**Polymer Bulletin**

# Tri-armed star polymers by living cationic polymerization

## 2. Synthesis of tri-armed amphiphilic block copolymers of isobutyl and 2-hydroxyethyl vinyl ethers*

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SUMMARY

Tri-armed amphiphilic block polymers ($\underset{\sim}{5}$ and $\underset{\sim}{6}$) of isobutyl and 2-hydroxyethyl vinyl ethers (IBVE and HOVE, respectively) were prepared. The synthesis was based on the sequential living cationic polymerization of IBVE and 2-acetoxyethyl vinyl ether (AcOVE) initiated with a trifunctional initiating system that consisted of a tris(trifluoroacetate) [$CH_3-C(C_6H_4OCH_2CH_2OCHMeOCOCF_3)_3$; $\underset{\sim}{1}$] and ethylaluminum dichloride (EtAlCl$_2$) coupled with an excess of 1,4-dioxane as a carbocation-stabilizing Lewis base. The subsequent hydrolysis of the ester pendant groups in the resulting poly(AcOVE) segments led to the target IBVE-HOVE amphiphilic tri-armed polymers. Depending on the polymerization sequence of IBVE and AcOVE, the hydrophilic poly(HOVE) chain could be placed either inner or outer segment of the tri-armed architecture. The solubility of these polymers ($\underset{\sim}{5}$ and $\underset{\sim}{6}$) was apparently determined by the nature of the outer segments.

INTRODUCTION

Quite recently, we have developed a trifunctional initiating system, consisting of a tris(trifluoroacetate) ($\underset{\sim}{1}$) and ethylaluminum dichloride (EtAlCl$_2$), that induces living cationic polymerization of isobutyl vinyl ether (IBVE) in the presence of 1,4-dioxane at relatively high temperatures up to +40°C (1). The initiator $\underset{\sim}{1}$ is derived from the corresponding trifunctional vinyl ether and, with aid of EtAlCl$_2$, each of the three vinyl ether-derived trifluoroacetate groups of $\underset{\sim}{1}$ initiates polymerization of IBVE to generate a trifunctional living polymer $\underset{\sim}{2}$ (eq. 1) where the active cationic site is stabilized by the added 1,4-dioxane as a mild base. The product is a tri-armed poly(IBVE) that is featured by the uniformity in length of three arm chains, in addition to a controlled overall molecular weight and a very narrow molecular weight distribution (MWD).
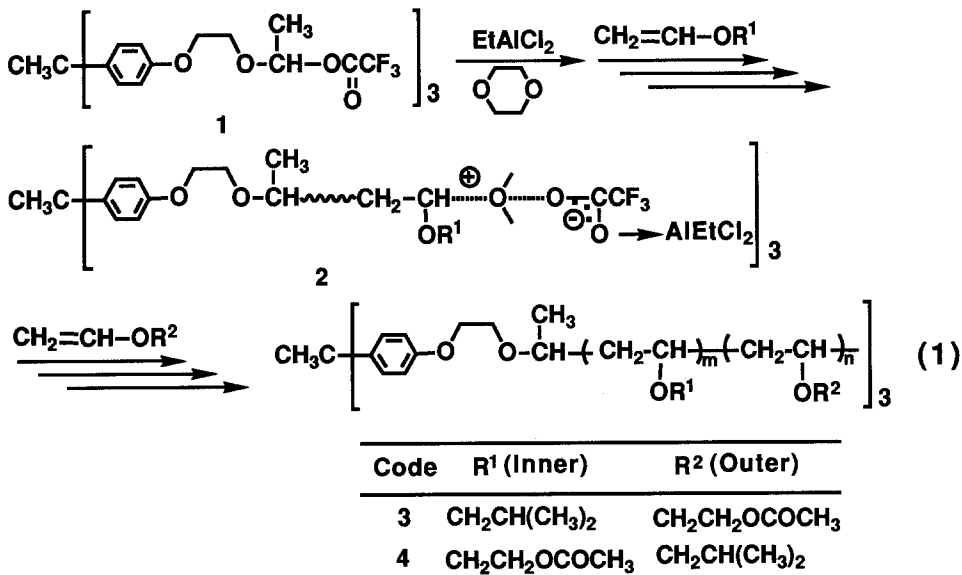


