Water-Soluble Fluorine-Containing Amphiphilic Block Copolymer: Synthesis and Aggregation Behavior in Aqueous Solution

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ABSTRACT: Fluorine-containing block copolymers consisting of poly(2-hydroxyethyl vinyl ether) (polyHOVE) and poly(2-(2,2,2-trifluoroethoxy)ethyl vinyl ether) (polyTFEOVE) with different degrees of polymerization were synthesized by sequential cationic polymerization of 2-(acetoxyethyl) vinyl ether (AcOVE) and TFEOVE, followed by hydrolysis of the acetyl protecting group. Poly(HOVE-*b*-TFEOVE) (m:n = 32:10, 28:13, 34:20, 34:31, where m and n represent the degree of polymerization of HOVE and TFEOVE segments, respectively) showed amphiphilic characters and was soluble in water and nonpolar solvents such as toluene. The surface tension of the polymer aqueous solution decreased to ca. 30 mN/m at polymer concentrations around 1×10^{-4} mol/L. SAXS measurement of the aqueous polymer solution revealed that the polymers formed core−shelled spherical micelles at concentrations of 1.0 wt %. Poly(HOVE-*b*-TFEOVE) (m:n = 34:31) aqueous solution solubilized more hexafluorobenzene than the nonfluorinated amphiphilic block polymer, poly(HOVE-*b*-*n*-butyl vinyl ether) did, which was confirmed by measurement of the UV absorption of each solution.

Introduction

Amphiphilic block copolymers have recently attracted much attention because they can form ordered structures by adsorption at the air−water interface or micellization in solution.[1] Their self-assembing properties can be controlled by a change of the chemical structure, the length, and the ratio of hydrophobic and hydrophilic segments.[2,3] On the other hand, it is well-known that fluorine-containing materials exhibit unique properties such as low surface energy, high contact angle, reduced coefficient of friction, biocompatibility, and oleo- and hydrophobicity.[4] Many studies have already been performed on the fluorinated surfactants from both academic and industrial points of view[5] but have mainly been limited to low molecular weight molecules, probably due to the difficulty in the synthesis of amphiphilic block copolymers. Despite some pioneering works on the synthesis of fluorine-containing amphiphilic polymers using controlled radical polymerization,[6] group transfer polymerization,[7] or anionic polymerization,[8] little work has been reported on the synthesis of water-soluble fluorine-containing amphiphilic block copolymers.[9] To obtain such polymers with desired lengths of hydrophobic and hydrophilic segments and sufficiently narrow molecular weight distributions, we applied living cationic polymerization of vinyl ethers,[10−12] which have been well-established by Sawamoto and Higashimura or other groups. Here, we describe the synthesis of water-soluble fluorine-containing amphiphilic block polymers as well as their surface activity and aggregation behavior in aqueous solution.

Experimental Section

Materials. 2-Hydroxylethyl vinyl ether was a kind gift from Professor Mitsuo Sawamoto of Kyoto University. 2-Acetoxyethyl vinyl ether (AcOVE) was prepared by the reported procedure.[13] Triethylamine, ethane sulfonyl chloride, sodium hydride (60% in oil), 1,4-dioxane, sodium hydroxide, and *n*-butyl vinyl ether were purchased from Wako Pure Chemical (Osaka, Japan), zinc chloride (1.0 M diethyl ether solution) was purchased from Aldrich (WI), and 2,2,2-trifluoroethanol was from Daikin (Tokyo) and used as delivered. Diethyl ether and tetrahydrofuran (THF) were freshly distilled over sodium benzophenone ketyl under an argon atmosphere and methylene chloride was distilled over calcium hydride before use.

