Macromolecules **2002,** *35,* 1091−1101

Micellar Polymers with Hydrocarbon and Fluorocarbon Hydrophobic Chains. A Strategy to Multicompartment Micelles

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Received June 19, 2001; Revised Manuscript Received November 9, 2001

ABSTRACT: Cationic ionenes bearing hydrophobic side chains were synthesized, which behave as micellar polymers of the polysoap type. The hydrophobic chains were either hydrocarbons or fluorocarbons, or a mixture of both, in the form of statistical as well as block copolymers. These amphiphilic polymers were studied and compared with each other and with low molar mass analogous surfactants, especially with respect to their hydrophobic association in aqueous solution. The particular molecular structure of the ionenes synthesized results in polymeric surfactants with high mobility of the fluorocarbon chains. Most noteworthy, the behavior of the hydrocarbon−fluorocarbon block copolymer soaps in aqueous solution indicates microphase separation into hydrocarbon-rich and fluorocarbon-rich hydrophobic domains, thus yielding multicompartment micelles.

Introduction

Amphiphiles bearing fluorocarbon chains as hydrophobic part have been investigated by virtue of a number of—compared to their hydrocarbon analogues—particular properties, for example with respect to increased stiffness, lower surface energy, and increased hydrophobicity, as well as to their poor compatibility with hydrocarbons.[1,2] Whereas numerous examples of fluorocarbon low molar mass surfactants have been described, reports on amphiphilic polymers bearing fluorocarbon hydrophobic chains are still rare. The few studies have been restricted mostly to block copolymer macrosurfactants[3−5] or to water-soluble polymers with only a small number of fluorocarbon chains, in the search for efficient thickeners.[6−11] Reports on water-soluble polymers that have a high content of fluorocarbon side chains in order to enable “polysoap” behavior[12−14] and thus to provide primarily intramolecular aggregation are exceptional.[15−19]

In fact, “polysoaps” represent a particular class of hydrophobically modified polymers, which present many similarities to micelle-forming standard surfactants.[12−14] They can be considered as individual low-molar-mass surfactant fragments, tied together by a polymer backbone. Characteristically, they show primarily intramolecular aggregation, thus being hardly viscosifying, and do not lose their solubilizing power even at high dilutions, as they have no or only negligibly low critical micelle concentrations. In the past, we established some structure−property relationships concerning the role of the molecular variables which are characteristic for polymers, such as the site of the anchoring of the surfactant fragment, the length of side chain spacers as well as of main chain spacers, the polarity of the polymer backbone, and the polymer topology.[13,20−23] Now, we readdress the question how to design polysoap properties by the choice of the surfactant fragments in the polymers. This includes the use of unusual hydrophobic chains, such as fluorocarbons.[15,19]

To benefit from the inherent low surface energy of fluorocarbons, the polysoaps should dispose of hydrophobic chains with CF_3− end groups. This means that the surfactant fragments cannot be attached to the polymer backbone via the end of the hydrophobic chains (the so-called “tail end” type geometry) but must be fixed via the middle of the hydrophobic chain only (“mid tail” type) or via the hydrophilic headgroups (“head” type). Unfortunately, the latter two cases cannot be prepared by homopolymerization of the usual polymerizable surfactants (often referred to as “surfmers”).[13,14] Typically, the steric constraints imposed by the short C_2 repeat unit of such functional vinyl oder vinylidene polymers (such as styrene, acrylic, or methacrylic derivatives) interfere with an efficient amphiphilic response of the surfactant side chains,[14,20,21] thus yielding water-insoluble homopolymers. This is independent of the nominal hydrophilic−hydrophobic balance of such compounds. Main chain spacer groups which separate the individual surfactant fragments are needed to overcome the steric restrictions.[14] Therefore, polysoaps of the “mid tail” type or of the “head” type are mostly synthesized by copolymerization of a surfmer (or of a hydrophobic monomer) with a large amount of hydrophilic comonomer.[21] Alternatively, partial modification of a precursor polymer with hydrophobic side chains is applied. Recently, we applied both strategies to prepare fluorocarbon polysoaps disposing of a polystyrene backbone.[19] But, these methods provide only a limited control on the molecular structure of the polysoaps obtained and are therefore e.g. less suited for model studies. The application of step growth polymerization instead of free radical polymerization can remedy this problem. However, the surfactant fragments are often very hygroscopic and require protic solvents, thus limiting the synthetic possibilities substantially. Nevertheless, some practical approaches exist, such as free radical polyaddition,[24,25] or the synthesis of ionenes by the Menshutkin

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10.1021/ma011047n CCC: $22.00

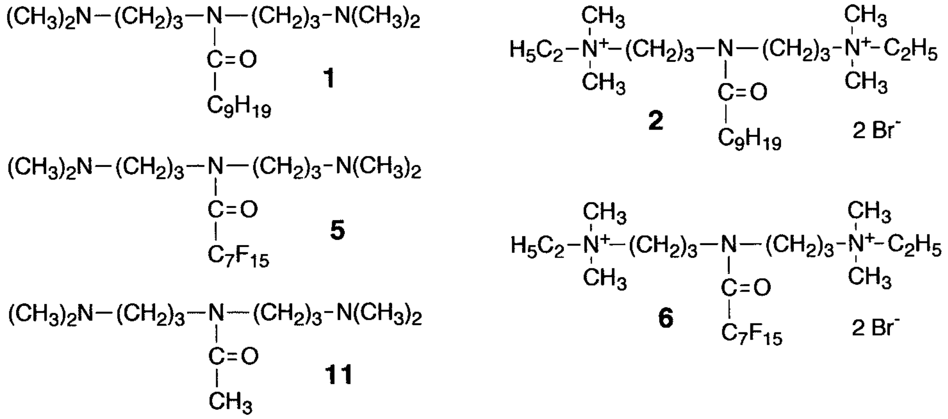

Figure 1. Monomers and monomer analogues synthesized and investigated.

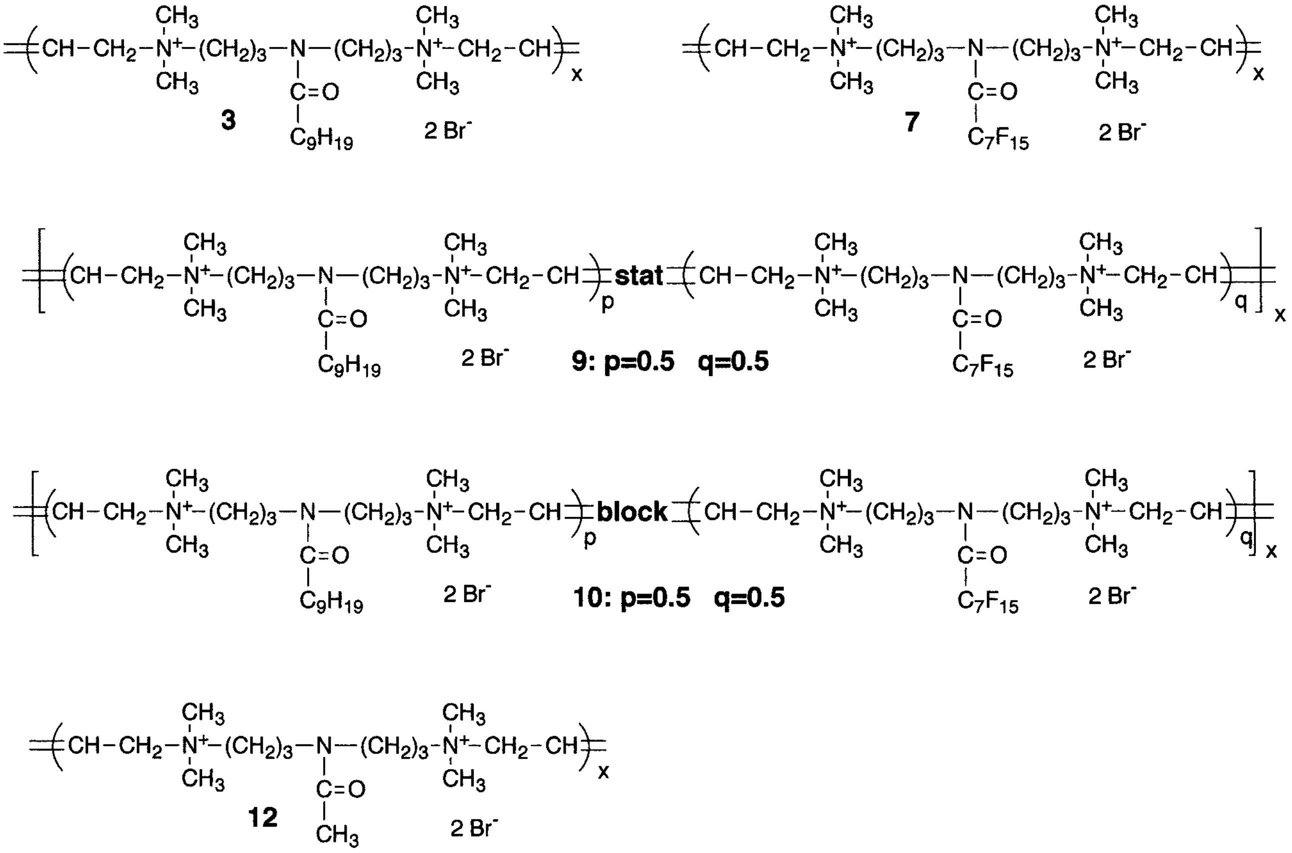

Figure 2. Ionene polymers synthesized and investigated.

reaction of α–ω-diamines with α–ω-dialkylating agents.[23,26,27]

