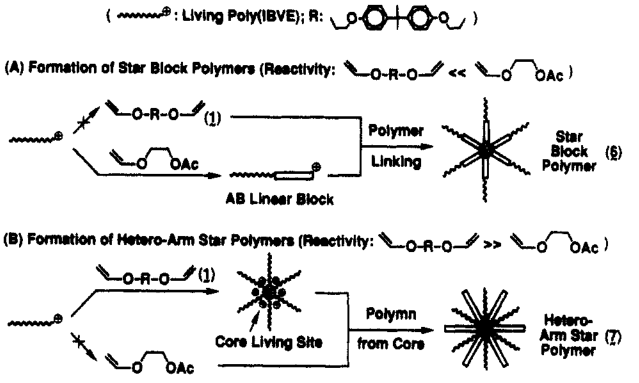
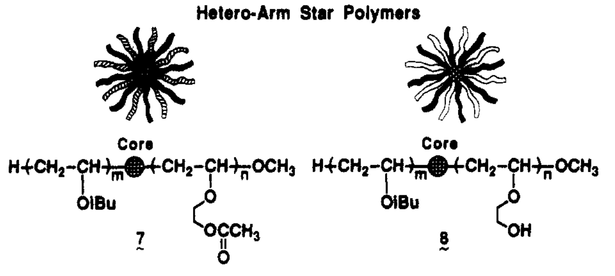


**Figure 2.** $^1$H NMR spectra in $CDCl_3$ at 25 °C: (A) core-functionalized star polymer 4 (sample 4-I); (B) heteroarm star polymer 7. IBVE/1/AcOVE in the polymers = 38/5/20 mole ratio.

### Scheme II
### Possible Undesired Reactions



"copolymerization" of the two monomers, they must have similar reactivity toward the vinyl ether living ends. In another extreme, namely, if the vinyl ether groups of 1 and AcOVE were very different in reactivity, the reaction of living polymer 2 with a mixture of these monomers would give either star block polymers or heteroarm star polymers (Scheme II). Thus, if the vinyl group's reactivity of AcOVE is much larger than that of 1 (Scheme IIA), the latter bifunctional monomer may remain unreacted until the quantitative consumption of AcOVE, to give a star block polymer (6) carrying IBVE–AcOVE block copolymer chains as arms.[6] In contrast, if the vinyl group's reactivity of AcOVE is much smaller than that of 1 (Scheme IIB), AcOVE may remain unreacted until the linking reaction of 2 with 1 alone is complete, and thereby a heteroarm star polymer (7) results.[7] Specifically for the pair of 1 and AcOVE, their vinyl groups are indeed similar in reactivity, but actually 1 is slightly more reactive than AcOVE, so that a heteroarm star polymer (7), rather than a star block copolymer (6), might be obtained.



$H{+}CH_2{-}\underset{OiBu}{CH}{+}_m{\bullet}{+}CH_2{-}\underset{OCH_2CH_2OCOCH_3}{CH}{+}_n OCH_3$ (7)

$H{+}CH_2{-}\underset{OiBu}{CH}{+}_m{\bullet}{+}CH_2{-}\underset{OCH_2CH_2OH}{CH}{+}_n OCH_3$ (8)

(▨ : Ester-Containing, ■ : Hydrophobic, □ : Hydrophilic)

By $^1$H and $^{13}$C NMR analysis, we therefore compared our products with a separately prepared heteroarm star polymer[7] to confirm the successful core functionalization according to Scheme I. Figure 2 compares the $^1$H NMR spectra of samples of the core-functionalized (sample 4-I; 7 arms/molecule) and the heteroarm (7; 14 arms/molecule) star polymers; in the latter, separate sets of poly(IBVE) and poly(AcOVE) arms (7 arms each) are independently attached to a single core. Both samples were prepared under formally the same reagent feed conditions (IBVE/1/AcOVE = 38/5/20 mole ratio). In the spectrum of the heteroarm version 7, the acetoxy methyl absorption (b, 2.1 ppm) of the AcOVE units was strong and sharp (Figure 2B), whereas the corresponding peak b for 4-I (Figure 2A) was clearly broader. The same trend is seen for the AcOVE methylene signals c. The broadening of the signals b and c shows that, in sample 4-I, the AcOVE units are more restricted in motion, because they reside in the microgel core.