Synthesis of 2-(2,2,2-Trifluoroethoxy)ethyl Vinyl Ether (TFEOVE). To a mixture of 2-hydroxyethyl vinyl ether (18.7 g, 212 mmol) and triethylamine (32.3 mL, 232 mmol) in diethyl ether (150 mL) was added ethanesulfonyl chloride (24.9 g, 194 mmol) under an argon atmosphere at 0 °C. The mixture was allowed to warm to room temperature and stirred for 10 h. Then the mixture was poured into aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was dried over Na_2SO_4 and concentrated. Distillation under reduced pressure gave 2-vinyloxyethyl ethanesulfonate (24.5 g, 136 mmol) in 70% yield: bp 78−80 °C/0.5 Torr; IR (neat) 2978, 2944, 1623, 1338, 1194, 1162, 972, 912, 798 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (t, J = 7.3 Hz, 3H), 3.19 (q, J = 7.3 Hz, 2H), 3.92−4.02 (m, 2H), 4.09 (dd, J = 6.6, 2.2 Hz, 1H), 4.23 (dd, J = 13.9, 2.2 Hz, 1H), 4.41−4.50 (m, 2H), 6.47 (dd, J = 13.9, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 8.06, 45.13, 65.59, 67.46, 87.61, 150.96. Anal. Calcd for $C_6H_{12}O_4S$: C, 39.98; H, 6.72. Found: C, 39.80; H, 6.83. Sodium hydride (60% in oil, 10.0 g, 250 mmol) was washed with 20 mL of THF four times under an argon atmosphere, and 80 mL of 2,2,2-trifluoroethanol was slowly added at 0 °C. To the suspension of sodium 2,2,2-trifluoroethoxide was added 2-vinyloxyethy ethanesulfonate (23.1 g, 128 mmol) prepared as above, and the mixture was stirred for 10 h under reflux. Then the mixture was poured into aqueous $NaHCO_3$ and extracted with diethyl ether (100 mL). The extract was dried over Na_2SO_4 and concentrated. The residual oil was distilled under reduced pressure over calcium hydride twice to give TFEOVE (4.93 g, 29.0 mmol) in 23% yield: bp 63−65 °C (100 Torr) IR (neat) 2934, 2878, 1639, 1620, 1459, 1315, 1277, 1143, 968, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 4H), 3.92 (q, J = 8.0 Hz, 2H), 4.05 (dd, J = 6.3, 2.0 Hz, 1H), 4.21 (dd, J = 13.5, 2.0 Hz, 1H), 6.49 (dd, J = 13.5, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 67.16, 68.79 (q, J_{CF} = 34 Hz), 70.90, 86.99, 123.94 (q, J_{CF} = 279 Hz), 151.44. Anal. Calcd for $C_6F_3H_9O_2$: C, 42.64; H, 5.21. Found: C, 42.36; H, 5.33.

Block Polymerization Procedure. The synthesis of poly(AcOVE-*b*-TFEOVE) (m:n = 28:13) is representative. Polymerizations were carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. Two Schlenk tubes

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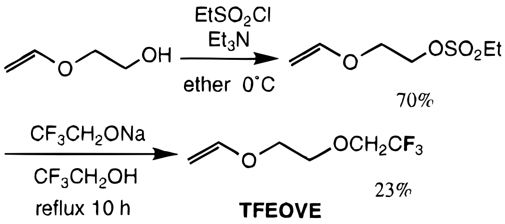
Scheme 1



were used. One (tube A) was for the synthesis of AcOVE homopolymers, and the other (tube B) was for the synthesis of block polymers. The reaction was initiated by sequential addition of a prechilled solution of *n*-butyl vinyl ether−HCl adduct[14] (0.135 M hexane solution, 1.3 mL, 0.175 mmol) and $ZnCl_2$ (0.1 M diethyl ether solution 0.40 mL, 0.04 mmol) into an AcOVE solution (686 mg, 5.28 mmol) in methylene chloride (11 mL) at −20 °C (tube A contained 0.4 mL of chlorobenzene as a GC internal standard). A small portion of the reaction mixture in tube A was taken by a syringe and quenched with methanol containing a small amount of ammonia, which was analyzed by GC, and the monomer conversion was determined. After 95% of AcOVE had been converted, the polymerization in tube A was terminated with ammonia-containing methanol. On the other hand, the mixture in tube B was cooled to −40 °C and TFEOVE (527 mg, 3.10 mmol) was added. The polymerization in tube B was terminated with ammonia-containing methanol 1.5 h after the second monomer had been added. The resulting mixtures in tube A and B were poured into water and the products were extracted with diethyl ether, respectively. The extracts were dried over Na_2SO_4 and concentrated in vacuo.

Poly(AcOVE-*b*-TFEOVE). IR (neat): 2936, 1729, 1378, 1231, 1094, 1053, 966 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J = 7.0 Hz, 3H), 1.09−1.22 (m, 3H), 1.25−2.00 (m, 86H), 2.09 (s, 84H), 3.32 (s, 3H), 3.35−3.75 (m, 139H), 3.75−3.93 (m, 26H), 4.07−4.23 (m, 56H), 4.61−4.72 (m, 1H).

