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Perfluoroalkyl-philic Character of Poly(2-hydroxyethyl vinyl ether)-*block*-poly[2-(2,2,2-trifluoroethoxy)ethyl vinyl ether] Micelles in Water: Selective Solubilization of Perfluorinated Compounds

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ABSTRACT: Two types of amphiphilic block copolymer, poly(2-hydroxyethyl vinyl ether)-*block*-poly[2-(2,2,2-trifluoroethoxy)ethyl vinyl ether] (poly(HOVE-*b*-TFEOVE)) (m:n = 78:23) and poly(2-hydroxyethyl vinyl ether)-*block*-poly(*n*-butyl vinyl ether) (poly(HOVE-*b*-NBVE)) (m:n = 74:23), having the same ratios of polymerization degree in hydrophilic and hydrophobic segments with the same total chain length were synthesized, and the properties of their aqueous solutions were investigated, where m and n represent number-averaged polymerization degree of HOVE and TFEOVE or NBVE, respectively. By water surface tension measurements, the critical micelle concentrations (cmc's) of poly(HOVE-*b*-TFEOVE) and poly(HOVE-*b*-NBVE) were both estimated at 1.0×10^{-4} mol/L. Solubilization of various fluoro and nonfluoro compounds using these polymer aqueous solutions was examined. It was confirmed that poly(HOVE-*b*-TFEOVE) solubilized more decafluorobiphenyl than did poly(HOVE-*b*-NBVE), whereas poly(HOVE-*b*-NBVE) solubilized more 2,6-dimethylnaphthalene than did poly(HOVE-*b*-TFEOVE). When a mixture of decafluorobiphenyl and 2,6-dimethylnaphthalene was added to the polymer solutions, poly(HOVE-*b*-TFEOVE) selectively solubilized decafluorobiphenyl, while poly(HOVE-*b*-NBVE) solubilized 2,6-dimethylnaphthalene predominantly, which was observed by the UV absorption spectrum of the polymer solutions.

Introduction

Fluorine-containing polymers have attracted much attention because of their unique properties such as low surface energy, high contact angle, reduced coefficient of friction, high biocompatibility, and lipo- and hydrophobicity, which conventional hydrocarbon polymers do not possess.[1] In particular, highly fluorinated polymers exhibit characteristic solubility. For example, they are not soluble in common organic solvents but are soluble in fluorinated solvents. Recently, DeSimmon and coworkers have reported that fluorinated polymers have CO_2-philicity and are soluble in the supercritical carbon dioxide.[2]

On the other hand, hydrophobic−hydrophilic block copolymers have recently been investigated extensively because they show high surface activity and can self-assemble to form various nanostructures such as micelles in selective solutions.[3] However, little has been known about the nature of water-soluble fluorinated block copolymers consisting of hydrophobic and hydrophilic segments. Saegusa et al. reported the first example of a water-soluble fluorine-containing block copolymer, poly(perfluoroalkyloxazoline)-*block*-poly(methyloxazoline).[4] We recently reported the synthesis and micelle formation of fluorine-containing amphiphilic block copolymer, poly(2-hydroxyethyl vinyl ether)-*block*-poly[2(2,2,2-trifluoroethoxy)ethyl vinyl ether] (poly(HOVE-*b*-TFEOVE)),[5] and observed an interesting property of poly(HOVE-*b*-TFEOVE) in the solubilization of hexafluorobenzene into water.

In this study, poly(HOVE-*b*-TFEOVE) and nonfluorinated poly(HOVE-*block*-poly(*n*-butyl vinyl ether) (poly(HOVE-*b*-NBVE)) having the same ratios of polymerization degree in hydrophilic and hydrophobic segments with the same total chain length were newly synthesized and the solubilization of fluorinated or nonfluorinated compounds by the polymer micelles formed in water was examined in detail. We found that poly(HOVE-*b*-TFEOVE) could selectively solubilize fluorinated compounds from a mixture of fluorinated and nonfluorinated compounds. We considered that this was due to a "perfluoroalkyl-philic" character of the polymer micelles.

