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Star-Shaped Polymers by Living Cationic Polymerization. 2. Synthesis of Amphiphilic Star-Shaped Block Polymers of Vinyl Ethers with Hydroxyl Groups

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ABSTRACT: Amphiphilic star-shaped polymers (**5**) of vinyl ethers (VEs) where the arms consist of a polyalcohol/poly(alkyl vinyl ether) AB block copolymer were prepared on the basis of living cationic polymerization. For example, a sequential polymerization of an ester-containing VE ($\mathrm{CH_2{=}CHOCH_2CH_2OCOCH_3}$) and isobutyl VE with $\mathrm{HI/ZnI_2}$ at −15 °C in toluene led to a living block polymer (**3a**), which was subsequently allowed to react with a small amount of a bifunctional vinyl ether [**1**; $\mathrm{CH_2{=}CHOCH_2CH_2OC_6H_4C(CH_3)_2C_6H_4\text{-}OCH_2CH_2OCH{=}CH_2}$] to give a star-shaped block copolymer (**4a**). Alkaline hydrolysis of the ester functions of **4a** gave the amphiphilic star polymer **5a**, $[\mathrm{H[\text{-}CH_2CH(OCH_2CH_2OH)]}_m\text{-}[\mathrm{CH_2CH(O}i\mathrm{Bu)]}_n\text{-}]_f\text{-}$(core), with hydrophilic polyalcohol segments in the outer region. Amphiphilic star polymers **5b**, $[\mathrm{H[\text{-}CH_2CH(O}i\mathrm{Bu)]}_m\text{-}[\mathrm{CH_2CH(OCH_2CH_2OH)]}_n\text{-}]_f\text{-}$(core), with an opposite segment sequence (inner polyalcohol chains) were also prepared. The star polymer **5a** (m = 10, n = 29, 8 arms/molecule) is soluble in methanol, whereas the corresponding linear block copolymer (identical with the arm chains) and the inner-alcohol counterpart **5b** are insoluble.

Introduction

Star-shaped polymers have been prepared by living anionic polymerization in several ways,[1] among which a typical one involves the linking reaction of a linear living polymer with a small amount of a divinyl compound like divinylbenzene.[2] Recently, we have shown that a similar synthesis of star-shaped polymers is possible via living cationic polymerization of alkyl vinyl ethers.[3] We have also clarified the pathway for formation of the star-shaped poly(vinyl ethers) as well as the factors that determine the molecular weight and the number (f) of arm chains per molecule. These multibranched polymers with interesting three-dimensional shapes are expected to possess properties that differ from those of linear polymers, particularly when they have functional groups. Among the typical multiarmed polymers with functional groups thus far known are dendritic polymers.[4] There are few examples of similar "functionalized" star-shaped polymers in anionic polymerization,[5] because of the difficulty in preparing living polymers with polar pendant groups.

The hydrogen iodide/Lewis acid initiating system ($\mathrm{HI/I_2}$, $\mathrm{HI/ZnI_2}$, etc.) induces living cationic polymerization of not only alkyl vinyl ethers but also those having a pendant ester group[6] that lead to water-soluble polymers. A recent study in our group showed that a series of amphiphilic polymers could also be prepared by sequential living cationic polymerization of a functional vinyl ether and an alkyl derivative.[7-9] These findings prompted us to synthesize amphiphilic star-shaped polymers **5** with pendant hydroxyl groups, new functionalized polymers with controlled spatial (three-dimensional) shapes.

As illustrated in Scheme I, the synthesis starts from the sequential living cationic polymerization of 2-acetoxyethyl vinyl ether (AcOVE; $\mathrm{CH_2{=}CHOCH_2CH_2OCOCH_3}$) and isobutyl vinyl ether [IBVE; $\mathrm{CH_2{=}CHOCH_2CH(CH_3)_2}$] by $\mathrm{HI/ZnI_2}$. The resulting living block polymer **3** (P*) is allowed to react with a small amount of bifunctional vinyl ether **1** to give a star-shaped block copolymer **4**. Alkaline hydrolysis of the ester pendant in **4** then leads to an amphiphile **5**, where the arms consist of hydrophilic polyalcohol [poly(2-hydroxyethyl vinyl ether); poly(HOVE)] and hydrophobic poly(IBVE) segments.