Hydrolysis of the Acetoxy Protecting Group. The acetoxy protecting groups of poly(AcOVE-*b*-TFEOVE) were hydrolyzed by treatment with an excess amount of 4 M aqueous sodium hydroxide in 1,4-dioxane (5 equiv of NaOH to acetoxy groups in 10 wt % polymer solution) for 3 days at room temperature. Removal of impurities by dialysis (Spectra/Pro 7, molecular weight cutoff 1000) in water, followed by freeze-drying in vacuo gave poly(HOVE-*b*-TFEOVE): IR (neat) 3250 (broad OH), 2916, 1458, 1278, 1046, 967 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.09−1.22 (m, 3H), 1.25−2.20 (m, 86H), 2.80−4.80 (m, 249H), 3.32 (s, 3H), 4.60−4.72 (m, 1H).

Molecular Characterization. The values of M_w/M_n were determined by GPC with a polystyrene standard calibration for the AcOVE−TFEOVE block polymer, where M_w and M_n are weight- and number-averaged molecular weights, respectively. The number-averaged degrees of polymerization of AcOVE (m) and TFEOVE (n) were evaluated by comparing the area of methyl peak (at 2.09 ppm) and methylene peak (at 3.75−3.93 ppm) with the methyl peak (at 0.92 ppm) of the initiation end butyl group by ^{1}H NMR. Although they were evaluated for poly(AcOVE-*b*-TFEOVE) precursor polymers, they can be applied for poly(HOVE-*b*-TFEOVE) as well, since it was confirmed by ^{1}H NMR that no subreaction had taken place during hydrolysis.

Measurements. Gel permeation chromatography was carried out in chloroform on a JASCO 880-PU chromatograph equipped with four polystyrene gel columns (Shodex K-802, K-803, K-804, and K-805) and JASCO 830-RI refractive index detector. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX 270 spectrometer in $CDCl_3$. IR spectra were measured on a JASCO IR-810 spectrometer. Surface tension was measured on a CBVP-Z automatic surface tensiometer (Kyowa Interface Science Co., Ltd.) using a Pt plate in full automatic mode. UV−visible spectra of dye solubilized polymer solutions were obtained using a U-3400 spectrometer (Hitachi, Ltd.). Small-angle X-ray scattering (SAXS) of polymer solution was measured using a Kratky-type camera manufactured by Rigaku Corporation installed on a rotating anode X-ray generator and a position-sensitive proportional counter. Details of the SAXS instrument were previously reported.[15]

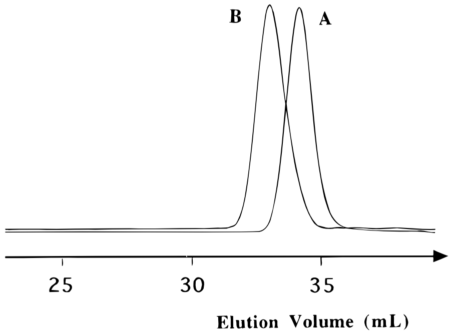


Figure 1. GPC charts: (A) polyAcOVE (m = 32); (B) poly(AcOVE-*b*-TFEOVE) (m:n = 33:12).

Results and Discussion

Synthesis of Fluorine-Containing Vinyl Monomer. Semifluorinated monomer, 2-(2,2,2-trifluoroethoxy)ethyl vinyl ether (TFEOVE), was obtained by treatment of 2-vinyloxyethyl ethanesulfonate with sodium 2,2,2-trifluoroethoxide as shown in Scheme 1.[16] 2-Vinyloxyethyl ethanesulfonate was prepared from 2-hydroxyethyl vinyl ether with ethanesulfonyl chloride in good yield. TFEOVE was miscible with AcOVE at any rate and showed high solubility to conventional organic solvents such as diethyl ether, dichloromethane, and toluene even at low temperatures. This is one of the characters essential for a fluorinated monomer to be copolymerized with hydrocarbon monomers.

