Amphiphilic Block Copolymers of Vinyl Ethers by Living Cationic Polymerization. 4. Macromolecular Amphiphiles with Multiple Hydroxyl Groups and a Cylindrical Topology

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ABSTRACT: Amphiphilic block polymers (3) of vinyl ethers, $[-CH_2CH(OCH_2CH_2R')-]_m[-CH_2CH(OR)-]_n$ $(R' = CH(CONHC(CH_2OH)_3)_2; R = n\text{-}C_{16}H_{33}, i\text{-}C_8H_{17}; m = 5\text{-}100, n = 10$ or $50)$, with narrow molecular weight distributions were prepared, in which the hydrophilic segment had a unique cylindrical shape that originates from the highly branched, bulky pendant substituent (R') with six hydroxyl groups. The precursor block polymers (2), $[-CH_2CH(OCH_2CH_2R'')-]_m[-CH_2CH(OR)-]_n$ $(R'' = CH(COOEt)_2)$, were obtained by the HI/ I_2-initiated sequential living cationic polymerization of vinyl ethers, $CH_2=CH(OCH_2CH_2R'')$ and $CH_2=CH(OR)$. Subsequent amidation of the pendant malonic ester in R'' with $H_2NC(CH_2OH)_3$ in the presence of anhydrous K_2CO_3 in dimethyl sulfoxide led to polymer 3. A similar reaction in methanol, on the other hand, gave another block polymer (4), $[-CH_2CH(OCH_2CH_2R')-]_m[-CH_2CH(OR)-]_n$ $(R' = CH(CONHC(CH_2OH)_3)COO^-K^+)$, with one carboxylate anion and three hydroxyl groups per pendant R'. These amphiphilic block polymers (3 and 4) were soluble in water and lowered the surface tension of their aqueous solutions (0.1 wt %, 25 °C) to a minimum 40 dyn/cm. Observation by transmission electron microscopy revealed that these block copolymers form molecular assemblies that include lamellae and vesicles (for $m = 5$, $n = 12$) and phase-separated microdomains (for $m = 30\text{-}100, n \cong 10$ or 50).

Introduction

Recent development of controlled polymerizations has permitted the synthesis of polymers with definite molecular weight, molecular weight distribution, pendant and end functions, and main-chain stereoregularity. In contrast, the spatial or three-dimensional shape of synthetic polymers, vinyl polymers in particular, has thus far eluded such elaborate control through regulation of polymerization reactions. It is indeed quite recently that such topologically controlled macromolecules as "arborols"[1] and "starburst dendrimers"[2] have been synthesized. The syntheses of these uniquely shaped compounds have been achieved by repetitive reactions where multifunctional reagents lead to treelike molecular frameworks that consist of a concentric regular branching and of a surface densely covered with polar functional groups like carboxylate and hydroxyl. In the synthesis of arborols by such a functional-group multiplication,[1] for example, Newkome utilized the following amidation reaction of an ester: $-COOR + H_2$-$NC(CH_2OH)_3 \rightarrow -CONHC(CH_2OH)_3 + ROH$.

Recently, we have synthesized homopolymers (1)[3] and block polymers (2)[4] of diethyl 2-(vinyloxy)ethylmalonate [VOEM; $CH_2=CHOCH_2CH_2CH(COOEt)_2$] by living cationic polymerization, where the products possess an array of pendant double ester functions (eq 1). It occurred to

$$\text{(1)}$$

2a: R = i-C_8H_17
2b: R = n-C_16H_33
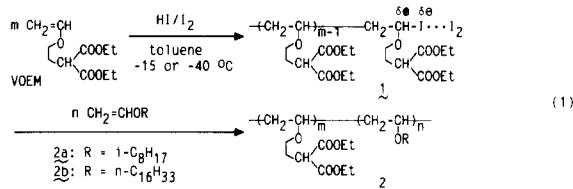
us that these ester groups might undergo the above-mentioned amidation[1] to give a regularly branched, treelike, and multifunctional pendant moiety with six hydroxyl groups (3; eq 2A). Inspection of molecular models suggests 3 to be an amphiphilic block polymer with a hydrophilic segment of a cylindrical shape whose surface is