Here, the synthesis and investigation of fluorocarbon and analogous hydrocarbon polysoaps of the ionene type and of the corresponding surfactant monomers are reported (Figures 1 and 2). The polysoaps are prepared by polyaddition of hydrophobically modified α–ω-diamines, bearing either a hydrocarbon or a perfluorocarbon hydrophobic chain, with 1,4-dibromobut-2-ene. This strategy allows for the preparation of statistical copolymers with mixed perfluorocarbon and a hydrocarbon chains, too. Furthermore, the irreversibility of the quaternization reaction at moderate temperatures enables to prepare block copolymers with perfluorocarbon and hydrocarbon micellar blocks in a multistep sequence (Figure 3). Such block copolymers are intriguing because the poor compatibility of the two kinds of hydrophobic chains[1,2] may induce an additional microphase separation.[19] This would lead to micellar polymers which bear two qualitatively different hydrophobic domains within the same molecule, in analogy of some natural transport proteins like serum albumine.[28] Very few approaches to such "multicompartment micelles" have been explored up to now, either using micellar copolymerization of coexisting micellar populations of hydrocarbon and fluorocarbon surfmers[29,30] or stepwise polymerization of such surfmers.[16,19,31]

Experimental Part

Methods. Elemental analysis was done by the University College of London. Analytical NMR spectra were taken with Gemini-200 and 300 spectrometers (Varian). $CFCl_3$ was used as internal standard for ^{19}F spectra. Relaxation times were measured with an Inova-400 spectrometer (Varian), using

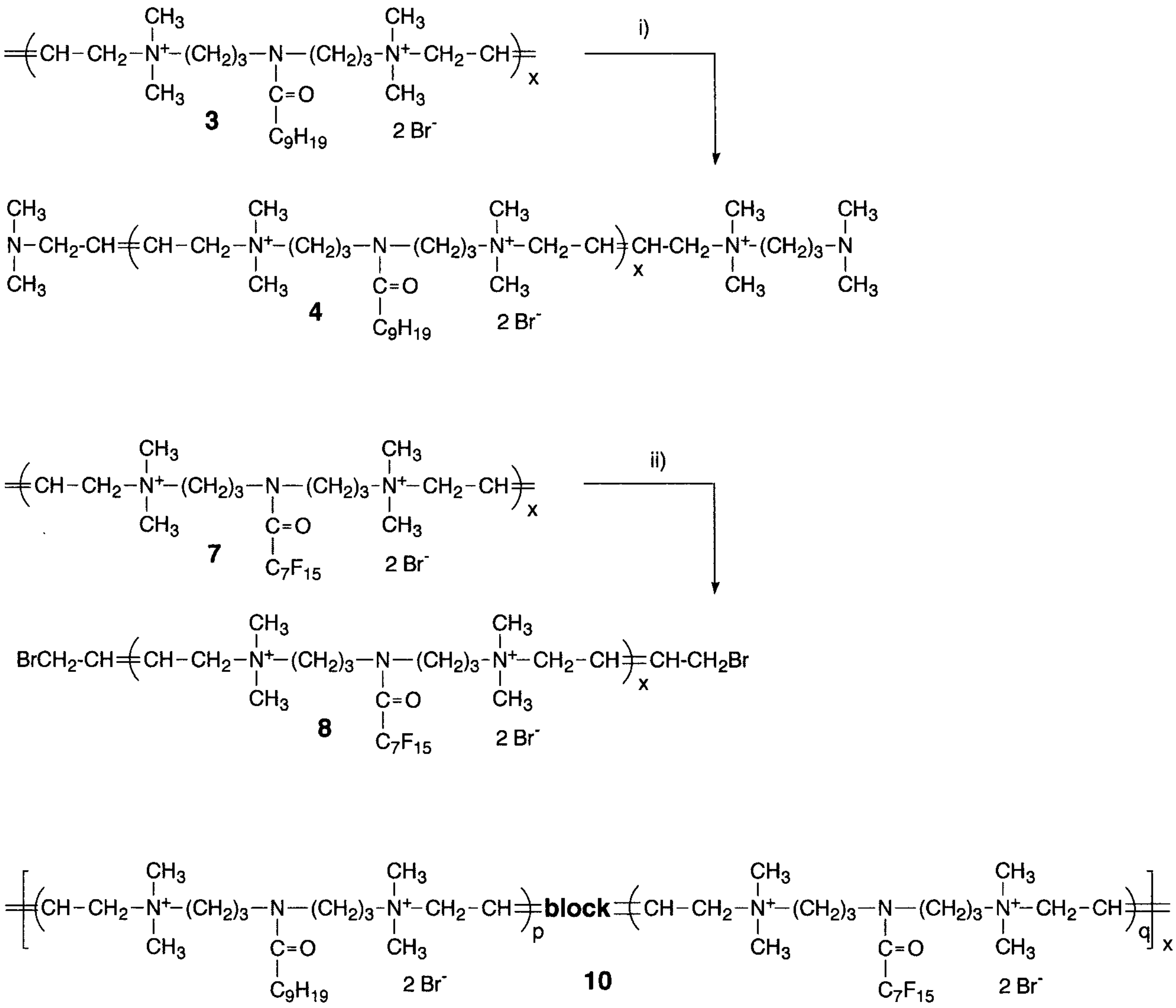

Figure 3. Synthetic pathway to block copolymer polysoaps with separated hydrocarbon and fluorocarbon segments.

aqueous solutions containing 18 mg/mL of polymer, employing the CPMG pulse sequence $(\pi/2)_x$−t_D−$(\pi_y$−$t_D)_n$−acquisition with $t_D = 0.4$ ms and $4nt_D$ the total time for T_2 relaxation. The latter is an array of 35 values varying from 1.6 ms to 0.6 s. For the fluorine NMR experiments, the array values are between 1.6 ms and 0.2 s. The proton and fluorine spin−lattice relaxation times (T_1) were measured by means of the inversion recovery pulse sequence. All relaxation experiments consisted of eight scans, a preparation delay of 5 s, an acquisition time of 2.5 s, and a $\pi/2$ pulse width of 5 μs (proton) or 6.5 μs (fluorine). For studying the solubilization capacity of the polymers by ^{1}H and ^{19}F NMR, 0.2 mL of 2,3-dimethylbutene or of hexafluorobenzene, respectively, are added to 1 mL of polymer solutions in D_2O (1 wt %). The sealed samples are agitated for 1 night at 25 °C. Then, the turbid emulsions are allowed to separate into two phases for 24 h, which become clear, and 0.8 mL of the aqueous phase is transferred to an NMR tube. The quantity of compounds dissolved in water was calibrated by adding a known amount of ethanol or of sodium trifluoroacetate as standard during the measurement. The reported values are averages over six measurements which all agreed within 10−20%.

Infrared spectra were recorded with a FTS 135 infrared Fourier transform spectrometer (BioRad). Viscosimetric studies were performed with an automatic Ubbelohde viscometer at 25 °C (Schott AVS 350). Surface tensions were measured with a manual tensiometer (Krüss 8501, De Noüy) at 22 °C. Monomer solutions were equilibrated for 24 h, and polymer solutions were equilibrated for 2 weeks in the measuring jar before measurements. Thermogravimetry was performed on a thermogravimetric analyzer TGA-500 SETARAM, with a heating rate of 10 °C/min in a nitrogen atmosphere. Differential scanning calorimetry was performed with a Perkin-Elmer DSC7, applying heating and cooling rates of 20 °C/min. X-ray scattering experiments were done with a diffractometer (Siemens D-5000), using the Ni-filtered Cu Kα line (λ = 0.1541 nm).

Materials. Water used for all experiments was purified by a Milli-Q water purification system (resistance 18 MΩ·cm). Column chromatography was performed on silica gel (Merck 203−400 mesh) or if stated explicitly on Al_2O_3 (Acros, basic, 150 mesh).

Synthesis of Monomers. *N,N-Bis(3-(dimethylamino)propyl)decanamide* (**1**). 7.60 g (0.0406 mol) of *N,N*-bis(3-(dimethylamino)propyl)amine are added dropwise to 7.00 g (0.0367 mol) of decanoyl chloride in dry acetone under an argon atmosphere at 0 °C. After stirring overnight at room temperature, 1 mL of water and 5.84 g (0.0551 mol) of $NaHCO_3$ are added, and the mixture is stirred for an additional 12 h. The insoluble parts are filtered off, the filtrate is evaporated, and the residue is purified by flash chromatography over Al_2O_3 (eluent: ethyl acetate/methanol 3v/1v) to give 9.40 g (75%) of yellowish oil (n_{20} = 1.4695).

^{1}H NMR (200 MHz in $CDCl_3$, δ in ppm): 3.20−3.40 (m, 4H, −CON−CH_2 cis and trans conformer), 2.15−2.35 (m, 18H, −CH_2−CON⟨, −CH_2N⟨, −N−$(CH_3)_2$), 1.50−1.80 (m, 6H, −CH_2−C−CON−, −CON−C−CH_2), 1.15−1.40 (m, 12H, −$(CH_2)_6$−), 0.85 (t, 6.5 Hz, 3H, CH_3).

^{13}C NMR (50 MHz in CDCl$_3$, δ in ppm): 173.0 (C=O), 56.6, 57.2 (−CH$_2$N⟨ cis and trans conformer), 45.4 (−N−(CH$_3$)$_2$), 44.0, 46.0 (−C(O)N−*C*H$_2$ cis and trans conformer), 33.1 (−*C*H$_2$−CON⟨⟩), 31.8 (CH$_3$−C−*C*H$_2$−), 29.2, 29.4, 29.5 (−(CH$_2$)$_4$−), 25.5, 25.9, 27.2 (−*C*H$_2$−C−CON−, −CON−C−*C*H$_2$), 22.6 (CH$_3$−*C*H$_2$−), 14.0 (CH$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 1647 (C=O stretch).

Elemental analysis (C$_{20}$H$_{43}$N$_3$O, M_r = 341.58): Calcd: C, 70.33%; H, 12.69%; N, 12.30%. Found: C, 69.95%; H, 12.78%; N, 12.28%.

