Star-Shaped Polymers by Living Cationic Polymerization. VII. Amphiphilic Graft Polymers of Vinyl Ethers with Hydroxyl Groups: Synthesis and Host–Guest Interaction*

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SYNOPSIS

Amphiphilic graft polymers of vinyl ethers (VEs) (6) where each branch consists of a hydrophilic polyalcohol and a hydrophobic poly(alkyl vinyl ether) segment were prepared on the basis of living cationic polymerization, and their properties and functions were compared with the corresponding amphiphilic star-shaped polymers. In toluene at $-15°C$, the HI/ZnI_2-initiated living block polymer 2 of an ester-containing VE ($CH_2\!=\!CHOCH_2CH_2OCOCH_3$) and isobutyl VE (IBVE) was terminated with the diethyl 2-(vinyloxy)ethylmalonate anion [3; $^{\ominus}C(COOEt)_2CH_2CH_2OCH\!=\!CH_2$] (2/3 = 1/2 mole ratio) to give a macromonomer (4), $H[CH_2CH(OCH_2CH_2OCOCH_3)]_m$-$[CH_2CH(OiBu)]_n\!-\!C(COOEt)_2CH_2CH_2OCH\!=\!CH_2$ (m = 5, n = 15; $\bar{M}_n$ = 2600, $\bar{M}_w/\bar{M}_n$ = 1.13, 1.10 vinyl groups/chain). Subsequently, 4 was homopolymerized with HI/ZnI_2 in toluene at $-15°C$. In 3 h, 85% of 4 was consumed and a graft polymer (5) was obtained [$\bar{M}_w$ = 15000, $\overline{DP}_n$ (for 4) = 6]. The apparent $\bar{M}_w$ (10,900) of 5 by size-exclusion chromatography (SEC) is smaller than that by light scattering as well as that (18,300) by SEC of the corresponding linear polymer with the almost same molecular weight, indicating the formation of a multi-branched structure. Hydrolysis of the pendant esters in 5 gave the amphiphilic graft polymer 6 where each branch consists of a hydrophilic polyalcohol and a hydrophobic poly(IBVE) segment. The graft polymer 6 was found to interact specifically with small organic molecules (guests) with polar functional groups, and 6 differed in solubility and host–guest interaction from the corresponding star-shaped polymer. © 1993 John Wiley & Sons, Inc.

Keywords: graft polymer • star-shaped polymer • living polymerization • cationic polymerization • amphiphilic polymer • host–guest interaction

INTRODUCTION

Living polymerization permits the synthesis of not only linear polymers with well-defined structures but also polymers with controlled three-dimensional shapes, which are usually attained by multi-branched structures. Such topologically controlled polymers are classified star-shaped,[1] dendritic,[2] and graft polymers, etc., depending on how the branches or arms are placed in the polymeric structure.

On the basis of living cationic polymerization, for example, we have recently synthesized three types of amphiphilic star-shaped polymers of vinyl ethers with hydroxyl or carboxyl groups: star-shaped block copolymers;[3,4] hetero-arm star polymers;[5] and core-functionalized star polymers.[6] All these star polymers have been obtained via linking reactions of linear living polymers mediated by bifunctional vinyl compounds.[3–6] The functionalized star poly(vinyl ether)s were found to possess properties and functions (like selective host–guest interaction with small molecules[7]) that differed from those of the corresponding linear block polymers.[3–7] In general, an important factor that affects the properties of star polymers is the number of arms per molecule.[1]

Although the relationship of the arm number with synthetic conditions is empirically known,[8,9] it is difficult to strictly predetermine the arm number, because it is statistically controlled in the linking reaction of living polymers with bifunctional monomers.[8,9]

Another method for the synthesis of multibranched polymers is the homo- or copolymerization of a macromonomer into a graft polymer.[10] In the course of our series of studies on star-shaped amphiphilic polymers,[3-8] we became interested in the synthesis of "amphiphilic" graft polymers with a predetermined number of arms (branches) via living cationic polymerization of macromonomers. Although a number of macromonomers have been prepared, there are no examples of polymerization of "block" macromonomers,[10] which consist of more than two different segments.

Herein we directed our study to the synthesis of amphiphilic graft polymers with a controlled branch number. As shown in Scheme 1, 2-acetoxyethyl vinyl ether (AcOVE; $CH_2 = CHOCH_2CH_2OCOCH_3$) and isobutyl vinyl ether (IBVE) are sequentially polymerized with the hydrogen iodide/zinc iodide (HI/ZnI_2) initiating system. The resultant living block polymer 2 is terminated with diethyl 2-(vinyloxy)ethylmalonate (VOEM) anion 3 in toluene at $-15°C$ to give a macromonomer 4, which bears a cationically polymerizable vinyl ether terminal.[11] The subsequent homopolymerization of 4 with HI/ZnI_2 in toluene at $-15°C$ affords a graft polymer 5. Alkaline hydrolysis of the ester groups in 5 then leads to the amphiphilic graft polymer 6 where each branch consists of a hydrophilic polyalcohol [poly(2-

hydroxyethyl vinyl ether)]: poly(HOVE)] and a hydrophobic poly(IBVE) segment.