Experimental Section

Materials. 2-Hydroxylethyl vinyl ether was a kind gift from Professor Mitsuo Sawamoto of Kyoto University. 2-Acetoxyethyl vinyl ether (AcOVE),[6] 2-(2,2,2-trifluoroethoxy)ethyl vinyl ether (TFEOVE),[5] and *n*-butyl vinyl ether−HCl adduct[7] were prepared by the reported procedures. Chlorobenzene, 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 (Milwaukee, WI) and used as delivered. Diethyl ether was freshly distilled over sodium benzophenone ketyl under an argon atmosphere, and methylene chloride was distilled over calcium hydride before use.

Block Copolymerization Procedure. Two Schlenk tubes equipped with a three-way stopcock were baked under nitrogen and used for synthesis of each block copolymer. One (tube A) was for the synthesis of a homopolymer, and the other (tube B) was for the synthesis of a block copolymer. The reaction was initiated by sequential addition of a solution of *n*-butyl vinyl ether−HCl adduct (0.10 M hexane solution, 2.5 mL, 0.25 mmol) and a solution of $ZnCl_2$ (0.1 M diethyl ether, 0.80 mL, 0.08 mmol) into a mixture of AcOVE (1.90 mL, 15 mmol) and chlorobenzene (0.5 mL, as a GC internal standard) in methylene chloride (20 mL) at −20 °C. A small portion of reaction

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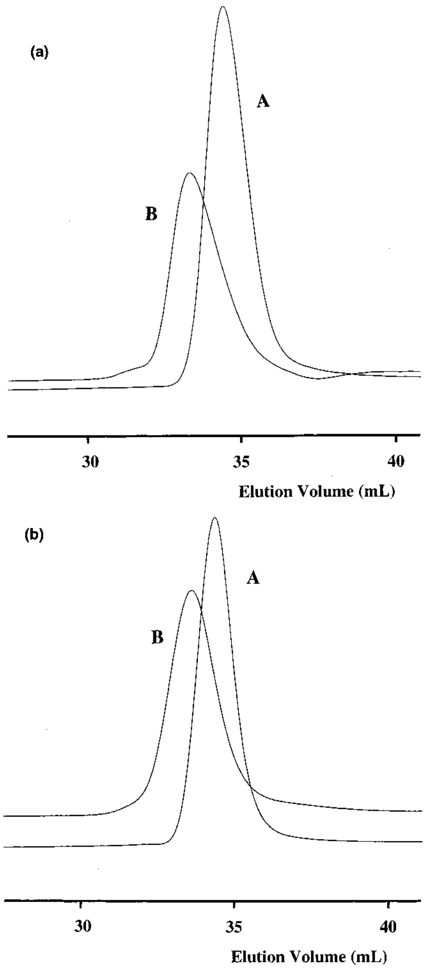


Figure 1. (a) GPC charts: (A) polyAcOVE homopolymer, (B) poly(AcOVE-*b*-TFEOVE) block copolymer. (b) GPC charts: (A) polyAcOVE homopolymer, (B) poly(AcOVE-*b*-NBVE) block copolymer.

mixture in tube A (ca. 0.1 mL) was taken with a syringe and quenched with ammonia-containing methanol (1.5 wt %, 0.3 mL), which was analyzed by GC to check the monomer conversion. After 95% of a monomer had been converted, the polymerization in tube A was terminated with ammonia-containing methanol (5 mL). On the other hand, tube B was cooled to −40 °C, and the second monomer (TFEOVE (0.66 mL, 5.0 mmol) or NBVE (0.80 mL, 5.0 mmol)) was added to the mixture. The polymerization in tube B was terminated with ammonia-containing methanol (5 mL) 4.0 h after the second monomer had been added. The resulting mixtures in tubes A and B were poured into water, and the products were extracted with diethyl ether. The extracts were dried over Na$_2$SO$_4$ and concentrated in vacuo to give polyAcOVE homopolymer and the desired block copolymer (poly(AcOVE-*b*-TFEOVE) or poly(AcOVE-*b*-NBVE)).