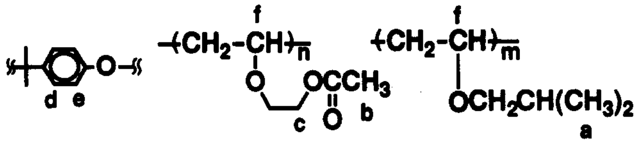
Another difference was found for the signals due to divinyl ether 1. The downfield absorptions (d and e, 6.5–7.2 ppm) were assigned to the aromatic protons of the core derived from 1. Sample 4-I clearly showed these signals (Figure 2A), whereas the corresponding signals were rather broader in the spectrum of 7 (Figure 2B). This is also consistent with core functionalization: in the heteroarm star polymers (7), two sets of poly(IBVE) and poly(AcOVE) arm chains may crowd around a core, and the core is most likely more restricted in thermal motion. On the other hand, for core-functionalized polymers (4) the smaller number of arms and the larger size of the core may facilitate the thermal motion of the core.

$^{13}$C NMR relaxation time ($T_1$) analysis also provided evidence for the successful core functionalization. For both core-functionalized (4-I) and heteroarm (7) versions, Table II summarizes the $T_1$ values for the acetoxy methyl ($C_b$), the aromatic ($C_d$ and $C_e$), and the main-chain methine ($C_f$) carbons. The $T_1$ of the methine carbon ($C_f$) in the main chain was independent of the polymer structure (f, 221 ms). With the acetoxy methyl carbon ($C_b$) of the AcOVE units, the $T_1$ for the core-functionalized star polymer 4 (301 ms) was shorter than that for the heteroarm counterpart 7 (324 ms). In contrast, with the aromatic carbons ($C_d$ and $C_e$), the $T_1$ for 4 (d, 233 ms; e, 218 ms) was longer than that for 7 (d, 210 ms; e, 202 ms). Evidently, the AcOVE units are indeed incorporated into the microgel core of 4, and thereby their thermal motion is more restricted, while the divinyl ether unit's motion is less restricted due to the incorporation of more flexible AcOVE units in the core.

**(d) Hydrolysis of Pendant Esters.** The pendant ester groups of the AcOVE units of 4 were hydrolyzed into hydroxyl functions in 1,4-dioxane under basic conditions (Scheme I; see the Experimental Section) to give amphiphilic star-shaped polymers 5, which carry the 2-hydroxyethyl vinyl ether (HOVE) units within the core.

Figure 3 compares the $^1$H NMR spectra of the precursor star polymer (4; with an AcOVE-based core) and its

Table II
$^{13}C$ NMR Spin-Lattice Relaxation Time ($T_1$) of the Various Carbons in Core-Functionalized Star Polymer 4 and Heteroarm Star Polymer 7[a]



| code | polymer structure[b] | $T_1$, ms $C_b$ | $C_d$ | $C_e$ | $C_f$ |
|---|---|---|---|---|---|
| 4-I | $(IBVE)_{38}$–[$(AcOVE)_{20}$ in the core] | 301 | 233 | 218 | 221 |
| 7 | $(IBVE)_{30}$–(core)–$(AcOVE)_{10}$ | 324 | 210 | 202 | 221 |

[a] The $T_1$ values for the various carbons in the polymer measured in $CDCl_3$ at 30 °C. [b] The unit ratios are the calculated values; see Table I. The number (*f*) of arms per molecule are as follows: 4-I, 7; 7, 20.

