Macromolecules

Volume 23, Number 7 April 2, 1990

Amphiphilic Block Copolymers of Vinyl Ethers by Living Cationic Polymerization. 3. Anionic Macromolecular Amphiphiles with Pendant Carboxylate Anions[1]

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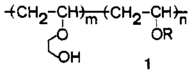
ABSTRACT: Anionic amphiphilic block polymers of vinyl ethers (VEs) $-[CH_2CH(OCH_2CH_2R')]_m-[CH_2CH(OR)]_n-$ ($R' = CH(COO^-Na^+)_2$, $CH_2COO^-Na^+$, CH_2COOH; $R = n\text{-}C_{16}H_{33}$, $i\text{-}C_8H_{17}$, $n\text{-}C_4H_9$; $m \cong 20$, $n = 1–17$) were prepared, in which the hydrophilic segment has pendant carboxylate anions or carboxylic acid groups and the hydrophobic segment has alkyl chains. Their precursors, $-[CH_2CH(OCH_2CH_2R'')]_m-[CH_2CH(OR)]_n-$ ($R'' = CH(COOEt)_2$), were obtained from a malonic ester containing VE ($CH_2{=}CHOCH_2CH_2CH(COOEt)_2$) and an alkyl VE by sequential living cationic polymerization initiated by a mixture of hydrogen iodide and iodine. Hydrolysis and decarboxylation of the malonic ester pendants of the precursors led to the target amphiphiles. These block polymers had excellent surface activity and lowered the surface tension of their aqueous solutions. For example, the highest surface activity was attained (minimum 25.8 dyn/cm; 1.0 wt %, 25 °C) when the number of total carbon atoms in the alkyl VE chain was 20–40 and $m \cong 20$ but independent of the kind of the hydrophilic group. The extent of the surface tension decrease was greatly affected by the structures and the combinations of the hydrophilic and the hydrophobic groups. The surface activity of these anionic amphiphiles was also compared with that of nonionic and cationic amphiphilic block polymers of VEs.

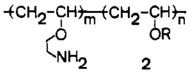
Introduction

Recently, we have synthesized a series of amphiphilic block polymers (**1**,[2] **2**,[3] and **3**[3]) by sequential living cationic polymerization of vinyl ethers (VEs) initiated by the hydrogen iodide/iodine (HI/I_2) system. The living process permitted us to control the molecular weight (or segment length), molecular weight distribution (MWD), and composition (m/n ratio) of **1**–**3**. Polymers **1** and **2** are nonionic amphiphiles that possess hydroxyl and primary amino groups, respectively, as hydrophilic function, whereas the protonated form **3** is a cationic analogue with ammonium substituents. Despite such structural differences, all these polymers exhibit excellent surface activity and lower the surface tension of their aqueous solutions (down to 30 dyn/cm or below) and the interfacial tension of the water/toluene interface.[2,3]



$-(CH_2-CH(OCH_2CH_2OH))_m-(CH_2-CH(OR))_n-$

1



$-(CH_2-CH(OCH_2CH_2NH_2))_m-(CH_2-CH(OR))_n-$

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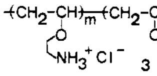

$-(CH_2-CH(OCH_2CH_2NH_3^+Cl^-))_m-(CH_2-CH(OR))_n-$

3

(R: $nC_{16}H_{33}$, iC_8H_{17}, nC_4H_9)

A recent study in our group showed that the HI/I_2 system induces living cationic polymerization of diethyl (2-(vinyloxy)ethyl)malonate ($CH_2{=}CHOCH_2CH_2CH(COOEt)_2$; VOEM),[4] a functionalized VE carrying a malonic ester in the pendant (see eq 1). Alkaline hydrolysis of the malonate moiety of poly(VOEM) **4**, followed by thermal decarboxylation, leads to three types of water-soluble polymers $-[CH_2CH(OCH_2CH_2R')]_m-$ ($R' = CH(COO^-Na^+)_2$, $CH_2COO^-Na^+$, and CH_2COOH) with dicarboxylate, monocarboxylate, or monocarboxyl groups, respectively.