Such amphiphilic graft polymers may have the almost uniform number of branches, provided that living polymerization of 4 is available. In addition, unlike the various types of the star-shaped polymers previously reported,[3-6] graft polymer 5 has no hydrophobic microgel core that may possess some dimensions. Therefore, the amphiphilic graft polymers are expected to possess properties and functions differing from those of the corresponding star block amphiphiles. In this study, we examined: (i) the synthesis of amphiphilic graft polymers 6 with the controlled number of branches and (ii) their solubility characteristics and host–guest interaction with small organic molecules, relative to those of the corresponding amphiphilic star-shaped and linear block polymers.

RESULTS AND DISCUSSION

Synthesis of Macromonomer 4

Macromonomer 4 was prepared by terminating the HI/ZnI_2-initiated living block polymer 2 with VOEM anion 3 in toluene at $-15°C$ (Scheme 1, see Experimental section). In a typical example, the first-stage polymerization of AcOVE ([AcOVE]$_0$ = 0.05M, [HI]$_0$ = 10 mM, [ZnI_2]$_0$ = 0.5 mM) reached 100% conversion in 35 min to give a living polymer with a narrow molecular weight distribution (MWD) [$\bar{M}_w/\bar{M}_n < 1.1$, Fig. 1(A)]. The subsequent polymerization of IBVE (AcOVE/IBVE
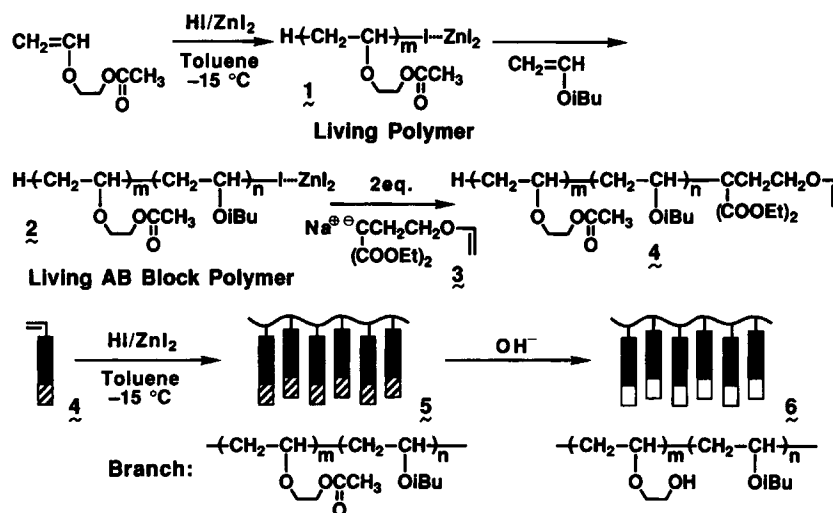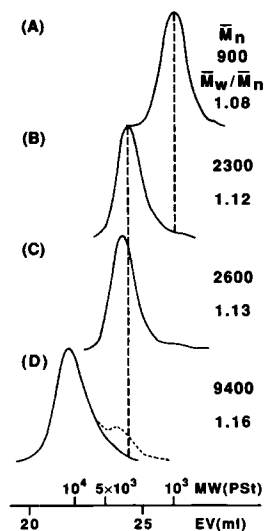

Scheme 1

Figure 1. MWD of the products obtained in the synthesis of graft polymer **5** at −15°C in toluene (Scheme 1): (A) starting living poly(AcOVE) **1**, [AcOVE]$_0$ = 0.05 M, [HI]$_0$ = 10 mM, [ZnI$_2$]$_0$ = 0.50 mM, monomer conversion = 100%; (B) linear living block polymers **2** (quenched with methanol), AcOVE/IBVE mole ratio = 5/15; (C) macromonomer **4** obtained from the end-capping reaction of **2** with sodio malonic ester anion **3**, [**3**]$_0$/[**2**]$_0$ = 2.0; (D) graft polymer **5** obtained from the polymerization of **4** with HI/ZnI$_2$, [**4**]$_0$ = 16 mM, [HI]$_0$ = 2.0 mM, [ZnI$_2$]$_0$ = 1.0 mM.

= 5/15 mole ratio, completed in 6 min) led to AcOVE–IBVE block polymer **2** [$\bar{M}_w/\bar{M}_n$ = 1.12, Fig. 1(B)]. Then, the living end of polymer **2** was allowed to react with the anion **3**, 2 equiv to the living ends, to give a product [Fig. 1(C)] whose $\bar{M}_n$ and MWD are very similar to the polymer **2** quenched with methanol [see Fig. 1(B)]. The nearly same MWDs indicate that the quenching with **3** is rapid and quantitative, and that no vinyl ether group of **3** reacted with the living growing ends of **2**.