Hydrolysis of Acetyl Protecting Group. The acetyl protecting groups of poly(AcOVE-*b*-TFEOVE) and poly(AcOVE-*b*-NBVE) were hydrolyzed by treatment with an excess amount of 4 M aqueous sodium hydroxide in 1,4-dioxane (5 equiv of NaOH to acetyl 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) and poly(HOVE-*b*-NBVE).

Molecular Characterization. The GPC charts of the block polymers are shown in Figure 1 along with those of the polyAcOVE prepolymers. In both figures, GPC charts clearly shifted to the high molecular weight region after addition of the second monomer, indicating the clean formation of the block copolymers. The values of M_w/M_n were determined by GPC with a polystyrene standard calibration for poly(AcOVE-*b*-TFEOVE) and poly(AcOVE-*b*-NBVE), where M_w and M_n are weight- and number-average molecular weights, respectively. The ^{1}H NMR spectra of poly(AcOVE-*b*-TFEOVE) and poly(AcOVE-*b*-NBVE) were similar to those of the analogous block copolymers reported previously.[5,8] The number-average degrees of polymerization of poly(AcOVE-*b*-TFEOVE) were evaluated by comparing the area of methyl peak (at 2.09 ppm) and methylene peak (at 3.75−3.93 ppm) with methyl peak (at 0.92 ppm) of the initiation end butyl group by ^{1}H NMR. Those of poly(AcOVE-*b*-NBVE) were evaluated as follows. First, the degree of polymerization for the AcOVE segment was determined by ^{1}H NMR measurement of the AcOVE homopolymer obtained from a termination of living polyAcOVE before addition of NBVE. Then, the degree of polymerization for the NBVE segment was estimated from the integral ratio of methyl peak of AcOVE segment at 2.09 ppm and methyl peak of NBVE segment at 0.92 ppm. The characteristics of the obtained poly(AcOVE-*b*-TFEOVE) and poly(AcOVE-*b*-NBVE) are summarized in Table 1.

Table 1. Characteristics of the Block Copolymers before Hydrolysis of Acetyl Groups

polymer	m:n ^{1}H NMR	M_n ^{1}H NMR	M_n GPC	M_w/M_n GPC
poly(AcOVE-*b*-TFEOVE)	78:23	14 200	8 800	1.12
poly(AcOVE-*b*-NBVE)	74:23	11 800	10 600	1.17

Although the values were obtained for poly(AcOVE-*b*-TFEOVE) and poly(AcOVE-*b*-NBVE) precursor polymers, the method can be applied for poly(HOVE-*b*-TFEOVE) and poly(HOVE-*b*-NBVE) as well, since it was confirmed by ^{1}H NMR that no subreaction had taken place during hydrolysis. The ^{1}H NMR spectra of poly(HOVE-*b*-TFEOVE) and poly(HOVE-*b*-NBVE) are shown in Figure 2.

Measurements. Gas chromatography was performed on Shimadzu GC-8A chromatograhy equipped with glass column (stationary phase: silicon-DC11(20%), support: Celite 545S). 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 reflective index detector. Proton NMR spectra were recorded on a JEOL GSX 270 spectrometer in CDCl$_3$. 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−vis spectra of dye-solubilized polymer solutions were taken on a U-3310 spectrophotometer (Hitachi, Ltd.) using the same concentration of the polymer solution as a reference. The dye-solubilized polymer solutions were prepared by addition of excess amount of powdered dye (300 mg) to an aqueous solution of block copolymers (10 mL) and stirring the mixture for 3 days at room temperature. In all cases examined in this study, the excess dyes were precipitated at the bottom of the sample containers, which indicated that the solutions were saturated with the dyes.

Results and Discussion

Synthesis of Water-Soluble Block Copolymer: Poly(HOVE-*b*-TFEOVE) and Poly(HOVE-*b*-NBVE). Fluorine-containing block copolymer poly(HOVE-*b*-TFEOVE) and non-fluorine-containing block copolymer poly(HOVE-*b*-NBVE)[9] having the same ratios of polymerization degree in hydrophilic and hydrophobic segments with the same total chain length were synthesized by a living cationic polymerization[10] of AcOVE with TFEOVE or NBVE, followed by hydrolysis of the acetyl protection group of polyAcOVE as shown in Schemes 1 and 2.