These results prompted us to synthesize new anionic amphiphilic block polymers [**6**–**8** ($n \geq 1$) and **10**–**12** ($n = 1$)] with controlled structure and molecular weight, as illustrated in eqs 1 and 2. For example, sequential living polymerization of VOEM and an alkyl VE affords a precursor block polymer **5**. The malonic ester groups in the pendant are then saponificated to give the dicarboxylate form **6**. Subsequent thermal decarboxylation yields the monoacid form **7**, which can be neutralized into the monocarboxylate counterpart **8**. Reaction 2 is specifically employed to prepare **10**–**12** with exactly one alkyl VE unit attached to the polymer terminal. The pendant group transformation of **9** into **10**–**12** is the same as for **5**.

Because of the intramolecular Coulombic charge repulsion among the pendant ions, in general, polyelectro-

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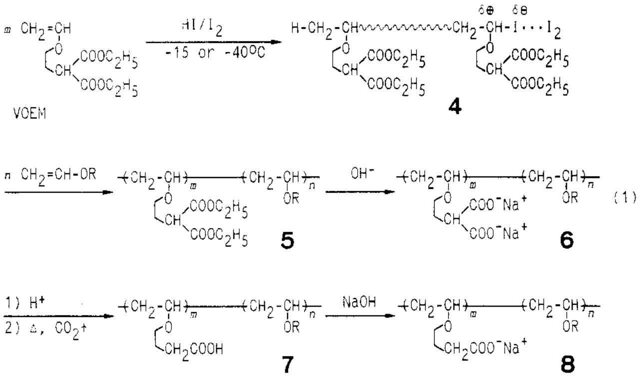
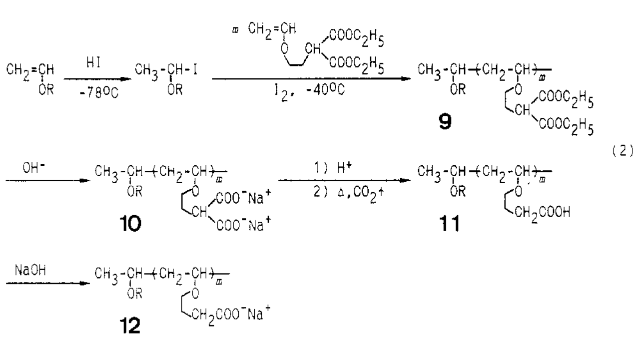


5a, **6a**, **7a**, **8a** (R: n-$C_{16}H_{33}$)
5b, **6b**, **7b**, **8b** (R: i-C_8H_{17})
5c, **6c**, **7c**, **8c** (R: n-C_4H_9)



9a, **10a**, **11a**, **12a** (R: n-$C_{16}H_{33}$)
9b, **10b**, **11b**, **12b** (R: n-C_4H_9)

lytes are more extended in conformation in aqueous solution than the corresponding nonionic polymers.[5] The same is the case for macromolecular amphiphiles and, therefore, the structures of the hydrophilic segments (ionic versus nonionic) will affect their conformation in solution and thereby the surface activity, which depends on how densely the amphiphilic polymers are packed and aligned at an air/water surface. As a result of these features, the structures (ionic versus nonionic) of the hydrophilic groups may affect the conformations of the macromolecular amphiphiles in their aqueous solutions;[6] consequently, the conformations appear to possibly influence the polymers' packing at the air/water interface.

In this study, we synthesized anionic amphiphilic block polymers (**6**–**8** and **10**–**12**) by living cationic polymerization (eqs 1 and 2) and determined their surface activity (surface tension) as a function of their segment molecular weight and composition as well as the nature of the hydrophilic and hydrophobic pendant substituents. The data were then compared with the surface activity of the nonionic (**1** and **2**) and the cationic amphiphiles (**3**) prepared previously by us via living cationic polymerization.