Synthesis of Poly(HOVE-*b*-TFEOVE). Aoshima et al. reported that cationic polymerization of 2-ethoxyethyl vinyl ether proceeded in a living fashion using 1-(isobutoxy)ethyl acetate $CH_3CH(O\text{-}i\text{-}Bu)OCOCH_3$ as an initiator and $Et_{1.5}AlCl_{1.5}$ as an activator in toluene in the presence of a small amount of THF.[11] First, we examined the polymerization of TFEOVE under this condition. However, the polymerization rate was unexpectedly slow, and complete conversion of TFEOVE was not achieved. Then we applied a more reactive polymerization condition, in which alkyl vinyl ether HCl adduct was used as an initiator and $ZnCl_2$ was used as an activator.[10a,b] Block copolymerization of 2-acetoxyethyl vinyl ether (AcOVE) with TFEOVE was carried out by sequential addition of TFEOVE at −40 °C to a cationic living polymer of AcOVE prepared with *n*-butyl vinyl ether initiator in the presence of $ZnCl_2$ activator in CH_2Cl_2 at −20 °C. The typical GPC trace of the obtained polymers before and after the addition of the second monomer is shown in Figure 1. The GPC trace shifted toward a higher molecular weight region, which indicates the clean formation of block copolymer. The proton NMR spectrum of poly(AcOVE-*b*-TFEOVE) is shown in Figure 2. The signals for the initiation end methyl proton of the butyl group (**f**) and termination end methyl proton of the methoxy group (**q**) are seen at 0.89 and 3.32 ppm, which can be used for the estimation of the degree of polymerization.(See Experimental Section) The acetal methyne proton **m′** at the termination end is also observed at 4.60−4.70 ppm. Several block polymers having different compositions of AcOVE and TFEOVE were synthesized by changing the feed ratios of these two monomers. The results are summarized in Table 1.The acetyl protecting group was easily hydro-

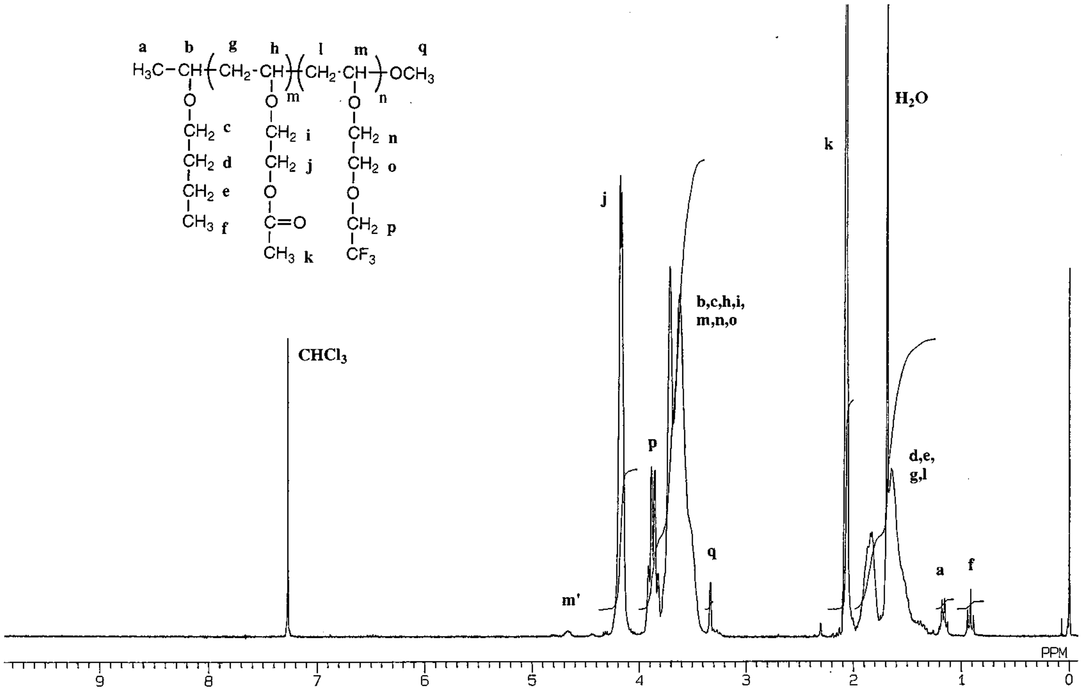


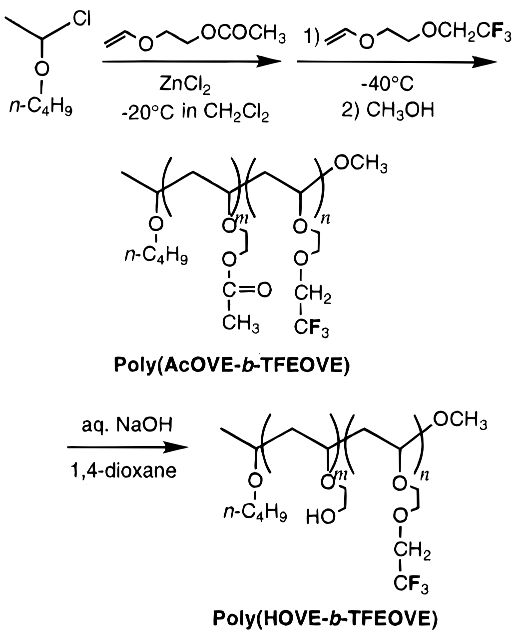
Figure 2. 270 MHz ^{1}H NMR spectrum of poly(AcOVE-*b*-TFEOVE) (m:n = 33:12) in CDCl$_3$.