$\underset{\sim}{1}$
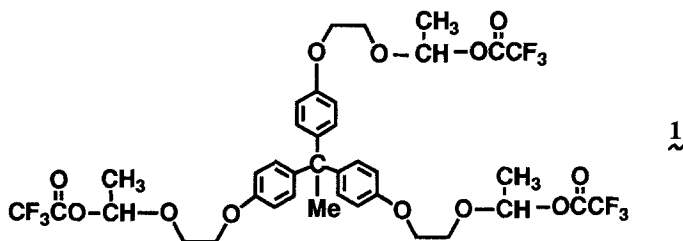
In this paper, we report the application of the $\underset{\sim}{1}$/EtAlCl$_2$/1,4-dioxane system to sequential living cationic polymerization of IBVE and an ester-

$$CH_3C\left[\underset{}{\bigcirc}-O\diagdown\diagup O-\overset{CH_3}{\underset{}{CH}}-O\underset{O}{\overset{\|}{C}}CF_3\right]_3 \xrightarrow[\underset{O\diagup\diagdown O}{EtAlCl_2}]{} \xrightarrow{CH_2=CH-OR^1} \Longrightarrow$$

**1**

$$CH_3C\left[\underset{}{\bigcirc}-O\diagdown\diagup O-\overset{CH_3}{\underset{}{CH}}\text{www}CH_2-\overset{\oplus}{\underset{OR^1}{CH}}\cdots O\diagup\diagdown\cdots O\overset{\ominus}{\underset{O\rightarrow AlEtCl_2}{\overset{\overline{}}{C}}}CF_3\right]_3$$

**2**

$$\xrightarrow{CH_2=CH-OR^2} CH_3C\left[\underset{}{\bigcirc}-O\diagdown\diagup O-\overset{CH_3}{\underset{}{CH}}\left(CH_2-\underset{OR^1}{CH}\right)_{\!\!m}\!\!\left(CH_2-\underset{OR^2}{CH}\right)_{\!\!n}\right]_3 \quad (1)$$

| Code | $R^1$ (Inner) | $R^2$ (Outer) |
|------|------|------|
| 3 | $CH_2CH(CH_3)_2$ | $CH_2CH_2OCOCH_3$ |
| 4 | $CH_2CH_2OCOCH_3$ | $CH_2CH(CH_3)_2$ |

functionalized vinyl ether [2-acetoxyethyl vinyl ether (AcOVE)] (eq. 1), which was directed to the synthesis of novel tri-armed amphihpilic block copolymers of IBVE (hydrophobic) and 2-hydroxyethyl vinyl ether (hydrophilic), the latter being derived from hydrolysis of the AcOVE segment. Such tri-armed block polymers with polar functional groups have not been obtained in cationic polymerization yet.
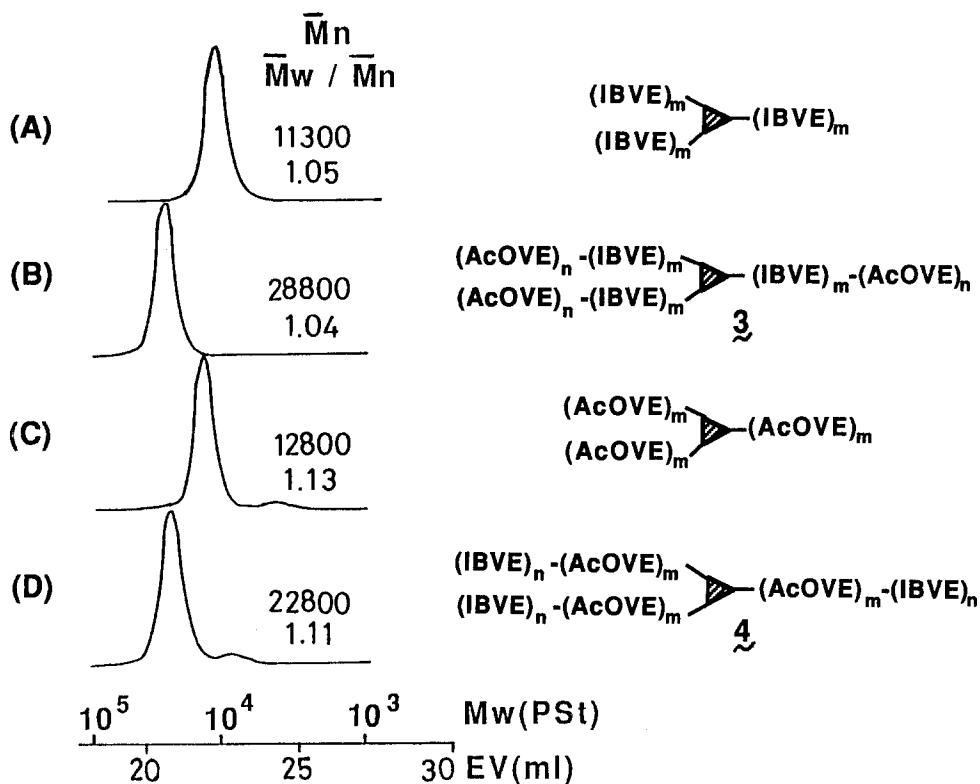
## RESULTS AND DISCUSSION