Results and Discussion

1. Synthesis of Amphiphilic Polymers. Block Copolymerization. In order to synthesize the block polymer **5**, VOEM and an alkyl VE ($CH_2{=}CHOR$; R = alkyl) were sequentially polymerized by the HI/I_2 initiating system in toluene at −15 or −40 °C (eq 1). The alkyl VEs employed were the n-hexadecyl, isooctyl, and n-butyl derivatives ($C_{16}VE$, C_8VE, and C_4VE, respectively). In a typical run ($[VOEM]_0 = 0.40$ M, $[HI]_0 = 22$ mM, $[I_2]_0 = 10$ mM at −40 °C), the first-stage polymerization of VOEM reached 100% conversion in 4 h. After addition of C_8VE (VOEM/C_8VE = 20/8 molar ratio), the second-stage polymerization was completed in an additional 4 h.

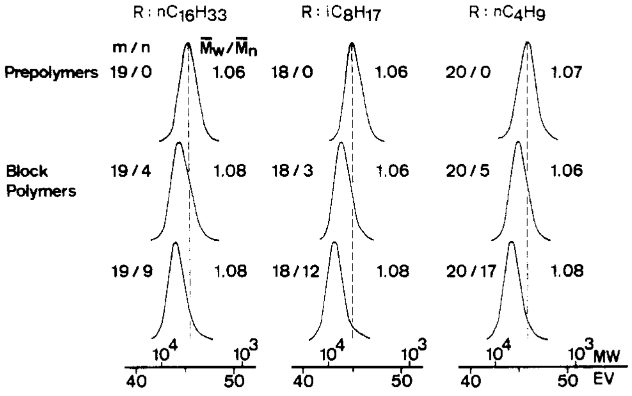


Figure 1. MWD of VOEM–alkyl VE block polymer **5** (middle and bottom rows) and precursor poly(VOEM) **4** (top row) obtained by the sequential polymerization of VOEM and an alkyl VE (eq 1) with HI/I_2 in toluene at −40 °C: $[VOEM]_0 = 0.40$ M; $[HI]_0 = 20$–22 mM; $[I_2]_0 = 10$ mM. Conversion was 100% in each step.

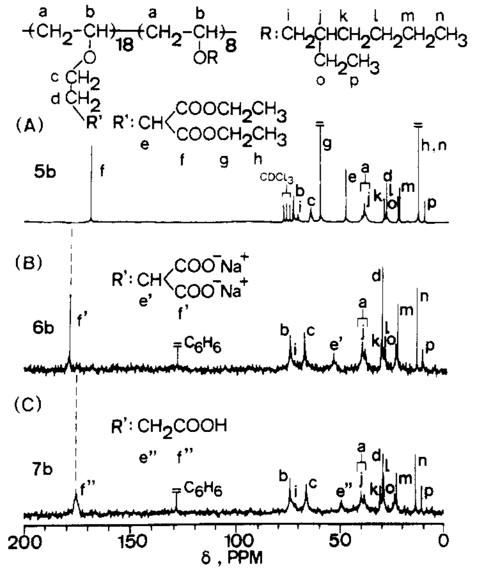


Figure 2. ^{13}C NMR spectra in $CDCl_3$ (A) and in D_2O (B and C): (A) precursor **5b** (m/n = 18.8; $\bar{M}_n$ = 4200, $\bar{M}_w/\bar{M}_n$ = 1.08); (B) hydrolysis product **6b** obtained from sample A; (C) decarboxylation product **7b** obtained from sample B.

Figure 1 shows the MWDs of the resultant block polymers **5** and their precursors [living poly(VOEM) **4**]. The poly(VOEM) has a very narrow MWD ($\bar{M}_w/\bar{M}_n < 1.1$) (Figure 1, top row). After the addition of an alkyl VE, the MWD curve shifted toward higher molecular weight, while maintaining its narrowness (Figure 1, middle and bottom row). The molecular weight of block polymer **5** increased proportionally to the quantity of the added alkyl VEs; the $\bar{M}_n$ of the starting living poly(VOEM) could be controlled by regulating the monomer-to-initiator (HI) feed ratio. Figure 1 thus indicates the quantitative formation of block polymers **5a**–**c** of controlled MWD by the use of any alkyl VE. The structures of **5a**–**c** were verified by ^1H and ^{13}C NMR spectroscopy (cf. Figure 2).