Hydrolysis of the acetyl protecting group was performed in 1,4-dioxane in the presence of aqueous NaOH. Poly(HOVE-*b*-NBVE) thus obtained was soluble in water but insoluble in a nonpolar solvent such as

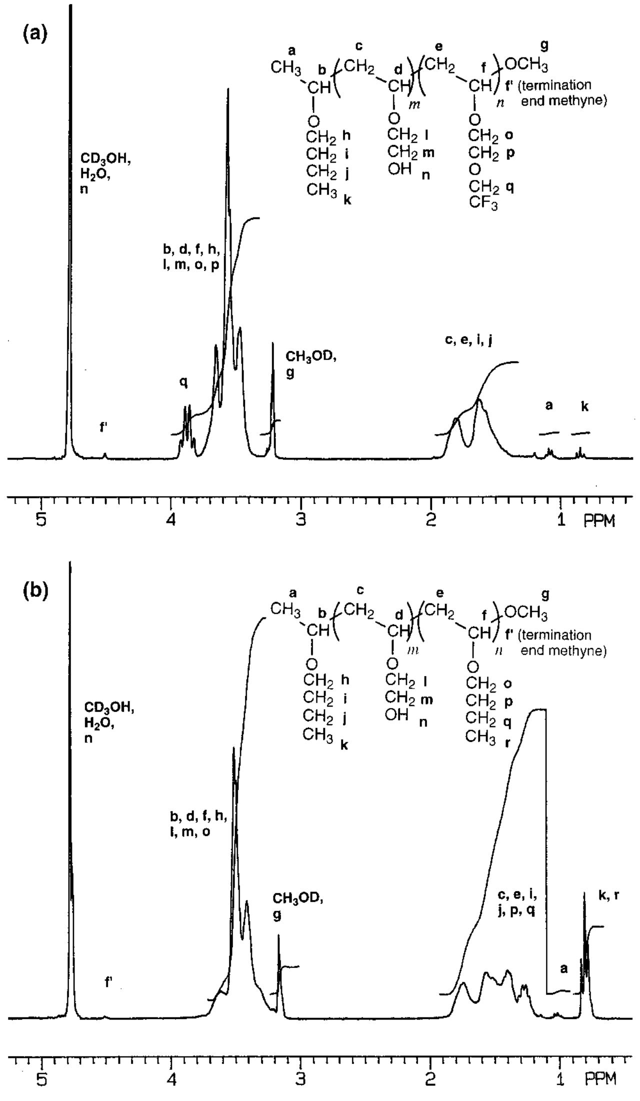
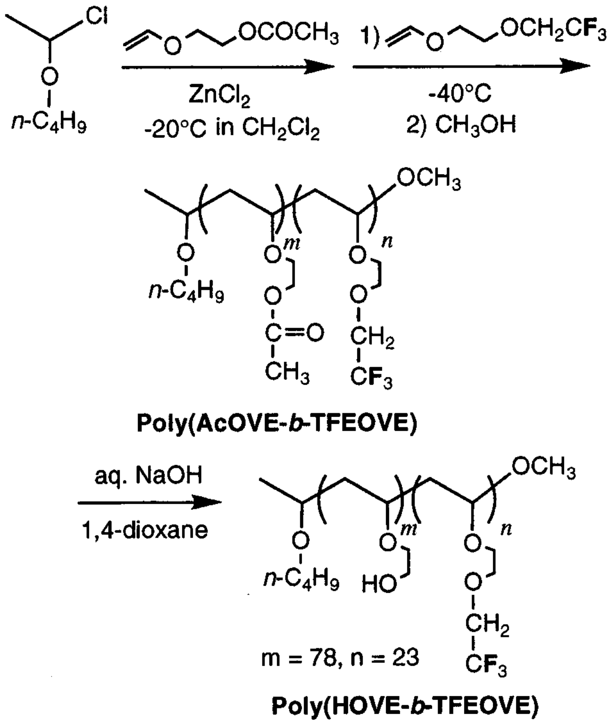
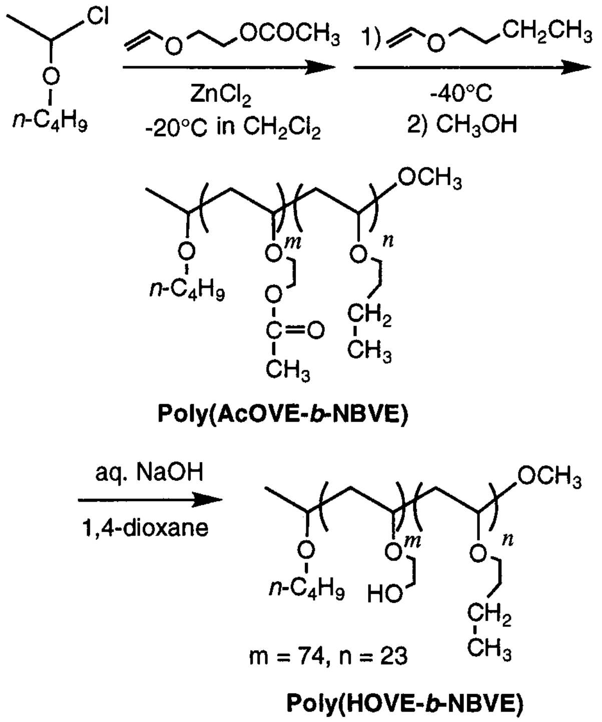