N,N-Dimethyl-N-ethylammoniotrimethylene-(N-decanoyl)iminotrimethylene-N′,N′-dimethyl-N′-ethylammonium Dibromide **(2)**. 2.30 g (0.00673 mol) of **1** and 3.30 g (0.0303 mol) of ethyl bromide are stirred for 72 h in 20 mL of dry acetone at room temperature. The solvent and the excess ethyl bromide are evaporated, and the residue is washed thrice with petrol ether to yield 3.51 g (93%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in CDCl$_3$, δ in ppm): 3.40−3.85 (m, 12H, −CON−CH$_2$−, −CH$_2$−N$^+$CH$_2$−), 3.30, 3.39 (s, 12H, −N$^+$(CH$_3$)$_2$ 2 conformers), 2.05−2.45 (m, 6H, −CH$_2$−CON⟨, −CON−C−CH$_2$−), 1.10−1.70 (m, 20 H, −(CH$_2$)$_7$−, CH$_3$−C−N$^+$), 0.85 (t, 6.9 Hz, 3H, CH$_3$).

^{13}C NMR (50 MHz in D$_2$O, δ in ppm): 177.7 (C=O), 61.1, 61.2, 61.5, 62.0 (−*C*H$_2$−N$^+$−*C*H$_2$−), 51.3 (−N$^+$(CH$_3$)$_2$), 44.0, 46.1 (−CON−*C*H$_2$− cis and trans conformer), 33.8 (−*C*H$_2$−CON⟨⟩), 32.5 (CH$_3$−C−*C*H$_2$−), 29.8, 29.9 (−(CH$_2$)$_4$−), 26.3 (−*C*H$_2$−C−CON−), 23.0, 23.3 (−CON−C−*C*H$_2$−), 21.8 (CH$_3$−*C*H$_2$−CH$_2$−), 14.8 (CH$_3$−), 8.8 (*C*H$_3$−C−N$^+$).

FT-IR (selected bands in cm^{-1}, KBr pellet): 1634 (C=O stretch).

Elemental analysis (C$_{24}$H$_{53}$Br$_2$N$_3$O, M_r = 559.51): Calcd: C, 51.52%; H, 19.55%; N, 7.51%; Br, 28.56%. Calcd (monohydrate): C, 49.91%; H, 9.60%; N, 7.28%; Br, 27.67%. Found: C, 49.60%; H, 9.92%; N, 7.21%; Br, 27.71%.

Mass spectrum (FAB): m/z = 480.1 ((M−Br)$^+$).

N,N-Bis(3-(dimethylamino)propyl)perfluorooctanamide **(5)**. The amide **5** is prepared in analogy to the procedure for **1** above, employing 3.78 g (0.0202 mol) of *N*,*N*-bis(3-(dimethylamino)propyl)amine and 8.12 g (0.0188 mol) of perfluorooctanoyl chloride. Purification by flash chromatography over Al$_2$O$_3$ (eluent: ethyl acetate/methanol 3v/1v) gives 7.42 g (68%) of yellowish oil (n_{20} = 1.3830).

^{1}H NMR (200 MHz in CDCl$_3$, δ in ppm): 3.35−3.55 (m, 4H, −CON−CH$_2$ cis and trans conformer), 2.26 (t, 8.25 Hz, 4H, −N−CH$_2$−), 2.19 (s, 12H, −N−(CH$_3$)$_2$), 1.65−1.90 (m, 4H, −CON−C−CH$_2$).

^{13}C NMR (50 MHz in CDCl$_3$, δ in ppm): 157.9 (C=O), 105.0−120.0 (CF$_3$(CF$_2$)$_6$), 57.3 (−CH$_2$N⟨⟩), 47.2 (−CON−*C*H$_2$), 45.9 (−N−(CH$_3$)$_2$), 25.6, 28.0 (−CON−C−*C*H$_2$).

^{19}F NMR (283 MHz in CD$_3$OD, δ in ppm): −125.8 (2F, CF$_3$−C*F*$_2$), −122.2 (2F, CF$_3$−C−C*F*$_2$), −121.6 (2F, −CF$_2$−C−C−C−CON⟨⟩), −120.3 (2F, −CF$_2$−C−C−CON⟨⟩), −119.9 (2F, −CF$_2$−C−CON⟨⟩), −110.9 (2F, −CF$_2$−CON⟨⟩), −80.4 (3F, CF$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 1685 (C=O stretch); 1242, 1209 (C−F stretch).

Elemental analysis (C$_{18}$H$_{24}$F$_{15}$N$_3$O, M_r = 583.38): Calcd: C, 37.05%; H, 4.12%; N, 7.20%. Found: C, 37.25%; H, 4.08%; N, 7.25%.

N,N-Dimethyl-N-ethylammoniotrimethylene-(N-perfluorooctanoyl)iminotrimethylene-N′,N′-dimethyl-N′-ethylammonium Dibromide **(6)**: 1.20 g (0.002 06 mol) of **5** and 1.20 g (0.0110 mol) of ethyl bromide are stirred for 72 h in 20 mL of dry acetone at room temperature. After evaporation of the solvent and the excess ethyl bromide, the residue is washed thrice with petrol ether/acetone (9v/1v) to yield 1.30 g (79%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in CDCl$_3$, δ in ppm): 3.45−3.65 (m, 4H, −CON−CH$_2$−), 3.15−3.40 (m, 8H, −CH$_2$−N$^+$−CH$_2$−), 2.95, 3.00 (s, 12H, −N$^+$(CH$_3$)$_2$ two conformers), 1.95−2.20 (m, 4H, −CON−C−CH$_2$−), 1.25 (t, 7.1 Hz, 6H, CH$_3$−C−N$^+$).

^{13}C NMR (50 MHz in D$_2$O, δ in ppm): 158.3 (C=O), 108.0−120.0 (CF$_3$(CF$_2$)$_6$−), 61.4, 61.8, 61.9 (−*C*H$_2$−N$^+$−*C*H$_2$−), 50.3, 50.9 (−N$^+$(CH$_3$)$_2$), 45.7, 45.9 (−CON-*C*H$_2$ cis and trans conformer), 21.6, 23.7 (−CON−C−*C*H$_2$−), 8.5 (*C*H$_3$−C−N$^+$).

^{19}F NMR (283 MHz in CDCl$_3$, δ in ppm): −123.8 (2F, CF$_3$−C*F*$_2$), −120.1 (2F, CF$_3$−C−C*F*$_2$), −119.5 (2F, −CF$_2$−C−C−C−CON⟨⟩), −118.0 (2F, −CF$_2$−C−C−CON⟨⟩), −117.4 (2F, −CF$_2$−C−CON⟨⟩), −109.0 (2F, −CF$_2$−CON⟨⟩), −78.9 (3F, CF$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 1679 (C=O stretch); 1240, 1206 (C−F stretch).

Elemental analysis (C$_{22}$H$_{34}$Br$_2$F$_{15}$N$_3$O, M_r = 801.31): Calcd: C, 32.98%; H, 4.28%; N, 5.24%; Br, 19.94%. Calcd (trihydrate): C, 30.89%; H, 4.71%; N, 4.91%; Br, 18.68%. Found: C, 30.77%; H, 4.72%; N, 4.87%; Br, 23.26%.

Mass spectrum (FAB): m/z = 721.9 ([M−Br]$^+$).

N,N-Bis(3-(dimethylamino)propyl)acetamide **(11)**. The amide **11** is prepared in analogy to the procedure for **1** above, employing 2.86 g (0.0153 mol) of *N*,*N*-bis(3-(dimethylamino)propyl)amine and 1.00 g (0.0127 mol) of acetyl chloride. Purification by flash chromatography over Al$_2$O$_3$ (eluent: ethyl acetate/methanol 4v/1v) gives 2.45 g (84%) of yellowish oil.

^{1}H NMR (200 MHz in CDCl$_3$, δ in ppm): 3.20−3.40 (m, 4H, −CON−CH$_2$− cis and trans conformer), 2.10−2.35 (m, 16H, −CH$_2$N⟨, −N−(CH$_3$)$_2$), 2.10 (s, 3H, CH$_3$CON⟨⟩), 1.60−1.80 (m, 6H, −CON−C−CH$_2$−).

^{13}C NMR (50 MHz in CDCl$_3$, δ in ppm): 170.3 (C=O), 56.9, 56.3 (−CH$_2$N⟨ cis and trans conformer), 45.3 (−N−(CH$_3$)$_2$), 43.7, 46.7 (−CON−*C*H$_2$− cis and trans conformer), 25.7, 26.8 (−CON−C−*C*H$_2$−), 21.4 (*C*H$_3$−CON⟨⟩).

FT-IR (selected bands in cm^{-1}, KBr pellet): 1626 (C=O stretch).

Mass spectrum (EI): m/z = 229.3 (M$^+$).

Polymers. *Poly(N,N-dimethylammoniotrimethylene-(N-decanoyl)iminotrimethylene-N,N-dimethylammonio-2-butenylene dibromide)* **(3)**. 1.7941 g (8.378 mmol) of 1,4-dibromobut-2-ene and 2.8618 g (8.384 mmol) of *N*,*N*-di(3-(dimethylamino)propyl)decanamide **(1)** are stirred in a mixture of 6 mL of dry DMF and 1 mL of dry methanol at room temperature for 2 weeks. The mixture is precipitated in 70 mL of ethyl acetate. The precipitate is redissolved in 10 mL of methanol and reprecipitated in 100 mL of ethyl acetate. Dissolution in 20 mL of water and lyophilization yield 3.82 g (82%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in D$_2$O, δ in ppm): 6.30−6.55 (m, 2H, =CH−), 3.90−4.30 (m, 4H, −CH$_2$−C=), 2.90−3.75 (m, 20H, −CON−C*H*$_2$−C−C*H*$_2$−N$^+$−(C*H*$_3$)$_2$), 2.25−2.50 (m, 2H, −CH$_2$−CON⟨⟩), 1.85−2.20 (m, 4H, −CON−C−CH$_2$−), 1.00−1.60 (m, 14 H, −(CH$_2$)$_7$−C−CON⟨⟩), 0.79 (m, 3H, CH$_3$).