An important feature of this methodology is that, by applying opposite polymerization sequences for AcOVE and IBVE, two types of amphiphilic star-shaped polymers may be prepared (**5a** and **5b**; Scheme I). Namely, polymer **5a** carries hydrophilic polyalcohol segments in its outer layer, whereas **5b** does in its inner layer. Therefore, **5a** and **5b** are expected to be different in their properties (solubility, etc.), even though they are the same in segment composition and degree of polymerization ($\overline{\mathrm{DP}}_n$). Noting these features of **5**, we examined herein (i) the controlled synthesis of amphiphilic star-shaped polymers **5** and (ii)

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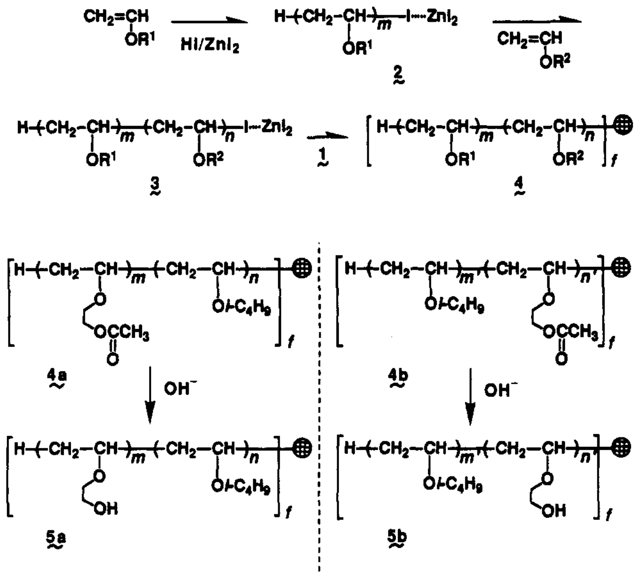
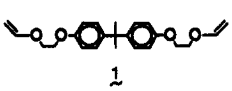
Scheme I



Code	R¹ (Outer Segment)	R² (Inner Segment)
2a, 3a, 4a	$CH_2CH_2OCCH_3$ (C=O)	i-C_4H_9
2b, 3b, 4b	i-C_4H_9	$CH_2CH_2OCCH_3$ (C=O)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⊕: Microgel Core of Poly(1)

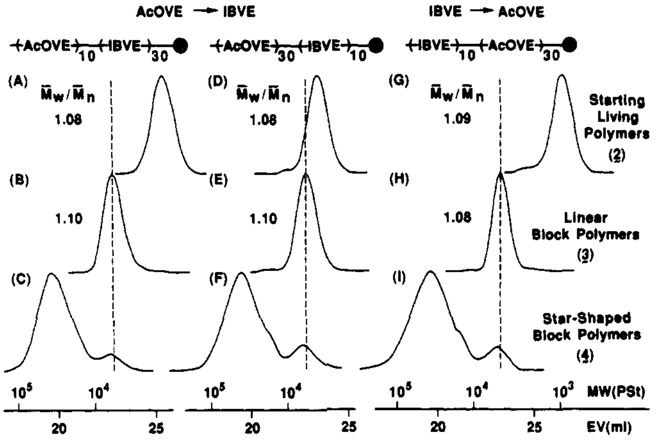

Figure 1. MWD of three series of products (A–C, D–F, and G–I) obtained in the synthesis of AcOVE–IBVE star-shaped block polymers 4 (Scheme I): $r = [1]_0/[P^*(3)] = 5.0$; (A, D, G) starting living polymers 2; (B, E, H) linear block polymers 3; (C, F, I) star-shaped block polymers 4. Other details of the synthesis are shown in the table given below:

series	A–C	D–F	G–I
polymn sequence	AcOVE → IBVE	AcOVE → IBVE	IBVE → AcOVE
(segment $\overline{DP}_n$ (calcd))	(10/30)	(30/10)	(10/30)
$[HI]_0$, mM	10.0	10.0	10.0
$[ZnI_2]_0$, mM	0.50	2.0	0.10 + 2.0[a]
solvent	toluene	toluene	CH_2CL_2
temp, °C	-15	-15	-40

[a] See text.

their solubility characteristics, specifically relative to those of the corresponding linear AB block polymers.