2a, 3a, 4a: R = i-C_8H_17
2b, 3b, 4b: R = n-C_16H_33
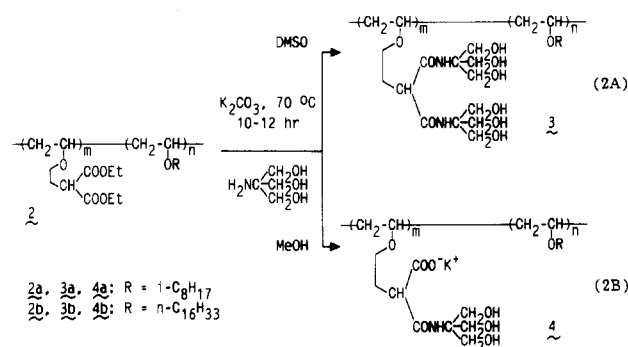
covered with a number of polar hydroxyl groups. Thus, 3 may possess a three-dimensional structure that differs from the spherical multibranched shapes of arborols and starburst dendrimers and would in turn show such specific properties as the formation of molecular assemblies.[5]

The first objective of this study was, therefore, to synthesize the uniquely shaped amphiphilic block polymer 3 with multiple pendant hydroxyl groups, according to the synthetic routes shown in eqs 1 and 2A. The second objective was to investigate how the multibranched amphiphile 3 aggregates on casting from solution. The morphological change of their molecular assemblies was studied by transmission electron microscopy as a function of their segment molecular weights and compositions.

Results and Discussion

1. Synthesis of Amphiphilic Block Polymers with Multiple Hydroxyl Groups. Block Copolymerization of Vinyl Ethers. As shown in eq 1, precursor block polymer 2 was synthesized by the HI/I_2-mediated sequential living cationic polymerization of VOEM and an alkyl vinyl ether (VE).[3,4] The employed alkyl VEs included the *i*-octyl (2-ethylhexyl) and *n*-hexadecyl derivatives (C_8-VE and C_{16}VE, respectively). The degree of polymerization (m) for the poly(VOEM) segment was varied in the range 5-100. The molecualr weight distributions (MWDs) of two series of block polymer samples are shown in Figure 1 (A, $m = 20$; B, $m = 92$).
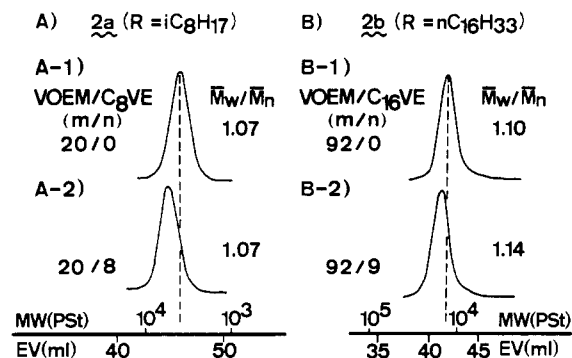
Figure 1. MWDs (SEC curves) of the products in sequential living cationic polymerizations of VOEM with C_8VE (A) or C_{16}-VE (B) initiated with HI/I_2 in toluene (eq 1). (A) $[VOEM]_0$ = 0.40 M, $[C_8VE]_0$ = 0.16 M, $[HI]_0$ = 20 mM, $[I_2]_0$ = 10 mM, at −40 °C; (A-1) living poly(VOEM) precursor (1); (A-2) VOEM-C_8VE block polymer (2a) from sample A-1 (m/n = 20/8). (B) $[VOEM]_0$ = 1.0 M, $[C_{16}VE]_0$ = 0.10 M; $[HI]_0$ = 11 mM, $[I_2]_0$ = 10 mM, at −15 °C; (B-1) living poly(VOEM) precursor (1); (B-2) VOEM-$C_{16}VE$ block polymer (2b) from sample B-1 (m/n = 92/9). Conversion was ca. 100% in each step.

In the synthesis of **2b**, for example, the living polymerization of VOEM was carried out with HI/I_2 in toluene at −15 °C: $[VOEM]_0$ = 1.0 M; $[HI]_0$ = 11 mM; $[I_2]_0$ = 10 mM. After near quantitative consumption of VOEM (within ca. 1 h), the second-stage polymerization was triggered by the addition of $C_{16}VE$ (VOEM/$C_{16}VE$ = 92/9 mole ratio) and completed in an additional 20 min. The resultant **2b** and its precursor exhibited unimodal, narrow MWDs (Figure 1B). The overall results of the block copolymerizations are summarized in Tables I (for **2a**) and II (for **2b**). These data show that the molecular weights and segmental compositions (m/n ratios) of **2a** and **2b** could be controlled by regulating the feed ratio of two monomers and the concentration of the initiator (HI).