^{13}C NMR (50 MHz in CD$_3$OD, δ in ppm): 176.0 (C=O), 131.5 (−C=C−), 66.0−66.4 (−N$^+$−*C*H$_2$−C=), 63.0−63.3 (−CH$_2$−*C*H$_2$−N$^+$−), 51.7 (−N$^+$−CH$_3$), 44.1, 46.1 (−CON-*C*H$_2$− cis and trans conformer), 34.1 (−*C*H$_2$−CON⟨⟩), 33.1 (CH$_3$−C−*C*H$_2$−), 30.5−30.8 (−(CH$_2$)$_4$−), 26.6 (−*C*H$_2$−C−CON⟨⟩), 23.7 (−CON−C−*C*H$_2$−), 22.7 (CH$_3$−*C*H$_2$−), 14.5 (CH$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 3021 (=*C*−*H* stretch), 1653 (C=O stretch).

Elemental analysis ((C$_{24}$H$_{49}$Br$_2$N$_3$O)$_x$, M_r = (555.47)$_x$): Calcd: C, 51.89%; H, 8.89%; N, 7.57%; Br, 28.77%. Calcd (tetrahydrate): C, 45.90%; H, 9.10%; N, 6.69%; Br, 25.25%. Found: C, 46.46%; H, 9.29%; N, 6.54%; Br, 25.86%.

Poly(N,N-dimethylammoniotrimethylene-(N-perfluorooctanoyl)iminotrimethylene-N,N-dimethylammonio-2-butenylene dibromide) **(7)**. 0.8926 g (4.170 mmol) of 1,4-dibromobut-2-ene and 2.4316 g (4.170 mmol) of *N*,*N*-di(3-(dimethylamino)propyl)perfluorooctanamide **(5)** are stirred in a mixture of 5 mL of dry DMF and 1 mL of dry methanol at room temperature for 2 weeks. The mixture is precipitated in 60 mL of ethyl acetate; the precipitate redissolved in 10 mL of methanol and reprecipitated in 100 mL of ethyl acetate. The solid is dissolved in 20 mL of deionized water, filtered, and lyophilized to give 2.90 g (87%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in D$_2$O, δ in ppm): 6.35−6.70 (m, 2H, =CH−), 3.85−4.30 (m, 4H, −N$^+$−CH$_2$−C=), 2.85−3.80 (m, 20H, −CON−C*H*$_2$−C−C*H*$_2$−N$^+$(C*H*$_3$)$_2$), 1.90−2.40 (m, 4H, −CON−C−CH$_2$−).

^{13}C NMR (50 MHz in CD$_3$OD, δ in ppm): 159.0 (C=O), 131.5 (C=C), 108.0−120.0 (*C*F$_3$(*C*F$_2$)$_6$), 66.5 (−N$^+$−*C*H$_2$−C=), 62.5 (−CH$_2$−*C*H$_2$−N$^+$−), 51.7 (CH$_3$N$^+$−), 45.8, 46.2 (−CON−*C*H$_2$− cis and trans conformer), 24.1 (−CON−C−*C*H$_2$−).

^{19}F NMR (283 MHz in CD$_3$OD, δ in ppm): −125.6 (2F, CF$_3$−C*F*$_2$−), −121.9 (2F, CF$_3$−C−C*F*$_2$−), −121.3 (2F, −CF$_2$−C−C−C−CON⟨), −119.8 (2F, −CF$_2$−C−C−CON⟨), −119.3 (2F, −CF$_2$−C−CON⟨), −110.6 (2F, −CF$_2$−CON⟨), −80.7 (3F, CF$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 3019 (C═*C*−*H* stretch), 1678 (C═O stretch), 1240, 1206 (C−F stretch).

Elemental analysis ((C$_{22}$H$_{30}$Br$_2$F$_{15}$N$_3$O)$_x$, M_r = (797.28)$_x$): Calcd: C, 33.14%; H, 3.79%; N, 5.27%; Br, 20.05%. Calcd (trihydrate): C, 31.01%; H, 4.23%; N, 4.93%; Br, 18.80%. Found: C, 31.25%; H, 3.92%; N, 4.97%; Br, 21.54%.

Poly[(N,N-dimethylammoniotrimethylene-(N-perfluorooctanoyl)iminotrimethylene-N,N-dimethylammonio-2-butenylene dibromide)-stat-(N,N-dimethylammoniotrimethylene-(N-decanoyl)iminotrimethylene-N,N-dimethylammonio-2-butenylene dibromide)] (**9**). 3.0318 g (14.08 mmol) of 1,4-dibromobut-2-ene, 4.1378 g (7.093 mmol) of *N*,*N*-di(3-(dimethylamino)propyl)perfluorooctanamide (**5**)**,** and 2.4147 g (7.069 mmol) of *N*,*N*-di(3-(dimethylamino)propyl)decanamide (**1**) are stirred in a mixture of 8 mL of dry DMF and 2 mL of dry methanol at room temperature for 2 weeks. The mixture is precipitated in 100 mL of ethyl acetate; the precipitate is redissolved in 12 mL of methanol and reprecipitated in 120 mL of ethyl acetate. The solid is dissolved in 25 mL of deionized water, filtered, and lyophilized to give 7.56 g (79%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in CD$_3$OD, δ in ppm): 6.40−6.70 (m, 4H, ═CH−), 4.00−4.35 (m, 8H, −N$^+$−CH$_2$−C═), 2.95−3.70 (m, 40H, −CON−C*H*$_2$−C−C*H*$_2$−N$^+$(C*H*$_3$)$_2$), 2.39 (t, 7.1 Hz, 2H, −CH$_2$−CON⟨), 1.85−2.30 (m, 8H, −CON−C−CH$_2$−), 1.40−1.60 (m, 2H, −CH$_2$−C−CON⟨), 1.00−1.35 (m, 12 H, −(CH$_2$)$_6$−C−C−CON⟨), 0.79 (t, 6.8 Hz, 3H, CH$_3$−).

^{13}C NMR (50 MHz in CD$_3$OD, δ in ppm): 176.0 (−CH$_2$−C═O), 158.0 (−CF$_2$−C═O), 131.5 (C═C), 65.9, 66.4 (−N$^+$−*C*H$_2$−C═), 62.5 (−N$^+$−*C*H$_2$CH$_2$), 51.5 (N$^+$CH$_3$), 44.1, 46.2 (−CON−*C*H$_2$−), 34.1 (−*C*H$_2$−CON⟨), 33.1 (CH$_3$−C−*C*H$_2$−), 30.5−30.8 (−(CH$_2$)$_4$−), 26.6 (−*C*H$_2$−C−CON⟨), 23.7 (−CON−C−*C*H$_2$−), 22.7 (CH$_3$−*C*H$_2$−), 14.5 (CH$_3$−).

^{19}F NMR (283 MHz in CD$_3$OD, δ in ppm): −125.6 (2F, CF$_3$−C*F*$_2$−), −121.8 (2F, CF$_3$−C−C*F*$_2$−), −121.2 (2F, −CF$_2$−C−C−C−CON⟨), −119.8 (2F, −CF$_2$−C−C−CON⟨), −119.3 (2F, −CF$_2$−C−CON⟨), −110.6 (2F, −CF$_2$−CON⟨), −80.6 (3F, CF$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 3019 (═*C*−*H* stretch), 1684, 1653 (C═O stretch), 1240, 1206 (C−F stretch).

Elemental analysis ((C$_{46}$H$_{79}$Br$_4$F$_{15}$N$_6$O$_2$)$_{x/2}$, M_r = (676.38)$_x$): Calcd (1:1 copolymer): C, 37.29%; H, 5.44%; N, 6.21%; Br, 23.63%. Found: C, 37.35%; H, 5.62%; N, 6.28%; Br, 25.65%.

Poly[(N,N-dimethylammoniotrimethylene-(N-perfluorooctanoyl)iminotrimethylene-N,N-dimethylammonio-2-butenylene dibromide)-block-(N,N-dimethylammoniotrimethylene-(N-decanoyl)iminotrimethylene-N,N-dimethyl-ammonio-2-butenylene dibromide)] **(10)**. 0.5602 g (7.03 mol of repeating units) of butenylene bromide end-capped poly(*N*,*N*-dimethylammoniotrimethylene-(*N*-perfluorooctanoyl)iminotrimethylene-*N*,*N*-dimethylammonio-2-butenylene dibromide) **(8)** and 0.3832 g (6.91 mmol of repeating units) of *N*,*N*-dimethylaminotrimethylene end-capped poly(*N*,*N*-dimethylammoniotrimethylene-(*N*-decanoyl)imino-trimethylene-*N*,*N*-dimethylammonio-2-butenylene dibromide) (**4**) are stirred in 5 mL of dry methanol at 50 °C for 3 weeks. The solvent is evaporated, and the residue is dissolved in 15 mL of deionized water, filtered, and lyophilized to give 0.942 g (99.9%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in CD$_3$OD, δ in ppm): 6.40−6.75 (m, 4H, ═CH−), 4.00−4.40 (m, 8H, −N$^+$−CH$_2$−C═), 2.90−3.80 (m, 40H, −CON−C*H*$_2$−C−C*H*$_2$−N$^+$−(C*H*$_3$)$_2$), 2.40 (t, 7.1 Hz, 2H, −CH$_2$−CON⟨), 1.95−2.35 (m, 8H, −CON−C−CH$_2$−), 1.10−1.70 (m, 14 H, −(CH$_2$)$_7$−C−CON⟨), 0.81 (t, 6.8 Hz, 3H, CH$_3$−).

