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Block Copolymers of 2-Hydroxyethyl Vinyl Ether and Alkyl Vinyl Ether by Living Cationic Polymerization: New Nonionic Macromolecular Amphiphiles

Masahiko Minoda, Mitsuo Sawamoto, and Toshinobu Higashimura*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan.

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ABSTRACT: Amphiphilic block polymers of vinyl ethers (VEs) $-[CH_2CH(OCH_2CH_2OH)]_m-[CH_2CH(OR)]_n-$ (R = n-$C_{16}H_{33}$, i-C_8H_{17}, n-C_4H_9; m = 20–100, n = 1–10) were prepared, which consist of a water-soluble polyalcohol segment and a hydrophobic poly(alkyl VE) segment. Their precursors $-[CH_2CH(OCH_2CH_2OCOR')]_m-[CH_2CH(OR)]_n-$ (R′ = CH_3, C_6H_5) were obtained from an ester-containing VE ($CH_2{=}CHOCH_2CH_2OCOR'$) and an alkyl VE by living cationic processes initiated by a mixture of hydrogen iodide and iodine. Alkaline hydrolysis of the ester pendants of the precursor block gave the target polymer amphiphiles. These block polymers remarkably lowered the surface tension of their aqueous solutions and the interfacial tension of the water/toluene interface. For example, the surface tension became minimum (<30 dyn/cm; 25 °C) when the number of total carbon atoms in the alkyl VE chain was 20–30 and $m \cong 40$.

Introduction

Block copolymers consisting of hydrophilic and hydrophobic segments are of interest as amphiphilic materials. Naturally occurring amphiphilic polymers and oligomers have a well-defined structure and a definite molecular weight that endow them with specific functions in vivo. In contrast, few of their synthetic counterparts possess such a controlled structure and molecular weight distribution (MWD), because of the difficulties in regulating these factors in the usual polymer syntheses except for those by a cumbersome stepwise process.

Living polymerization is one of the most useful methods to control the structure and molecular weight of polymers. Recently we found living cationic polymerizations of vinyl ethers (VEs) initiated by the hydrogen iodide/iodine (HI/I_2) initiating system where polymers having a very narrow MWD are readily prepared.[1] The VEs applicable to these living processes include not only alkyl derivatives ($CH_2{=}CHOR_1$, R_1 = alkyl)[2,3] but also those having a pendant ester group, e.g., 2-acetoxyethyl vinyl ether (AcOVE, $CH_2{=}CHOCH_2CH_2OCOCH_3$)[4] and 2-(benzoyloxy)ethyl vinyl ether (BzOVE, $CH_2{=}CHOCH_2CH_2OCOC_6H_5$).[5] The latter two are particularly important in that the hydrolysis of their polymers leads to poly(2-hydroxyethyl vinyl ether) (poly(HOVE), $-[CH_2CH(OCH_2CH_2OH)]_m-$), a water soluble polymer with controlled molecular weight and narrow MWD.[4]

An important application of living processes is the synthesis of block copolymers by sequential polymerization of two (or more) monomers.[1c] The living polymerizations of AcOVE and BzOVE offer a way to incorporate a hydrophilic (water-soluble) segment into block copolymers. Specifically, sequential living polymerization of AcOVE or BzOVE and a hydrophobic alkyl VE, followed by hydrolysis of the ester pendants, will give amphiphilic AB block copolymers. Thanks to the living nature of each blocking step, one can control the length (or compositions) of both hydrophilic and hydrophobic segments, achieve a narrow MWD, and thereby clarify the relationships between the structure of the amphiphilic block polymers and their properties (e.g., surface activity).

Despite these expected advantages, however, block copolymerizations involving an ester-containing VE as a comonomer have not been investigated yet. Currently available amphiphilic block polymers with a controlled molecular weight by living polymerization include ethylene oxide–propylene oxide ABA triblock copolymers (commercially available as Pluronics, etc.)[6] and oxazoline copolymers;[7] as vinyl-type polymeric amphiphiles, only di- and triblock polymers of methyl VE and cetyl VE were prepared by us.[8] Although apparently amphiphilic, the hitherto obtained samples of the methyl VE–cetyl VE block polymers were insoluble in water, and thus their surface activity could not be determined.