Amidation of 2 into Multibranched Amphiphilic Block Polymers. The pendant malonate groups of the block polymer **2** were then treated with $H_2NC(CH_2OH)_3$ in the presence of anhydrous K_2CO_3 at 70 °C, according to a modified method after Newkome,[1a] in order to prepare amphiphilic block polymer **3** carrying six hydroxyl groups in each pendant (eq 2). Interestingly, it turned out that the structure of the amidation products is critically dependent on the reaction media and the amounts of the reagents (structural analysis was described below).

For example, with dimethyl sulfoxide as a solvent and with a large excess of $H_2NC(CH_2OH)_3$ and a small amount of K_2CO_3 (12 and 0.8 equiv to the COOEt units in **2**, respectively), both ester groups of the malonate moiety reacted almost quantitatively with the amine to afford polymer **3** (six hydroxyl groups per pendant; eq 2A). In sharp contrast, the reaction in methanol, using the amine and K_2CO_3, 2 equiv each to the ester units, gave another polymer **4** (eq 2B), where only one ester group of the pendant malonate was converted into the expected amide form, whereas the other was hydrolyzed into the corresponding carboxylate. Thus, **3** is a nonionic amphiphile carrying hydroxyl groups only, while **4** bears both nonionic (hydroxyl) and anionic (carboxylate) hydrophilic groups.

After the unreacted amine was removed by reprecipitation into methanol and subsequent dialysis, **3** and **4** were recovered as pale yellow, transparent, and fragile films. Although the precursor **2** was soluble in common organic solvents but insoluble in water, both **3** and **4** (e.g., m = 20; n = 2–13) were completely water-soluble at room temperature.

Figure 2 compares the ^1H NMR spectra of precursor **2a** ($R = i\text{-}C_8H_{17}$; m = 20, n = 8.8) and its amidation product

3a (obtained in dimethyl sulfoxide). After the amidation (spectrum B), the absorptions f (COOCH_2) and g (COOCH$_2$CH_3) of the pendant ester of **2a** (spectrum A) completely disappeared, and a new peak assignable to the methylene adjacent to the hydroxyl group (k; CH_2OH) instead appeared, whereas those of the C_8VE unit (peaks i and j) remained unchanged. The complete disappearance of the ester functions was also observed for the other product, **4a**, too; however, the products obtained in dimethyl sulfoxide (**3**) and in methanol (**4**) were virtually indistinguishable by ^1H NMR spectroscopy.

In contrast, ^{13}C NMR analysis indeed provided evidence for the structural difference between **3** and **4**, particularly upon comparison of the chemical shifts of their carbonyl carbons (Figure 3). Namely, characteristic carbonyl absorptions that were distinct from that of precursor **2a** (spectrum A) were observed for **3a** (spectrum B) and for **4a** (spectrum C), which supported the expected structures of them: (δ): (A) **2a**, 169.0 [f, $(COOEt)_2$]; (B) **3a**, 172.7 [f^1, $(CONHC(CH_2OH)_3)_2$]; (C) **4a**, 175.1 [f^2, $CONHC(CH_2\text{-}OH)_3$] and 177.7 (f^3, COO^-K^+). In particular, **4a** (obtained in methanol) gave double carbonyl absorptions, and the chemical shift of its amide carbonyl (f^2) differed from that of **3a** (f^1). Therefore, we could exclude an alternative possibility that some of the pendants carry six hydroxyl groups (complete amidation as in **3a**) and others bear two carboxylate salts (complete hydrolysis). Spectrum B also showed traces of peaks f^2 and f^3 besides the intense peak of amide carbonyl (peak f^1), indicating that a small amount of malonic ester groups underwent partial hydrolysis even when dimethyl sulfoxide was used as a reaction medium.

The structural difference between **3** and **4** was further proved by IR spectroscopy. For example, in the spectrum for product **3a** in dimethyl sulfoxide, the carbonyl stretching band (1730 cm^{-1}) of starting polymer **2a** completely disappeared, and new strong bands due to the double amide moiety in turn appeared (in cm^{-1}): 1520, N–H bending; 1660, C=O stretching; ca. 3400, O–H stretching. Along with these absorptions for the amide, in contrast, the spectrum for product **4a** in methanol showed an additional peak at 1590 cm^{-1} assignable to the asymmetric C=O stretching of a carboxylate salt that resulted from a partial hydrolysis of the malonate group.

As summarized in Table I, the segment compositions (m/n; m and n = degree of polymerization) of polymers **2a**, **3a**, and **4a** were determined by ^1H NMR spectroscopy (cf. Figure 2) from the following peak intensity ratios: **2a**, f/j; **3a** and **4a**, (d + a + i)/j. The m/n ratios before and after the amidation were in fair agreement with each other, irrespective of the kind of reaction media employed, which indicates that the amidation reaction does not affect the main-chain structures.