^{13}C NMR (50 MHz in CD$_3$OD, δ in ppm): 176.0 (−CH$_2$−C═O), 158.0 (−CF$_2$−C═O), 131.5 (C═C), 66.0, 66.4 (−N$^+$−*C*H$_2$−C═), 62.5, 63.3 (−CH$_2$−*C*H$_2$−N$^+$), 51.8 (N$^+$CH$_3$), 44.1, 45.9, 46.0, 46.2 (−CON−*C*H$_2$− cis and trans conformer), 34.1 (−*C*H$_2$−CON⟨), 33.1 (CH$_3$−C−*C*H$_2$−), 30.5−30.8 (−(CH$_2$)$_4$−), 26.6 (−*C*H$_2$−C−CON⟨), 23.7 (−CON−C−*C*H$_2$−), 22.6 (CH$_3$−*C*H$_2$−), 14.5 (CH$_3$−).

^{19}F NMR (283 MHz in CD$_3$OD, δ in ppm): −125.6 (2F, CF$_3$−C*F*$_2$−), −121.9 (2F, CF$_3$−C−C*F*$_2$−), −121.3 (2F, −CF$_2$−C−C−C−CON⟨), −119.8 (2F, −CF$_2$−C−C−CON⟨), −119.3 (2F, −CF$_2$−C−CON⟨), −110.6 (2F, −CF$_2$−CON⟨), −80.5 (3F, CF$_3$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 3025 (C═*C*−*H* stretch), 1682, 1642 (C═O stretch), 1233, 1200 (C−F stretch).

Elemental analysis ((C$_{46}$H$_{79}$Br$_4$F$_{15}$N$_6$O$_2$)$_{x/2}$, M_r = (676.38)$_x$): Calcd (1:1 copolymer): C, 37.29%; H, 5.44%; N, 6.21%; Br, 23.63%. Found: C, 37.15%; H, 5.48%; N, 6.57%; Br, 25.48%.

Poly(N,N-dimethylammoniotrimethylene-(N-acetyl)iminotrimethylene-N,N-dimethylammonio-2-butenylene dibromide) **(12)**. 0.870 g (4.07 mmol) of 1,4-dibromobut-2-ene and 0.930 g (4.06 mmol) of *N*,*N*-di(3-(dimethylamino)propyl)acetamide (**11)** are stirred in a mixture of 4 mL of dry DMF and 1 mL of dry methanol at room temperature for 2 weeks. The mixture is precipitated in 50 mL of ethyl acetate. The precipitate is redissolved in 10 mL of methanol and reprecipitated in 100 mL of ethyl acetate. The solid is dissolved in 20 mL of deionized water, filtered, and lyophilized to give 1.60 g (89%) of colorless hygroscopic powder.

^{1}H NMR (200 MHz in D$_2$O, δ in ppm): 6.30−6.45 (m, 2H, ═CH−), 4.00−4.20 (m, 4H, −N$^+$−CH$_2$−C═), 3.20−3.50 (m, 8H, −CON−C*H*$_2$−C−C*H*$_2$−N$^+$−), 2.90−3.20 (m, 12H, CH$_3$N$^+$−), 1.90−2.20 (m, 7H, C*H*$_3$−CON−C−C*H*$_2$−).

^{13}C NMR (50 MHz in CD$_3$OD, δ in ppm): 174.0 (C═O), 131.5 (−C═C−), 66.2 (−N$^+$−*C*H$_2$−C═), 62.8 (−CH$_2$−*C*H$_2$−N$^+$−), 51.7 (−N$^+$CH$_3$), 43.8, 46.8 (−CON−*C*H$_2$− cis and trans conformer), 23.4 (*C*H$_3$−CON−C−*C*H$_2$−), 22.3 (−CON−C−*C*H$_2$−).

FT-IR (selected bands in cm^{-1}, KBr pellet): 3027 (═*CH* stretch), 1654 (C═O stretch).

Elemental analysis ((C$_{16}$H$_{33}$Br$_2$N$_3$O)$_x$, M_r = (443.26)$_x$): Calcd: C, 43.35%; H, 7.50%; N, 9.48%; Br, 36.05%. Calcd (dihydrate): C, 40.09%; H, 7.78%; N, 8.77%; Br, 33.34%. Found: C, 40.64%; H, 7.89%; N, 8.80%; Br, 34.08%.

The 1:1 composition of the copolymers was determined from the ^{1}H NMR spectra in CD$_3$OD, using the integration of the signals of the long hydrocarbon chains between 0.5 and 1.7 ppm in comparison with the signals of the allylic protons as well as of the olefinic protons in the polymer backbone at about 4.2 ppm and at 6.5 ppm, respectively. The results were corroborated by elemental analysis.

For estimating the molar masses by end group analysis, the individual polymers were submitted to exhaustive alkylation with a large excess of 1,4-dibromobut-2-ene, followed by quaternization of the allyl bromide end groups by pyridine, or by *N*,*N*-dimethylhexadecylamine in the case of the fluorinated ionene **7**. Alternatively, the polymers were submitted to exhaustive reaction with a large excess of 1,3-bis(dimethylamino)propane, followed by quaternization with benzyl bromide. Average molar masses and degrees of polymerization were estimated from the integrals of the ^{1}H NMR signals, assuming two functional end groups per polymer chain.

Results and Discussion

Macromolecular Design. There are several possibilities to link the surfactant fragments of polysoaps together.[13,14] We decided to attach the surfactants to the polymer backbone via the hydrophilic headgroup (the so-called “head type”), because the hydrophobic chains in other polysoap architectures are subject to very particular steric as well as mobility restrictions, due to the anchoring of the hydrophobic chain on the polymer backbone.[14,32,33] But whereas the “head type” geometry leads to polysoaps with closest ressemblance to low molar mass surfactants concerning mobility and hydrophilic−hydrophobic profile,[14] it asks for the appropriate choice of main chain spacer entitites to overcome the problem of steric overcrowding of the polymer backbone. The diameter of a densely packed hydrocarbon chain is about 0.5 nm, the one of a fluorocarbon chain somewhat larger than 0.6 nm due to the increased C−F bond

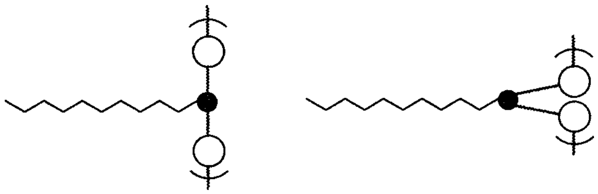

Figure 4. Model of possible amphiphilic conformations of the ionenes with favorable polarity profiles.

length and to the increased van der Waals radius of fluorine compared to hydrogen. Thus, the minimum spacer length required for hydrocarbon polysoaps equals about four carbon−carbon bonds (i.e., a C_4 repeat unit in average), whereas fluorocarbon polysoaps ask for a minimum spacer length of about five carbon−carbon bonds.

To satisfy these requirements and to ensure a certain flexibility in the system with an advantageous hydrophilic−hydrophobic profile, i.e., the most hydrophilic groups can be easily positioned at the “outer” side of the polymers, while the most hydrophobic groups can be placed on the “inner” side (or into the interior of micellar aggregates), we designed ionenes **3**, **7**, **9**, and **10** (Figure 2). In these polymers, the hydrophobic chains are not attached to the polymer backbone via the major hydrophilic groups, i.e., the ammonium groups, as mostly found.[34−37] Instead, they are attached in between of them via a moderately hydrophilic moiety, namely the tertiary amide group. On one hand, this modular design enables a facile, independent variation of the size and nature of the hydrophobic chain, by choice of the acylating agent. Also, the length and nature of the spacer group are easily varied by choice of the $\alpha-\omega$-dialkylating agent. On the other hand, this design enables a continuous variation of the packing of the hydrophobic chains in response to the environment, without creating unduly many unfavorable contacts, such as hydrophobic fragments being exposed to an aqueous environment, or vice versa, strongly hydrophilic fragments being exposed to a hydrophobic environment (Figure 4). Although we have used this design only for a small number of polysoaps in this work, it is general and extremely versatile. Most noteworthy, the irreversibility of the quaternization reaction at moderate temperatures enables the preparation of block copolymers with perfluorocarbon and hydrocarbon micellar blocks in a multistep sequence (cf. Figure 3). The choice of the perfluoroctanoyl chain was a compromise between a sufficient size of the hydrophobic chain to ensure hydrophobic association and the solubility in water. The choice of the decanoyl chain for the hydrocarbon analogue was a compromise between having a hydrophobic chain of comparable hydrophobicity (which would be dodecanoyl)[2] and a chain of comparable length (which would be octanoyl).

Still, this molecular approach has an inherent difficulty. Step growth polymerizations require virtually quantitative yields to provide high molar mass polymers, thus asking for absolutely clean reactions with close to 100% conversion (inherently, or by displacing the reaction equilibrium). This is, however, not the case for the quaternization of tertiary amines, so that typically low to moderate degrees of polymerization are only obtained for ionenes.[26,38] Therefore, we tried to limit these problems by reacting activated alkylating agents which cannot undergo E_2-type eliminations, such as allyl halogenides, with sterically undemanding $\alpha-\alpha$-diamines, such as *N*,*N*-dimethylamines. The limited size of the polymers presents at least the advantage of allowing to estimate the average degrees of polymerization from end group analysis,[38] what otherwise is extremely tricky for associative polyelectrolytes. The number-average degrees of polymerization obtained and the average number molar masses are given in Table 1. From these figures, an average number of 2.3 blocks per block copolymer is calculated, i.e., the majority of polymers should be diblock copolymers, though some homopolymers and some triblock copolymers should be present.