Table 1. Results of Block Polymerization of AcOVE with TFEOVE

initial ratio of [I]^a:[AcOVE]:[TFEOVE]	m^b	n^c	M_w/M_n^{d}
1:30:12	32	10	1.13
1:30:18	28	13	1.08
1:30:25	34	20	1.16
1:30:30	34	31	*e*

[a] Concentration of the initiator. [b] Average degree of polymerizaton of AcOVE determined by ^{1}H NMR. [c] Average degree of polymerization of TFEOVE determined by ^{1}H NMR. [d] Determined by GPC using a polystyrene standard. [e] The polydispersity index could not be determined by GPC because the block polymer was not detected by the RI detector.

Scheme 2



lyzed by treatment with aqueous sodium hydroxide in 1,4-dioxane. The proton NMR spectrum of the polymer after hydrolysis is shown in Figure 3. The complete hydrolysis was confirmed by disappearance of acetoxy methyl signal **k** at 2.09 ppm and by higher field shift of methylene proton **j** from 4.07–4.23 ppm to 3.70–3.95 ppm. These polymers were soluble in not only water but also nonpolar organic solvents such as chloroform, methylene chloride, and toluene, indicating the amphiphilic character.

Surface Activity of Poly(HOVE-*b*-TFEOVE). Surface activities of the block copolymers in aqueous media were determined by measuring the surface tension of the water solutions. Figure 4 depicts the surface tensions for the poly(HOVE-*b*-TFEOVE)s as a function of polymer concentration. All block polymers show a declining surface tension down to around 30 mN/m with increasing polymer concentrations. Obscure breakpoints of the declining surface tensions were observed around 1×10^{-5} to 1×10^{-4} mol/L for all polymers. It seemed that the critical micelle concentrations (cmcs) existed around those polymer concentrations.

Small-Angle X-ray Scattering (SAXS) Measurement. To investigate the aggregation behavior of the block polymer in water, SAXS measurements of 1.0 wt % aqueous solutions were carried out. The SAXS profiles for poly(HOVE-*b*-TFEOVE)s (m:n = 32:10, 28:13, 34:20, 34:31) are shown in Figure 5. In all cases, strong X-ray scattering were observed at small angles, indicating the existence of aggregates, and particularly in the case of poly(HOVE-*b*-TFEOVE) (m:n = 34:31), the scattering curve exhibited a well-marked second maximum, indicating a well-defined structure of micelles (Figure 5d).

To evaluate the size of the aggregates, we fitted the experimental profiles by theoretical curves. For calculation, a spherical core–shell model was assumed as the micelle structure, where the central core consisted of a TFEOVE segment and the outer shell consisted of a HOVE segment swollen by water. Theoretical curves for the models were calculated as follows:

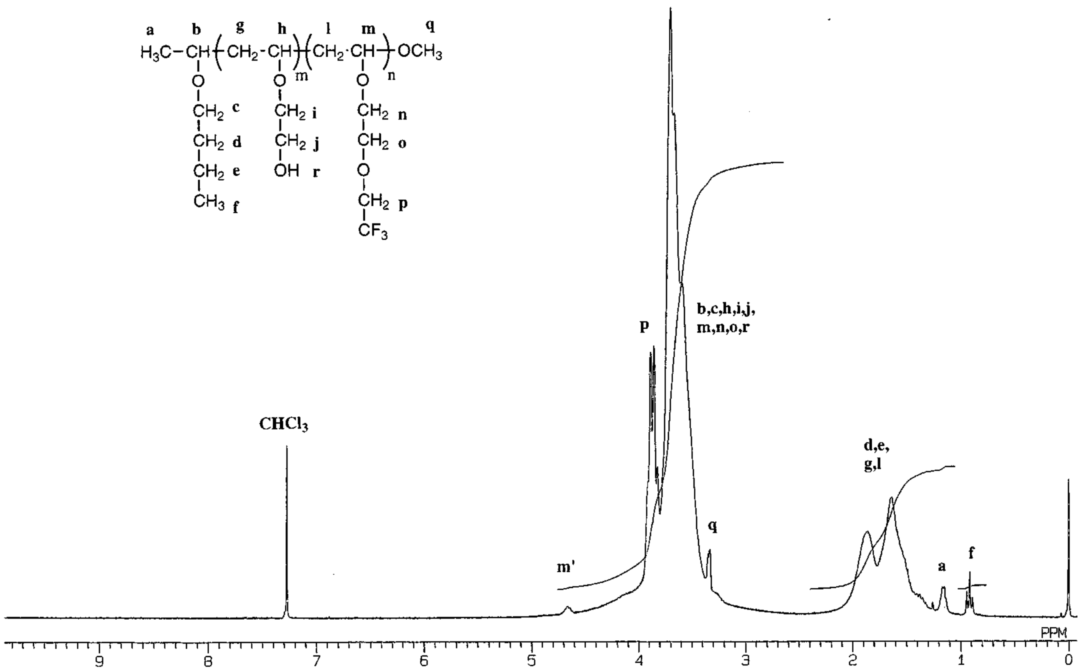


Figure 3. 270 MHz ^{1}H NMR spectrum of poly(HOVE-*b*-TFEOVE) (m:n = 33:12) in CDCl$_3$.

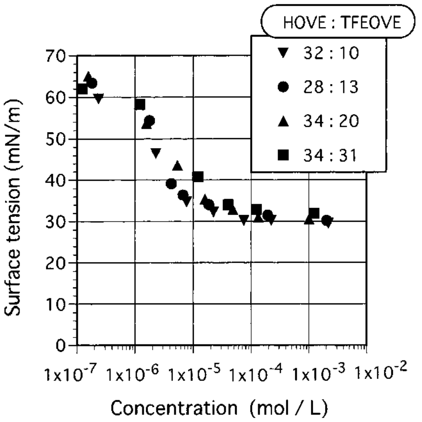


Figure 4. Surface tension of poly(HOVE-*b*-TFEOVE) aqueous solutions.

$$I(q) = fn_p[(4\pi/3)R_c^{\,3}(\rho_c - \rho_s)\Phi(R_c\mathbf{q}) + (4\pi/3)R_s^{\,3}(\rho_s - \rho_0)\Phi(R_s\mathbf{q})]^2$$

$$\Phi(x) = 3[(\sin x - x\cos x)/x^3] \qquad (1)$$

where n_p is the number density of the micelle; R_c and R_s are the radii of the core and of the whole micelle, respectively; and ρ_c, ρ_s, and ρ_0 are the electron densities of the core, shell, and solvent, respectively. **q** (scattering vector) is $4\pi(\sin\theta)/\lambda$ with X-ray wavelength λ and scattering angle 2θ. f is a shift factor (it is necessary to introduce a shift factor, since the intensities of the experimental data are obtained in arbitrary units because the data have not been calibrated to an absolute scale). Here, we assume homogeneous electron density distributions inside the core and the shell. Using the calculable values of the electron densities of the monomer unit ρ_{TFEOVE} and ρ_{HOVE}, ρ_c and ρ_s are given by

$$\rho_c = \rho_{\mathrm{TFEOVE}} \qquad (2)$$

$$\rho_s = \phi_{\mathrm{sol}}\rho_0 + (1 - \phi_{\mathrm{sol}})\rho_{\mathrm{HOVE}} \qquad (3)$$

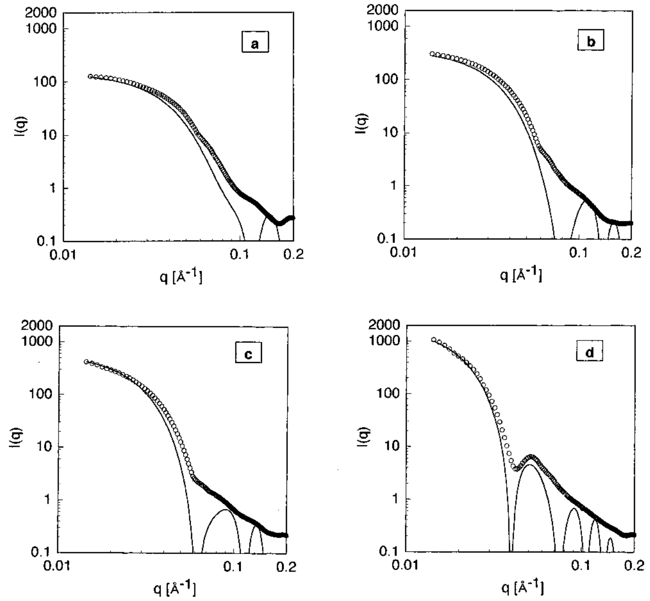


Figure 5. SAXS profiles of poly(HOVE-*b*-TFEOVE) 1.0 wt % aqueous solutions. (a) m:n = 32:10, (b) m:n = 28:13, (c) m:n = 34:20, (d) m:n = 34:31. Solid lines are theoretical curves of core–shell spheres.