Also, the number of hydroxyl groups per repeat unit was determined for **3a** and **4a** from the peak intensity ratio of k/j ($-CH_2OH$/pendant CH$_3$; cf. Figure 2B) and the m/n ratio. Each pendant of **4a** possessed nearly three hydroxyl groups, being consistent with its expected structure. The hydroxyl numbers for **3a** (4.2–4.9 per pendant) were clearly larger than those for **4a** but smaller than the theoretical value (six per pendant). Besides the side reaction (partial hydrolysis, see above), the discrepancy may be due to an underestimation of the NMR absorption of the $-CH_2OH$ units (peak k), which are embedded in the densely packed, rigid, and branched pendant group (with as many as six hydroxyl groups) and which are thereby less movable than those in **4a**.

To summarize, the careful choice of the reaction media (dimethyl sulfoxide versus methanol) permitted the se-
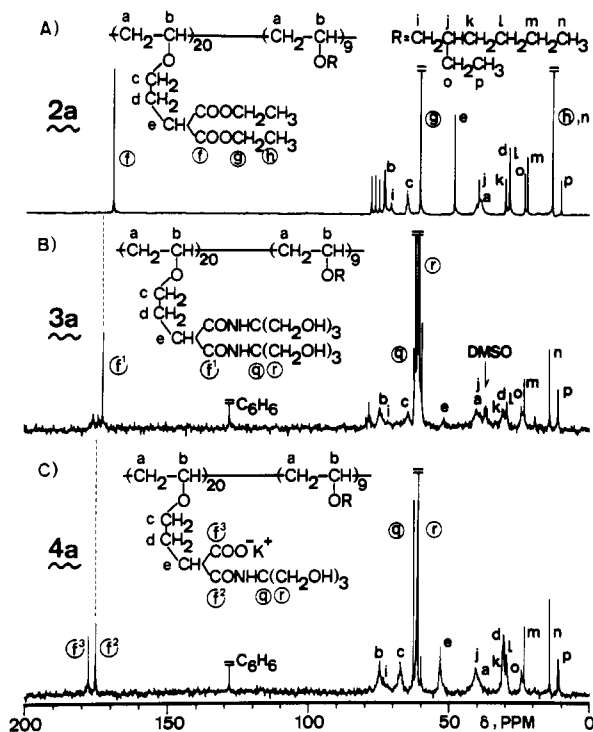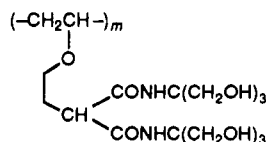
Table I
Characterization of VOEM–C$_8$VE Block Polymer 2a and Its Amidation Products 3a and 4a

code	reaction medium	R'	VOEM/C$_8$VE (m/n) calcd[a]	precursor 2a m/n	amidation product m/n	OH groups per pendant[b]	surface tension[c] $\gamma_{W/A}$
3a	DMSO	CH⟨CONHC(CH$_2$OH)$_3$ / CONHC(CH$_2$OH)$_3$	20/8	20/8.8	20/13	4.3	56.0
			20/4	20/4.9	20/5.7	4.9	48.0
			20/2	20/2.8	20/2.9	4.2	42.0
4a	MeOH	CH⟨COO⁻K⁺ / CONHC(CH$_2$OH)$_3$	20/8	20/9.0	20/8.6	2.9	60.0
			20/4	20/4.3	20/4.6	3.1	47.5
			20/2	20/2.4	20/2.0	2.9	55.0

[a] Degree of polymerization of the two segments, calculated on the basis of [HI]$_0$ and the feed ratio: m = [VOEM]$_0$/[HI]$_0$; n = m([C$_8$VE]$_0$/[VOEM]$_0$). [b] Determined by ^{1}H NMR; m is assumed to be the calculated value (footnote a); n is determined from the observed m/n ratio and the calculated m; see text. [c] In dyn/cm (=10^{-3} N/m); 0.1 wt % at 25 °C.