Table 1. Molecular Characteristics of the Ionene Polymers Prepared: Number-Average Degrees of Polymerization (DP_n) and Molar Masses (M_n)

polymer	yield (%)	DP_n	M_n
3	82	35	19 400
7	87	65	51 800
9	79	22	14 900
10		115	77 800
12	89	53	23 500

General Properties of the Ionenes. All polymers prepared are hygroscopic compounds, which are easily soluble in water and in methanol but not soluble in ethyl acetate, $CHCl_3$, or pure DMF. According to thermogravimetric analysis, they undergo thermal decomposition at temperatures above 200−210 °C. For dried samples, no thermal transition could be detected by differential scanning calorimetry below the onset of thermal decomposition. Powder diffractograms of dried samples by small-angle X-ray scattering exhibited one peak in the small angle region only for the hydrocarbon homopolymer **3** at $2\theta = 2.8°$, corresponding to a characteristic distance of 3.2 nm. The peak is somewhat broadened and has a half-width of about 0.3° (2θ). This suggests a microphase separation between the polar backbone and the hydrophobic chains in a bilayer type structure.[27,37] However, no peak was found for the fluorocarbon homopolymer **7** or for the statistical copolymer **9**. Normally when comparing similar series of polymers bearing comparably long hydrocarbon and fluorocarbon chains, opposite results are reported; i.e., the fluorocarbon polymers show more ordered structures.[15,19,37,39−41] We cannot give a good explanation for this unusual finding at present, but obviously, the particular molecular architecture of the ionenes prepared prevents the fluorocarbon chains from tightly associating.

Associative Properties in Aqueous Solution. As mentioned above, all ionenes prepared are easily soluble in water. But comparing the ^{1}H NMR spectra of the polymers in water with the ones taken in methanol, a notable broadening of the signals of the hydrophobic alkyl chains is observed in water for polymers **3**, **9**, and **10**, indicating hydrophobic association of the chains on the molecular level (Figure 5). This is particular visible for the terminal methyl group of the alkyl chain (signal at about 0.85 ppm) and for the methylene group next to the carbonyl moiety (signal at 2.35 ppm). Analogously, ^{19}F NMR spectra of the polymers in water compared to the ones taken in methanol exhibit a notable broadening of all signals of the perfluoroalkyl chains in water for polymers **7**, **9**, and **10** (Figure 6). By virtue of the molecular design of the polymers, these findings are not surprising. But most noteworthy, though somewhat broadened, the signals in the ^{19}F NMR spectra in water are much narrower than typically

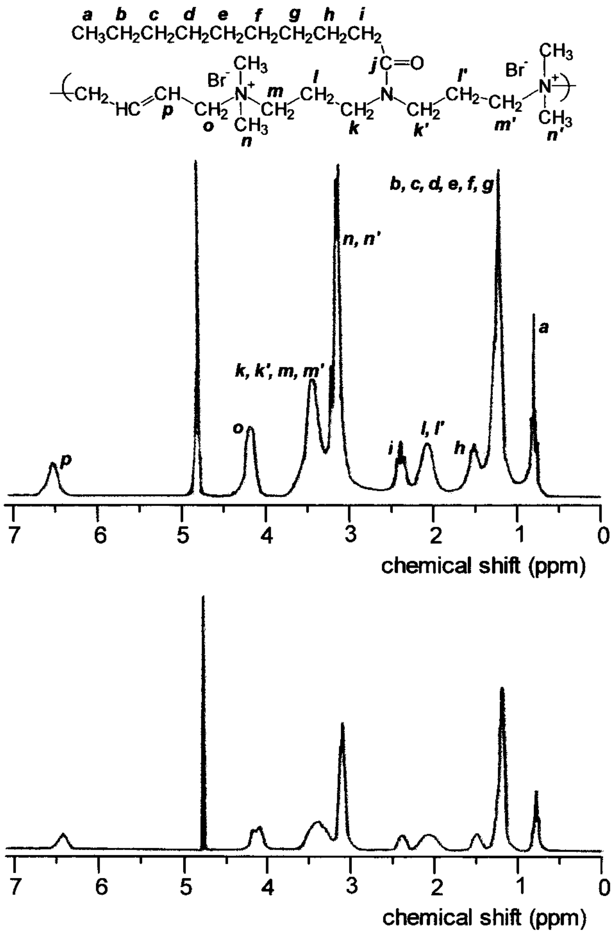

Figure 5. ^1H NMR spectra (200 MHz) of hydrocarbon polymer **3** in in CD_3OD (top) and in D_2O (bottom).

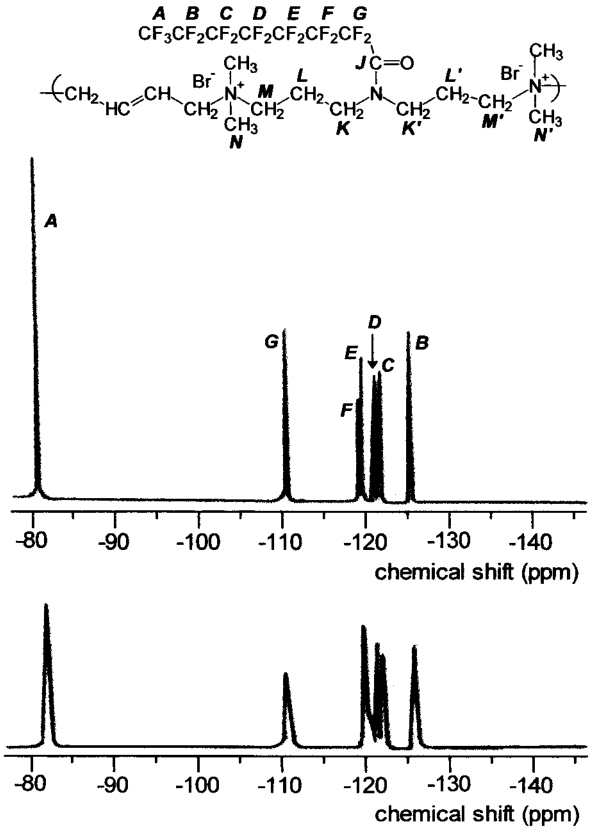

Figure 6. ^{19}F NMR spectra (283 MHz) of fluorocarbon polymer **7** in in CD_3OD (top) and in D_2O (bottom).

Table 2. ^1H Relaxation Times T_1 (Longitudinal) for Hydrophobized Ionenes in Water (±0.01 s 95% Condfidence); the Notation of the Assigned Signals Refers to Figures 5 and 6

		relaxation time (s) for polymer				
assignt	δ (ppm)	**3**	**7**	**3** + **7**	**9**	**10**
a	0.78	0.85		0.87	0.71	0.86
b−g	1.18	0.55		0.56	0.51	0.54
h	1.48	0.42		0.43	0.45	0.43
i	2.36	0.43		0.42	0.46	0.45
k + m	3.34	0.43	0.50	0.45	0.48	0.47
l	2.08	0.40	0.51	0.44	0.47	0.45
n	3.09	0.29	0.35	0.32	0.34	0.32
o	4.11	0.51	0.52	0.50	0.48	0.47
p	6.39	0.58	0.57	0.56	0.54	0.57

reported for polymers hydrophobized with long perfluorocarbon chains,[19,42−45] and no splitting of the signal of the terminal CF_3- group is observed. This implies that the perfluorocarbon chains are in a liquidlike state and not in a solidlike state as observed frequently.

This remarkable finding can be correlated with the absence of a small-angle signal in the solid-state powder diffractograms discussed above. The apparently weaker tendency of association of the perfluorocarbon chains, in the solid as well as in the dissolved state, might derive from the lack of a flexible side chain spacer group decoupling the side chains from the polymer backbone. This would prevent the fluorocarbon chains from tight association. A somewhat similar, though less pronounced, side chain spacer effect on associative perfluorocarbon thickeners was reported before.[6,46] In any case, the effect is fortunate for polysoaps because a liquidlike interior of the hydrophobic domains in water will favor the solubilization capacity for hydrophobic compounds (vide infra), as in ordinary surfactant micelles.

Looking in more detail into the mobility of the various molecular fragments in aqueous solution, we studied their ^1H and ^{19}F relaxation times T_1 (longitudinal) and T_2 (transversal), as listed in Tables 2−5. All relaxations showed monoexponential decay, suggesting a similar state of association and similar mobilities for the majority of the macromolecules of a given sample on the NMR time scale.

^1H relaxation times T_1 (Table 2) are rather similar for most protons, with the notable exception of the methylammonium groups which show markedly shorter decay times and of the methyl groups at the end of the hydrophobic chains (for polymers **3**, **9**, and **10** and their mixtures) which exhibit markedly longer decay times due to their high rotational frequency. Note that the T_1 value for this signal is virtually the same for hydrocarbon polysoap **3**, its 1:1 mixture with the fluorocarbon polysoap **7**, and block copolymer soap **10**, whereas the relaxation is significantly faster for the statistical copolymer **9**.