Figure 2. (a) ^{1}H NMR spectrum of poly(HOVE-*b*-TFEOVE) in CD_3OD. (b) ^{1}H NMR spectrum of poly(HOVE-*b*-NBVE) in CD_3OD.

Scheme 1



Scheme 2



chloroform, dichloromethane, toluene, and benzene. Poly(HOVE-*b*-TFEOVE) was soluble in water, chloroform, and dichloromethane but insoluble in highly nonpolar hydrocarbons such as benzene and toluene.

Surface Activity. To examine the surface activities of poly(HOVE-*b*-TFEOVE) and poly(HOVE-*b*-NBVE) in aqueous media, the surface tension of the water solution was measured. Figures 3 shows the surface tension of aqueous block copolymer solutions. In the case of poly(HOVE-*b*-TFEOVE), the surface tension declined to 35 mN/m with increasing polymer concentrations, indicating high surface activity of the polymer. We previously reported that an aqueous poly(HOVE-*b*-TFEOVE) with shorter chain length (m:n = 32:10) showed lower surface tension (32 mN/m at its critical micelle concentration (cmc) (1.0×10^{-4} mol/L)).[5] In comparison with this result, it was supposed that the surface activity of the block copolymer decreases as the total chain length increases. The breakpoint of the declining surface tension was observed around 1.0×10^{-4} mol/L, where the cmc of the solution should exist. On the other hand, the surface tension of aqueous poly(HOVE-*b*-NBVE) declined to 38 mN/m, showing less surface activity. Nevertheless, the breakpoint of the declining surface tension was also observed around 1.0×10^{-4} mol/L, which was in the same range as the cmc observed for poly(HOVE-*b*-TFEOVE). It can be expected that multimolecular micelles with inner cores consisting of polyTFEOVE or polyNBVE are formed in the aqueous solutions at the concentration higher than 1.0×10^{-4} mol/L.

Dye-Solubilization by Poly(HOVE-*b*-TFEOVE) or Poly(HOVE-*b*-NBVE) Micelles. We examined the solubilization of fluorinated or nonfluorinated compounds using the aqueous block copolymer solutions.[11] Perfluorinated or nonfluorinated aromatic compounds were used as solubilizates because they have strong UV