Table II
Characterization of VOEM–C$_{16}$VE Block Polymer 2b and Its Amidation Product 3b

		precursor 2b			amidation product (3b) molecular weight[c]		
code	structure	composition ($\overline{DP}_n$)[a] m/n	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_n$[b]	total	hydrophilic segment	hydrophobic segment
7	homopolymer	92/0	1.10	12 300	35 000	35 000	
3b-1	block polymer	102/46	1.20	15 000	51 100	38 800	12 300
3b-2	block polymer	92/13	1.14	13 600	38 500	35 000	3 500
3b-3	block polymer	58/13	1.13	8 100	25 500	22 000	3 500
3b-4	block polymer	29/11	1.17	6 900	14 000	11 000	3 000
3b-5	block polymer	5/12	1.17	3 750	5 100	1 900	3 200

[a] Determined by ^{1}H NMR; m is assumed to be equal to the feed molar ratio of VOEM and hydrogen iodide (initiator); n is determined from the observed m/n ratio and the calculated m value; see text. [b] By SEC; polystyrene calibration. [c] Based on the calculated degrees of polymerization (m and n) of the two segments of precursor 2b: m = [VOEM]$_0$/[HI]$_0$; n = m([C$_{16}$VE]$_0$/[VOEM]$_0$).

Figure 2. ^{1}H NMR spectra in CDCl$_3$ (A) and in D$_2$O (B): (A) precursor 2a (m/n = 20/9); (B) amidation product 3a obtained from sample A in dimethyl sulfoxide (eq 2A).

2. Surface Activity of Amphiphilic Block Polymers 3 and 4.

In this section, we focus on the surface activity of 3a and 4a, which consist of poly(C$_8$VE) as the hydrophobic segment. To evaluate their surface activity, we determined the surface tension $\gamma_{W/A}$ of their aqueous solutions (1.0 wt %). As shown in Table I, both 3a and 4a proved surface active, lowering the surface tension from 72.8 dyn/cm for pure water down to 42.0 dyn/cm; the lowest value was achieved with a sample of 3a with m = 20 and n = 2.8. When the poly(C$_8$VE) segment was the shortest (n = 2–3), 3a gave a lower $\gamma_{W/A}$ value than 4a, whereas the samples of other compositions gave no difference.

Though efficiently surface active, however, 3 and 4 turned out inferior to other vinyl ether-based amphiphilic block copolymers (5[6] and 6[4]) that have less bulky hydro-

lective synthesis of the two types of amphiphilic block polymers (3 and 4) with different multibranched hydrophilic pendant groups. It was also confirmed that homopolymers (1) of VOEM can undergo a similar amidation reaction to give the corresponding multibranched, water-soluble homopolymers.

philic segments. For example, the lowest $\gamma_{W/A}$ values for 3a and 4a are over 10 dyn/cm higher than that for the corresponding sample of 5 [$\gamma_{W/A}$ in dyn/cm (m/n): 3a, 48.0 (20/5); 4a, 47.5 (20/4); 5, 33.9 (44/8)]. Because of the steric hindrance as well as Coulombic charge repulsion

Figure 3. ^{13}C NMR spectra in $CDCl_3$ (A) and in D_2O (B and C): (A) precursor **2a** (m/n = 20/9); (B) amidation product **3a** obtained from sample A in dimethyl sulfoxide (eq 2A); (C) amidation product **4a** obtained from sample A in methanol (eq 2B).

(specifically for **4a** only) among the neighboring bulky pendants, **3a** and **4a** may assume extended conformations, but their large cross-sectional area may render these amphiphiles less efficient in packing at an air/water interface than **5** and **6**.

3. Morphological Analysis by Transmission Electron Microscopy. In addition to lowering surface tension, amphiphilic block copolymers **3** and **4** are expected to form molecular aggregates in water. Thus, the aggregate morphology of thin films of **3** was analyzed by transmission electron microscopy (TEM), as a function of the degree of polymerization (or molecular weight) and the segmental composition.

Samples. The samples for aggregate morphology analysis were $C_{16}VE$-based block polymers **3b** (specified as **3b-1** to **3b-5** in Table II); the precursors **2** of all these samples had narrow MWDs ($\bar{M}_w/\bar{M}_n \leq 1.20$). The degree of polymerization (m) of the hydrophilic segment ranged from 5 to 100, while that (n) of the hydrophobic poly-($C_{16}VE$) segment was set at ca. 10 or 50; the molecular weights, calculated from the structural formulas were in the range from 5×10^3 to 5×10^4. For comparison, a polymer (**7**) with the corresponding hydrophilic segment only was also prepared through the amidation of a homopolymer (**1**) of VOEM in dimethyl sulfoxide.