### Block Polymerization

With use of the $\underset{\sim}{1}$/EtAlCl$_2$ trifunctional initiating system, sequential living polymerization of IBVE and AcOVE was examined (eq. 1), starting either with IBVE (for $\underset{\sim}{3}$) or with AcOVE (for $\underset{\sim}{4}$). For example, in the presence of 1,4-dioxane, IBVE was first polymerized in toluene at 0°C with $\underset{\sim}{1}$/EtAlCl$_2$ (1). The polymerization reached quantitative monomer conversion in 6 min. To the solution of the resulting tri-armed living polymer ($\underset{\sim}{2}$), AcOVE was added, and the temperature was raised to +40°C to accelerate the polymerization of AcOVE, which is less reactive than IBVE. The added AcOVE feed was polymerized completely in 3 h.

The reverse order of monomer addition, i.e., from AcOVE to IBVE, was also examined. Thus, AcOVE was first polymerized with $\underset{\sim}{1}$/EtAlCl$_2$ in the presence of 1,4-dioxane at +40°C. The polymerization was completed after 2 h, at which moment IBVE was added, and it was quantitatively polymerized in an additional 1 h at the same temperature. Figure 1 shows the MWD curves for the products of these two series of sequential polymerizations.

The first-stage polymerizations led to polymers of narrow MWDs ($\bar{M}w/\bar{M}n$ < 1.1), not only from IBVE as already reported (Fig. 1A) (1) but also from AcOVE (Fig. 1C). The MWDs obtained after the second monomer addition (Figs. 1B and 1D) were as narrow as those of the first-stage polymers and clearly shifted toward higher molecular weight without tailings in the regions

$$\overline{Mn}$$

$$\overline{Mw} / \overline{Mn}$$

**(A)**   11300
   1.05

(IBVE)$_m$ ▷—(IBVE)$_m$
(IBVE)$_m$

**(B)**   28800
   1.04

(AcOVE)$_n$-(IBVE)$_m$ ▷—(IBVE)$_m$-(AcOVE)$_n$
(AcOVE)$_n$-(IBVE)$_m$
**3**

**(C)**   12800
   1.13

(AcOVE)$_m$ ▷—(AcOVE)$_m$
(AcOVE)$_m$

**(D)**   22800
   1.11

(IBVE)$_n$-(AcOVE)$_m$ ▷—(AcOVE)$_m$-(IBVE)$_n$
(IBVE)$_n$-(AcOVE)$_m$
**4**

$10^5$     $10^4$     $10^3$   Mw(PSt)

20        25       30 EV(ml)

