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ORIGINAL CONTRIBUTION

D. Cochin
P. Hendlinger
A. Laschewsky

Polysoaps with fluorocarbon hydrophobic chains

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D. Cochin · P. Hendlinger
Prof. Dr. A. Laschewsky (✉)
Université Catholique de Louvain
Dépt. de Chimie
Place L. Pasteur
1348 Louvain-la-Neuve, Belgium

Abstract A series of amphiphilic copolymers is prepared by copolymerization of choline methacrylate with 1,1,2,2-tetrahydroperfluorooctyl methacrylate in varying amounts. The copolymers bearing fluorocarbon chains are studied concerning their effects on viscosity, solubilization and surface activity in aqueous solution, exhibiting a general behavior characteristic for polysoaps. The results are compared with the ones obtained for an analogous series of amphiphilic copolymers bearing hydrocarbon chains.

Key words Amphiphilic polymers – fluorocarbon polymers – associating polymers – polysoaps

Introduction

By virtue of their strong tendency to self-organize in aqueous media and of their industrial importance, water-soluble amphiphilic polymers attract increasing attention. "Polysoaps" [1–3] represent a particular class within such polymers which is characterized by many analogies to micelle-forming surfactants.

Though the hydrophobic parts of amphiphiles are generally made from hydrocarbon chains, a number of alternatives exists, including, e.g., siloxanes, oligo (propylene oxides) or fluorocarbons. Such alternative hydrophobic groups have been increasingly explored in low molecular weight surfactants due to their different qualities – such as flexibility, surface energy, hydrophobicity and oleophobicity [4] – but their use in amphiphilic polymers is exceptional. In particular, the use of fluorocarbon hydrophobic chains in polymers has so far been very limited. The few studies have been restricted basically to water-soluble polymers which are weakly substituted with fluorocarbon chains to provide efficient thickeners [5–10], or to block copolymers [11–15] or oligomers [16, 17] respectively. Examples for water-soluble polymers which are heavily substituted with fluorocarbon chains, as needed for polysoaps to enable intramolecular aggregation, are virtually missing.

Here, the synthesis and investigation of fluorocarbon polysoaps is reported. The polysoaps 3a–3d are prepared by random copolymerization of the hydrophilic monomer choline methacrylate 1 with the 1,1,2,2-tetrahydro-perfluorooctyl methacrylate 2 in varying amounts (Fig. 1). These fluorocarbon polysoaps are of the so-called "head-type" geometry [3, 18], having a chemical structure similar to the known hydrocarbon polysoaps 4a–4c [18].

Experimental Part

Monomer 1 was a gift from B. Schlarb, monomer 2 was a gift from Hoechst Co. (Germany). Monomers 1 and 2 are copolymerized at 60 °C for 12 h, reacting 0.200 g of 2 dissolved in 5 ml of ethanol with the calculated amount of 1 and 1 mol% of azobis (isobutyronitrile) AIBN as initiator, to give copolymers 3a–3d. Copolymers 3a and 3b precipitate during polymerization; they are separated by filtration, extracted with ethanol, dissolved in water, and precipitated in acetone. Copolymers 3c and 3d are repeatedly precipitated in acetone from ethanol solutions.

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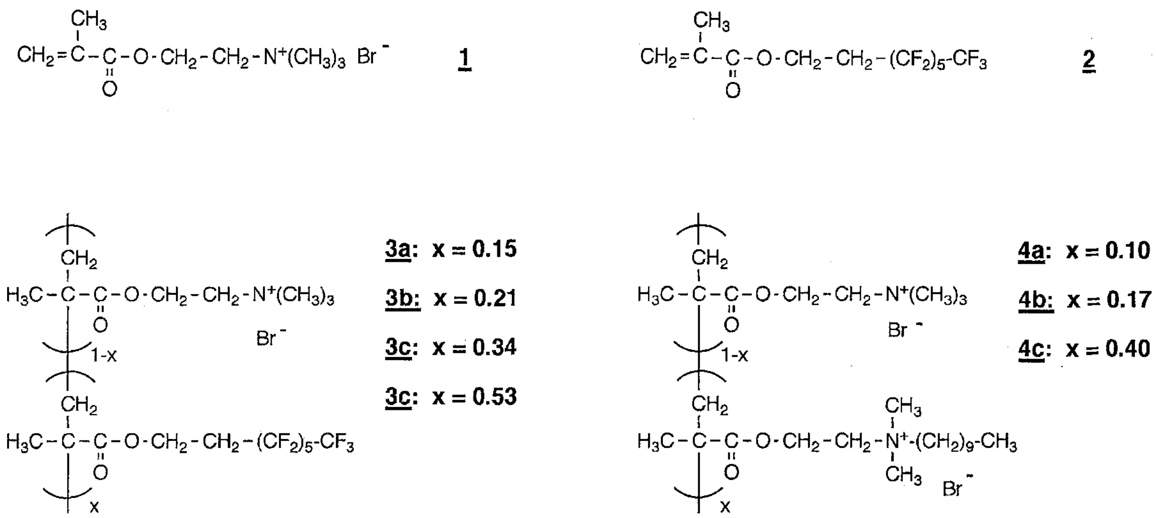