7

Solvent-Cast Thin Films. For TEM observation, four samples of amphiphilic polymer **3b** were employed: **3b-1** to **3b-4** with calculated molecular weights > 10^4 (Table II). Among these, samples **3b-1** and **3b-2** had long hydrophilic segments of similar lengths (m = ca. 100) but

hydrophobic segments of different lengths (n = 46 and 13); in another series, samples **3b-2** to **3b-4**, the length of the hydrophilic segments was varied (m = 90–30) but that of the hydrophobic segments was relatively short and nearly the same (n = ca. 10). For comparison, a sample of hydrophilic homopolymer **7** (corresponding to the hydrophilic segments of **3b-1** and **3b-2**) was also employed. From these samples, transparent thin films were cast from a water/methanol (1/1, v/v) mixed solvent, negatively stained with uranyl acetate (2 wt % aqueous solution), and subjected to TEM observation (Figure 4), where hydrophilic domains are stained and appear black.

Homopolymer **7**, which consists of a hydrophilic segment only, showed virtually no ordered structure (Figure 4A). In contrast, all of the block polymers **3b-1** to **3b-4** exhibited clear microphase separation (Figure 4B–E), the morphology of which appears to depend on the segment compositions and lengths (m and n). For example, comparison between images B and C indicates that the size of the hydrophobic domain (the white region) becomes smaller (**3b-1** > **3b-2**) with decreasing length (n) of the hydrophobic segment, with that (m) of the hydrophilic segment being similar. Along with the change in the domain size with n, a morphological transition also developed. Namely, **3b-2** (m/n = 92/13; Figure 4C) showed roughly spherical hydrophobic domains (150–200 Å in diameter; appearing as white circular images) that were embedded in a continuous matrix of the hydrophilic segment, whereas the longer hydrophobic segment of **3b-1** (m/n = 102/46; Figure 4B) led to cylindrical domains (300 × 1000–1500 Å; appearing as white rodlike images) as well as spherical domains (ca. 300 Å in diameter).

When the hydrophobic segment length (n) was kept short and nearly unchanged (ca. 10; polymers **3b-2** to **3b-4**; Figure 4C–E), a variation in the hydrophilic segment length (m, from 30 to 90) also induced another morphological transition. Thus, the shorter the hydrophilic segment (m) (C < D < E), the greater the area of the hydrophobic microdomains (the white regions); also, the microdomain patterns changed from spherical (C) to cylindrical (E).

It should be noted that the above-discussed observations (Figure 4) are for the solvent-cast thin films and not for microtomed layers that may be obtained from thermally equilibrated large samples of **3**. Therefore, we could not discuss the general relationships between the microphase structure and the polymer structure in further detail. It is noteworthy, however, that the vinyl ether block polymers **3b**, even sample **3b-4** with a fairly low degree of polymerization (m + n = 40), undergo microphase separation, and the systematic morphological transition among the four samples of **3b** certainly results from their well-controlled molecular weights, narrow MWDs, and segmental compositions.

Sonicated Samples. In contrast to samples **3b-1** through **3b-4**, where the hydrophilic segment is much longer than the hydrophobic segment ($m \gg n$), another sample of **3b** (**3b-5**, Table II; m/n = 5/12) is featured by a short hydrophilic segment and a relatively low overall molecular weight (calculated, 4600). This particular sample of **3b-5** was found to form interesting molecular aggregates (Figure 5) that are apparently similar to vesicles and lamellae common to lipids and related amphiphiles.