where ϕ_{sol} is the volume fraction of the solvent in the shell, which can be calculated by the following equation with the degree of polymerization of HOVE (m), the volume of HOVE repeated units (ν_{HOVE}), the volume of the core (V_c), and the volume of the overall micelle (V_s):

$$\phi_{\mathrm{sol}} = 1 - N_{\mathrm{agg}}m\nu_{\mathrm{HOVE}}/(V_s - V_c) \qquad (4)$$

N_{agg} denotes the aggregation number of the micelles, which is calculated from V_c, the degree of polymerization of TFEOVE (n), and the volume of TFEOVE repeated units (ν_{TFEOVE}):

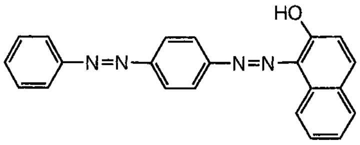
$$N_{\mathrm{agg}} = V_c/(n\nu_{\mathrm{TFEOVE}}) \qquad (5)$$

Assuming that all polymers contribute to the micelle

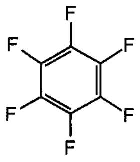
Table 2. Structural Parameters of Poly(HOVE-*b*-TFEOVE) Micelles in 1.0 wt % Aqueous Solutions

poly(HOVE-*b*-TFEOVE) *m*:*n*	R_c[a] (Å)	R_s[b] (Å)	N_{agg}[c]	Φ_{sol}[d]
32:10	41	81	140	0.71
28:13	57	99	290	0.69
34:20	69	112	340	0.68
34:31	105	152	770	0.67

[a] Radius of the core. [b] Radius of the shell. [c] Aggregation number. [d] Volume fraction of water in the shell.



a. Sudane III



b. hexafluorobenzene

Figure 6. Chemical structure of Sudan III (a) and hexafluorobenzene (b).

formation, the number density n_p of the micelles is then calculated

$$n_p = \phi/(N_{agg}(n\nu_{TFEOVE} + m\nu_{HOVE})) \qquad (6)$$

where ϕ is the volume fraction of copolymer in solution.

The values of $\rho_{TFEOVE} = 0.433$ Å^{-3}, $\rho_{HOVE} = 0.382$ Å^{-3}, and $\rho_0 = 0.334$ Å^{-3} were fixed, which were calculated from electron numbers, unit formula weights, and bulk densities of polyTFEOVE, polyHOVE, and H_2O. The bulk densities of 1.39 g/cm^3 for polyTFEOVE and 1.17 g/cm^3 for polyHOVE were used. Three parameters, R_c, R_s, and f, were variables in the fitting procedure, while the value of f was arranged to be the same for all data. The SAXS curves were well reproduced by the theoretical curves for core–shell spheres as shown in Figure 5, whereas simple theoretical curves for homogeneous spherical particles did not fit the experimental data. The fitting results are summarized in Table 2. The results indicated that there was a qualitative relationship between polymer composition and micellar structure. The aggregation number N_{agg} or core size R_c increased with the increase of TFEOVE chain length (n). A similar increase in aggregation number was observed for other amphiphilic vinyl ether block copolymers.[3e]