This study aims (i) to synthesize, by the HI/I_2-initiated living polymerization, amphiphilic block polymers that consist of hydrophilic poly(HOVE) and hydrophobic poly(alkyl VE) segments with definite molecular weights and structures (see eq 1 and 2 below) and (ii) to determine

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Table I
Block Copolymers 1 and 2 Obtained from AcOVE and Alkyl VE by Sequential Living Polymerization (Eq 1)

R_1	unit ratio,[a] m/n	content, mol %[a] 1 AcOVE/alkyl VE	2 HOVE/alkyl VE	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	$\gamma_{W/A}$,[c] dyn/cm
C_{16}	95/8	92/8	96/4	7100	1.64	42.2
C_{16}	40/7	85/15	96/4	5300	1.29	38.5
C_{16}	40/3	92/8	95/5	5600	1.33	33.0
C_{16}	40/2	96/4	97/3	6100	1.31	29.0
C_8	44/8	84/16	77/23	5700	1.20	33.9
C_8	44/5	89/11	85/15	5700	1.18	31.0
C_8	44/3	94/6	90/10	5600	1.21	30.2
C_8	44/1	97/3	96/4	5600	1.26	29.8
C_4	100/10	91/9	91/9	9300	1.51	31.2
C_4	42/9	82/8	84/16	5800	1.34	33.0
C_4	42/5	89/11	89/11	5900	1.33	31.8
C_4	42/2	96/4	97/3	5200	1.41	41.8

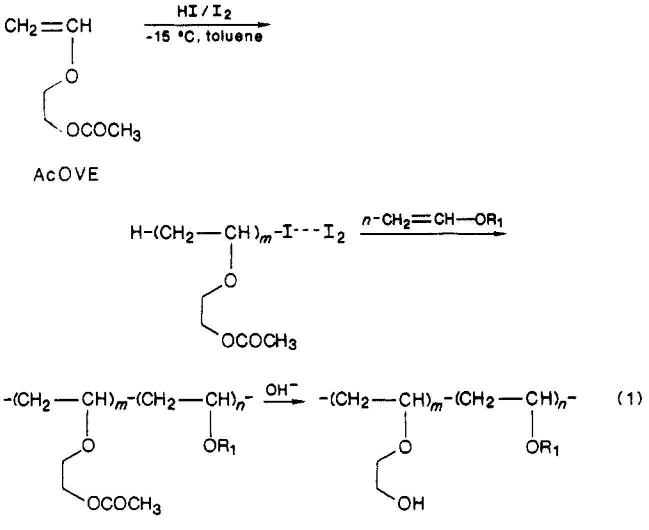
[a] Determined by ^1H NMR. [b] By SEC for 1; polystyrene calibration. [c] Surface tension of aqueous solution (0.1 wt %) at 25 °C; dyn/cm = 10^{-3} N/m.

their surface activity as a function of their segment molecular weight, their composition, and the nature of the hydrophobic alkyl pendant, all of which affect the balance of their hydrophilicity and hydrophobicity. As a hydrophilic segment, we selected poly(HOVE) because it is more hydrophilic than poly(methyl VE) and might give water-soluble amphiphilic block polymers. The surface activity was evaluated from the surface tension and the interfacial tension (with pure toluene) of aqueous solutions of the block copolymers.

Results and Discussion

1. Synthesis of Amphiphilic Polymers. We obtained amphiphilic polymers consisting of HOVE and hydrophobic alkyl VE segments by the following methods (eq 1 and 2).

Block Copolymerization. In this first method (eq 1), AcOVE and an alkyl VE ($CH_2{=}CHOR_1$) were sequentially polymerized by the HI/I_2 initiating system, which is known as an effective initiator for living polymerization of VEs.[1]



(1)

1 2

1a, 2a: $R_1 = n\text{-}C_{16}H_{33}$
1b, 2b: $R_1 = i\text{-}C_8H_{17}$
1c, 2c: $R_1 = n\text{-}C_4H_9$

The alkyl VEs employed were *n*-butyl, isooctyl, and *n*-hexadecyl derivatives (C_4VE, C_8VE, and $C_{16}VE$, respectively). Preliminary experiments showed that, for efficient block copolymerization, AcOVE should be polymerized first, followed by the addition of an alkyl VE; the reversed sequence (alkyl VE first, then AcOVE) did give block copolymers but the blocking efficiency was below 100%.