$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}N^+(CH_3)_3\ Br^-$ **1**

$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}(CF_2)_5{-}CF_3$ **2**

Fig. 1 Monomers and copolymers used

The synthesis of copolymers 4a–4c was described previously [18]. The azodye 4-(4-butylphenylazo)-N,N-diethylaniline 5 was synthesized by standard coupling reaction of 4-butylaniline and N,N-diethylaniline [19].

Water used for all experiments was purified by a Milli-Q water purification system (resistance 18 MΩ).

NMR-spectra were recorded by a Gemini 300 MHz spectrometer. $CFCl_3$ was used as internal standard for ^{19}F-spectra. IR-spectra were recorded by a Nicolet type 205 FT-IR spectrometer. Elemental analysis was done by the University College of London. Viscometry was performed by a semi-automatic Ubbelohde capillary viscometer (Schott) in water at 25 °C. Solubilization experiments were done by shaking 4 wt % aqueous solutions of the polymers with an excess of dye for 4 weeks at 18 °C, followed by centrifugation and filtration to give clear, colored solutions which are measured by UV/Vis spectroscopy (SLM AMINCO DW-2000 spectrometer).

Thermogravimetry was performed on a thermogravimetric analyzer TGA-500 SETARAM, with a heating rate of 10 °C/min in nitrogen atmosphere. Differential scanning calorimetry d.s.c 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-500 Siemens, using the Ni-filtered Cu-K_α-line ($\lambda = 0.1541$ nm).

Results and Discussion

Synthesis and general properties of the copolymers

Copolymers 3a–3d are prepared by free radical copolymerization of the cationic methacrylate 1 with the fluorocarbon methacrylate 2 in solution. Table 1 lists the composition of the respective monomer feeds and of the resulting copolymers. As both compositions are rather close even at moderate conversions with a slight preference for monomer 2, we can assume a copolymerization behavior not too different from ideal statistical copolymerization of both methacrylates.

Table 1 Composition of the monomer feeds of 1 and 2, and of the resulting copolymers 3a–3d as determined by elemental analysis of N and Br

Copolymer	Molar fraction of monomer 2 in the feed	Yield (%)	Molar fraction of monomer 2 in the copolymer	
			X_2(N)	X_2(Br)
3a	0.091	80	0.15	0.17
3b	0.17	48	0.21	0.20
3c	0.33	34	0.34	0.33
3d	0.50	30	0.53	0.63

Copolymers 3a–3d were characterized by ^1H-NMR, ^{19}F-NMR and FT-IR spectroscopy, and by elemental analysis, to give satisfactory results (cf. Table 1, Fig. 2). Thermogravimetric analysis indicated decomposition above 190 °C; no thermal transition could be observed by d.s.c.. Unlike the homopolymers, x-ray powder diffractograms of copolymers 3b–3d exhibit one small angle signal at $2\theta = 2°$ in addition to the halo around $2\theta = 17°$. This behavior is similar to the one of the hydrocarbon analog 4c [18]. The small-angle peak was attributed to a lamellar superstructure due to microphase separation of the ionic and the hydrophobic fragments of the copolymers. That