The overall results of the block copolymerizations were summarized in Table I. All the samples were prepared so as to keep the degree of polymerization (m) of the poly(VOEM) segment about 20 and that (n) of the alkyl VE segment in the range 2–17. The compositions (m/n) were determined from the integrated signal intensity ratio of the ^1H NMR spectra, which are in good agreement with the monomer feed ratio.

The two samples with one $C_{16}VE$ or C_4VE unit (n =

Table I
Block Copolymers 5 and 9 Obtained from VOEM and Alkyl VE by Sequential Living Polymerization (Eqs 1 and 2)

		block copolymer		
VOEM/alkyl VE (m/n), calcd[a]	R	VOEM/alkyl VE (m/n), obsd[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
19/8	C_{16}	19/8.5	6000	1.08
19/4	C_{16}	19/3.8	5300	1.08
19/2	C_{16}	19/2.4	4700	1.07
20/1	C_{16}	20/1.0	4900	1.07
18/15	C_8	18/12	4900	1.08
18/7	C_8	18/6.5	4000	1.08
18/4	C_8	18/3.0	4000	1.06
18/1	C_8	18/1.1	3800	1.06
20/16	C_4	20/17	5700	1.08
20/8	C_4	20/9.6	5300	1.06
20/4	C_4	20/4.7	4800	1.06
20/1	C_4	20/1.0	4600	1.06

[a] Degrees of polymerization of the two segments, calculated on the basis of $[HI]_0$ and the feed ratio: $m = [VOEM]_0/[HI]_0$; $n = m([alkyl\ VE]_0/[VOEM]_0)$. [b] Determined by ^1H NMR. [c] By SEC; polystyrene calibration.

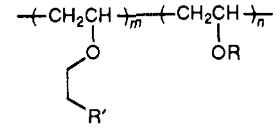
1) were prepared via reaction 2.[2] Thus, an alkyl VE was first treated with an equimolar amount of HI in toluene at −78 °C, and with the resulting adduct as the initiator, VOEM was polymerized at −15 °C in the presence of iodine, to give block polymer **9**. This method was very useful for the synthesis of the block polymer with one particular alkyl VE unit in the first (head) repeat unit.

Hydrolysis and Decarboxylation of Block Polymers 5 and 9. Block polymers **5** and **9**, differing in the alkyl pendant (R) and composition (m/n), were thus prepared. These copolymers were then hydrolyzed in acetone under basic conditions, to give **6** and **10** with dicarboxylate anions. The precursors **5** and **9** were soluble in common organic solvents (toluene, chloroform, etc.) but insoluble in water; however, the hydrolysis products were completely water soluble. The dianionic polymers **6** and **10** were then converted into the carboxylic acid forms (**7** and **11**, respectively) by the treatment with hydrochloric acid and subsequent thermal decarboxylation in water at 90 °C. Both **7** and **11** were water soluble. The treatment of **7** and **11** with sodium hydroxide gave the polymers **8** and **12** with monocarboxylate anions.

Figure 2 compares the ^{13}C NMR spectra of a series of block polymers **5b**–**7b** thus prepared (R = $i\text{-}C_8H_{17}$, m = 20, n = 8). Comparison of the spectra confirmed that precursor **5b** was quantitatively converted into **6b** and then to **7b**. For example, after the hydrolysis and subsequent decarboxylation (Figure 2B), the absorption of the ester ethyl carbons (g, CH_2CH_3, δ 61.0; h, CH_2CH_3, δ 13.9; Figure 2A) of **5b** completely disappeared, whereas the peaks of the C_8VE unit (i–p) remained unchanged. The three samples gave the signals of the carbonyl carbons at different chemical shifts that are consistent with their expected structures: **5b**, δ 169.0 [f, $(COOEt)_2$]; **6b**, δ 178.8 [f′, $(COO^-Na^+)_2$]; **7b**, δ 175.6 (f″, COOH). The other block polymers (**5a** and **5c**) also underwent similar chemical modifications.