Figure 2 (A) shows the ^{1}H-NMR spectrum of the quenching product [see Fig. 1 (C)] thus obtained. The spectrum exhibits the absorptions assignable to the terminal vinyl protons (peaks d and f), in addition to those of the AcOVE and the IBVE units (peaks a, c, and e), and was fully consistent with the macromonomer structure **4** (Scheme 1). The segment composition and the number ($\bar{F}_n$) of the vinyl terminal per polymer chain were determined from the ^{1}H-NMR peak intensity ratios of the acetoxy methyl protons (peak b) of the AcOVE units to the methyl protons (peak a) of the IBVE units and to the vinyl protons (peak f) of the terminal VOEM units, respectively. The $\overline{DP}_n$ of the poly(AcOVE) segment was taken to be 5, which was

calculated from AcOVE/HI feed ratio. The observed segment composition was 5/15.4, in good agreement with the calculated ratio (5/15). The end functionality $\bar{F}_n$ was 1.10, showing the attachment of nearly one vinyl ether group per chain. Thus, "block" macromonomer **4**, which consists of poly(AcOVE) and poly(IBVE) segments, was quantitatively obtained via the reaction of living block polymer **2** with **3**. Macromonomers **4** with a longer chain (e.g., total $\overline{DP}_n$ = 40, AcOVE/IBVE = 10/30) were also obtained in a similar manner.

Cationic Polymerization of Macromonomer 4

Macromonomer **4** (AcOVE/IBVE = m/n = 10/30, [**4**]$_0$ = 16 mM) was homopolymerized with boron trifluoride etherate (BF$_3$OEt$_2$, 10 mM)[12] and the HI/ZnI$_2$ (2.0/5.0 mM) initiating system at −15°C
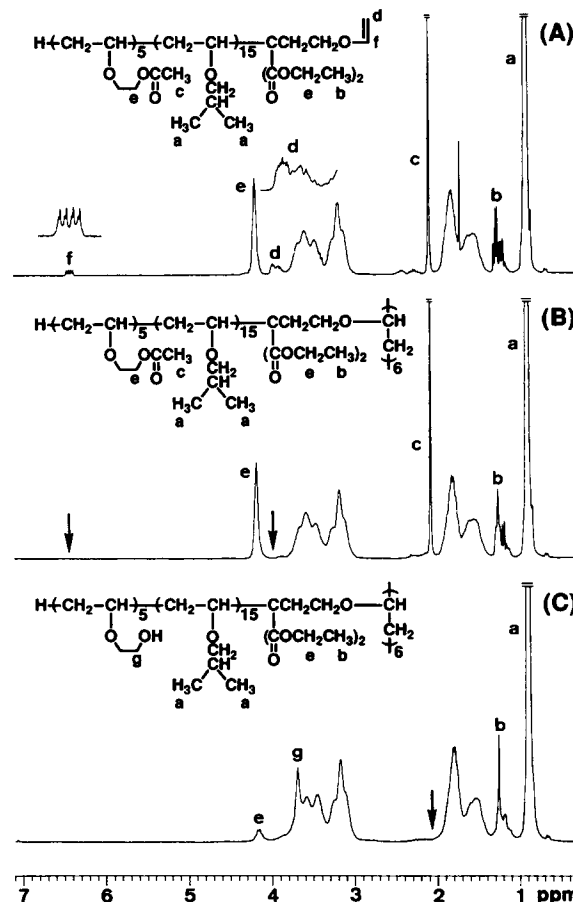

Figure 2. ^{1}H-NMR spectra in CDCl$_3$ at 25°C: (A) macromonomer **4**, (B) precursor graft polymer **5** from sample A after polymerization, (C) amphiphilic graft polymer **6** from sample (B) after hydrolysis. DP$_n$ of arm chains is as indicated.

in toluene. After a sufficiently long reaction time,[13] both polymerizations led to soluble products containing polymers of clearly higher molecular weight relative to 4 [Figs. 3 (A) and (B)]. These polymers are likely graft polymers of 4, but they were accompanied by a large amount of unreacted 4 (indicated by the arrow in each SEC curve, see Fig. 3). The conversions of 4 were determined from the integration of the MWD curve, and they were 35–45% for both initiators. Thus, the cationic homopolymerization of 4 turned out to be possible but not quantitative under these conditions.

The factors that render the polymerization of 4 not highly efficient may be the steric hindrance of the main chain and/or the polar nature of the pendant ester groups of the AcOVE units in 4; the latter can complex ZnI_2 to reduce its effective concentration. Thus, we examined the effects of these two factors on the yield of graft polymers.

To examine the steric effect on the polymerization, we herein employed two poly(IBVE)-based macromonomers 7, whose degree $(\overline{DP}_n)$ of polymerization was 10 or 38. As shown in Figure 4, the shorter the chain length of the poly(IBVE) chain, the higher the yield of the graft polymer (A > B) from 7. When the $\overline{DP}_n$ was 10, the macromonomer 7 was almost completely consumed in 1 h [Fig. 4 (A)]. Furthermore, the MWD of the product was unimodal and apparently narrow $(\overline{M}_w/\overline{M}_n = 1.10)$.