Figure 1. MWD of tri-armed homopolymers and block polymers of IBVE and AcOVE obtained by sequential living polymerization with $\underline{1}$/EtAlCl$_2$ at +40°C in toluene containing 1,4-dioxane: [IBVE]$_0$ = [AcOVE]$_0$ = 0.38 M; [$\underline{1}$]$_0$ = 3.5 mM; [EtAlCl$_2$]$_0$ = 10.0 mM; [1,4-dioxane] = 1.2 M (10 vol%); conversion = 100 % for all monomers. Samples and reaction times: (A) starting poly(IBVE), 6 min (at 0°C); (B) poly(IBVE-$\underline{b}$-AcOVE)($\underline{3}$) from sample A, 3 h after AcOVE addition; (C) starting poly(AcOVE), 2 h; (D) poly(AcOVE-$\underline{b}$-IBVE)($\underline{4}$) from sample C, 1 h after IBVE addition. ▷ shows the aromatic core derived from initiator $\underline{1}$ (see eq. 1).

where the starting polymers eluted. The MWD analysis thus suggests the formation of living polymers in all these sequential polymerizations (see below).

The structure and segment compositions of these block polymerization products were determined by ^{1}H NMR spectroscopy (Fig. 2 and 3). These samples are the same for those shown in Figure 1, and they were quenched with methanol, which is known to give a methoxide (acetal) terminal [∿∿CH$_2$CH(OR)-OCH$_3$] (1). For example, Figure 2 presents typical ^{1}H NMR spectra of the starting poly(IBVE) (Fig. 2A) and the product after the addition of AcOVE (Fig. 2B).