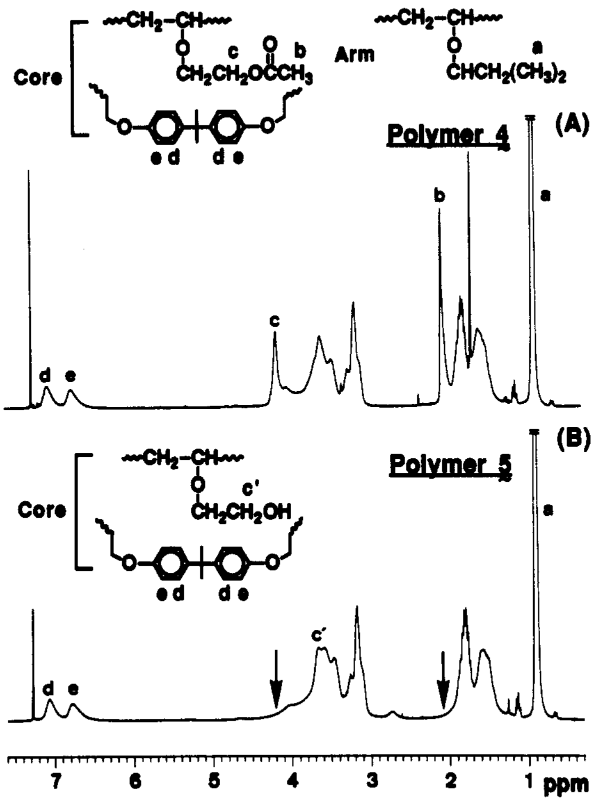


**Figure 3.** Hydrolysis of 4 (sample 4-I, IBVE/1/AcOVE in the polymer = 38/5/20 mole ratio) monitored by $^1H$ NMR spectroscopy in $CDCl_3$ at 25 °C: (A) IBVE–AcOVE core-functionalized star polymer 4 ($f = 7$); (B) amphiphilic star polymer 5 from sample A after hydrolysis.

hydrolysis product (5). After the hydrolysis, the absorption of the pendant acetoxy groups (b, 2.1 ppm; Figure 3A) completely disappeared; and signal c (4.2 ppm; Figure 3A), due to the methylene protons adjacent to the ester group, shifted upfield as peak c′ and became indistinguishable from that of the methine adjacent to the ether oxygen (Figure 3B). In contrast to these, all other signals of the poly(IBVE) units and the core moiety (a, 0.9 ppm; d and e, 6.5–7.2 ppm) remained unchanged upon hydrolysis.

Figure 4 compares the $^1H$ NMR spectra taken in a $CDCl_3/CD_3OD$ mixture (1:1, v/v) of 5 and heteroarm amphiphile 8 (obtained from 7 by hydrolysis), showing the signal of the hydroxyethyl (c′) of the HOVE units. The signal c′ in the spectrum of 5 (Figure 4A) was broader than that in the spectrum of 8 (Figure 4B). This indicated more restriction of the thermal motion of the hydroxyl groups in 5 and also confirmed the successful core functionalization.