^1H relaxation times T_2 (Table 3) are more differentiated between the various polymers. The decay times are rather short for all protons on the polymer backbone but increase markedly for the protons in the hydrocarbon side chains and this with increasing distance from the backbone. This indicates an increasing degree of mobility, as expected for “head type” polysoaps.[32] Comparing the T_2 values for the different polymers, we note that the hydrocarbon polysoap **3** shows always the highest T_2 value for a given proton, suggesting the highest mobility. The fluorocarbon analogue **7** shows

Table 3. ^{1}H Relaxation Times T_2 (Transversal) for Hydrophobized Ionenes in Water (±0.5 ms 95% Condfidence); the Notation of the Assigned Signals Refers to Figures 5 and 6

		relaxation time (s) for polymer				
assignt	δ (ppm)	**3**	**7**	**3 + 7**	**9**	**10**
a	0.78	0.32		0.33	0.12	0.29
b−g	1.18	0.17		0.18	0.07	0.14
h	1.48	0.11		0.12	0.05	0.09
i	2.36	0.052		0.051	0.025	0.042
k + m	3.34	0.037	0.016	0.027	0.017	0.026
l	2.08	0.035	0.012	0.026	0.016	0.025
n	3.09	0.056	0.029	0.036	0.029	0.041
o	4.11	0.039	0.015	0.027	0.017	0.025
p	6.39	0.072	0.045	0.052	0.041	0.062

Table 4. ^{19}F Relaxation Times T_1 (Longitudinal) for Hydrophobized Ionenes in Water (±0.01 s 95% Condfidence); the Notation of the Assigned Signals Refers to Figure 6

		relaxation time (s) for polymer			
assignt	δ (ppm)	**7**	**3 + 7**	**9**	**10**
A	−80.50	0.54	0.54	0.55	0.54
B	−125.26	0.58	0.58	0.56	0.59
C	−121.43	0.56	0.56	0.52	0.57
D	−120.66	0.55	0.55	0.52	0.57
E + F	−119.25	0.53	0.53	0.50	0.54
G	−109.88	0.44	0.44	0.42	0.46

considerably lower T_2 value for a given proton on the polymer backbone indicating a lower mobility, thus suggesting a more tight aggregation of the perfluorocarbon chains. The physical mixture of the hydrocarbon polysoap **3** and its fluorocarbon analogue **7** provides virtually the same T_2 values for the protons of the hydrophobic chain as the pure homopolymer **3**, whereas the T_2 values for the protons on the polymer backbone are intermediate between the values of the two homopolymers. Accordingly, the mixture of the polymers behaves as a mere superposition.

The T_2 values for block copolymer soap **10** are throughout somewhat lower than for homopolymer **3**. While T_2 values of the protons attributed to the fragments of the hydrophilic backbone are thus very similar to the values found for the mixture of the hydrocarbon polysoap **3** and fluorocarbon analogue **7**, T_2 values of the protons attributed to the hydrophobic chains are somewhat lower than determined for the mixture of **3** and **7**. These findings indicate a somewhat different environment (or association) for the hydrocarbon chains with slightly reduced mobility in the case of the block copolymer.

But most notably for the statistical copolymer **9**, the T_2 values of the protons of the hydrophobic chain are markedly reduced in comparison with the other polysoaps. Even the T_2 values of the protons attributed to the fragments of the hydrophilic backbone are markedly low, being comparable to those of homopolymer **7** bearing only fluorocarbon hydrophobic chains. This suggests a very different environment and in particular a markedly reduced mobility of both the polymer's hydrophobic fragments and the backbone, presumably due to intermolecular association as discussed below.

Different from the proton relaxation times, ^{19}F relaxation times can only probe the hydrophobic side chains of the polymers. Typically, values for T_1 (Table 4) do not evolve much with increasing distance from the backbone. The values of a given fluorine position are similar for polymer **7**, the mixture of **7** with **3**, and block copolymer **10**. For the statistical copolymer **9**, T_1 decay times seem to be somewhat shorter, except for the terminal CF_3− group. The presentation of ^{19}F relaxation times T_2 is somewhat more complex (Table 5). But with the exception of the superposed signals of positions E and F, there is a general trend that the T_2 values increase with increasing distance from the backbone. Again, T_2 values of a given fluorine position are similar for polymer **7**, the mixture of **7** with **3**, and block copolymer **10**, whereas some of the T_2 values for the statistical copolymer **9** are significantly shorter. Again, this points to a different environment as well as to a reduced molecular mobility of the hydrophobic side chains of the statistical copolymer soap **9**.

Table 5. ^{19}F Relaxation Times T_2 (Transversal) for Hydrophobized Ionenes in Water (±0.2 ms 95% Condfidence); the Notation of the Assigned Signals Refers to Figure 6

		relaxation time (s) for polymer			
assignt	δ (ppm)	**7**	**3+7**	**9**	**10**
A	−80.50	0.064	0.065	0.050	0.065
B	−125.26	0.012	0.011	0.011	0.011
C	−121.43	0.012	0.011	0.0085	0.011
D	−120.66	0.0094	0.0094	0.0089	0.0090
E + F	−119.25	0.013	0.012	0.0096	0.012
G	−109.88	0.0078	0.0074	0.0072	0.0077

Combining the findings of the different measurements, it emerges that the mixture of the hydrocarbon and the fluorocarbon polysoaps **3** and **7** behaves like a superposition of the individual polymers, therefore strongly suggesting the nonmixing of the two types of hydrophobic chains in the hydrophobic aggregates in water. The behavior of block copolymer **10** differs slightly but is still rather similar. Therefore, nonmiscibility or at most very limited miscibility of the hydrocarbon and fluorocarbon chains may be assumed for **10**, too. In contrast, the behavior of the statistical copolymer soap **9** in water differs substantially from the behavior of the other polymers, pointing to a different form of hydrophobic association, that is, namely to intermolecular association taking the viscometric data into account (see below).

In addition to the NMR studies, viscometric studies were performed in order to learn about the macroscopic associative behavior of the ionene polysoaps in water. Figure 7 illustrates the reduced viscosities of the polymer solutions, either in water (Figure 7a) or, for comparison, in methanol (Figure 7b) as a solvent that does not promote hydrophobic association. Also, to estimate the effect of the hydrophobic chains attached to the ionene polymer backbone, a reference polymer without hydrophobic side chains, namely ionene **12**, was compared in water. All polymers show typical polyelectrolyte behavior in both solvents; this means increasing reduced viscosities for decreasing concentrations. Though the average molar masses M_n or the degrees of polymerization DP_n of the ionenes studied (cf. Table 1) are not identical, they are in the same order of the magnitude and thus enable at least a semiquantitative discussion.

We find that the reduced viscosity in water decreases in the order **9** $\gg$ **12** > **3** > **7** > **10**, whereas in methanol the sequence is **9** $\gg$ **3** > **10** > **7**. Importantly, we observe that the reduced viscosity of a given hydrophobized polymer increases significantly in methanol compared to in water, with the notable exception of statistical copolymer **9**, which behaves in the opposite way. These

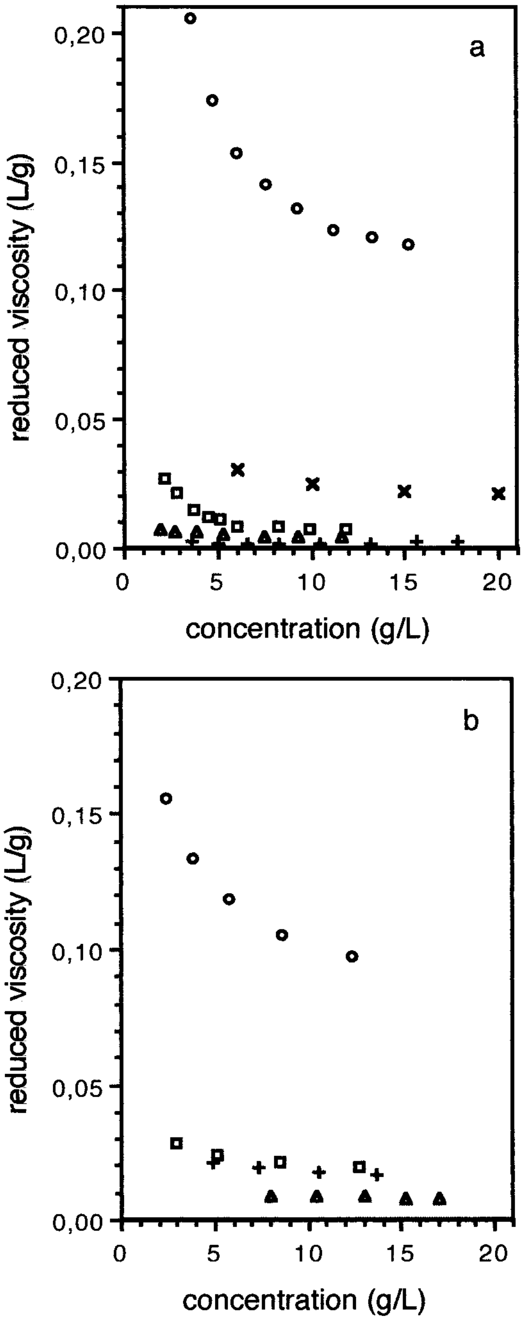

Figure 7. Viscosifying effect of polymers **3** (□), **7** (△), **9** (○) **10** (+), and **12** (×): (a) in aqueous solution; (b) in methanol.

effects are not linked to the relative evolution of M_n or of DP_n. On the contrary, ionene **9**, which has the lowest M_n, is by distance the most viscosifying polymer in water. Also, aqueous solutions of the hydrocarbon polysoap **3** and the fluorocarbon polysoap **7** exhibit considerably lower intrinsic viscosities compared to those of solutions of the not hydrophobized reference polymer **12**. Note that for the latter three polymers the average degrees of polymerization are similar. All these observations strongly suggest that ionene **9** undergoes intermolecular associations of the hydrophobic chains in water, whereas ionenes **3**, **7**, and **10** undergo primarily intramolecular association.

This set of observations can be easily rationalized by assuming (i) a strong tendency of hydrophobic association of neighboring side chains in water due to their high content within the polymers, (ii) steric and dynamic limitations in the possible arrangements of the hydrophobic chains due to their anchoring on a polymer backbone, confining intramolecular association to chains in close vicinity, and (iii) a poor compatibility of the hydrocarbon and the fluorocarbon side chains. Thus, the primarily intramolecular association of ionenes **3**, **7**, and **10** results from the high content of neighboring hydrophobic side chains of the same kind in these polymers. In contrast, the preferred intermolecular association of statistical copolymer **9** may be explained by the superposition of the anchoring of the hydrophobic chains to the polymer backbone with the poor compatibility of the hydrocarbon and the fluorocarbon side chains. Because the statistical distribution of the different hydrophobic chains along the polymer backbone does not enable an efficient local clustering of alike chains on an intramolecular base, microphase separation cannot take place within a given macromolecule but requires the association with others.