Figure 2A is completely consistent with the tri-armed poly(IBVE) derived from the initiator $\underline{1}$, showing, for instance, the absorptions of the pendant methyl groups (peak d) and the aromatic initiator residue (peak
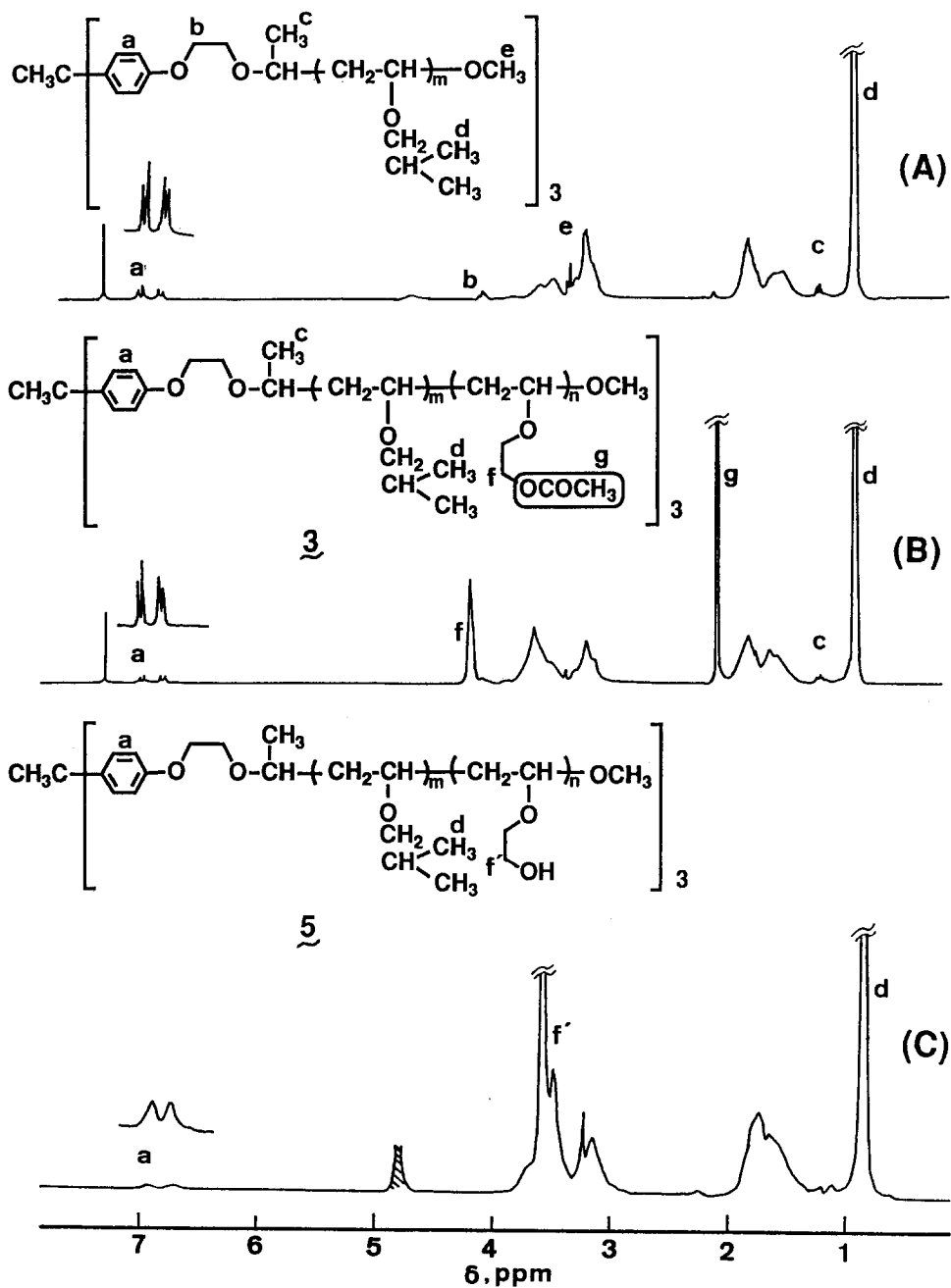
Figure 2. $^1$H NMR spectra in $CDCl_3$ (A and B) or $CD_3OD$ (C):
(A) tri-armed poly(IBVE);
(B) tri-armed poly(IBVE-b-AcOVE) 3 from sample A;
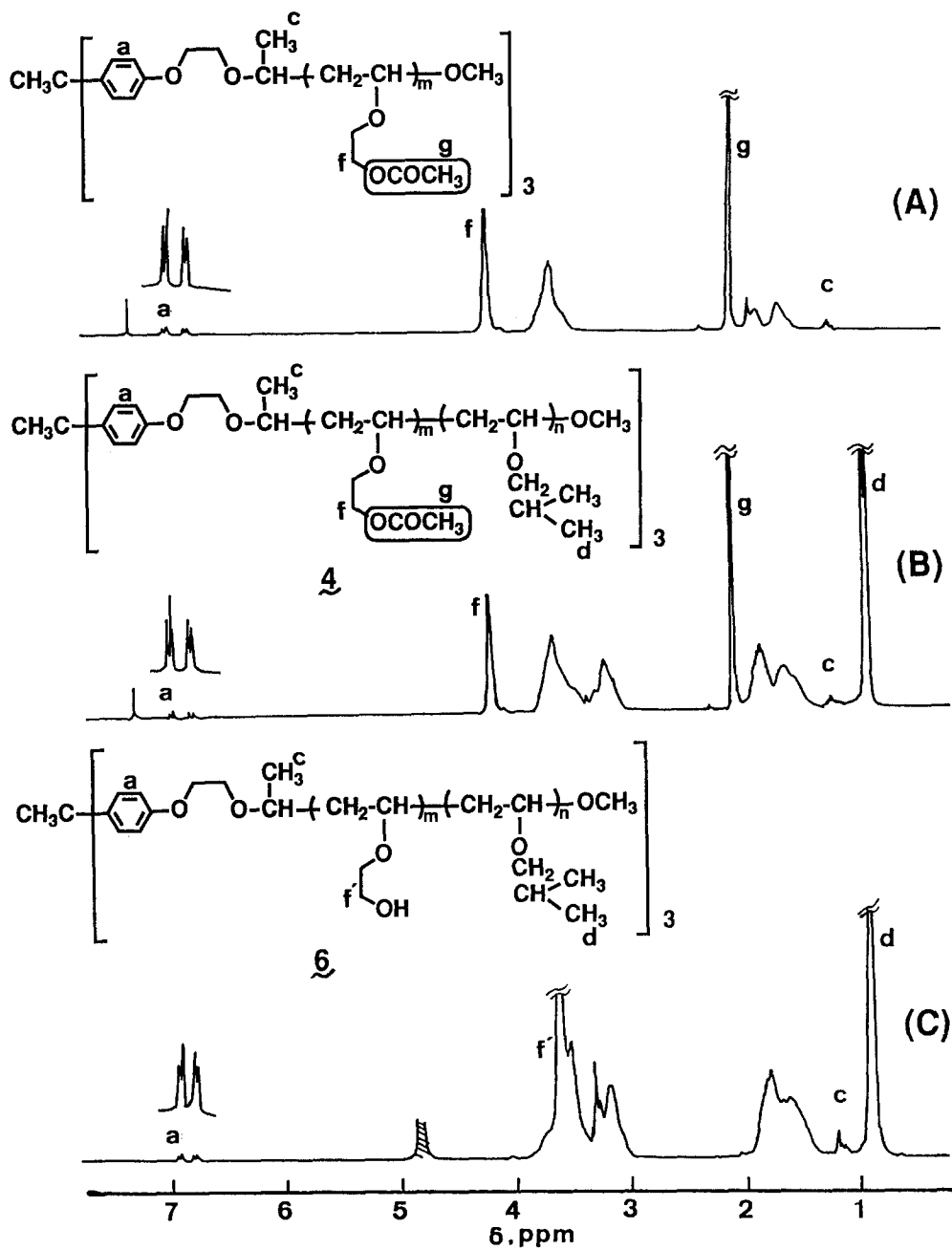(C) tri-armed poly(IBVE-b-HOVE) 5 from sample B after hydrolysis.