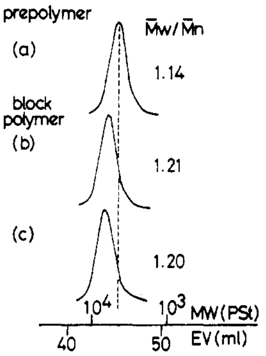


Figure 1. MWD of AcOVE–C_8VE block polymer **1b** and its precursor poly(AcOVE) obtained by the sequential polymerization of AcOVE and C_8VE (eq 1) with HI/I_2 in toluene at -15 °C: (a) starting poly(AcOVE), $[AcOVE]_0 = 0.44$ M, $[HI]_0 = 9.7$ mM, $[I_2]_0 = 10$ mM, conversion = 83%; (b, c) **1b** from sample a. AcOVE/C_8VE composition (unit ratio): (b) 44/3; (c) 44/8.

Thus, AcOVE was polymerized by HI/I_2 at -15 °C in toluene, and then one of the three alkyl VEs was polymerized from the resultant living propagating end to give AB block polymer 1. In a typical run ($[AcOVE]_0 = 0.44$ M, $[HI]_0 = 9.7$ mM, $[I_2]_0 = 10$ mM), the first-stage polymerization reached ca. 100% conversion in 1 h. On addition of C_8VE (AcOVE/C_8VE = 44/6 molar ratio) to this solution, a second-stage polymerization ensued and was completed in 6 h.

Figure 1 shows the MWDs of two samples of the blocking products (C_8VE as the alkyl VE) and their precursor poly(AcOVE). The poly(AcOVE) has a relatively narrow MWD ($\bar{M}_w/\bar{M}_n \sim 1.1$) (Figure 1a). After the addition of C_8VE, the MWD curve shifted toward higher molecular weight, while keeping its narrowness (Figure 1b,c), and no peak was observed in the region where the precursor polymer was eluted. Figure 1 thus indicates the quantitative formation of block polymer **1b**. Similar results were obtained for the block polymerizations using $C_{16}VE$ and C_4VE.

The molecular weight of block polymer 1 increased proportionally to the quantity of the added alkyl VEs and could be controlled by regulating the monomer-to-initiator (HI) feed ratio. The overall results of the block copolymerizations were summarized in Table I; see the following for further discussion.

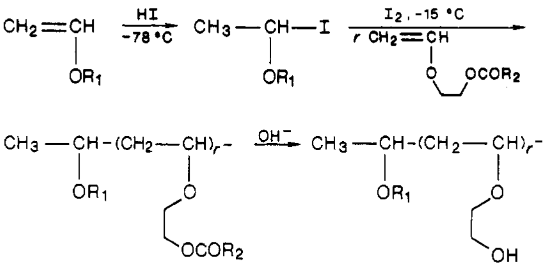
Synthesis of Copolymers with One Hydrophobic Unit. Although the segment composition of block polymer 1 was controllable by the AcOVE/alkyl VE feed ratio, it was rather difficult to attach exactly one hydrophobic VE

Table II
Copolymers 3 and 4 with One Hydrophobic Unit Obtained from Alkyl VE and BzOVE (Eq 2)

			content, mol %[a]				
R_1	r	alkyl VE unit[a]	3 BzOVE/alkyl VE	4 HOVE/alkyl VE	$\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[b]	$\gamma_{W/A}$,[c] dyn/cm
C_{16}	39	1.2	97/3	97/3	4800	1.15	42.0
C_{16}	20	1.0	95/5	93/7	3200	1.08	40.5
C_8	38	0.9	98/2	98/2	5200	1.10	49.0
C_8	19	0.9	95/5	93/7	3100	1.09	40.0
C_4	39	0.9	98/2	98/2	5300	1.16	55.5
C_4	20	0.9	95/5	90/10	3300	1.15	54.8