2. Surface Activity of the Amphiphilic Block Polymers. Surface Tension Measurement. To evaluate the surface activity of our polymer amphiphiles, we determined the surface tension $\gamma_{W/A}$ of their aqueous solutions (1.0 wt %). All the samples were completely soluble in water and desalted by dialysis. The overall results of the surface tension measurement were summarized in Table II. With a few exceptions, these polymers turned out to be highly surface active and lowered the surface tension from 72.8 dyn/cm for pure water down to 30 dyn/cm or below. The surface activity remarkably changed, depending upon the combinations of the hydrophilic groups and the hydrophobic alkyl pendants (see below).

Table II
Surface Tension ($\gamma_{W/A}$)[a] of Amphiphilic Block Polymers



		hydrophilic substituent (R′)		
R	unit ratio[b] m/n	$CH(COO^-Na^+)_2$ (**6, 10**)	CH_2COOH (**7, 11**)	$CH_2COO^-Na^+$ (**8, 12**)
C_{16}	19/8.5	72.0	49.5	45.1
C_{16}	19/3.8	66.0	38.0	37.9
C_{16}	19/2.4	45.0	31.3	27.7
C_{16}	20/1.0	32.8	43.0	25.8
C_8	18/12	57.0	50.7	60.2
C_8	18/6.5	46.3	40.3	48.6
C_8	18/3.0	36.8	36.6	43.0
C_8	18/1.1	39.0	34.0	41.8
C_4	20/17	46.9	40.1	38.0
C_4	20/9.6	40.2	37.8	39.0
C_4	20/4.7	37.1	35.0	40.6
C_4	20/1.0	53.2	65.4	72.0

[a] In dyn/cm (=10^{-3} N/m), 1.0 wt % at 25 °C in water. [b] Determined by ^1H NMR.

The surface tension values in Table II were obtained at 1.0 wt % concentration. When diluted to 0.1 wt %, most of the samples gave $\gamma_{W/A}$ values a few dynes per centimeter or even 10–20 dyn/cm higher than those at 1.0 wt %. Such a concentration dependence is absent for nonionic amphiphile **1** and does reflect the extended conformations of the anionic block polymers due to the intramolecular charge repulsion.

Effects of the Hydrophilic Substituents. Figure 3 shows the relationships between the surface activity and structure of the hydrophilic groups [$(COO^-)_2$, COO^-, and COOH]. In Figure 3A, the $\gamma_{W/A}$ value for the C_{16}VE-containing polymers **6a**–**8a** (and **10a**–**12a**) are plotted as a function of N, the number of carbon atoms in the hydrophobic segment; Figure 3B gives the corresponding plots for the C_4VE-containing analogues (1.0 wt %; $m \cong 20$). In both cases, the surface tension was minimal at N = 20–40 and independent of the kind of the hydrophilic groups. In particular (Figure 3A), polymer **12a** (R = $n\text{-}C_{16}H_{33}$, R′ = $CH_2COO^-Na^+$; m/n = 20/1) remarkably decreased the $\gamma_{W/A}$ value down to 25.8 dyn/cm, which is the lowest value among the nonionic, cationic, and anionic amphiphilic VE block polymers thus far prepared.

Overall, each sample exhibits a common dependence, i.e., a gradual rise of $\gamma_{W/A}$ for $N > 20$ and a sharp increase in $\gamma_{W/A}$ for $N < 10$; the latter region is absent in Figure 3A because the minimum N is as large as 18 for R = $n\text{-}C_{16}H_{33}$. Thus, the surface activity appears to depend little on the structure of the hydrophilic groups. The only exception is polymer **6a** [R = $n\text{-}C_{16}H_{33}$, R′ = $CH(COO^-)_2$], for which $\gamma_{W/A}$ sharply increased with increasing N. This probably results from the bulkiness of the long alkyl pendant group, coupled with the strong interionic repulsion of the dianions, both of which may render polymer **6a** highly rigid and inefficient in packing at an air/water interface, particularly when N is large.