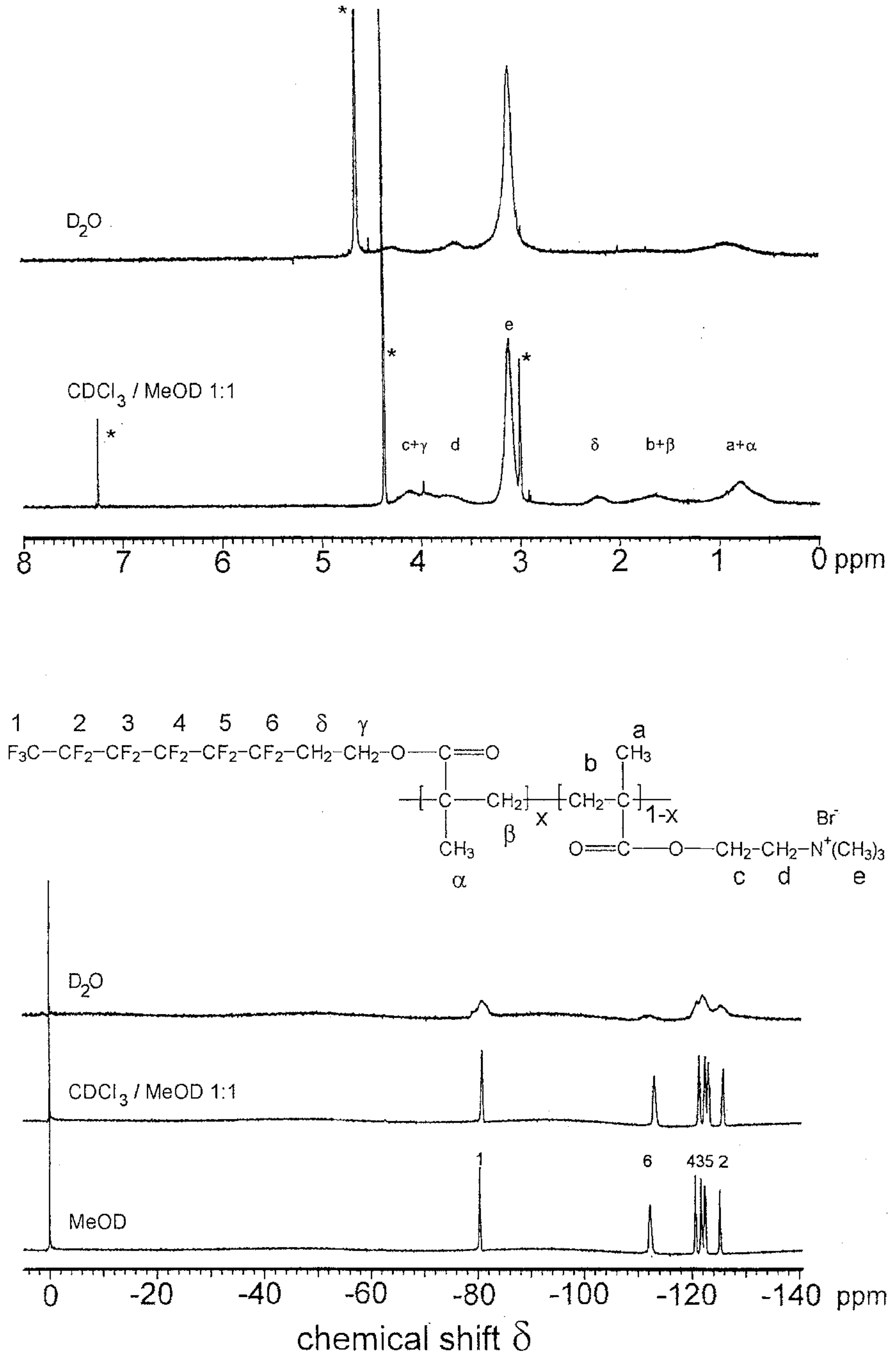

Fig. 2 ^{1}H-NMR (300 MHz) and ^{19}F-NMR (188 MHz) spectra of copolymer **3c** at room temperature (x: = 0.34). from top to bottom: ^{1}H-NMR in D_2O, ^{1}H-NMR in $CDCl_3/CD_3OD$, ^{19}F-NMR, in D_2O, ^{19}F-NMR in $CDCl_3/CD_3OD$ 1v/1v, ^{19}F-NMR in CD_3OD

superstructure formation in the series 3a–3d occurs at lower hydrophobe contents than in the series of their hydrocarbon analogs 4a–4c, can be explained by the stronger hydrophobicity of the fluorocarbon chains.

Attempts to characterize the degree of polymerization of copolymers 3a–3d by GPC failed. End group analysis by NMR and FT-IR spectroscopy enabled however an estimation of the lower limit: as nitrile end-groups could not be detected, the degree of polymerization of the copolymers must exceed 20.

Copolymers 3a–3d are insoluble in acetone, dioxane and $CHCl_3$. They are soluble in methanol and 1v/1v mixtures of methanol and $CHCl_3$. Copolymers 3a–3c are water-soluble, whereas 3d swells only. This observation agrees well with previous findings on the limits of water solubility of copolymers of the "head type" geometry hydrophobized by hydrocarbon chains which were explained by a spacer model [3, 18, 20].