Results and Discussion

Synthesis of Amphiphilic Star-Shaped Polymers 5. (a) Star-Shaped Block Copolymers 4. IBVE and AcOVE were sequentially polymerized by the HI/ZnI$_2$ initiating system, and then the resultant linear block polymer 3 was allowed to react with a small amount of bifunctional vinyl ether 1 to afford precursor polymer 4 (Scheme I). We employed two types of linear block polymers (**3a** and **3b**) for the synthesis: **3a**, prepared by polymerizing AcOVE first, would lead to amphiphilic star-shaped polymer **5a** with outer polyalcohol segments; and **3b**, obtained via the reverse polymerization sequence, would give the inner-alcohol counterpart **5b**. For all these samples, the total degree of polymerization for the arm chains was invariably ca. 40, where the $\overline{DP}_n$ for the longer and the shorter segments were 30 and 10, respectively.

We first examined the synthesis of star block polymer 4 in toluene at -15 °C via the reaction of 1 and block polymer **3a** that was prepared by polymerizing AcOVE first and then IBVE with HI/ZnI$_2$. The first-stage polymerization of AcOVE reached 100% conversion in ca. 2.5 h to afford a living polymer with a very narrow molecular weight distribution (MWD) ($\bar{M}_w/\bar{M}_n \leq 1.1$; Figure 1A). On addition of IBVE (AcOVE/IBVE = 10/30 molar ratio) to this solution, the second-stage polymerization immediately ensued, being completed in 1 h. The MWD of the resulting AcOVE–IBVE block polymer **3a** shifted toward higher molecular weight and was relatively narrower than that of the block polymer of AcOVE and an alkyl vinyl ether with HI/I$_2$[7] ($\bar{M}_w/\bar{M}_n = 1.1$; Figure 1B).

The linear block polymer **3a** was then allowed to react with 1, 5 equiv to the living ends (P*) ($r = [1]_0/[P^*] = 5.0$). In 7 h, 1 and P* were consumed quantitatively, and a soluble polymer of a clearly higher molecular weight was obtained in yields as high as those for the star-shaped poly(IBVE)[3] (Figure 1C). The product was completely soluble in common organic solvents (toluene, chloroform, etc.). The weight-average molecular weight ($\bar{M}_w$) of this polymer (by light scattering) was 51 300, clearly higher than that of the arm chain (**3a**; $\bar{M}_w = 4300$). Thus, the star-shaped polymer **4a** was obtained via the reaction of **3a** with 1 (see below for structural verification). The high yield of **4a** was also attained with AcOVE/IBVE = 30/10 (Figure 1F).

Although obtained in high yield, polymers **4a** are accompanied by a small amount of low molecular weight polymers (Figure 1C,F). This byproduct had a peak molecular weight slightly higher than that of **3a** and is most likely a copolymer of **3a** and 1, where an oligomeric segment of 1 is attached to the poly(AcOVE-*b*-IBVE) living end.

A similar synthesis but with the opposite polymerization sequence (from IBVE to AcOVE) was also examined. Thus, the living polymerization of IBVE by HI/ZnI$_2$ was first carried out at -40 °C in CH$_2$Cl$_2$ at a low ZnI$_2$ concentration (0.1 mM; $[HI]_0 = 10$ mM),[10] which reached quantitative monomer conversion in 30 min to give a living polymer with a narrow MWD (Figure 1G). As already reported,[11] the living polymerization of AcOVE (less reactive than IBVE) needs a larger amount of ZnI$_2$ than that for alkyl vinyl ethers. Accordingly, in the second-phase polymerization of AcOVE from living poly(IBVE), an additional dose of ZnI$_2$ (2.0 mM) was added to the reaction mixture as soon as AcOVE was added. The polymerization of AcOVE reached ca. 100% conversion in an additional 18 h to give living block polymer **3b** (Figure 1H). The subsequent reaction of **3b** with 1 gave the star-shaped polymer **4b** in high yield (Figure 1I), which carries the poly(AcOVE) segments in its inner layer.