We next examined the polymerization of two samples of 4 that differed in segment composition. On the basis of the results for the steric effect, the total $\overline{DP}_n$ of the two samples was set 20, where the $\overline{DP}_n$ for the AcOVE segment was 5 and 10 (4a and

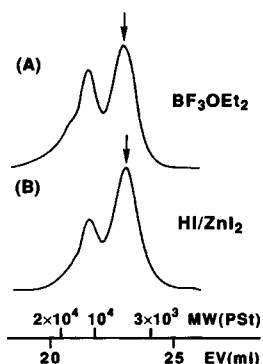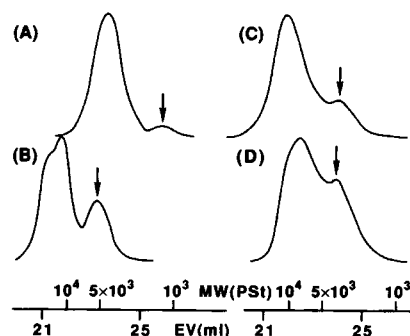**Figure 4.** MWD of the products obtained in the homopolymerization of poly(IBVE)-based macromonomer 7 [(A) and (B)] or macromonomer 4 (total $\overline{DP}_n$ = 20) with the varying number of the AcOVE units [(C) and (D)] at −15°C in toluene; [7 or 4]$_0$ = 16 mM, [HI]$_0$ = 2.0 mM. $\overline{DP}_n$ for IBVE and [ZnI$_2$]$_0$: (A) 10, 2.0 mM; (B) 38, 4.0 mM. Segment $\overline{DP}_n$ for AcOVE and [ZnI$_2$]$_0$: (C) 5, 1.0 mM; (D) 10, 2.0 mM. The arrow, attached to each MWD curve, indicates the unreacted macromonomer 4 or 7.

4b, respectively). Depending on the segment composition, the amount of ZnI_2 was varied (1.0 and 2.0 mM for 4a and 4b, respectively), namely, the more ZnI_2 for the macromonomer with a longer AcOVE segment. Although the two macromonomers had the same total $\overline{DP}_n$, the yield of the graft polymer was clearly higher with 4a [Fig. 4, (C) > (D)]. In general, the larger amount of AcOVE units retards its polymerization, because the ester group of AcOVE may complex ZnI_2 to reduce its effective concentration. Both the retardation and the steric effect render 4b much less reactive to induce termination or chain transfer reactions and eventually lead to the lower yield of 5 with the longer poly(AcOVE) segment.

Amphiphilic Graft Polymers 6

Precursor Graft Polymers 5

According to the results described in the preceding section, both the total $\overline{DP}_n$ and the AcOVE segment $\overline{DP}_n$ of macromonomer 4 should be relatively low to achieve its successful homopolymerization. Thus, for the synthesis of amphiphilic graft polymer 6 (and its precursor 5, Scheme 1), we selected 4 with total $\overline{DP}_n$ = 20 and AcOVE/IBVE segment $\overline{DP}_n$ ratio = 5/15. In toluene at −15°C, the macromonomer 4 was homopolymerized with HI/ZnI$_2$ ([4]$_0$ = 16 mM, [HI]$_0$ = 2.0 mM, [ZnI$_2$]$_0$ = 1.0 mM). In 3 h, 85% of 4 was consumed and higher molecular weight polymers were obtained [Fig. 1 (D)]. The product was completely soluble in common organic solvents

Figure 3. MWD of the products obtained from the homopolymerization of macromonomer 4 at −15°C in toluene (Scheme 1); [4]$_0$ = 16 mM. Initiator: (A) BF$_3$OEt$_2$, 10 mM; (B) HI/ZnI$_2$, 2.0 mM ([ZnI$_2$]$_0$ = 5.0 mM). The arrow, attached to each MWD curve, indicates the unreacted macromonomer 4.

(toluene, chloroform, etc.). For subsequent experiments, the unreacted **4** was removed from the sample by preparative SEC [see Fig. 1 (D) where the SEC curve in broken line indicates the excluded macromonomer fraction]. The weight-average molecular weight ($\bar{M}_w$) of this fractionated graft polymer (by light scattering) was 15,000, and the apparent MWD by SEC was narrow ($\bar{M}_w/\bar{M}_n = 1.16$). The $\overline{DP}_n$ for **4**, calculated on the basis of $\bar{M}_w$, was 6.3, which was close to the calculated value (= 6.8) based on the $[4]_0/[HI]_0$ ratio and the conversion of **4**. These results support that **4** is polymerized with HI/ZnI_2 in a living fashion to give the graft polymer **5** with the *controlled* number of branches.

Figure 2 (B) shows the ^1H-NMR spectrum of the graft polymer **5** obtained from **4**. After the polymerization of **4**, the peaks [d and f: Fig. 2(A)] due to the vinyl groups completely disappeared, whereas all other signals of the AcOVE and the IBVE units remained unchanged [peaks a, c, and e: Fig. 2(B)]. Thus, the precursor graft polymer **5** was obtained.

Hydrolysis of Pendant Esters

The pendant ester groups of the AcOVE units of the graft polymer **5** were hydrolyzed into hydroxyl functions in 1,4-dioxane under basic conditions (Scheme 1, see Experimental section) to give amphiphilic graft polymer **6**.