[a] Determined by ^{1}H NMR. [b] By SEC for 3; polystyrene calibration. [c] Surface tension of aqueous solution (0.1 wt %) at 25 °C; dyn/cm = 10^{-3} N/m.

unit to a poly(AcOVE) chain by the sequential living polymerization shown in eq 1. Since amphiphilic blocks with a very small lipophilic segment are of interest, we then adopted another approach (eq 2) to prepare copolymer 3 that carries exactly one alkyl VE unit attached to a poly(AcOVE) backbone. This method is based on the fact[9] that, in the HI/I_2-initiated living polymerization, the initial product is the 1:1 adduct [CH_3–CH(OR)–I] between HI and a VE, the carbon–iodine bond of which is then activated by coexisting iodine to initiate living propagation. The VE residue of the adduct is thus attached to the resulting polymer as the first (head) repeat unit. Thus, a hydrophobic alkyl VE (C_{16}VE, C_8VE, or C_4VE) was first treated with an equimolar amount of HI in toluene at −78 °C, and with resulting adduct as the initiator, AcOVE or BzOVE was polymerized at −15 °C in the presence of iodine. AcOVE and BzOVE were polymerized without an induction phase up to 100% conversion, as in the living polymerizations by HI/I_2 otherwise under the same conditions.[4,5]



(2)

3

4a: $R_1 = n\text{-}C_{16}H_{33}$
b: $R_1 = i\text{-}C_8H_{17}$
c: $R_1 = n\text{-}C_4H_9$

	R_1	R_2
3a	$n\text{-}C_{16}H_{33}$	CH_3
3b	$i\text{-}C_8H_{17}$	CH_3
3c	$n\text{-}C_4H_9$	CH_3
3a′	$n\text{-}C_{16}H_{33}$	C_6H_5
3b′	$i\text{-}C_8H_{17}$	C_6H_5
3c′	$n\text{-}C_4H_9$	C_6H_5

Figure 2 illustrates examples of the MWDs of copolymer 3b′ thus obtained from C_8VE and BzOVE; the degree of polymerization (DP) of the poly(BzOVE) part was ca. 40 or 20. Both MWDs are narrow ($\bar{M}_w/\bar{M}_n \sim 1.1$) and the molecular weight can be controlled by regulating the monomer-to-initiator (C_8VE–HI adduct) feed reatio. Polymers 3a′ and 3c′ were also obtained by using C_{16}VE and C_4VE as the alkyl VEs. Table II summarizes the composition data for 3a′–c′ determined by ^{1}H NMR spectroscopy. Independent of the kind of the alkyl VEs, the number of the alkyl VE unit per chain is close to one, indicating the formation of polymers 3a′–c′ with one hydrophobic VE unit at the chain end of poly(BzOVE).

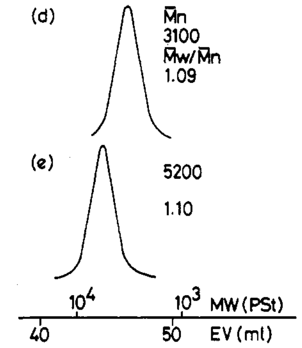


Figure 2. MWD of 3b′ obtained by reaction 2 in toluene at −15 °C: $[C_8VE]_0 = [HI]_0 = 10$ mM; $[I_2]_0 = 10$ mM. $[BzOVE]_0$: (d) 0.40 M; (e) 0.20 M.

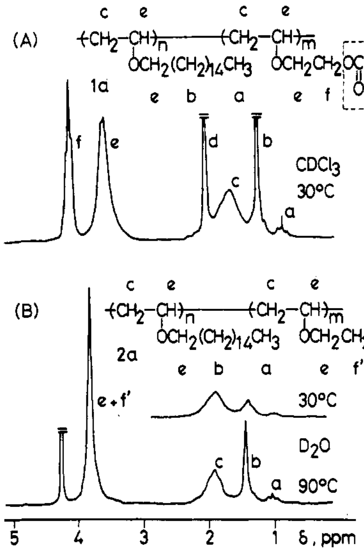


Figure 3. Hydrolysis of 1a (AcOVE/C_{16}VE = 40/3) monitored by ^{1}H NMR spectroscopy: (A) 1a in $CDCl_3$ at 30 °C; (B) hydrolysis product 2a from sample a in D_2O at 90 °C and 30 °C (inset).