Solubilization of Sudan III and Hexafluorobenzene in Polymer Micelles. Solubilization of water-insoluble compounds in water is one of the most important functions of the polymer surfactants. To investigate the property of fluorine-containing amphiphilic block polymers, we examined the solubilization of two water-insoluble compounds to aqueous poly(HOVE-*b*-TFEOVE) (m:n = 34:31) solution. One was a nonfluorinated compound, Sudan III (molar absorptivity: $\epsilon = 1.3 \times 10^4$ at $\lambda = 328$ nm in $CHCl_3$), and the other was a fluorinated compound, hexafluorobenzene ($\epsilon = 4.3 \times 10^2$ at $\lambda = 231$ nm in $CHCl_3$). Their chemical structures are given in Figure 6. For comparison, solubilization of the same compounds to the nonfluorinated block polymer, poly(HOVE-*b*-*n*-butyl vinyl ether) (poly(HOVE-*b*-NBVE), m:n = 40:20),[17] in solution was also examined. The chemical structure of poly(HOVE-*b*-NBVE) is depicted in Figure 7. The UV absorption of the aqueous polymer solution in the presence of an excess amount of Sudan III and hexafluorobenzene as a function of polymer concentration is shown in Figures 8 and 9. As shown in Figure 8, a significant increase of UV absorption was observed at concentrations higher than 1×10^{-5} mol/L for both poly(HOVE-*b*-TFEOVE) and poly(HOVE-*b*-NBVE). These concentrations were regarded as the cmcs of the amphiphilic polymers. The cmc of poly(HOVE-*b*-TFEOVE) observed from sulubilization experiments was in agreement with that estimated from the surface tension experiments. In Figure 8, it is clear that poly(HOVE-*b*-NBVE) solution solubilized more Sudan III than poly(HOVE-*b*-TFEOVE) did. This is probably due to the oleophobicity of the fluorinated segment of poly(HOVE-*b*-TFEOVE). In Figure 9, the increase of UV absorption was also seen above the concentration of 1×10^{-5} mol/L regardless of the solubilizate. In this case, however, poly(HOVE-*b*-TFEOVE) solubilized more hexafluorobenzene than poly(HOVE-*b*-NBVE) did. These results suggested the existence of an attractive interaction between a poly(HOVE-*b*-TFEOVE) micelle and a fluorinated compound.

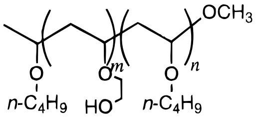


Figure 7. Chemical structure of poly(HOVE-*b*-NBVE).

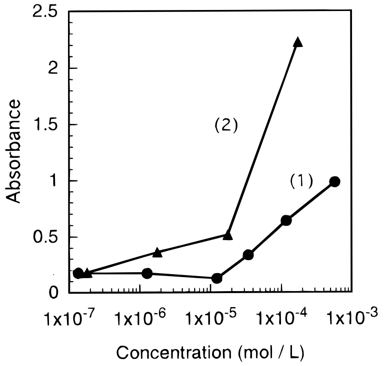


Figure 8. Absorbance by Sudan III in aqueous solutions of (1) poly(HOVE-*b*-TFEOVE) (m:n = 34:31) and (2) poly(HOVE-*b*-NBVE) (m:n = 40:20) at 328 nm.

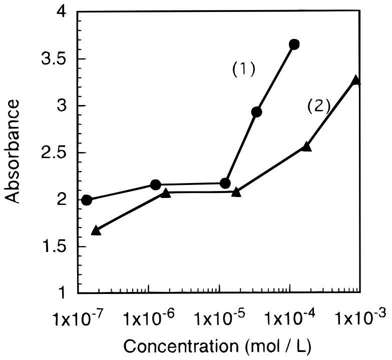


Figure 9. Absorbance by hexafluorobenzene in aqueous solutions of (1) poly(HOVE-*b*-TFEOVE) (m:n = 34:31) and (2) poly(HOVE-*b*-NBVE) (m:n = 40:20) at 231 nm.

Conclusions

Water-soluble fluorine-containing amphiphilic block copolymers, poly(HOVE-*b*-TFEOVE)s, were synthesized by a living cationic polymerization and subsequent hydrolysis. They showed high surface activity. The surface tension of the polymer aqueous solutions decreased to 30 mN/m. Critical micelle concentrations of the block polymers were found to be around 1×10^{-5} to 1×10^{-4} mol/L by surface tension measurements. The micelle formations of the block polymers in water were confirmed by SAXS measurements. Analysis of the SAXS profiles by theoretical calculations revealed that the micelle had a core−shell spherical morphology and the aggregation number increased as the length of TFEOVE segment increased. Solubilization experiments revealed that poly(HOVE-*b*-TFEOVE) had a high ability to solubilize a fluorinated compound compared to nonfluorinated amphiphilic block copolymers.

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References and Notes

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(17) Poly(HOVE-*b*-NBVE) (m:n = 40:20) was prepared as reported in ref 3e. We have reported that the block polymer poly(HOVE-*b*-NBVE) (m:n = 39:21) formed a core−shell ellipsoidal micelle in aqueous solution in ref 3d.

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