Parts A and C of Figure 2 show typical ^{1}H NMR spectra of the product obtained from the reactions of the living block polymer 3 with 1. Spectra A and C both exhibit a

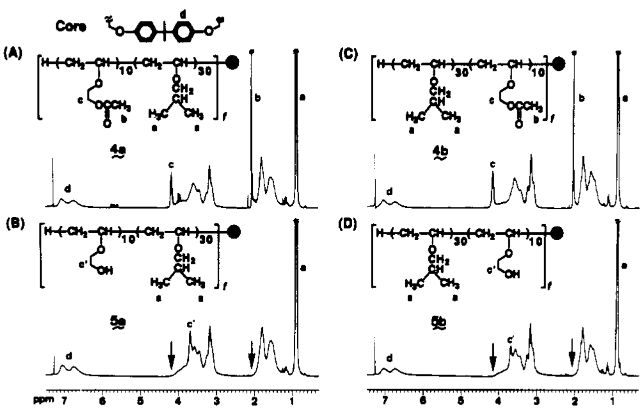

Figure 2. ^{1}H NMR spectra in $CDCl_3$ at 25 °C: (A) AcOVE–IBVE star block polymer **4a** (f = 8); (B) amphiphilic star polymer **5a** from sample A after hydrolysis; (C) IBVE–AcOVE star polymer **4b** (f = 8); (D) amphiphilic star polymer **5b** from sample C after hydrolysis. $\overline{DP}_n$ of arm chains as indicated.

Table I
Star-Shaped Block Polymer 4 Obtained from Linear Block Polymer 3 and Divinyl Ether 1 by Living Cationic Polymerization[a]

code	polymer structure[b]	$\overline{DP}_n$(obsd)[c]	$\bar{M}_w$(star),[d] ×10^{-4}	f[e]
4a	$(AcOVE)_{10}$–$(IBVE)_{30}$–(core)	10/29	5.13	8
4a	$(AcOVE)_{30}$–$(IBVE)_{10}$–(core)	30/9	10.9	16
4b	$(IBVE)_{10}$–$(AcOVE)_{30}$–(core)	10/31	9.54	14
4b	$(IBVE)_{30}$–$(AcOVE)_{10}$–(core)	30/10	4.67	8

[a] Reaction conditions: with HI/ZnI_2, in toluene at −15 °C for **4a**; in CH_2Cl_2 at −40 °C for **4b**; conversions of IBVE, AcOVE, and **1** are 100%; r = $[1]_0/[P^*]$ = 5.0; see Scheme I. [b] The segment $\overline{DP}_n$(calcd), shown in the formula, is based on the feed ratio of the monomers to hydrogen iodide. [c] The observed degree of polymerization of segments, determined by ^{1}H NMR (see text). [d] Determined by light scattering. [e] The number of arms per molecule; see the Experimental Section.

broad absorption assignable to the aromatic protons of **1** (d, 6.5–7.2 ppm), in addition to those of the IBVE and the AcOVE units (e.g., peaks a–c, Figure 2A,C). These results also support the formation of the star-shaped block polymer **4**, which consists of poly(AcOVE-*b*-IBVE) arm chains and a microgel core of poly(**1**).

Table I summarizes the $\bar{M}_w$ values (by light scattering), the arm numbers (f) per molecule (see the Experimental Section), and the segment compositions (AcOVE/IBVE; by ^{1}H NMR) of the star-shaped block polymers **4**. The $\bar{M}_w$ of **4** ranged from 4.7 × 10^4 to 1.1 × 10^5 and the arm numbers f from 8 to 16. The arm number f was larger for star polymers **4** (lines 2 and 3, Table I) with longer poly(AcOVE) segments, whether they are placed in the inner or the outer layer. This indicates that the longer the poly(AcOVE) segment is, the less sterically hindered is the linking reaction of the linear block polymer **3**. The segment composition of the arm was determined from the ^{1}H NMR peak intensity ratio of the methoxyl protons (peak b) of the AcOVE units to the methyl protons (peak a) of the IBVE units. The $\overline{DP}_n$ of the outer segment was obtained from the monomer (AcOVE or IBVE)/HI feed ratio. As shown in Table I, the observed segment compositions were in good agreement with the calculated values.