Table 2. Solubilized Dye Concentrations in the Aqueous Solution of Poly(HOVE-*b*-TFEOVE) and Poly(HOVE-*b*-NBVE)[a]

polymer	mixed dye	concentrations (mol/L) [F]	concentrations (mol/L) [non-F]	[F]/[non-F]
poly(HOVE-*b*-TFEOVE)	$(CH_3)_2C_{10}H_6 + (C_6F_5)_2$	2.64×10^{-4}	1.18×10^{-4}	2.24
	$(CH_3C_6H_4)_2 + C_{10}F_8$	3.16×10^{-4}	1.80×10^{-5}	17.7
	$C_{14}H_{10} + (C_6F_5)_2$	3.84×10^{-4}	7.67×10^{-6}	50.1
poly(HOVE-*b*-NBVE)	$(CH_3)_2C_{10}H_6 + (C_6F_5)_2$	1.34×10^{-4}	1.75×10^{-4}	0.77
	$(CH_3C_6H_4)_2 + C_{10}F_8$	1.92×10^{-4}	1.46×10^{-5}	13.2
	$C_{14}H_{10} + (C_6F_5)_2$	2.20×10^{-4}	8.46×10^{-6}	26.0

[a] $(CH_3)_2C_{10}H_6$ = 2,6-dimethylnaphthalene, $(C_6F_5)_2$ = decafluorobiphenyl, $(CH_3C_6H_4)_2$ = 4,4′-dimethylbiphenyl, $C_{10}F_8$ = octafluoronaphthalene, $C_{14}H_{10}$ = anthracene, [F] = molar concentration of fluorinated dye, [non-F] = molar concentration of nonfluorinated dye.

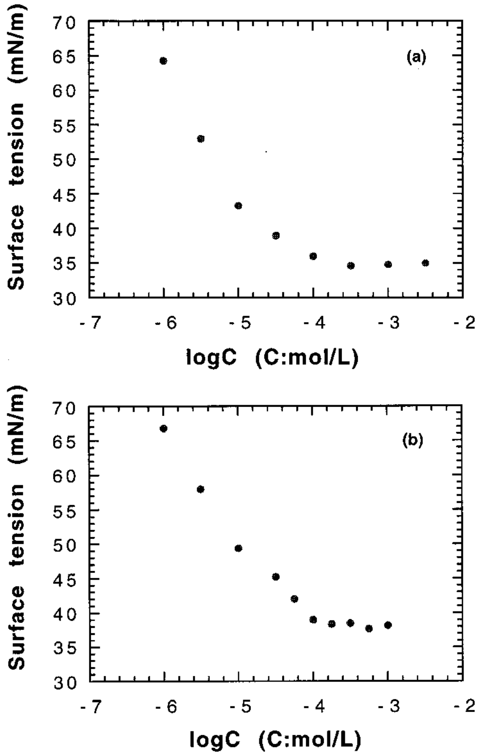


Figure 3. (a) Surface tension of poly(HOVE-*b*-TFEOVE) aqueous solutions. (b) Surface tension of poly(HOVE-*b*-NBVE) aqueous solutions.

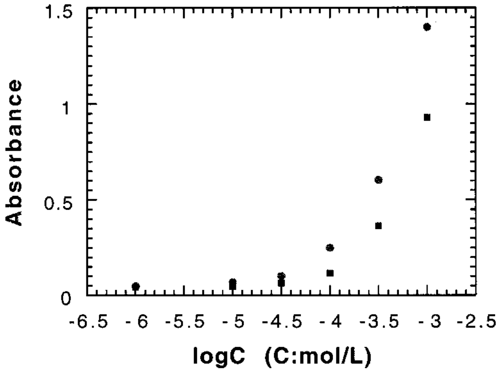


Figure 4. UV absorbance of aqueous solution of (■) poly(HOVE-*b*-TFEOVE) (m:n = 78:23) and (●) poly(HOVE-*b*-NBVE) (m:n = 74:23) in the presence of 2,6-dimethylnaphthalene at 274 nm.