Similarly, living polymerization of AcOVE according to eq 2 gave polymers 3a–c. Their MWD was somewhat broader ($\bar{M}_w/\bar{M}_n$ = 1.3–1.45) than that of the corresponding poly(BzOVE)-based polymers (3a′–c′); the number of the head alkyl VE units was slightly above unity (1.1–1.6).

Hydrolysis of Polymers 1 and 3. Block copolymers 1 and 3, differing in structure and composition, were thus prepared by the two methods discussed above. The pendant ester groups of these copolymers were then hydrolyzed into alcohols to give amphiphilic polymers 2 and 4, respectively (eq 1 and 2). The hydrolysis was carried out in an acetone/water mixture in the presence of sodium hydroxide (see Experimental Section).[4]

Figure 3 compares the ^{1}H NMR spectra of AcOVE–C_{16}VE block polymer 1a (in $CDCl_3$) and its hydrolysis product 2a (in D_2O). Comparison of both spectra confirmed that the AcOVE units were quantitatively con-

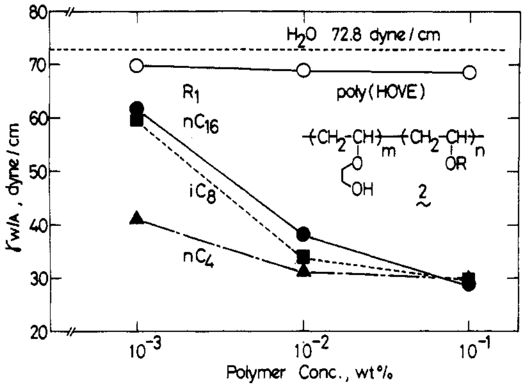


Figure 4. Relationships between the surface tension $\gamma_{W/A}$ of block polymers 2 and their concentrations in water at 25 °C; dyn/cm = 10^{-3} N/m. R_1 and composition (*m*/*n*): (●) *n*-$C_{16}H_{33}$, 40/2; (■) *i*-C_8H_{17}, 44/1; (▲) *n*-C_4H_9, 45/4; (○) poly(HOVE), *m* = 86.

verted to the HOVE units (-[$CH_2CH(OCH_2CH_2OH)]_m$-). For example, after the hydrolysis, the absorption of the pendant methoxyl group of the AcOVE unit (d, 2.1 ppm) completely disappeared, and that of the spacer methylene adjacent to the ester group (f, 4.2 ppm) shifted toward higher magnetic field (3.8 ppm), whereas the signals of the C_{16}VE unit [a, $(CH_2)_{14}CH_3$; b, $(CH_2)_{14}$] remained unchanged. Although the precursor block **1a** was insoluble in water, the hydrolysis product readily dissolved in it. These results support not only the quantitative hydrolysis of the ester pendants but also the efficient blocking of both segments of HOVE and C_{16}VE.

The ^{1}H NMR spectrum of the hydrolysis product **2a** in D_2O greatly changed with temperature, which also provided evidence for the successful hydrolysis of **1** into **2**. On going from 90 to 30 °C, the signals of the pendant alkyl group of the C_{16}VE unit (a and b, Figure 3B), which were strong and sharp at 90 °C, became smaller in intensity and broader (Figure 3B, inset), while no changes were observed in the shape and intensity of the other peaks. The broadening and decrease in intensity of the alkyl pendant peaks indicates that at 30 °C, amphiphilic polymer **2** forms micelles where the thermal movement of the alkyl groups is restricted by hydrophobic interaction.