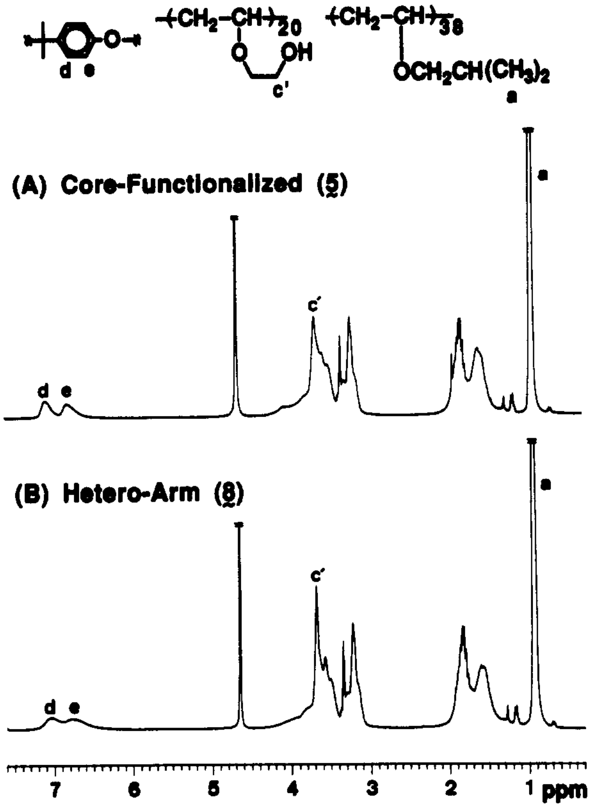


**Figure 4.** $^1H$ NMR spectra of core-functionalized star polymer 5-I (A) and heteroarm star polymer 8-I (B) at 25 °C in a $CDCl_3/CD_3OD$ (1:1, v/v) mixture. IBVE/HOVE in the polymer = 38/20 mole ratio. In spectra A and B, the sharp peaks at 4.6–4.7 ppm are due to water in the $CD_3OD$ solvent.

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

| code | polymer structure[b] | solvent hexane | toluene | $CHCl_3$ | $CH_3OH$ |
|---|---|---|---|---|---|
| 5-I | $(IBVE)_{38}$–[$(HOVE)_{20}$ in the core] | ○ | ○ | ○ | × |
| 5-II | $(IBVE)_{30}$–[$(HOVE)_{10}$ in the core] | ○ | ○ | ○ | × |
| 8-I | $(IBVE)_{38}$–(core)–$(HOVE)_{20}$ | △ | ○ | ○ | *c* |
| 8-II | $(IBVE)_{30}$–(core)–$(HOVE)_{10}$ | ○ | ○ | ○ | × |

[a] ○, soluble; △, swelling; ×, insoluble; at room temperature, ca. 3 wt %. [b] The unit ratios are the calculated values before hydrolysis; see Table I. The number (*f*) of arms per molecule are as follows: 5-I, 7; 5-II, 10; 8-I, 14; 8-II, 20. [c] Cloudy solution.

**Solubility Characteristics: Core-Functionalized vs Heteroarm Star.** Table III summarizes the solubility characteristics of two types of amphiphilic star polymers: core-functionalized (5) and heteroarm star (8). For both series of samples, the degree of polymerization for the poly(IBVE) arm chain was 38 or 30, and the mole ratio of IBVE and HOVE was 38/20 or 30/10. The ester-containing precursors, irrespective of their structure, were soluble in hexane, toluene, and chloroform but insoluble in methanol.

As shown in Table III, core-functionalized star 5 and heteroarm star 8 differ in solubility. Polymers 5-I and 8-I (IBVE/HOVE = 38/20) are both soluble in toluene and chloroform. Polymer 5-I is soluble in hexane but insoluble in methanol. In contrast, 8-I is insoluble in hexane, and a cloudy solution was obtained on addition of methanol. Such affinity of 5-I to a nonpolar solvent relative to 8-I