absorption in the range 200–350 nm and because it is well-known that biphenyl and naphthalene derivatives are captured by the core of the micelle instead of the shell.[12] Figure 4 shows the UV absorbance of the poly(HOVE-*b*-TFEOVE) solution and that of the poly(HOVE-*b*-NBVE) solution at 274 nm ($\epsilon_{274\ nm} = 5.26 \times 10^3$) in the presence of 2,6-dimethylnaphthalene as a function of the copolymer concentration. A significant increase of UV absorption was observed at concentrations higher than 1.0×10^{-4} mol/L for both poly(HOVE-*b*-TFEOVE) solution and poly(HOVE-*b*-NBVE) solution. These concentrations mean the cmc's estimated by the dye solubilization method and are in good agreement with the values estimated by surface tension measurements. When 2,6-dimethylnaphthalene was used as solubilizate, poly(HOVE-*b*-NBVE) solubilized it more than poly(HOVE-*b*-TFEOVE) did at any polymer concentrations. Figure 5 shows the UV absorbance of each polymer solution at 265 nm ($\epsilon_{265\ nm} = 2.04 \times 10^3$) in the presence of decafluorobiphenyl. The cmc's of poly(HOVE-*b*-TFEOVE) and poly(HOVE-*b*-NBVE) were observed at 1.0×10^{-4} and 3.2×10^{-5} mol/L, respectively, which are similar to the cmc's obtained by surface tension measurements.

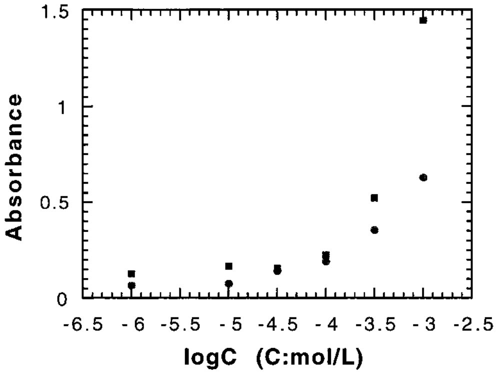


Figure 5. UV absorbance of aqueous solution of (■) poly(HOVE-*b*-TFEOVE) (m:n = 78:23) and (●) poly(HOVE-*b*-NBVE) (m:n = 74:23) in the presence of decafluorobiphenyl at 265 nm.

In contrast with Figure 4, when decafluorobiphenyl was used as a solubilizate, poly(HOVE-*b*-TFEOVE) solubilized it more than poly(HOVE-*b*-NBVE) did. In other words, a fluorine-containing polymer could solubilize fluorinated compounds more than a non-fluorine-containing polymer could. The same tendency was observed in a previous experiment using Sudan III and hexafluorobenzene as solubilizates.[5] However, since much simpler solubilizates were used for this experiment, these results showed that a fluorine-containing polymer had a high ability to solubilize fluorinated compounds compared to a non-fluorine-containing polymer.

Next, we examined the solubilization of a mixture of various perfluorinated and nonfluorinated compounds by an aqueous poly(HOVE-*b*-TFEOVE) solution or poly(HOVE-*b*-NBVE) solution at a concentration of 3.2×10^{-4} mol/L, which is higher than the cmc of both polymers. The UV absorption spectra of pure 2,6-dimethylnaphthalene and pure decafluorobiphenyl in

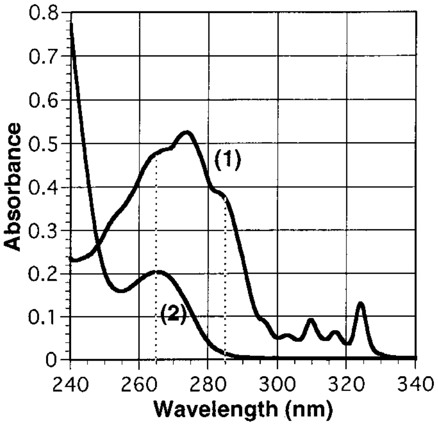


Figure 6. UV absorption spectra of (1) 2,6-dimethylnaphthalene and (2) decafluorobiphenyl (1.00 × 10^{-4} mol/L *n*-octane solution).