Figure 3. $^1$H NMR spectra in $CDCl_3$ (A and B) or $CD_3OD$ (C):
(A) tri-armed poly(AcOVE);
(B) tri-armed poly(AcOVE-b-IBVE) 4 from sample A;
(C) tri-armed poly(HOVE-b-IBVE) 6 from sample B after hydrolysis.

TABLE I
Tri-Armed Star Block Copolymers of IBVE and AcOVE via Sequential
Living Cationic Polymerization with $\underset{\sim}{1}$/EtAlCl$_2$[a]

| Code | Triarmed Polymer $\blacktriangleright$-(A-*b*-B)- [b] | Segment $\overline{DP}n$, A/B[b,c] | |
|------|------|------|------|
| | | calcd[d] | obsd[e] |
| | $\blacktriangleright$- IBVE | 38 | 36 |
| $\underset{\sim}{3}$ | $\blacktriangleright$- IBVE-AcOVE | 38/38 | 36/38 |
| | $\blacktriangleright$-AcOVE-IBVE | 38 | 35 |
| $\underset{\sim}{4}$ | $\blacktriangleright$- AcOVE | 38/38 | 35/34 |

a) See the caption of Figure $\underset{\sim}{1}$ for detailed reaction conditions.
b) A indicates the monomer that was first polymerized into a living polymer from which the second monomer B is polymerized; $\blacktriangleright$ shows the aromatic core derived from initiator $\underset{\sim}{1}$ (see eq. 1).
c) The number-average degree of polymerization ($\overline{DP}_n$) for each segment.
d) Calculated from the initial concentrations of the monomers and $\underset{\sim}{1}$: segment $\overline{DP}n$(calcd) = [M]$_0$/[$\underset{\sim}{1}$]$_0$.
e) By ^{1}H NMR spectroscopy; see text.