Effects of the Hydrophobic Substituents. In Figure 4, the $\gamma_{W/A}$ values were plotted against N for a series

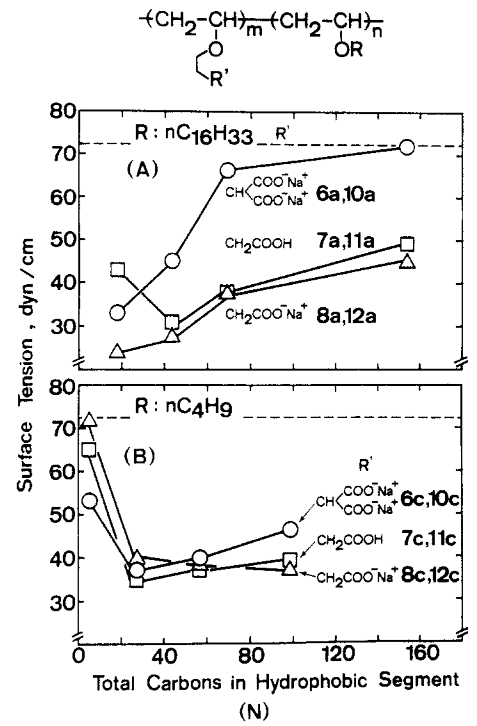


Figure 3. Effects of the hydrophilic substituents R′ on the surface tension $\gamma_{W/A}$ (1.0 wt %, 25 °C), plotted against the number of carbon atoms in the hydrophobic segment (N): $m \cong 20$, $n = 1$–17; dyn/cm = 10^{-3} N/m. R = (A) n-$C_{16}H_{33}$; (B) n-C_4H_9. R′ = (○) $CH(COO^-Na^+)_2$; (□) CH_2COOH; (△) $CH_2COO^-Na^+$.

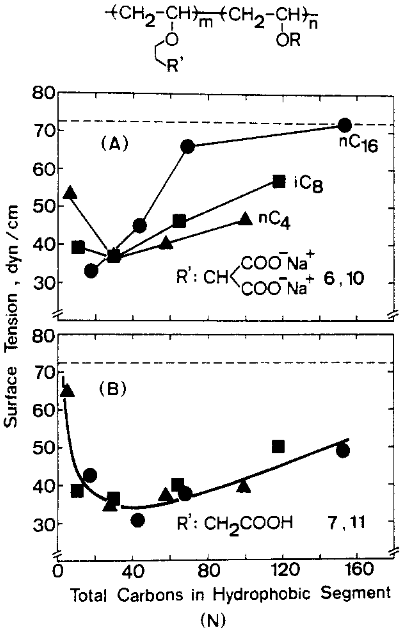


Figure 4. Effects of the hydrophobic substituents R on the surface tension $\gamma_{W/A}$ (1.0 wt %, 25 °C), plotted against the number of carbon atoms in the hydrophobic segment (N): $m \cong 20$, $n = 1$–17; dyn/cm = 10^{-3} N/m. R′ = (A) $CH(COO^-Na^+)_2$; (B) CH_2COOH. R = (●) n-$C_{16}H_{33}$; (■) i-C_8H_{17}; (▲) n-C_4H_9.

of polymers having common hydrophilic groups but differing in alkyl substituents: (A) dicarboxylate-type polymers 6 and 10; (B) monoacid forms 7 and 11. Figure 4A clearly indicates that the surface tensions for 6 and 10 are related to the hydrophobicity of the alkyl VE; thus, the longer the alkyl substituents R, the greater the effects of N on $\gamma_{W/A}$. In contrast, a single $\gamma_{W/A}$–N curve was obtained for 7 and 11 (Figure 4B), indicating that their surface tension is minimal at N = 20–40 and almost independent of the hydrophobic alkyl VEs. A very similar tendency has been observed for the nonionic amphiphile 1 with a polyalcohol as the hydrophilic segment.[2] The similarity to the nonionic form 1 suggests that the carboxyl moieties of 7 and 11 are weakly acidic and hardly dissociated under our conditions. We may therefore regard 7 and 11 as nonionic macromolecular amphiphiles.