Figures 2 (B) and (C) compare the ^1H-NMR spectra of the precursor graft polymer (**5**) and its hydrolysis product (**6**), respectively. After the hydrolysis, the absorption of the pendant acetoxy groups [c, 2.1 ppm: Fig. 2 (B)] completely disappeared; and signal e [4.2 ppm: Fig. 2 (B)], due to the methylene protons adjacent to the ester group, shifted upfield as peak g and became indistinguishable from that of the methine proton adjacent to the ether oxygen [Fig. 2 (C)]. In contrast to these, all other signals of the poly(IBVE) units (a, 0.9 ppm) remained unchanged upon hydrolysis. A small peak at 4.2 ppm is assignable to the methylene protons of the VOEM units [Fig. 2 (C)].[14] These spectral observations show the complete hydrolysis of the pendant acetoxy groups and the formation of the amphiphilic form **6**.

Graft vs. Star Block Polymers

Both graft and star-shaped polymers are multibranched macromolecules but differ in structure from each other, and hence difference in properties and functions would be expected between them. We therefore compared the graft polymers **5** (precursor)

and **6** (amphiphile) with the corresponding star block polymers[3] in terms of molecular weight, solubility, and host–guest interaction.

Molecular Weight

Figure 5 compares the MWD curves of samples of the graft (**5**, 6 branches/molecule) and the star block (**8**, 7 arms/molecule) precursor polymers before hydrolysis. For both samples, the $\overline{DP}_n$ for the poly(AcOVE) and the poly(IBVE) segments were 5 and 15, respectively. The peak molecular weight of **5** [Fig. 5 (B)] was slightly smaller than that of **8** [Fig. 5 (C)], indicating that **5** may possess smaller hydrodynamic volume than **8**. Such difference most likely stems from a microgel core of a bifunctional vinyl ether.[3]

Table I lists the $\bar{M}_w$ values (by light scattering and SEC) and the branch (or arm) numbers (f) per molecule (see Experimental section). Both $\bar{M}_w$ values of **5** and **8** by SEC were smaller than the corresponding values by light scattering as well as that of the corresponding linear polymer formally with the same total numbers of repeat units (AcOVE/IBVE = 30/90 mole ratio) per molecule as that of the graft polymer **5** [AcOVE/IBVE = (5/15) × 6 arms = 30/90]. This also supports the formation of a multi-branched structure like **5** and **8** that is more compact[15] than the linear counterpart with the same molecular weight. The $\bar{M}_w$ of **5** (by light
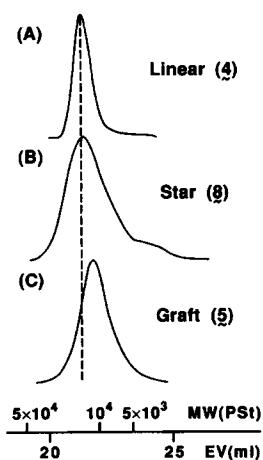
Figure 5. MWD of (A) linear block polymer **4**, (B) star block polymer **8**, and (C) precursor graft polymer **5**. Reaction conditions (in toluene at −15°C): (A) $[AcOVE]_0$ = 0.30 M, $[HI]_0$ = 10 mM, $[ZnI_2]_0$ = 0.5 mM, AcOVE/IBVE mole ratio = 30/90; (B) $[AcOVE]_0$ = 0.05M, $[HI]_0$ = 10 mM, $[ZnI_2]_0$ = 0.5 mM, AcOEV/IBVE mole ratio = 5/15, [divinyl ether]$_0$/[**2**] = 2.0; (C) $[4]_0$ = 16 mM, $[HI]_0$ = 2.0 mM, $[ZnI_2]_0$ = 1.0 mM.

Table I. The Weight-Average Molecular Weight $(\bar{M}_w)$ of Graft Polymer 5 and Star-Shaped Block Polymer 8 by Light Scattering and SEC[a]

Code	Shape	$\overline{DP}_n$ (obsd)[b] m/n	$\bar{M}_w \times 10^{-4}$ [c] LS	$\bar{M}_w \times 10^{-4}$ [c] SEC	$\bar{M}_w$ (core) $\times 10^{-3}$ [d]	f [e]
4	linear	30/102	—	1.83	—	—
5	graft	5/15.4 per branch	1.50	1.09	0	6
8	star	5/15.5 per arm	1.93	1.25	4.9	7

[a] Reaction conditions: with HI/ZnI_2 in toluene at $-15°C$. $[HI]_0$ and $[ZnI_2]_0$: (4 and 8) 10 mM, 0.5 mM; (5) 2.0 mM, 1.0 mM. In the synthesis of 8: [divinyl ether]$_0$ = 20 mM; r = [divinyl ether]$_0$/[HI]$_0$ = 2.0; see Reference 3.

[b] The observed segment compositions of the branch (arm), determined by ^{1}H-NMR (see text); the calculated values are 5/15 for 5 and 8, and 30/90 for 4.

[c] LS, by light scattering; SEC, by size-exclusion chromatography.

[d] See Reference 8.

[e] The number of branches (arms) per molecule; see Experimental section.

scattering) was smaller than that of the star block polymer 8, and the difference was very similar to the calculated $\bar{M}_w$(core) value for the microgel core of 8 (Table I).