(b) Hydrolysis of Pendant Esters. The pendant ester groups 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**.

Figure 2 compares the ^{1}H NMR spectra of the AcOVE–IBVE precursor star block polymers (**4a** and **4b**), and their hydrolysis products (**5a** and **5b**, respectively). Comparison between spectra A and B, as well as C and D, proved that the ester groups were quantitatively converted into hydroxyl functions. For example, after the hydrolysis, the absorption of the pendant acetoxy groups (b, 2.1 ppm; Figure 2A) completely disappeared; and signal c (4.2 ppm; Figure 2A), due to the methylene protons adjacent to the ester group, shifted upfield to give an absorption at 3.7 ppm (c′; Figure 2B). 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.

Very similar results were obtained for **4b**, which led to the inner-polyalcohol counterpart **5b** (Figure 2C,D). After the hydrolysis, for instance, peaks b and c of the acetate groups (Figure 2C) disappeared, and peak c′ of the hydroxymethylene in turn appeared (Figure 2D). Thus, the amphiphilic star-shaped polymers were obtained, independent of segment arrangement.

Solubility Characteristics. Table II summarizes the solubility characteristics of four amphiphilic star polymers (**5a** and **5b**) and the corresponding linear block polymers (**3**). Note that **5a** and **5b** are the same in segment composition (IBVE/HOVE = 30/10 or 10/30 in $\overline{DP}_n$) but are opposite in segment arrangement; the polyalcohol segments are placed outside the molecules in **5a** but inside in **5b** (C vs B or E vs D). The AcOVE-based precursors **4a** and **4b**, irrespective of their segment composition and arrangement, were soluble in toluene and chloroform but insoluble in methanol and water.

The four amphiphiles fall into two groups; samples B and C carry arm chains with longer hydrophobic segments, whereas D and F involve longer hydrophilic arm segments. As shown in the first group, sample C and the corresponding linear chain (A) clearly differ in solubility, whereas sample B, with an inner polyalcohol moiety, is the same in solubility as sample A, being soluble in toluene and chloroform but insoluble in methanol and water. Interestingly, placing short poly(HOVE) segments in the outer region of **5** renders sample C soluble in even methanol, in addition to toluene and chloroform.

A similar phenomenon was observed for the second group of polymers (D–F), which are all soluble in methanol but insoluble in toluene. Sample E and linear block polymer F are also completely soluble in water, but sample D, with outer hydrophobic poly(IBVE) segments, is now not totally soluble in water. Samples D and E are insoluble in chloroform, which is a good solvent for sample F, simply because their molecular weights are too large. Thus, the solubility of these amphiphilic star-shaped polymers was primarily governed by the structure of the outer segments, even when their length is short (C and D).

Conformational Changes with Solvents. In general, hydrophilic segments extend in conformation with increasing solvent polarity, whereas hydrophobic segments extend in less polar media. The amphiphilic star-shaped polymers **5a** and **5b** would thus change their conformation with solvent polarity. We examined the conformational changes of the amphiphile **5** by ^{1}H and ^{13}C NMR analysis. We herein selected sample C, which is soluble in various solvents of differing polarity. Figure 3 shows a series of ^{1}H NMR spectra showing the signals of the hydroxyethyl (c′) of the arm chains and the aromatic protons (d) of the core moiety in various solvents.