Tables I and II list the molecular weights and the compositions of copolymers **1** and **3** and of their hydrolysis products **2** and **4**. The compositions were obtained from the integrated signal intensity ratio of the ^{1}H NMR spectra. The segment compositions before and after the hydrolysis are in fair agreement with each other. The discrepancies between them seen for some samples are most likely due to that the composition data by ^{1}H NMR are less accurate for the hydrolysis products than for their precursors; the NMR signal intensities of the former may not reflect exactly the segment composition, because they are affected by micelle formation (see above). In the following discussion, therefore, we adopted the values before the hydrolysis as the segment compositions of our amphiphilic copolymers.

2. Surface Activity of the Amphiphilic Block Polymers. Surface Tension. All of the amphiphilic polymers **2** and **4** thus prepared were completely soluble in water at room temperature. To evaluate their surface activity as amphiphiles, we determined the surface tension $\gamma_{W/A}$ of their aqueous solutions. The overall results are summarized in Tables I and II; selected data are discussed.

Figure 4 shows the $\gamma_{W/A}$ values for polymers **2a–c** as a function of their concentration in the range from 10^{-1} to 10^{-3} wt %. The DP of their poly(HOVE) segments was all ca. 40.

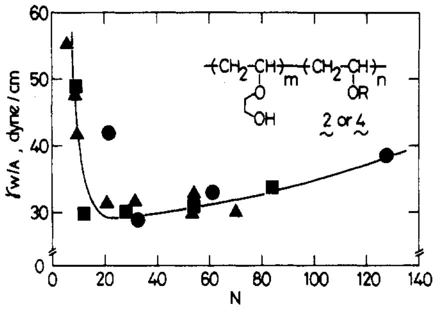


Figure 5. Surface tension $\gamma_{W/A}$ of aqueous solutions (0.1 wt %, 25 °C) of **2** and **4** as a function of *N*, the number of carbon atoms in the hydrophobic segment; dyn/cm = 10^{-3} N/m. R_1 (●) *n*-$16H_{33}$, (■) *i*-C_8H_{17}, (▲) *n*-C_4H_9; *m* ≅ 40, *n* = 1-10.

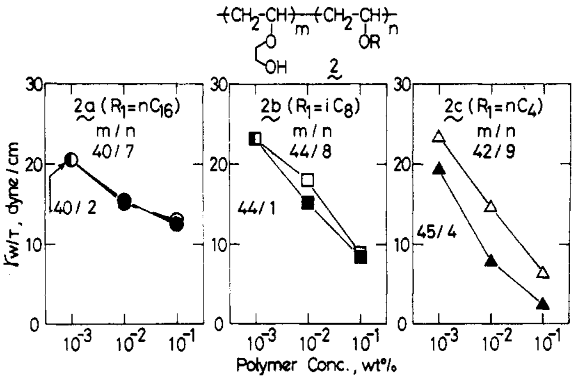


Figure 6. Relationships between the toluene/water interfacial tension $\gamma_{W/T}$ of block polymers **2** and their concentrations at 25 °C; dyn/cm = 10^{-3} N/m.

In contrast to the corresponding HOVE homopolymer, which induced little decrease in $\gamma_{W/A}$, block polymer **2** remarkably lowered the surface tension from 72.8 dyn/cm for pure water down to 30 dyn/cm or below at a concentration as low as 10^{-1} wt %; the extent of the $\gamma_{W/A}$ reduction was almost independent of the kind of the hydrophobic alkyl pendants in **2**. With all samples listed in Table I and II, low $\gamma_{W/A}$ values (29–55 dyn/cm) were obtained at 10^{-1} wt % concentration. Thus, the surface activity of HOVE–alkyl VE (block) copolymers **2** and **4** can compete with or exceed that of commercial nonionic macromolecular surfactants (e.g., Pluronics)[6] consisting of C, H, and O. The $\gamma_{W/A}$ values decreased with decreasing polymer concentration; no distinct critical micelle concentrations were observed, however, in the concentration range examined.

In Figure 5, the $\gamma_{W/A}$ values for polymers **2** and **4** (10^{-1} wt %; DP of the HOVE segment ≅40) are plotted as a function of *N*, the number of carbon atoms in the hydrophobic (alkyl VE) segments as a measure of the hydrophobicity of the copolymers. A single curve with a minimum at *N* = 20–30 was obtained for all samples, indicating that the surface activity of **2** and **4** is maximal in this region and almost independent of the kind of the alkyl pendants of the hydrophobic segments. Figure 5 also shows that the balance of hydrophobicity and hydrophilicity plays an important role in attaining the excellent surface activity of **2** and **4**.