Solubility Characteristics

Table II summarizes the solubility characteristics of both graft (6) and star block (9) amphiphilic polymers. For both samples, the $\overline{DP}_n$ for the poly(HOVE) and the poly(IBVE) segments were 5 and 15, respectively. The ester-containing precursors (5 and 8), irrespective of their structure, were soluble in hexane, toluene, and chloroform but insoluble in methanol.

Both 6 (sample B) and 9 (C) clearly differ in solubility from the corresponding linear polymer 10 (A). Sample A is soluble in hexane, toluene, chloroform, and methanol, whereas both 6 and 9 are insoluble in hexane. Placing polar hydroxyl groups in the outer region of the molecule rendered 6 and 9 insoluble in a nonpolar solvent like hexane.

The graft polymer 6 (B) is insoluble in methanol where the star block counterpart 9 (C) is soluble. In a polar solvent, the arms of 9 may be located radially enough for hydrophilic segments to surround the hydrophobic poly(IBVE) segments and the central core. On the other hand, the graft polymer 6 may differ in conformation from the star polymer 9 due to the lack of a central core; in other words, the arms of 6 can hardly be extend radially as those of 9 do. The hydrophobic segments of 6 are not well "shielded" from the polar solvent, and thus 6 becomes insoluble in methanol.

Host–Guest Interaction of Amphiphilic Graft Polymers 6 with Small Organic Molecules

Quite recently, we have found the selective host–guest interaction of the amphiphilic star-shaped poly(vinyl ether)s with small organic molecules carrying a particular functional group.[7] In this study, we examined the host–guest interaction between amphiphilic graft polymer 6 (host) and benzoic acid

Table II. Solubility of Amphiphilic Graft Polymer 6 and Related Polymers[a]

Code	Polymer Structure[b]	Solvent Hexane	Solvent Toluene	Solvent CHCl$_3$	Solvent CH$_3$OH
10	(HOVE)$_5$-(IBVE)$_{15}$	O	O	O	O
6	(HOVE)$_5$-(IBVE)$_{15}$—⟨	×	O	O	×
9	(HOVE)$_5$-(IBVE)$_{15}$-(core)	×	O	O	O

[a] (O) soluble; (×) insoluble; at room temperature, ca. 3 wt %.

[b] The segment compositions are the calculated values before hydrolysis. The number (f) of branches (arms) per molecule: (6) 6, (9) 7.

(**11**) or n-pentylbenzene (**12**) in $CDCl_3$ at 30°C. The occurrence of the host–guest interaction was evaluated from the changes in the ^{13}C-NMR spin-lattice relaxation time (T_1)[16,17] of the aromatic carbons of **11** and **12** in the absence or presence of **6** ([guest] = 0.30M). Table III summarizes the T_1 for the asterisked carbon of **11** or **12** in the presence of the graft (**6**), the corresponding star (**9**), and linear (**10**) polymers. For all polymers, their concentrations were set so as to give the hydroxyl groups 0.5 equiv to the guest ([guest]/[OH in the polymer] = 2.0).[7] Table III also lists the characterization data of the polymers [the observed $\overline{DP}_n$ (m/n) and the arm number (f) per molecule].

The amphiphilic graft polymer **6** turned out to be effective as a host polymer and lowered the T_1 of **11** by 50%. It gave the lower T_1 value (1.90 s) than the linear polymer **10** (2.18 s). This trend demonstrates that, for efficient interactions, the host polymers need a branched or multi-armed structure which would lead to a higher accumulation of polar hydroxyl groups per molecule. Thus, the larger amount of the hydroxyl groups may facilitate the interaction with the guest and may capture more guest molecules. As seen in Table III, however, the star polymer **9** was inferior to the graft polymer **6** as well as to the linear polymer **10**. The central core may be so large for these short arm chains that the accumulation of the hydroxyl groups is not high

enough to afford an effective host–guest interaction. For example, the star amphiphile with the longer arm chains (total $\overline{DP}_n$ = 40, HOVE/IBVE = 10/30 mole ratio) in fact gave the lower T_1 relative to the corresponding linear polymer.[7]

On the other hand, the T_1 of **12** remained unchanged upon treating with **6**, **9**, and **10**, irrespective of the structure of the host polymers (Table II). These results show that for efficient interactions with **6**, guests need polar hydrophilic groups, such as carboxyl, that can be hydrogen-bonded to the hydroxyl groups in **6**, as observed for the star-shaped polymers.[7]

With the star block polymers, the host–guest interaction exhibited a concentration dependence because guest molecules are in an equilibrium between free and complexed states.[7] Figure 6 plots the T_1 values of m-carbon in **11** as a function of the molar ratio ([OH in polymer]/[guest]) of the hydroxyl groups in **6** or **9** to the guest. The samples were prepared by the addition of varying doses of **11**, while keeping the concentration of the hydroxyl groups in the polymer constant ([OH in **6** or **9**] = 0.15M).