**Table IV**
**$T_1$ Values of Benzoic Acid in the Presence of Various Amphiphilic Star-Shaped Poly(vinyl ethers)[a]**

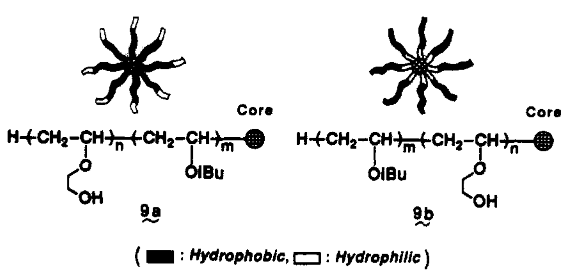
| code | shape[b] | polymer structure | unit ratio[c] $m/n$ | $f$[d] | $T_1$, s |
|---|---|---|---|---|---|
| | | no polymer | | | 3.77 |
| A | block (**9a**) | $(HOVE)_n$–$(IBVE)_m$–(core) | 29/10 | 8 | 1.92 |
| B | block (**9b**) | $(IBVE)_m$–$(HOVE)_n$–(core) | 30/9 | 8 | 1.67 |
| C | hetero (**8-II**) | $(IBVE)_m$–(core)–$(HOVE)_n$ | 30/11 | 20 | 1.75 |
| D | hetero (**8-I**) | $(IBVE)_m$–(core)–$(HOVE)_n$ | 38/21 | 14 | 1.73 |
| E | core (**5-II**) | $(IBVE)_m$– [$(HOVE)_n$ in the core] | 30/10 | 10 | 1.82 |
| F | core (**5-I**) | $(IBVE)_m$– [$(HOVE)_n$ in the core] | 38/20 | 7 | 1.53 |

[a] The $T_1$ values for the *m*-carbon of benzoic acid in $CDCl_3$ at 30 °C; [benzoic acid]/[OH in polymer] = 2.0. [b] **9a** and **9b**, star block polymers; **8**, heteroarm polymers; **5**, core-functionalized polymers. [c] The observed unit ratio, determined by $^1H$ NMR: see text and refs 6 and 7. [d] The number of arms per molecule determined by light scattering.

also supports the formation of the core-functionalized star amphiphile **5** where the hydrophilic core is better insulated from the solvent by the nonpolar poly(IBVE) arms.

Another pair of **5** and **8** with a smaller amount of the hydroxyl groups (**5-II** and **8-II**; IBVE/HOVE = 30/10) is similar in solubility, irrespective of their polymer structure, being soluble in hexane, toluene, and chloroform but insoluble in methanol. In heteroarm sample **8-II**, the short hydrophilic arms are probably buried in the inner region (almost core region), and hence **5-II** and **8-II** showed no difference in solubility. Such similarity in solubility is not due to the formation of the heteroarm star polymers in the synthesis of **4** (Scheme IIB), because, for example, the conversion data for AcOVE support its incorporation into the core parallelly with **1** (see the caption for Figure 1).

**Host–Guest Interaction of Core-Functionalized Amphiphilic Star Polymers 5 with Small Organic Molecules.** Following a similar study with star block polymers,[8] we examined the host–guest interaction between benzoic acid (guest) and amphiphilic star polymers **5-I** and **5-II** (hosts) in $CDCl_3$ at 30 °C. The occurrence of the host–guest interaction was evaluated from the changes in the $^{13}C$ spin–lattice relaxation time $(T_1)$[11,12] of the aromatic carbons of benzoic acid in the absence or presence of **5** ([benzoic acid] = 0.30 M; [benzoic acid]/[OH in **5**] = 2).[8] Table IV compares the $T_1$ for the *m*-carbon of benzoic acid in the presence of the three types of star amphiphiles (**5**, **8**, and **9**); core-functionalized (**5**; E and F), heteroarm (**8**; C and D),[7] and star block polymers with outer [A (**9a**)] or inner [B (**9b**)] polyalcohol arm segments. For all polymers, their concentrations were set so as to give the hydroxyl groups 0.5 equiv to the acid ([benzoic acid]/[OH in the polymer] = 2.0). Table IV also lists the characterization data of the polymers [the unit ratios (*m*/*n*) and the arm number (*f*) per molecule]; Figure 5 presents selected $T_1$ data in a bar chart form to visualize the results in Table IV.