The upfield absorption (c′, 3.7 ppm), assigned to the methylene adjacent to the hydroxyl group, was strong and sharp in CD_3OD (Figure 3A). Upon decreasing solvent polarity, this signal broadened (Figure 3B; in $CDCl_3$) and

Table II
Solubility of Amphiphilic Star-Shaped Polymers 5[a]

entry	shape	polymer structure[b]	solvent: toluene	solvent: $CHCl_3$	solvent: CH_3OH	solvent: H_2O
A	linear	$(HOVE)_{10}$-$(IBVE)_{30}$	○	○	×	×
B	star	$(IBVE)_{30}$-$(HOVE)_{10}$-(core)	○	○	×	×
C	star	$(HOVE)_{10}$-$(IBVE)_{30}$-(core)	○	○	○	×
D	star	$(IBVE)_{10}$-$(HOVE)_{30}$-(core)	×	×	○	△
E	star	$(HOVE)_{30}$-$(IBVE)_{10}$-(core)	×	×	○	○
F	linear	$(HOVE)_{30}$-$(IBVE)_{10}$	×	○	○	○

[a] ○, soluble; △, turbid; ×, insoluble; at room temperature, ca. 3 wt %. [b] The segment compositions ($\overline{DP}_n$) are the calculated values before hydrolysis; see Table I.

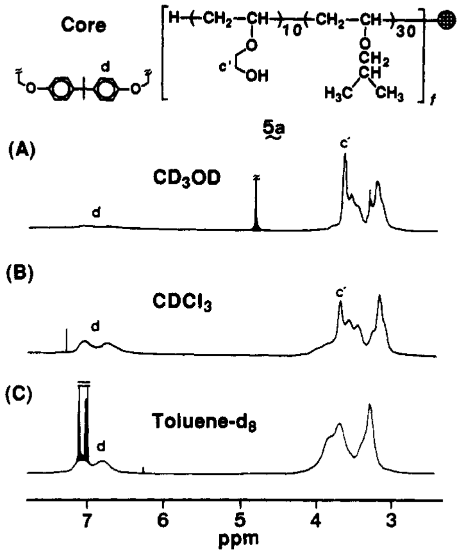

Figure 3. ^1H NMR spectra of the hydroxyethyl and the aromatic core moieties of amphiphilic star polymer **5a** (f = 8) at 25 °C in various solvents. $\overline{DP}_n$ of arm chains as indicated.

finally became indistinguishable from that of the methine adjacent to the ether oxygen (Figure 3C; in $C_6D_5CD_3$). The broadening and decrease in intensity of the peak arising from the HOVE units indicate that, in nonpolar solvent, the hydrophilic segments move into the inner region of the molecule and assemble intramolecularly.

The downfield absorption (d, 6.5–7.2 ppm) was assigned to the aromatic protons of the core derived from 1. As shown in Figure 3, the spectra of polymer C in $CDCl_3$ and $C_6D_5CD_3$ showed this signal (Figure 3B,C), whereas the signal could be hardly seen in the spectrum taken in CD_3OD (Figure 3A). This indicates that the hydrophobic inner poly(IBVE) segments in polymer C shrink in relatively polar CD_3OD solvent and render the core highly restricted in motion not to be observed by ^1H NMR.

^{13}C NMR analysis also provided evidence for these conformational changes. In $CDCl_3$, the absorptions due to the aromatic protons [from the microgel core of poly(1)] were clearly observed in the range from 115 to 160 ppm (Figure 4A). On the other hand, they could not be seen in CD_3OD (Figure 4B), where all other peaks of the poly(IBVE) and the poly(HOVE) units (a, 19.5 ppm; b, 28.8 ppm; c, 61.8 ppm) were seen. The disappearance of these signals is not due to the poor affinity of 1 units to CD_3OD. For example, the star-shaped poly(HOVE) (6), which was obtained via the reaction of living poly(AcOVE) (homopolymer) with 1, followed by hydrolysis, exhibited the ^{13}C NMR absorptions of the aromatic protons in the same solvent (Figure 4C).