Chart I

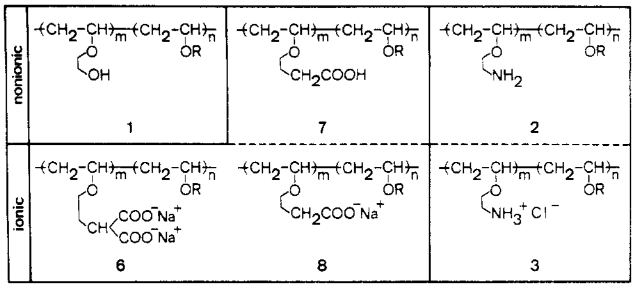
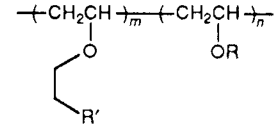


Table III
Surface Activity of Amphiphilic Block Polymers



	nonionic					
R′	OH (1)[c]		CH_2COOH (7)		NH_2 (2)[d]	
R	C_{16}	C_4	C_{16}	C_4	C_{16}	C_4
$\gamma_{W/A}$[a]	29.0	31.8	31.3	35.0	42.0	31.0
m[b]	40	42	19	20	40	40
n	1.8	5.3	2.4	4.7	1.1	3.9

	ionic					
R′	$CH(COO^-Na^+)_2$ (6)		$CH_2COO^-Na^+$ (8)		$NH_3^+Cl^-$ (3)[d]	
R	C_{16}	C_4	C_{16}	C_4	C_{16}	C_4
$\gamma_{W/A}$[a]	45.0	35.0	27.7	40.6	50.0	35.7
m[b]	19	20	19	20	40	40
n	2.4	4.7	2.4	4.7	1.1	3.9

[a] Minimum surface tension of aqueous solution: in dyn/cm (=10^{-3} N/m); 0.1 wt % for 1–3 and 1.0 wt % for 6–8, at 25 °C. [b] Degrees of polymerization of the two segments for the sample that gives the minimum $\gamma_{W/A}$ value. [c] From ref 2. [d] From ref 3.

As shown in Figures 3 and 4, the hydrophobic units affected the surface activity more clearly than did the hydrophilic substituents. This characteristic is rather unique for the anionic amphiphilic polymers and absent for the nonionic analogue 1.[2]

Comparison of the Surface Activity among Amphiphilic VE Block Polymers. We have now a variety of VE-based polymeric amphiphiles (Chart I). The hydrophilic segments include cationic, anionic, and nonionic; the hydrophobic substituents cover alkyl groups of 4–16 carbons. It is therefore interesting to compare their surface activity (Table III).

Table III compares the lowest $\gamma_{W/A}$ values obtained for the six types of amphiphilic polymers (1–3 and 6–8). The surface tension was measured at 0.1 or 1.0 wt % concentration, depending on the kind of the block polymers. Because 6–8 exhibited lower $\gamma_{W/A}$ values at higher concentrations, as described above, the data for 1.0 wt % are listed in Table III. All these block polymers exhibit excellent surface activity and in most cases reduce the surface tension down to 30 dyn/cm or below for selected composition (m/n) and the alkyl pendant R. Equally important, the carboxyl and carboxylate groups in 6–8 are so polar that the polymers need only short hydrophilic segments ($m \cong 20$) to dissolve in water, whereas **1**–**3** with less hydrophilic hydroxyl and primary amino groups require hydrophilic segments ($m \cong 40$) to be doubled in length for enough solubility.