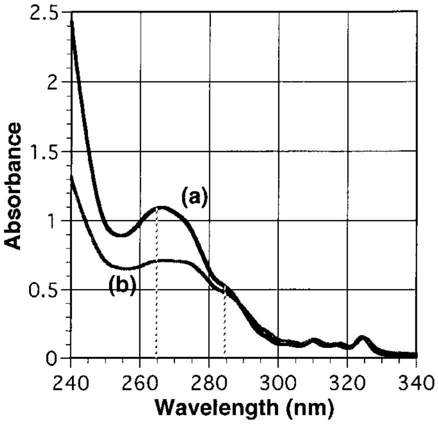


Figure 7. UV absorption spectrum of (a) poly(HOVE-*b*-TFEOVE) (*n*:*m* = 78:23) 3.2 × 10^{-4} mol/L aqueous solution and (b) poly(HOVE-*b*-NBVE) (*n*:*m* = 74:23) 3.2 × 10^{-4} mol/L aqueous solution in the presence of a mixture of 2,6-dimethylnaphthalene and decafluorobiphenyl.

octane are shown in Figure 6. From these spectra, molar absorptivities (ϵ) of 2,6-dimethylnaphthalene were determined to be 4.78 × 10^3 (265 nm) and 3.72 × 10^3 (285 nm), while those of decafluorobiphenyl were determined to be 2.04 × 10^3 (265 nm) and 1.40 × 10^2 (285 nm). The UV absorption spectra of poly(HOVE-*b*-TFEOVE) solution and poly(HOVE-*b*-NBVE) solution in the presence of a mixture of 2,6-dimethylnaphthalene and decafluorobiphenyl are depicted in Figure 7. The shapes of these two spectra suggested that the poly(HOVE-*b*-TFEOVE) micelle solubilized both 2,6-dimethylnaphthalene and decafluorobiphenyl as well as did the poly(HOVE-*b*-NBVE) micelle. However, the concentrations[13] of 2,6-dimethylnaphthalene and decafluorobiphenyl calculated from the absorbances at 265 and 285 nm revealed that the poly(HOVE-*b*-TFEOVE) micelle solublized more decafluorobiphenyl than 2,6-dimethylnaphthalene ([F]/[non-F] = 2.24), while the poly(HOVE-*b*-NBVE) micelle solubilized slightly less decafluorobiphenyl than 2,6-dimethylnaphthalene ([F]/[non-F] = 0.77), as shown in Table 2. As other examples in the combination of fluorinated and nonfluorinated solubilizates, a mixture of octafluoronaphthalene and 4,4′-dimethylbiphenyl and a mixture of anthracene and decafluorobiphenyl were examined. The calculated dye concentrations[13] from the UV absorbance at each partial absorption maximum wavelength are listed in Table 2. Although even the poly(HOVE-*b*-NBVE) micelle solubilized more fluorinated compounds than nonfluorinated compounds, the ratio of the solubilized concentration of fluorinated compounds to nonfluorinated compounds in the case of poly(HOVE-*b*-TFEOVE) micelle ([F]/[non-F] = 17.7 and 50.1) was higher than that in the case of poly(HOVE-*b*-NBVE) in both combinations ([F]/[non-F] = 13.2 and 26.0). These results suggest that the fluorine-containing block copolymer micelle enhanced the solubilization selectivity of perfluorinated compounds.

Conclusions

We synthesized fluorine-containing and non-fluorine-containing block copolymers having the same ratios of polymerization degree of hydrophilic and hydrophobic segments with the same total chain length. Critical micelle concentrations of the block polymers were found to be around 1 × 10^{-4} mol/L by surface tension measurements. It was demonstrated that the fluorine-containing polymer micelle could solubilize fluorinated compounds more than non-fluorine-containing polymer micelles could. Solubilization experiments using a mixture of perfluorinated and nonfluorinated solubilizates revealed that the fluorine-containing polymer micelle could preferentially solubilize the perfluorinated solubilizates. Although the hydrophobic segments of the polymers synthesized here were not fully fluorinated, they exhibited the unique characteristics of fluorinated materials, that is, a “perfluoroalkyl-philic” property. It is expected that such block copolymers can be applied to emulsion polymerization of fluorinated monomers, recovery of fluorinated compounds such as freone, and drug delivery systems.

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(13) The dye concentrations (mol/L) obtained by these experiments represent the mole amount of the solubilized dye in 1 L of the block copolymer solution satulated with the dye.

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