As described above, we demonstrated that amphiphilic star-shaped block polymers of vinyl ethers can be synthesized, where the arm chain consists of hydrophilic poly-

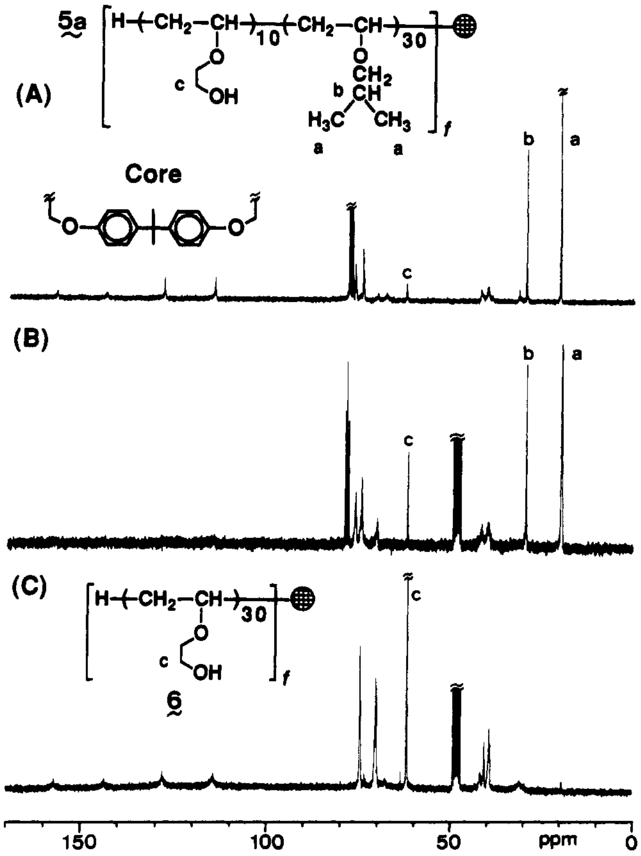

Figure 4. ^{13}C NMR spectra in $CDCl_3$ (A) and in CD_3OD (B and C) at 25 °C: (A and B) amphiphilic star-shaped polymer **5a** (f = 8); (C) star-shaped poly(HOVE) **6** (f = 15). $\overline{DP}_n$ of arm chains as indicated.

alcohol and hydrophobic poly(IBVE) segments, on the basis of the living cationic polymerization. The solubility characteristics of these polymers depend primarily on the properties of the outer segments and clearly differ from those of the corresponding linear block copolymers.

Experimental Section

Materials. AcOVE was prepared by the reaction of 2-chloroethyl vinyl ether with sodium acetate as reported previously.[12] 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[13] 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.[14] 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 diethyl ether just before use. Toluene and methylene chloride (polymerization solvents) were washed by the usual methods[14] and distilled over calcium hydride at least twice before use. Diethyl ether (anhydrous; Wako Chemicals) was distilled over $LiAlH_4$ before use.

Polymerization Procedures. Block copolymerization of vinyl ethers was carried out with HI/ZnI_2 at −15 or −40 °C under dry nitrogen in a baked flask equipped with a three-way stopcock.[14] After the polymerization had reached ca. 100% conversion, a solution of divinyl ether 1 was added, 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 Star-Shaped Polymers 4. A sample of polymer 4 (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. Depending on the segment composition, the hydrolyzed polymers were either soluble or insoluble in water. The water-soluble samples were dissolved in water (ca. 10 mL) and dialyzed for 2 days (Spectra/Por 7, molecular weight cutoff ca. 1000); the water-insoluble samples carrying arm chains with longer hydrophobic segments were dissolved in chloroform and washed with water. These purified samples were finally recovered by evaporation and vacuum dried 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 tetrahydrofuran (THF) at 25 °C on a Chromatix KMX-6 photometer (λ = 633 nm; five-point measurements; $c = 1 \times 10^{-3}$–2×10^{-3} g/mL). The refractive index increment (dn/dc) was measured in THF at 25 °C on a Chromatix KMX-6 refractometer (λ = 633 nm). The dn/dc value of 4 was taken as the weight average of the values for the star-shaped poly(IBVE) (7.994×10^{-2} mL/g) and the star-shaped poly(AcOVE) (7.411×10^{-2} mL/g). On the basis of the $\bar{M}_w$(star) value, the number (f) of the arms was calculated from the following relation[15]

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

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

The $\bar{M}_w$ was also measured, relative to standard polystyrene samples, by size exclusion chromatography in chloroform on a Jasco Trirotar 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.

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