Both interactions of **6** and **9** with **11** also showed concentration dependence (Fig. 6). Interestingly, upon increasing [OH in polymer]/[guest] ratio (by decreasing the guest concentration), the T_1 decreased more sharply in the presence of graft **6** than

Table III. T_1 Values of Benzoic Acid (**11**) or n-Pentylbenzene (**12**) in the Presence of Various Amphiphilic Poly(vinyl ethers)[a]

COOH $(CH_2)_4CH_3$

11   **12**

Code	Polymer Structure	$\overline{DP}_n$ (obsd)[b] m/n	f^c	T_1(s) 11	T_1(s) 12
	no polymer			3.84	4.81
10 (linear block)	(HOVE)$_m$-(IBVE)$_n$	5/15.4	—	2.13	4.88
6 (graft)	(HOVE)$_m$-(IBVE)$_n$—⟩	5/15.4	6	1.90	4.44
9 (star)	(HOVE)$_m$-(IBVE)$_n$-(core)	5/15.5	7	2.38	4.82

[a] The T_1 values for the asterisked carbon of **11** or **12** in $CDCl_3$ at 30°C; [guest]/[OH in polymer] = 2.0.

[b] The segment compositions are the observed values before hydrolysis determined by ^1H-NMR: see text and Reference 3. For **6** and **9**, the m/n values (in $\overline{DP}_n$) are for each branch or arm.

[b] The number of branches (arms) per molecule determined by light scattering.
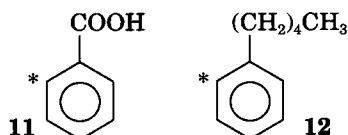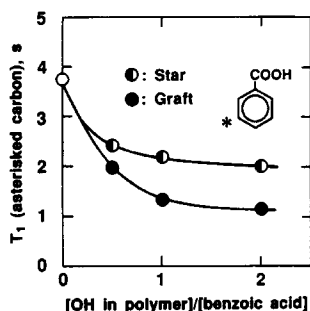
Figure 6. ^{13}C-NMR spin-lattice relaxation times (T_1) for the m-carbons of benzoic acid (**11**) in the presence of graft (**6**) and star (**9**) amphiphilic polymers as a function of [OH in **6** or **9**]/[benzoic acid] in CDCl$_3$ at 30°C: [OH in **6** or **9**] = 0.15 M.

in the presence of star **9**, and the difference in T_1 became much larger at a higher [OH in polymer]/[guest] ratio. The absence of the central core would lead to the higher accumulation of the hydroxyl groups per molecule, and hence the guest molecules' release from captivity may be suppressed.

In conclusion, we demonstrated that, on the basis of the living cationic polymerization (Scheme 1), the amphiphilic graft polymers (**6**) of vinyl ethers with the definite structure and the predetermined arm number can be synthesized, where each branch consists of a hydrophilic polyalcohol and a hydrophobic poly(IBVE) segment. In terms of solubility and the host–guest interaction with small organic molecules, these polymers clearly differ from the corresponding star block and linear amphiphiles.

EXPERIMENTAL

Materials

AcOVE[18] and VOEM[19] were prepared by the reaction of 2-chloroethyl vinyl ether with sodium acetate and sodio malonic ester, respectively. This monomer and commercial IBVE were purified by double distillation over calcium hydride before use. The stock solution (ca. 200 mM) of VOEM anion **3** was obtained by treating VOEM with sodium hydride in a 1,4-dioxane/toluene mixture [1 : 1 (v/v)] as reported previously.[11,19] 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.[20] The solution was sealed in brown ampoules 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 dry-

box and dissolved in dry and distilled diethyl ether just before use. Toluene (polymerization solvent) was washed by the usual methods[20] and distilled over calcium hydride at least twice before use. Diethyl ether (anhydrous, Wako Chemicals) was distilled over LiAlH$_4$ before use.

Synthesis of Macromonomer 4

Sequential block copolymerization of AcOVE and IBVE was carried out with HI/ZnI$_2$ in toluene at −15°C under dry nitrogen in a baked flask equipped with a three-way stopcock.[20] After the polymerization had reached ca. 100% conversion, a solution of **3** (two-fold molar excess over the living end) in a 1,4-dioxane/toluene mixture was added. 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 macromonomer **4**.

Polymerization of Macromonomer 4

Polymerization of macromonomer **4** was carried out with HI/ZnI$_2$ in toluene at −15°C under dry nitrogen in a baked flask equipped with a three-way stopcock.[20] The reactions were run under magnetically stirring for a sufficiently long time until the reaction mixtures turned light yellow, which was attributed to the decay reaction of the living end in the absence of monomers. The product polymers were recovered from the quenched reaction mixtures as mentioned in the previous section.

Hydrolysis of Polymer 5 into Amphiphilic Form 6

A sample of polymer **5** (0.6–1.0 g) 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 2–3 days, and the solvent was removed by evaporation. The hydrolyzed polymers were dissolved in chloroform and washed with water at least three times, and then the solvent was removed by evaporation. These purified samples were finally vacuum dried overnight to give polymer **6**.