When compared with the cationic analogue **3**, the nonionic polymer **2** was superior in surface activity. The influence of the length of the alkyl pendants was also remarkable for **2** and **3**, and the surface activity of the C_4VE-containing polymers was the highest in general. For polymers **1** and **6**–**8**, in contrast, those with C_{16}VE units are similar in surface activity to, or in some cases even better than, the C_4VE counterparts.

As shown in Table II, **10a**–**12a** also gave low $\gamma_{W/A}$ values, indicating that even one terminal C_{16}VE unit can effectively reduce the surface tension. For example, the minimum $\gamma_{W/A}$ values are as follows ($m = 20$, dyn/cm): **10a**, 32.8; **11a**, 43.0; **12a**, 25.8.

In conclusion, this study has provided anionic amphiphilic poly(vinyl ethers) with definite structures and various hydrophilic units, all of which exhibit excellent surface activity that paralells those of ethylene oxide–propylene oxide ABA triblock copolymers (Pluronics)[7] and of block polymers of oxazolines.[8]

Experimental Section

Materials. VOEM was prepared from 2-chloroethyl vinyl ether and ethyl malonate as reported previously.[4] This monomer and commercial alkyl VEs (CH_2=CHOR; R = n-$C_{16}H_{33}$, i-C_8H_{17}, and n-C_4H_9) were purified by double distillation over calcium hydride before use (gas chromatographic purity >99%). Anhydrous hydrogen iodide (as an n-hexane solution) was obtained by dehydration of commercial hydroiodic acid with phosphorus pentoxide. Iodine was sublimed over potassium iodide. These compounds were sealed in brown ampules under dry nitrogen and stored in a freezer. Toluene as polymerization solvent was purified by the usual method[9] and distilled over calcium hydride at least twice prior to 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. The reaction was initiated by adding an initiator solution to a monomer solution via a dry syringe and was quenched with prechilled ammoniacal methanol. The quenched reaction mixture was washed with 10% aqueous sodium thiosulfate solution and then with water, evaporated to dryness, and vacuum dried to give the product polymers.

Hydrolysis and Decarboxylation. A sample of polymer **5** (100–150 mg) was dissolved in acetone (15 mL), and 5 N sodium hydroxide (5 equiv to the COOEt units in the polymer) was added. The mixture was magnetically stirred at room temperature for about 10 h. The acetone was then evaporated off under reduced pressure, water (10 mL) was added, and stirring was continued at room temperature for an additional 2 or 3 days. The excess sodium hydroxide was removed by dialysis (Spectra/Por 7, molecular weight cutoff ca. 1000) to afford the dicarboxylate form **6**.

For decarboxylation, the hydrolysis product was treated with hydrochloric acid (equimolar to the sodium hydroxide used for the saponification), and then its aqueous solution was heated to 90 °C for about 3 h, followed by dialysis, to give the monoacid form **7**. Neutralization of **7** with sodium hydroxide (equimolar to the pendant carboxylic acid) gave the sodium salt form **8**. **10**–**12** were obtained from **9** in the same manner.

Measurement. The molecular weight distribution (MWD) of the precursor block polymers **5** and **9** was measured by size-exclusion chromatography (SEC) in chloroform on a Jasco Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex A-802, A-803, and A-834; exclusion limits: 5×10^3, 7×10^4, and 5×10^5, respectively; 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 obtained from the SEC eluograms on the basis of a polystyrene calibration. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or D_2O at room temperature on a Jeol FX-90Q spectrometer. The surface tensions of aqueous polymer solutions (1.0 and 0.1 wt %) were measured at 25 °C on a Shimadzu ST-1 tensiometer.

Acknowledgment. This work was supported in part by the Asahi Glass Foundation for Industrial Technology, for which T.H. is grateful.

References and Notes

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Registry No. (VOEM)(VE, R = n-$C_{16}H_{33}$) (block copolymer), 125197-74-2; (VOEM)(VE, R = i-C_8H_{17}) (block copolymer), 125197-77-5; (VOEM)(VE, R = n-C_4H_9) (block copolymer), 125197-75-3.