Characteristically, ^{1}H-NMR and ^{19}F-NMR spectra of copolymers 3a–3c have the usual polymeric appearance in organic solvents such as $CDCl_3/CD_3OD$ mixtures or CD_3OD, whereas the signals of the hydrophobic fragments are strongly broadened in D_2O, or are even missing (Fig. 2). The broadening effect is particularly visible in the ^{19}F-spectra. This behavior points to a reduced mobility due to hydrophobic aggregation in aqueous media, as observed for many other hydrophobized water-soluble polymers [21–24]. But noteworthy despite their strong broadening, fluorine signals are still observed, in contrast to reports on polyacrylamides with low contents of fluorocarbon groups [25].

Polysoap behavior

Within the water-soluble amphiphilic polymers, polysoaps are characterized by two prominent properties: i) relatively low reduced viscosities in water, compared to their analogs lacking hydrophobic groups, and ii) the ability to solubilize hydrophobic compounds in water. Both properties are attributed to the intramolecular formation of hydrophobic domains, often referred to as "polymeric micelles", in analogy with micelles formed from standard surfactants. For standard surfactants, surface activity has to be added as key property, whereas polysoaps may or may not be surface active, depending on their detailed structure [3].

Hence, these three key properties, reduced viscosity, solubilization capacity and surface activity were investigated for the fluorocarbon copolymers 3a–3c (Figs. 3–5), and compared with the behavior of the known hydrocarbon copolymers 4a–4c of similar chemical structure and hydrophobe content.

Viscosimetry

The reduced viscosities $\eta_{red} = \eta_{spec}/c$ of aqueous solutions of 3a–3c are plotted in Fig. 3 as function of the copolymer concentration. For comparison, the results for the homopolymer of choline methacrylate **poly-1** and for the hydrocarbon analogs 4b and 4c are added.

Characteristically, all polymers exhibit polyelectrolyte behavior: in the low concentration range, the values of η_{red} increase with decreasing concentration. Still, it is evident that the hydrophobized copolymer series 3a–3c and 4b–4c exhibit substantially lower η_{red} values than **poly-1** There is no indication of thickening effects as observed fo watersoluble copolymers with a very small fluorocarbon hydrophobe content [5–11, 25]. Though effects due to strongly differing degrees of polymerization cannot be rigorously excluded as the molar masses are unknown, they are highly improbable as the polymerization conditions for the polymers were virtually identical. Therefore, the behavior of the fluorinated copolymers is qualitatively in agreement with the one of classical polysoaps which is attributed to an intramolecular hydrophobic aggregation [26–30]. Noteworthy is that polysoap behavior is already observed for copolymer 3a which contains 10 mol % of 1,1,2,2-tetrahydro-perfluorooctyl chains, whereas much higher contents of octyl chains are usually needed [30, 31], thus demonstrating once more the higher hydrophobicity of fluorocarbon chains.

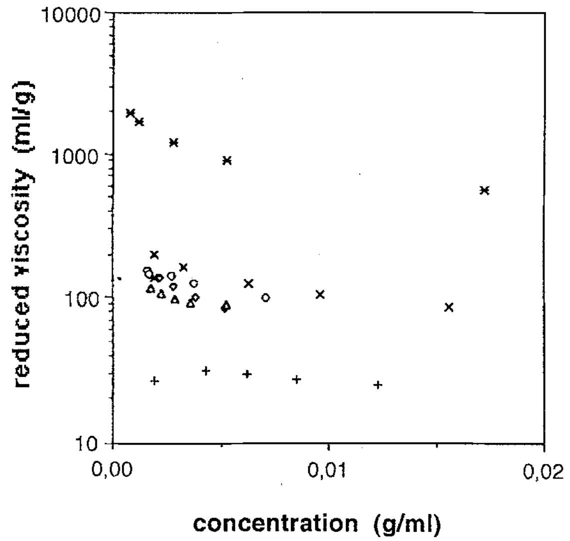

Fig. 3 Reduced viscosity η_{red} of aqueous polymer solutions at 25 °C, as function of the concentration for **poly-1** (∗), copolymers 3a(○), 3b(△) and 3c (◇), copolymers 4b (×), 4c (+)

A more detailed look at the viscometry data shows that the reduced viscosity of the hydrocarbon copolymers strongly decreases with increasing hydrophobic content from 4b to 4c, as reported for other polysoaps in the literature. This behavior is attributed to an increasing intramolecular hydrophobic aggregation. In contrast, all three fluorocarbon copolymers 3a–3c exhibit comparable reduced viscosities. Unfortunately, it cannot be decided whether this is a characteristic feature for such fluorinated polysoaps, or whether differences in the molecular weights are responsible.