a)(1). In addition to these, the absoption of the acetoxy groups arising from AcOVE (peaks f and g) are seen in Figure 2B, confirming the structure expected for the tri-armed star block poly(IBVE-b-AcOVE) $\underset{\sim}{3}$.
    Very similar results were obtained for the samples prepared through the opposite polymerization sequence (AcOVE→IBVE) (Fig. 3A and 3B) and corroborated the formation of a tri-armed poly(AcOVE-b-IBVE) ($\underset{\sim}{4}$, eq. 1). The starting homopolymer of AcOVE (Fig. 3A), for example, exhibited a spectrum indicative of the tri-armed structure, as evidenced by peaks f and g for the pendant acetoxyethyl groups and peak a for the initiator aromatic protons. The second-stage polymerization of IBVE led to the spectrum shown in Figure 3B, which is almost identical to Figure 2B and shows the resonances of poly(IBVE) segment (e.g., peak d) in addition to those for the poly(AcOVE) segments.
    To demonstrate the formation of true AB-type tri-armed block copolymers ($\underset{\sim}{3}$ and $\underset{\sim}{4}$), the number-avarage degree of polymerization ($\overline{DP}_n$) of each segment was determined by ^{1}H NMR from the peak intensity ratio of the aromatic initiator residue (peak a; both Figs. 2 and 3) to the pendant resonance of the poly(IBVE) or poly(AcOVE) segments; the key pendant signals: the methyl protons of the isobutyl group (peak d; 0.9 ppm) for IBVE and the methylene protons associated with the acetate group (peak f; 4.2 ppm) for AcOVE. As Table I summarizes, the observed $\overline{DP}_n$ values were in good agreement with the calculated values based on the feed molar ratios of IBVE or AcOVE to the initiator $\underset{\sim}{1}$. The spectral analysis thus confirmed the formation of the desired tri-armed AB block copolymers of IBVE and AcOVE in nearly perfect blocking efficiency. It should also be important that living cationic polymerization with $\underset{\sim}{1}$/EtAlCl$_2$ (+ 1,4-dioxane) is now feasible for AcOVE, an ester functionalized polar vinyl ether.


**Amphiphilic Block Copolymers**
    The acetate groups of the tri-armed IBVE-AcOVE block copolymers $\underset{\sim}{3}$ and $\underset{\sim}{4}$ were then hydrolyzed to give amphiphilic tri-armed star block polymers $\underset{\sim}{5}$ and $\underset{\sim}{6}$, respectively, carrying polyalcohol [poly(HOVE)] segments derived from AcOVE. Note that polymers $\underset{\sim}{5}$ and $\underset{\sim}{6}$ are the same in segment $\overline{DP}_n$ and composition (IBVE/HOVE = 38/38 in $\overline{DP}n$) but are opposite in segment

arrangement; the polyalcohol hydrophilic segments are located outside the molecules in 5, whereas inside in 6 (see schematic illustrations below where [▬▬] and ∿∿∿∿ show the hydrophilic poly(HOVE) and the hydrophobic poly(IBVE) segments, respectively):



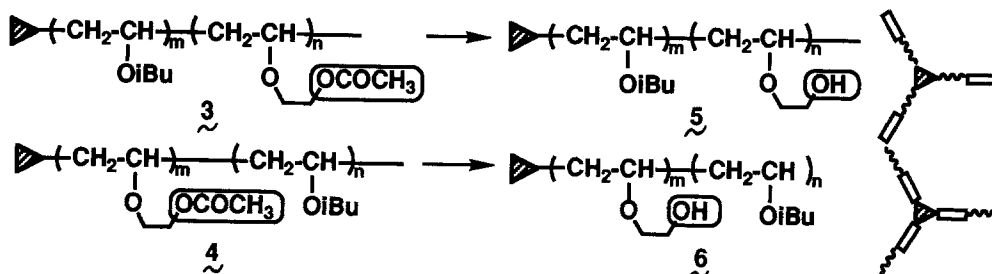Figure 2C illustrates the ^{1}H NMR spectrum (in $CD_3OD$) of the hydrolysis product obtained from 3 [with outer poly(AcOVE) chains; Fig. 2B]. Comparison between spectra 2B and 2C shows the complete conversion of the pendant acetoxy group into the corresponding alcohol. For example, signals f and g in Figure 2B, associated with the acetoxy group, are absent in Figure 2C, where the methylene protons due to the alcohol group are in turn seen around 3.6 ppm (peak f'). The spectral analysis shows the formation of the new amphiphilic tri-armed block copolymer (5) with outer polyalcohol segments. In a similar manner, as Figure 3C illustrates, the hydrolysis of 4 led to another tri-armed amphiphile 6 with inner polyalcohol segments (Fig. 3B and 3C). Interestingly, the aromatic protons' signals of the initiator core (peak a; 6.6-7.0 ppm) were clearly broader for 5 (with outer polyalcohol; Fig. 2C) than for 6 (with inner polyalcohol; Fig. 3C), probably because, the hydrophobic inner poly(IBVE) segments in 5, to which the aromatic core is attached, shrink in relatively polar $CD_3OD$ solvent and thereby restrict the thermal movement of the core.