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 an Otsuka Electronics SLS-600R photometer (λ = 633 nm, an-

gle = 30–150°, three-concentration measurements, $c = 1 \times 10^{-3}$–2×10^{-3} g/mL). The refractive index increment (dn/dc) was measured in ethyl acetate at 25°C on an Otsuka Electronics DRM-1020 double beam differential refractometer ($\lambda = 633$ nm, three-point measurements, $c = 2 \times 10^{-3}$–8×10^{-3} g/mL). The dn/dc values of **4** (AcOVE/IBVE = 5/15) was 8.524×10^{-2} mL/g. On the basis of the $\bar{M}_w$(graft) value, the number (f) of the branches was calculated from the following relation:

$$f = \bar{M}_w(\text{graft})/\bar{M}_w(\text{branch})$$

where $\bar{M}_w$(branch) is the weight-average molecular weight of the repeat unit (identical with **3**), which is assumed to be equal to the number-average molecular weight [$\bar{M}_n$(branch)] of **3**, based on the feed ratio of AcOVE, IBVE, and HI.[3] The arm number of the star-shaped block polymer **8** was calculated from the relation reported previously.[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, 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. ^{1}H- 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.[7,21]

REFERENCES AND NOTES

1. For reviews, see: (a) B. J. Bauer and L. J. Fetters, *Rubber Chem. Technol.*, **51**, 406 (1978); (b) S. Bywater, *Adv. Polym. Sci.*, **30**, 90 (1979).
2. For a review, see: D. A. Tomalia, A. M. Naylor, and W. A. Goddard III, *Angew. Chem. Int. Ed. Engl.*, **29**, 138 (1990).
3. Part II of this series: S. Kanaoka, M. Sawamoto, and T. Higashimura, *Macromolecules*, **24**, 5741 (1991).
4. Part VI of this series: S. Kanaoka, M. Sawamoto, and T. Higashimura, *Makromol. Chem.*, in press.
5. Part III of this series: S. Kanaoka, T. Omura, M. Sawamoto, and T. Higashimura, *Macromolecules*, **25**, 6407 (1992).
6. Part V of this series: S. Kanaoka, M. Sawamoto, and T. Higashimura, *Macromolecules*, **26**, 254 (1993).
7. Part IV of this series: S. Kanaoka, M. Sawamoto, and T. Higashimura, *Macromolecules*, **25**, 6414 (1992).
8. Part I of this series: S. Kanaoka, M. Sawamoto, and T. Higashimura, *Macromolecules*, **24**, 2309 (1991).
9. (a) J. G. Zilliox, P. Rempp, and J. Parrod, *J. Polym. Sci. C*, **22**, 145 (1968); (b) D. J. Worsfold, J. G. Zilliox, and P. Rempp, *Can. J. Chem.*, **47**, 3379 (1969).
10. For a review, see: P. Rempp and E. Franta, *Adv. Polym. Sci.*, **58**, 1 (1984).
11. M. Sawamoto, T. Enoki, and T. Higashimura, *Polym. Bull. (Berlin)*, **16**, 117 (1986).
12. BF$_3$OEt$_2$ in conjunction with a small amount of adventitious water initiates cationic polymerization of vinyl monomers such as vinyl ethers and styrene. However, with the smaller concentration of BF$_3$OEt$_2$ (below 5 mM), cationic polymerization can be hardly induced under our reaction conditions.
13. The homopolymerization of **4** was run for a sufficiently long time until the reaction mixture turns light yellow which was attributed to the decay reaction of the living end in the absence of monomers; see: (a) S. Aoshima and T. Higashimura, *Polym. J.*, **16**, 249 (1984); (b) W. O. Choi, M. Sawamoto, and T. Higashimura, *Macromolecules*, **23**, 48 (1990).
14. The ^{1}H-NMR peak intensity ratio indicates that 87% of the ester groups remained unreacted. As previously reported,[5] the restriction of the VOEM units in motion may lead to the broadening and decrease in intensity of the peak from which the amount of the VOEM units per molecule is estimated. These results indicate that almost all the ester functions of the VOEM units in **5** may remain unreacted under our hydrolysis conditions.
15. G. C. Berry and T. A. Orofino, *J. Chem. Phys.*, **40**, 1614 (1964).
16. F. M. Menger and J. M. Jerkunica, *J. Am. Chem. Soc.*, **100**, 688 (1978).
17. A. M. Naylor, W. A. Goddard III, G. E. Kiefer, and D. A. Tomalia, *J. Am. Chem. Soc.*, **111**, 2339 (1989).
18. S. Aoshima, T. Nakamura, N. Uesugi, M. Sawamoto, and T. Higashimura, *Macromolecules*, **18**, 2097 (1985).
19. (a) M. Sawamoto, T. Enoki, and T. Higashimura, *Macromolecules*, **20**, 1 (1987); (b) T. Higashimura, T. Enoki, and M. Sawamoto, *Polym. J.*, **19**, 515 (1987).
20. M. Miyamoto, M. Sawamoto, and T. Higashimura, *Macromolecules*, **17**, 265, 2228 (1984).
21. In all cases, magnetization recoveries showed an excellent and reproducible single exponential. For example, when plotted against time in the range from msec to sec, the natural logarithmic magnetization data showed variance from linearity only below 3×10^{-3}. This also indicates that benzoic acid molecules exchange rapidly between the free and the complexed states.