Solubilization

The ability of copolymers 3a–3c to solubilize hydrophobic compounds in water was studied for the azo dye 5. This

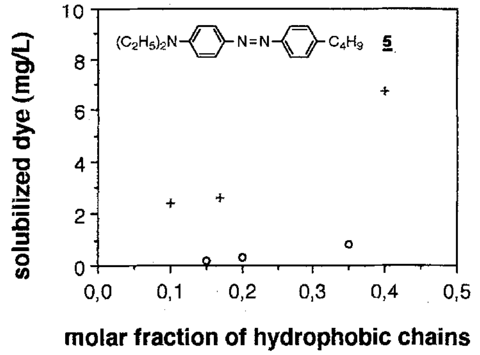

Fig. 4 Solubilization of azo dye 5 in water by copolymers 3a–3c (○) and by copolymers 4a–4c (+ , data taken from ref. [19]), (polymer concentration: = 4 g/L)

compound was used previously in studies of the analogous hydrocarbon copolymers 4a–4c [19, 32]. The results are shown in Fig. 4.

The figure basically demonstrates that the fluorocarbon copolymers are indeed capable of solubilizing hydrophobic compounds. Solubilization capacities increase with increasing hydrophobe content. However, compared to hydrocarbon analogs 4a–4c the capacities are much smaller [19]. Realizing the reduced length of the hydrophobic chains (octyl versus decyl), and keeping in mind that fluorocarbon chains are both hydrophobic and oleophobic, i.e., per se not particularly suited to accommodate hydrocarbon solubilizates, this finding is not surprising. Nevertheless, the observed solubilization capacities, albeit small, corrobate the presence of hydrophobic microdomains for 3a–3c.

Surface tension measurements

Surface tension measurements of copolymers 3a–3c are shown in Fig. 5. The copolymers show a notable surface activity, in particular at elevated concentrations, but no break point pointing to a critical micelle concentration (CMC) can be identified.

This general behavior agrees well with the one reported for other polysoaps of the "head type" geometry [18, 33, 34], such as copolymers 4a–4c. However, in contrast to such hydrocarbon polysoaps, the surface tension of aqueous solutions is not reduced with increasing content of hydrophobic chains in the copolymers: on the contrary, the surface tension is most reduced for copolymer 3a, increasing for a given concentration in the series 3a < 3b < 3c, i.e., with increasing content of fluorocarbon chains.

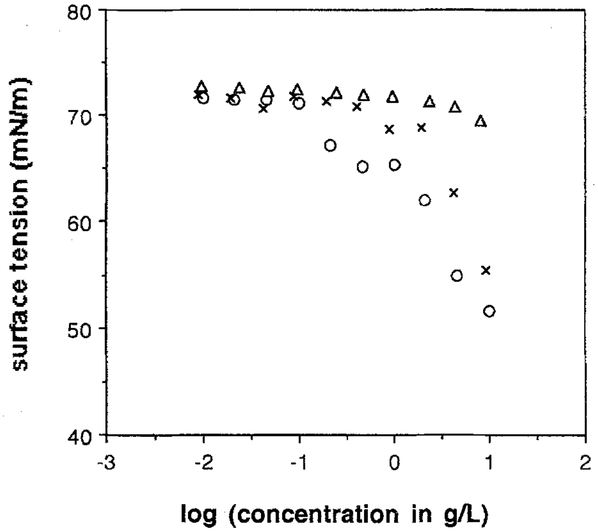

Fig. 5 Surface activity of fluorinated polysoaps: ○ = 3a, x = 3b and △ = 3c

There is no obvious explanation for this unexpected result, though it is not unparalleled in the literature [35, 36]. It clearly requires further investigation. Possibly, the strong hydrophobic effect of fluorocarbons could cause the superposition of intramolecular and intermolecular hydrophobic aggregation whose relative contributions would change with the fluorocarbon content in the copolymers. This putative explanation might also play a role in the weak dependence of the reduced viscosities of 3a–3c with increasing fluorocarbon content (cf. Fig. 3).

Conclusions

The fluorocarbon copolymers studied exhibit hydrophobic aggregation in water with characteristic behavior of polysoaps, concerning effects on viscosity, solubilization and surface activity. Nevertheless, the detailed properties show some marked differences compared to the ones of hydrocarbon analogs. Although the reasons for these differences remain to be clarified, the present results demonstrate the usefulness of replacing hydrocarbon chains by fluorocarbon ones to create polysoaps with a modified spectrum of properties.

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