## Solubility Characteristics

Table II summarizes the solubility characteristics of the tri-armed block polymers obtained in this study. First, the four AcOVE-based polymers B-E are all soluble in toluene but insoluble in water, whereas their hydrolysis products (HOVE-based polymers, F-I) are more polar, as expected, now insoluble in toluene and n-hexane but soluble or swellable in water. These trends are fully consistent with the transformation of the poly(AcOVE) segments into more polar poly(HOVE) counterparts.

As seen in the first group (B-D), moreover, the overall solubility characteristics of the tri-armed block polymers (C and D) appear to be governed primarily by the nature of the outer segments. Thus, sample C is the same in solubility as homopoly(AcOVE) (B), and sample D as homopoly(IBVE) (A). The corresponding linear analog (E), however, has intermediate solubility properties between C and D. It is equally interesting that even moving the modelately polar AcOVE segment from the inner (D) to the outer (C) region of the tri-armed architecture renders sample C insoluble in n-hexane and ethanol, which are good solvents for sample D.

In contrast, the HOVE-based polymers (F-I) are more or less similar in solubility, regardless of the placement of the polar polyalcohol segments (G vs. H) or even of the presence and absence of the nonpolar poly(IBVE) part (F vs. G and H). However, the poly(HOVE) segment in the outer region (G) indeed increased the solubility in water and ethanol, where the inner-alcohol version (H) just swells but remains not totally soluble.

TABLE II
Solubility of Tri-Armed Star Poly(vinyl Ethers)[a,b]

| Entry | Shape | Inner/Outer | toluene | hexane | ethanol | methanol | $H_2O$ |
|-------|-------|-------------|---------|--------|---------|----------|--------|
| A | Tri-armed | IBVE | O | O | O | X | X |
| B | " | AcOVE | O | X | X | O | X |
| C | " | IBVE/AcOVE (3) | O | X | X | O | X |
| D | " | AcOVE/IBVE (4) | O | O | O | X | X |
| E | Linear | AcOVE/IBVE | O | O | O | O | X |
| F | Tri-armed | HOVE | X | X | O | O | O |
| G | " | IBVE/HOVE (5) | X | X | O | O | O |
| H | " | HOVE/IBVE (6) | X | X | △ | O | △ |
| I | Linear | HOVE/IBVE | X | X | △ | O | △ |

a) O ,soluble; △ ,swelling; X ,insoluble. At room temperature ca. 0.5 wt%. $\overline{M}w/\overline{M}n < 1.1$ for all samples.
b) The calculated values for respective segments. $\overline{DP}_n$ is invariably 38 for each arm segment; e.g., sample A consists of three homopoly(IBVE) arms each with 38 IBVE units; sample C carries three AB block arms, each with 38 IBVE and 38 AcOVE units.

EXPERIMENTAL
    The syntheses of initiator 1 (1) and AcOVE (2) have already been described. IBVE, toluene, 1,4-dioxane, and $EtAlCl_2$ were employed as reported (3). Block polymerizations of IBVE and AcOVE were carried out under dry nitrogen (1) by sequential addition of solutions of 1 (in toluene; 0.50 mL) and $EtAlCl_2$ (in n-hexane; 0.50 mL) into a mixture of the first monomer and 1,4-dioxane (0.50 mL; 1.2 M; 10 vol%) in toluene (3.50 mL). Immediately before the end of the first-stage polymerization, the second monomer in bulk was added to the reaction mixture; see the caption for Firure 1 for reaction times, reagent concentrations, etc. After the complete consumption of the second monomer, the polymerization was terminated with prechilled methanol (2.0 mL) containing a small amount of ammonia. The alkaline hydrolysis of the block polymers was carried out as reported (2,4).

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