In agreement with this interpretation, the viscosifying effects of the fluorocarbon containing ionenes **7** and **10** are particularly low in water, keeping in mind that a perfluoroheptyl chain is more hydrophobic than a nonyl chain. But methanol is apparently a solvent of lower quality for the fluorocarbon polymers, too, in comparison with their hydrocarbon analogue **3**. The particularly low viscosifying effect of the block copolymer **10** in aqueous solution contrasts with the considerably higher molar masses of this polymer compared to the other ones and differs markedly from the behavior in methanol. This points to a particularly compact hydrophobic association in water. In fact, if **10** showed a mere superposition of the behavior of the two homopolymers **3** and **7**, the viscosifying effect of **10** should be either in between the behavior of the two homopolymers (as actually observed in methanol) or higher than both because of the higher molar mass. Hence, the exceptionally low viscosifying effect of **10** in water points to a particular conformation and association of the hydrophobic domains (cf. the discussion of solubilization capacity below).

Surface Activity of Aqueous Solutions. Polysoaps of the "head" type are known to be weakly or moderately surface active.[13,14,21] For the sake of completeness, we have therefore studied the static surface tensions of aqueous solutions of the polymers and compared them with the behavior of their monomeric structures, i.e., with surfactants **2** and **6** (Figure 8). The low molar mass analogues **2** and **6** exhibit well-defined critical micellar concentrations (cmc), the cmc of the fluorocarbon surfactant **6** being lower than the one of its hydrocarbon analogue **2**. This was expected because the hydrophobicity of fluorocarbon chains is about 1.5 times the one of hydrocarbon chains of identical length.[2] Though the lower surface tensions obtained for solutions of the fluorocarbon surfactant **6** are normal, too, the remarkably low absolute surface tensions found at the cmc of ca. 27 mN/m for **2**, and of 16 mN/m for **6** came to a surprise. Such low surface tensions imply normally a tight packing of the hydrophobic chains in the soluble monolayer which is counterintuitive to the surfactants' structure bearing two hydrophilic groups on one hydrophobic chain only. The surface tensions of the various ionene polysoaps show a continuous decrease with increasing concentration but no break point indicative of a cmc. The surface activity increases slightly in the series **3** ≈ **9** < **7** ≈ **10**, thus giving a slight advantage for the polymers bearing fluorocarbon chains. Other-

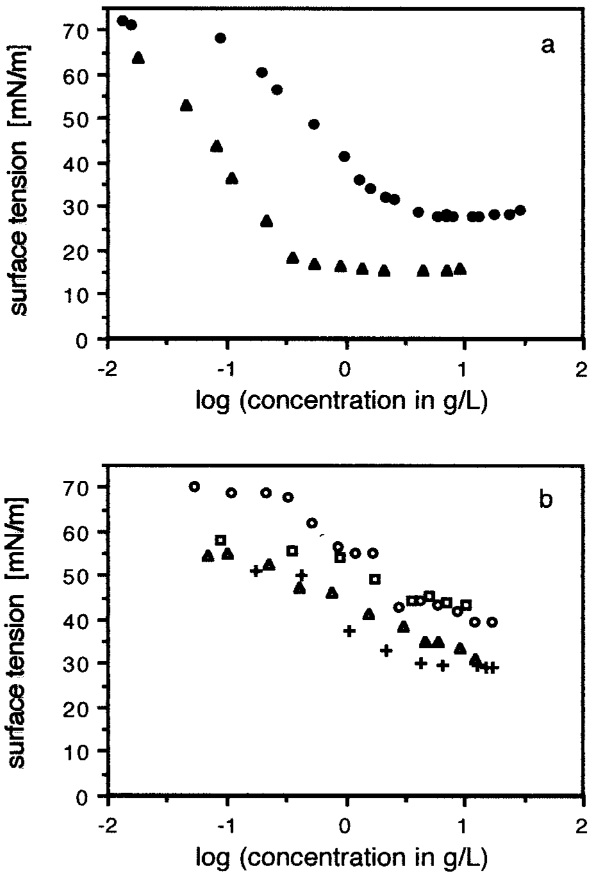

Figure 8. Surface tension vs concentration curves of aqueous solutions of (a) surfactants **2** (●) and **6** (▲) and (b) of polysoaps **3** (□), **7** (△), **9** (○), and **10** (+).

wise, the behavior of the polysoaps compares well at the first sight with many other polysoaps of the head type geometry.[12−14,21,22] A more detailed investigation of the adsorption properties and surface activity of such ionene polysoaps is given elsewhere.[49]

Selective Solubilization of Hydrocarbon and Fluorocarbon Compounds. Characteristically, the hydrophobic domains formed by polysoaps are capable of solubilizing sparingly water-soluble compounds, alike low molar mass surfactants.[47,48] As stated above, hydrocarbon and fluorocarbon compounds are poorly compatible, though both being hydrophobic. Therefore, disposing of polysoaps that bear hydrocarbon or fluorocarbon chains, or both of them, we wanted to study whether these systems show selectivities concerning the solubilization power toward hydrocarbon and fluorocarbon compounds.[29,50] For solubilization probes, we choose 2,3-dimethylbut-2-ene and hexafluorobenzene. Both compounds are liquids of moderate boiling points, thus being easy to handle. Importantly, both compounds do not bear heteroatoms, etc., which would render them amphiphilic, thus shifting their solubilization sites more to the surface and away of the different hydrophobic chains. Further, both compounds give one intense singlet in the ^{1}H spectra at about 1.70 ppm or in the ^{19}F spectra at 161 ppm, which are well resolved from the signals of the polysoaps. Thus, they can be exploited for direct quantification of the solubilized amounts. The results are listed in Table 6. Characteristically, we find that the hydrocarbon ionene **3** has a higher solubilizing power for the hydrocarbon probe than fluorocarbon ionene **7**, whereas **7** has a higher solubilizing power for the fluorocarbon probe than **3**. So indeed, selective solubilization sites exist for hydrocarbon and fluorocarbon compounds. The copolymers **9** and **10** show intermediate solubilizing power for these probes, as expected. However, it is striking that the block copolymer soap **10** shows a substantially higher solubilizing power for the hydrocarbon probe as well as for the fluorocarbon probe than the statistical copolymer **9**: the solubilizing power of **10** is always significantly higher than the average of the two homopolymers, whereas the solubilizing power of **9** is somewhat lower. These findings support once more the picture that the statistical copolymer provides a “mixed” CH/CF hydrophobic environment, whereas the block copolymer associates in multicompartment micelles containing separate hydrocarbon and perfluorocarbon domains. It appears that these two different types of hydrophobic domains can selectively solubilize hydrophobic compounds of their own kind. A particularly efficient solubilization by a mixed hydrocarbon−fluorocarbon block copolymer soap was reported recently for a very different system[29] as well as by vesicles made of blocky hydrocarbon−fluorocarbon lipids,[51] but a convincing explanation is missing yet. Taking also into account the particularly strong hydrophobic association as evidenced in the viscometric studies in aqueous solution (see above), it appears that hydrocarbon−fluorocarbon block copolymer soaps do form somewhat special hydrophobic associates.

Table 6. Solubilization Power of Aqueous Solutions of Hydrophobized Ionenes for 2,3-Dimethylbut-2-ene and for Hexafluorobenzene (Polymer Concentration = 10 g/L)

	probe $(CH_3)_2C{=}C(CH_3)_2$		probe C_6F_6	
polymer	mol probe/L	probe/ hydrophobic chain	mol probe/L	probe/ hydrophobic chain
none	0.01×10^{-4}		0.96×10^{-3}	
3	3.9×10^{-4}	0.022	1.1×10^{-3}	0.008
7	1.7×10^{-4}	0.014	5.2×10^{-3}	0.34
9	2.1×10^{-4}	0.014	3.3×10^{-3}	0.16
10	3.4×10^{-4}	0.023	4.9×10^{-3}	0.27

Conclusions

The amphiphilic fluorocarbon ionenes studied and their hydrocarbon analogues exhibit hydrophobic aggregation in water with the characteristic behavior of polysoaps, concerning surface activity, very weak viscosifying effects, and moderate NMR line broadening in aqueous media. Different from most amphiphilic polymers with a high content of fluorocarbon chains, the ^{19}F NMR spectra suggest a liquidlike behavior of the fluorocarbon chains in water. The ability for hydrophobic self-organization in aqueous solution makes such polymers well-suited for obtaining complex supramolecular systems. Copolymer soaps with hydrocarbon and fluorocarbon chains statistically distributed over the molecule prefer intermolecular hydrophobic association, presumably in order to minimize unfavorable interactions between unlike hydrophobic chains while favoring interactions of like chains. This leads to viscosifying behavior, despite the high density of hydrophobic chains in the polymer, and to reduced solubilizing power. In contrast, segmented block copolymers with blocks disposing of hydrocarbon and of fluorocarbon chains allow to prepare multicompartment micellar systems with two distinctly different types of hydrophobic domains. Such copolymers undergo tight intramolecular association, thus leading to very low viscosifying effects, while providing particularly high solubilizing power.

Acknowledgment. We thank F. Candau (CNRS Charles Sadron, Strasbourg, France) and H. Ringsdorf (Universität Mainz, Germany) for stimulating discussions and A. M. Jonas (Université catholique de Louvain) for help with X-ray facilities. The work was supported by the Belgian State (Services du Premier Ministre—Services fédéraux des Affaires Scientifiques, program PAI4/11).

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MA011047N