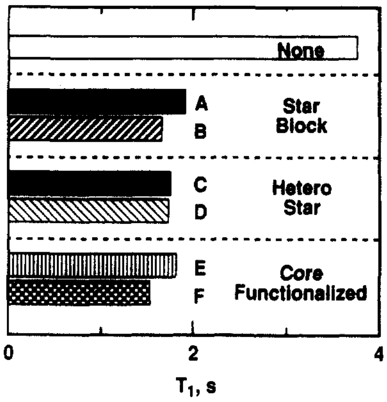


**Figure 5.** Relaxation time $T_1$ for *m*-carbon of benzoic acid in the presence and absence of amphiphilic star poly(vinyl ethers) A–F in $CDCl_3$ at 30 °C: [benzoic acid] = 0.30 M; [benzoic acid]/[OH in host polymer] = 2.0. (A and B) Star block polymers **9a** and **9b**, respectively. *m*/*n*: 30/10. (C and D) Heteroarm star polymers **8**. *m*/*n*: (C) 30/10; (D) 38/20. (E and F) Core-functionalized star polymers **5**. *m*/*n*: (E) 30/10; (F) 38/20; see also Table IV.

Both samples (E and F) of the core-functionalized star polymers **5** turned out to be effective as host polymers and lowered the $T_1$ of benzoic acid from 3.77 s for the polymer-free state to ca. 2.0 s or below in their presence. Between the two samples, interestingly, the $T_1$ decreased more for the larger number of the hydroxyl groups (**5-II** > **5-I**). The $T_1$ value (1.53 s) in the presence of F (polymer **5-I**) was also lower than those with the star block and the heteroarm star polymers (A–D). Although carrying the hydroxyl groups within the core, polymer E with the smaller amount of the hydroxyl groups induced a similar decrease in $T_1$ relative to the corresponding star block (A and B) and heteroarm star (C) polymers. These results demonstrate that, for efficient interactions, the host polymers need not only the higher accumulation of polar hydroxyl groups in the smaller region to which the core functionalization would lead but also the rather larger size of the core. Thus, as seen for the solubility data (Table III), the larger amount of the hydroxyl groups within the core affects the properties of **5** and may facilitate the interaction with the guest and capture guest molecules more efficiently.

In conclusion, we demonstrated that, on the basis of the living cationic polymerization (Scheme I), the core-functionalized amphiphilic star-shaped polymers (**5**) of vinyl ethers can be synthesized, where hydrophobic arm chains are attached to a hydrophilic single core carrying hydroxyl groups. In terms of solubility and the host–guest interaction with small organic molecules, these polymers clearly differ from the corresponding star block and heteroarm star amphiphiles.

## Experimental Section

**Materials.** AcOVE was prepared by the reaction of 2-chloroethyl vinyl ether with sodium acetate, as previously reported.[13] This monomer and commercial IBVE were purified by double distillation over calcium hydride before use. Bifunctional vinyl ether **1** was prepared according to the literature method[14] and doubly recrystallized from ethanol. 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%) using phosphorus pentoxide.[15] 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 transferred to a flask in a nitrogen-filled drybox and dissolved in dry and distilled diethyl ether just before use. Toluene (polymerization solvent) was washed by the usual methods[15] and distilled over calcium hydride at least twice before use. Diethyl ether (anhydrous; Wako Chemicals) was distilled over $LiAlH_4$ before use.

**Synthesis of Core-Functionalized Precursor Polymer 4 (Scheme I).** Living cationic polymerization of IBVE was carried out with $HI/ZnI_2$ at -15 °C in toluene under dry nitrogen in a baked flask equipped with a three-way stopcock.[9,15] After the polymerization had reached ca. 100% conversion, a mixture of divinyl ether **1** and AcOVE in toluene was added; see the caption for Figure 1 for reagent concentrations and other reaction conditions. Immediately after the monomer addition, an ether solution of $ZnI_2$ was added to increase its concentration to 0.50–1.0 mM, 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.

**Hydrolysis of Polymer 4 into Amphiphilic Form 5.** A sample of polymer **4** (400–500 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 chloroform and washed with water at least twice, and then the solvent was removed by evaporation. These purified samples were finally vacuum dried overnight to give polymer **5**.