When dispersed in water, **3b-5** gave a turbid mixture, which was subsequently cast to give a TEM sample (Figure 5F). The observed stripe patterns suggest the formation of lamellae whose periodicity distance was 30–60 Å. Upon sonication of its aqueous dispersion, on the other hand,
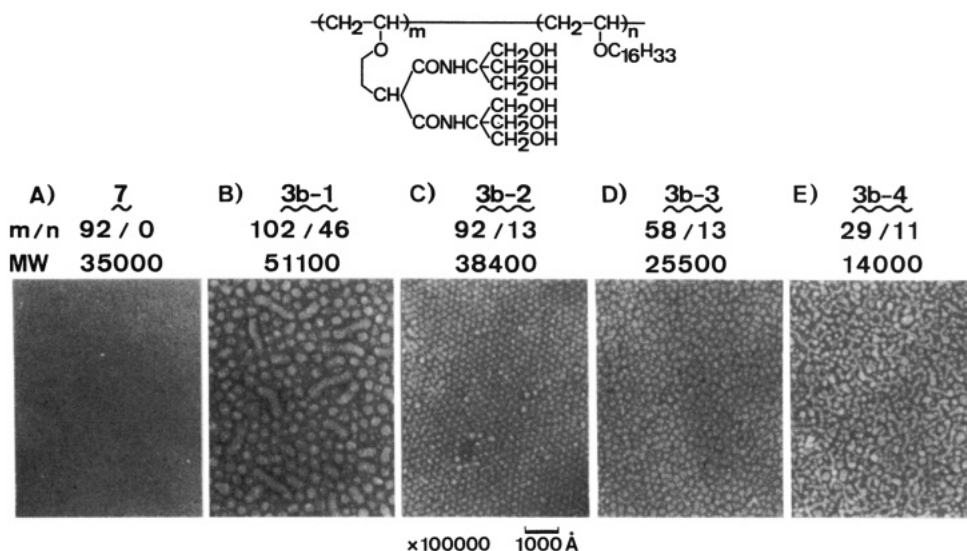
Figure 4. Transmission electron micrographs for homopolymer **7** (A) and amphiphilic block polymers **3b-1** to **3b-4** (B–E). Overall molecular weights and segment degrees of polymerization (m/n) are as indicated.
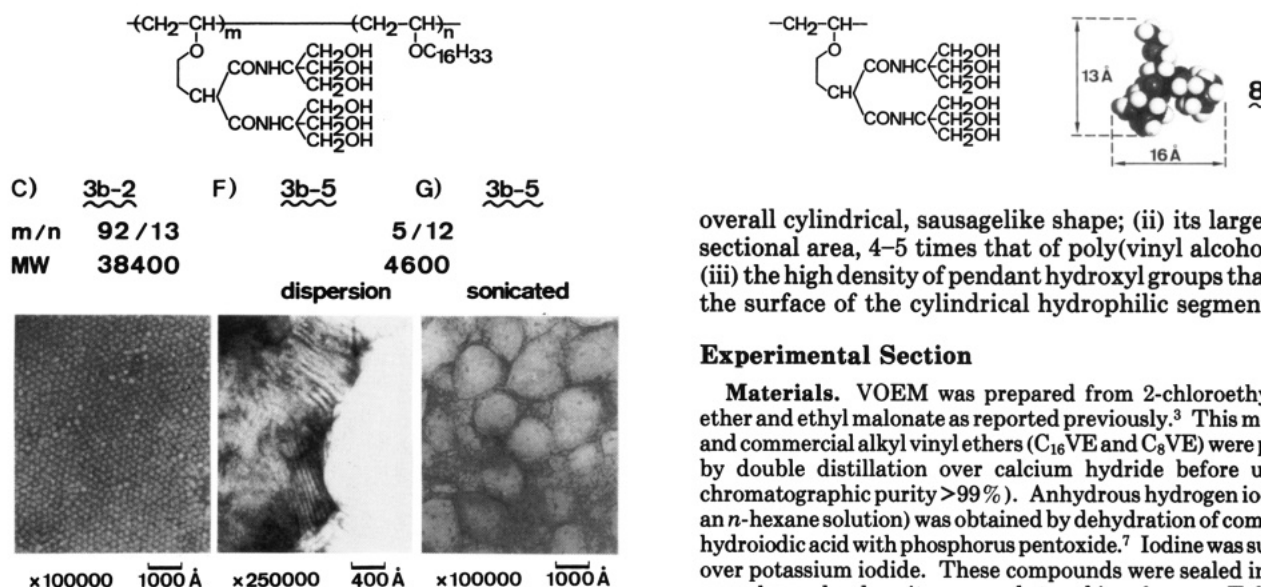

Figure 5. Transmission electron micrographs for amphiphilic block polymers **3b-2** (C) and **3b-5** (F and G) cast from aqueous dispersions: (C and F) without sonication; (G) after sonication (70 W, 8 min). Overall molecular weights and segment degrees of polymerization (m/n) are as indicated.

3b-5 led to Figure 5G, showing vesicles or disklike molecular aggregates (1000–2000 Å in diameter). Followup investigations are now in progress, specifically to observe internal aqueous compartments and the mode of aggregation.

As seen in Figures 4 and 5, the TEM observation has revealed that the molecular assemblies of **3b** changed from phase-separated microdomains (Figure 4) to lamellae or vesicles (Figure 5), depending on the degrees of polymerization of the hydrophilic and hydrophobic segments (m and n) and their balance (m/n ratio).

Spatial Shape. To visualize the spatial shape of the hydrophilic segment of amphiphilic block polymer **3**, structure **8** shows a CPK space-filling model of its repeat unit. Inspection of the model indicates that the highly branched repeat unit may take a triangular shape of 13 × 16 Å dimensions; and because of this bulky pendant substituent, the main chain of the hydrophilic segment may assume a 3–1 helix of a 23-Å diameter. If this model is valid, the hydrophilic segment of **3** is featured by (i) an

overall cylindrical, sausagelike shape; (ii) its large cross-sectional area, 4–5 times that of poly(vinyl alcohol), and (iii) the high density of pendant hydroxyl groups that cover the surface of the cylindrical hydrophilic segment.