Interfacial Tension. Another parameter to evaluate the surface activity of amphiphilic polymers is the interfacial tension between a aqueous polymer solution and a nonpolar organic solvent.[10] Thus, the water/toluene interfacial tension ($\gamma_{W/T}$) was measured for some samples of **2a–c** (cf. Table I) at 25 °C in the concentration range from 10^{-1} to 10^{-3} wt % (Figure 6). In each of the three pairs of **2a–c**, the DP of the HOVE segments is nearly the same ($\simeq$40), whereas that of the alkyl VE moiety is varied.

Block polymer **2** remarkably decreased $\gamma_{W/T}$ from 32 dyn/cm for the pure water/toluene interface to 5 dyn/cm at the lowest. The interfacial tension decreased with increasing polymer concentration; the minimal $\gamma_{W/T}$ values were in the order **2a** > **2b** > **2c**. Among these polymers, the lowest $\gamma_{W/T}$ value was obtained when **2c** has the HOVE/C_4VE ratio = 45/4. This sample has the most compact hydrophobic segment (the shortest (C_4) alkyl pendant and the smaller DP) that can be effectively and densely packed in the water/toluene interface. Thus, the excellent surface activity of our amphiphilic polymers was also shown by the $\gamma_{W/T}$ measurement.

Experimental Section

Materials. AcOVE and BzOVE were synthesized as described previously.[4,5] These monomers and commercial C_4VE, C_8VE, and C_{16}VE were purified by double distillation over calcium hydride before use (gas chromatographic purity >99%). Hydrogen iodide was obtained as an *n*-hexane solution from 57% aqueous solution by dehydration with phosphorus pentoxide.[2,3] Iodine was sublimed at 100 °C in the presence of potassium iodide. They were stored under dry nitrogen in ampules in the dark. Toluene as polymerization solvent was purified by the usual methods and distilled over calcium hydride at least twice before use.

Polymerization Procedures. Polymerization was carried out at −15 to −78 °C under dry nitrogen in a baked glass tube equipped with a three-way stopcock.[2,3] The reaction was terminated with prechilled ammoniacal methanol. The quenched reaction mixture was washed with aqueous sodium thiosulfate solution and then with water, evaporated to dryness under reduce pressure, and vacuum dried to give the product polymers (250–900 mg for each batch).

Hydrolysis of Copolymers 1 and 3. The hydrolysis of the pendant ester groups of **1** and **3** was carried out under basic conditions in an acetone/water mixture (1:1 v/v),[4] followed by the removal of sodium acetate or benzoate by dialysis (Spectra/Por 7, molecular weight cutoff 1000).

Measurements. The MWD of the polymers (**1** and **3**) was determined by size-exclusion chromatography (SEC) in chloroform on a Jasco Trirotar chromatograph equipped with polystyrene gel columns and ultraviolet/refractive index dual-mode detectors; the column set consisted of Shodex A-802 and A-804 (×2) (8.0-mm i.d. × 500 mm each). The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from SEC curves on the basis of a polystyrene calibration. ^{1}H NMR spectra were recorded on a Jeol FX-90Q spectrometer. The surface tension and the water/toluene interfacial tension of aqueous polymer solutions (10^{-1}–10^{-3} wt %) were measured at 25 °C on a Shimadzu ST-1 and a Shimadzu Du Nöuy tensiometer, respectively.

Acknowledgment. We thank Professor K. Nakamae and his co-workers of Kobe University for their helpful discussion and advice in the interfacial tension measurement.

Registry No. **1a** (block copolymer), 109088-94-0; **1b** (block copolymer), 109088-95-1; **1c** (block copolymer), 109088-96-2; **3a′** (block copolymer), 109088-97-3; **3b′** (block copolymer), 109088-98-4; **3c′** (block copolymer), 109088-99-5.

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