**Synthesis of Star Block (9a and 9b) and Heteroarm Star (8) Amphiphilic Polymers.** These samples (samples A–D, Table IV) were prepared as already reported.[6,7]

**Polymer Characterization.** The weight-average molecular weight ($\bar{M}_w$) of the polymers was determined by small-angle laser light scattering in tetrahydrofuran at 25 °C on a Chromatix KMX-6 photometer ($\lambda = 633$ nm; five-point measurements; $c = 6 \times 10^{-4}$–$3 \times 10^{-3}$ g/mL). The refractive index increment (d$n$/d$c$) was measured in tetrahydrofuran at 25 °C on an Otsuka Electronics DRM-1020 double-beam differential refractometer ($\lambda = 633$ nm; three-point measurements; $c = 3 \times 10^{-3}$–$9 \times 10^{-3}$ g/mL). The d$n$/d$c$ values of **4** were $8.119 \times 10^{-2}$ mL/g for IBVE/AcOVE/**1** = 38/20/5 (sample 4-I) and $9.351 \times 10^{-2}$ mL/g for IBVE/AcOVE/**1** = 30/10/5 (sample 4-II). On the basis of the $\bar{M}_w$(star) value, the number ($f$) of the arms was calculated from the following relation:[16]

$$f = (\text{wt fraction of IBVE}) \times \bar{M}_w(\text{star})/\bar{M}_w(\text{arm})$$

where $\bar{M}_w$(arm) is the weight-average molecular weight of the arm chain (**2**), which is assumed to be equal to the number-average molecular weight [$\bar{M}_n$(arm)] of **2**, based on the feed ratio of IBVE and HI.[9]

The apparent $\bar{M}_w$ 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, and 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. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL GSX-270 (270 MHz) spectrometer at 25 °C. $^{13}C$ NMR spin-lattice relaxation times ($T_1$) were obtained by the inversion-recovery method at 30 °C, as previously reported.[8]

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## References and Notes

(1) Part 1 of this series: Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309.

(2) (a) Zilliox, J. G.; Rempp, P.; Parrod, J. *J. Polym. Sci., Part C* **1968**, *22*, 145. (b) Worsfold, D. J.; Zilliox, J. G.; Rempp, P. *Can. J. Chem.* **1969**, *47*, 3379.

(3) For reviews, see: (a) Bauer, B. J.; Fetters, L. J. *Rubber Chem. Technol.* **1978**, *51*, 406. (b) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 90.

(4) Tsitsilianis, C.; Lutz, P.; Graff, S.; Lamps, J. Ph.; Rempp, P. *Macromolecules* **1991**, *24*, 5897.

(5) For reviews, see: (a) Higashimura, T.; Aoshima, S.; Sawamoto, M. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 457, 513. (b) Higashimura, T.; Sawamoto, M. *Comprehensive Polymer Science*; Pergamon: London, 1989; Vol. 3, Part I, Chapter 42.

(6) Part 2 of this series: Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 5741.

(7) Part 3 of this series: Kanaoka, S.; Omura, T.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6407.

(8) (a) Part 4 of this series: Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6414. (b) Kanaoka, S.; Omura, T.; Sawamoto, M.; Higashimura, T. *Polym. Prepr., Jpn.* **1991**, *40*, E759.

(9) Sawamoto, M.; Okamoto, C.; Higashimura, T. *Macromolecules* **1987**, *20*, 2693.

(10) The MWD curves C and F show an additional peak in the lower molecular weight region. Such byproducts are most likely a copolymer (**3**) of IBVE, **1**, and AcOVE (see Scheme I).[1,6]

(11) Menger, F. M.; Jerkunica, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 688.

(12) Naylor, A. M.; Goddard, W. A., III; Kiefer, G. E.; Tomalia, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2339.

(13) Aoshima, S.; Nakamura, T.; Uesugi, N.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1985**, *18*, 2097.

(14) Crivello, J. V.; Conlon, D. A. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1785.

(15) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265, 2228.

(16) Eschwey, H.; Burchard, W. *Polymer* **1975**, *16*, 180.