Experimental Section

Materials. VOEM was prepared from 2-chloroethyl vinyl ether and ethyl malonate as reported previously.[3] This monomer and commercial alkyl vinyl ethers (C_{16}VE and C_8VE) 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.[7] Iodine was sublimed over potassium iodide. These compounds were sealed in brown ampules under dry nitrogen and stored in a freezer. Toluene as a polymerization solvent was purified by the usual method[3] and distilled over calcium hydride at least twice prior to use. $H_2NC(CH_2OH)_3$ and K_2CO_3 (anhydrous) were obtained commercially (Wako Chemicals; guaranteed reagents) and used without further purification. Dimethyl sulfoxide and methanol (Wako Chemicals; guaranteed reagents) were dried over molecular sieves before use.

Polymerization Procedures. Polymerization was carried out at −15 to −40 °C under dry nitrogen in a baked glass tube equipped with a three-way stopcock.[7] The reaction was initiated by adding an initiator solution to a monomer solution via a dry syringe and was quenched with prechilled methanol containing a small amount of ammonia. The quenched reaction mixture was washed with 10% aqueous sodium thiosulfate solution and then with water to remove iodine-containing residues, evaporated to dryness, and vacuum dried to give the product polymers.

Amidation. The basic procedures for this reaction were similar to Newkome's[1a] but with modifications, particularly in reagent concentrations and reaction media. In a typical reaction, a sample of block polymer **2** (400–500 mg) was dissolved in dimethyl sulfoxide (100–150 mL), and to this solution were added $H_2NC(CH_2OH)_3$ and anhydrous K_2CO_3, 12 and 0.8 equiv to the COOEt units in the polymer, respectively. The mixture was magnetically stirred at 70 °C for 10–12 h. The dimethyl sulfoxide was evaporated off under reduced pressure; methanol (ca. 100 mL) was added; and the mixture was vigorously stirred and allowed to stand to give polymeric precipitates and a turbid supernatant, the latter being removed by decantation. To remove unreacted

$H_2NC(CH_2OH)_3$ and the residual dimethyl sulfoxide, the precipitated polymer was washed with methanol once and finally purified by dialysis (Spectra/Por 7, molecular cutoff ca. 1000) to give the target amphiphile **3**.

The other polymeric amphiphile **4** (eq 2B) was obtained in a similar way but with use of methanol as the reaction medium and different amounts of the reagents [$H_2NC(CH_2OH)_3$ and K_2CO_3, both 2 equiv to the COOEt units in the precursor **2**].

Measurements. The MWD of the precursor block polymer **2** 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-804) that were calibrated against standard polystyrene samples in the molecular weight range 10^2–10^5. The polydispersity ratios ($\bar{M}_w/\bar{M}_n$) were obtained from the SEC eluograms on the basis of a polystyrene calibration; relative changes in polymer molecular weights were also estimated from the apparent number-average molecular weights ($\bar{M}_n$) (Table II). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or D_2O at 25–90 °C on a Jeol FX-90Q spectrometer. The surface tension of aqueous polymer solutions (1.0 and 0.1 wt %) was measured at 25 °C on a Shimadzu ST-1 tensiometer.

The samples for TEM observation were prepared by the following procedures (samples shown in Table II). For **7** and **3b-1** to **3b-4**, a dilute solution of the polymer (0.01 wt %) in a water/methanol (1/1, v/v) mixture was applied on a 400-mesh copper grid (covered with a thin carbon film) and was allowed to air-dry. The cast film was stained with a drop of 2 wt % aqueous solution of uranyl acetate. On the other hand, **3b-5** was dispersed in water (0.1 wt %) on a vortex mixer and heated to ca. 50 °C to give a turbid dispersion. A protion of the dispersion was sonicated on a probe-type sonicator at 70 W for 8 min in a water bath. The aqueous dispersion and the sonicated mixture were then treated in the same manner as for the cast films. TEM images were obtained on a Jeol JEM-200CS (200-kV) or a Hitachi H-600 (100-kV) electron microscope.

References and Notes

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Registry No. 2a, 139943-04-7; **2b**, 125197-74-2; $H_2NC(CH_2OH)_3$, 77-86-1; H_2O, 7732-18-5.