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Polysoaps via alternating olefin/SO_2 copolymers

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Introduction

Recently, the irradiation-induced homopolymerization of olefinic surfactants has been studied[1,2], yielding oligomeric polysoaps[3] only. But instead of the poor homopolymerization, various simple and functionalized olefins have been shown to undergo easily a strictly alternating copolymerization with SO_2, to yield aliphatic polysulfones[4,5]. In principle, such olefin/SO_2 copolymers should be well suited for polysoap systems, too, offering the same advantages as simple polyolefins, viz. hydrolytic stability of the polymer backbone and easy monomer storage and handling. Hence, we studied the use of some olefinic zwitterionic surfactants, bearing single non-activated double bonds and their copolymers with SO_2, as an alternative to simple olefinic[1,2] and acrylic[6-8] polymerizable surfactants, and the polysoaps derived therefrom.

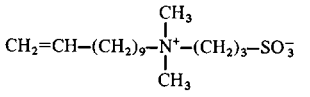
Results and discussion

Monomers studied

The olefinic zwitterionic surfactant monomers **1**–**3** were synthesized and the corresponding olefin/SO_2 copolymers copoly(**1**), copoly(**2**) and copoly(**3**) prepared using 2,2′-azoisobutyronitrile and the naphthyl-labelled azoinitiator **4**. All monomers bear the zwitterionic ammoniopropanenesulfonate head group. Noteworthy, monomer **3** is a diastereomeric mixture due to 2 chiral centres, the asymmetric ammonium nitrogen and the asymmetric carbon of the secondary alcohol group. Monomers **1** and **2** have the double bond at the end of the hydrophobic tail, because only polymerizable surfactants with the reactive moiety at this position are known to yield water-soluble polymers[7,8]. In contrast, monomer **3** bears the double bond attached to the nitrogen of the betain head group via a short hydrophilic spacer group. We wanted to investigate whether the elongated polymer backbone of olefin/SO_2 copolymers would improve the water solubility of such "head-bound" polysoaps, in comparison with analogous acrylic polymers[8].

Monomer properties

All three monomers are water-soluble at 25 °C showing characteristic surfactant properties, e. g. strongly foaming aqueous solutions, and the formation of lyotropic liquid crystals in the concentrated regime. The fan-shaped textures point to the presence of hexagonal phases, in agreement with previous observations of similar compounds[9]. As the hydrophobic tails are equivalent to ca. 11 methylene units, the measured critical micelle concentrations (cmc's) in Tab. 1 compare well with the cmc's of



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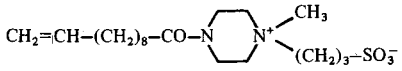

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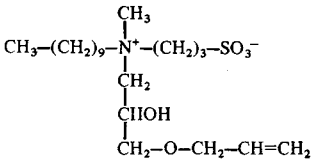

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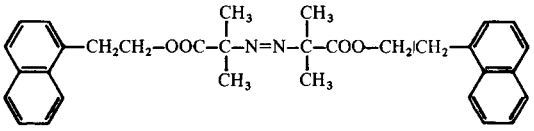

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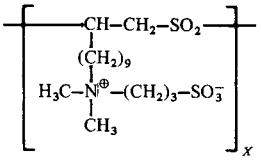
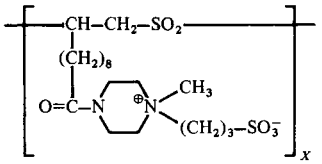
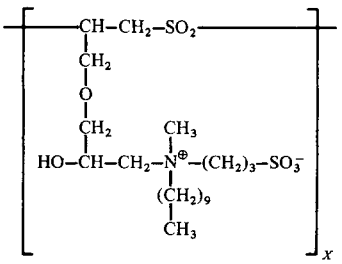


copoly (**1**)



copoly (**2**)



copoly (**3**)

the reference substances *N*-decyl-*N,N*-dimethylammoniopropane-1-sulfonate of $3{,}9 \cdot 10^{-2}$ mol/L, and of its dodecyl homologue of $3{,}6 \cdot 10^{-3}$ mol/L, respectively[10]. Within the series, monomer **3** exhibits the lowest cmc and minimum surface tension values, whereas monomer **1** exhibits the highest ones, indicating increasing hydrophobicity from **1** to **2** to **3** (Fig. 1a; Tab. 1).

As observed for a number of surfactants[11], monomer **1** is a thermotropic liquid crystal and exhibits complex melting behaviour (k_1 107 k_2 132 lc_1 148 lc_2 153 i). In contrast, monomer **2** has a simple melting point of 193 °C, which is significantly higher, suggesting the presence of additional attractive interactions due to the piperazine ring. Above the melting point, **2** degrades rapidly. Monomer **3** shows a glass transition at −15 °C only, presumably because of the diastereomeric mixture.

Polymerization, copolymer composition and general properties

The monomers were copolymerized with SO_2 in water at concentrations above their cmc, using 2,2′-azoisobutyronitrile (AIBN) as initiator. The purified polymers were free from monomer according to thin layer chromatography, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. As typical for polymers, the signals in the

Tab. 1. Thermal behaviour in bulk, critical micelle concentration (cmc) and minimum surface tension values γ_{min} of surfactant monomers **1**, **2** and **3**

Monomer	Thermal[a] behaviour in bulk in °C	cmc in g/L	cmc in mol/L	$\frac{\gamma_{min}}{mN/m}$	cmc in g/L (pyrene probe)
1	k_1 107 k_2 132 LC_1 148 LC_2 153 i	7,9	$2{,}4 \cdot 10^{-2}$	42,0	9,9
2	k 193 i (d)	3,6	$9{,}3 \cdot 10^{-3}$	38,5	3,6
3	g-15 i	1,5	$3{,}7 \cdot 10^{-3}$	33,5	

[a] k = crystalline, LC = liquid-crystalline, i = isotropic, d = decomposition, g = glassy.

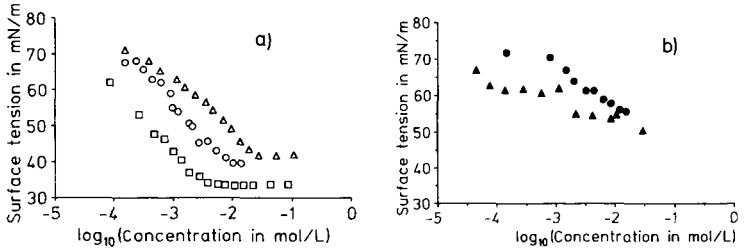


Fig. 1. Surface tension in water at 25 °C as a function of the logarithm of concentration for (a) surfactant monomers **1** (△), **2** (○) and **3** (□), and (b) for olefin/SO_2 copolymers copoly(**1**) (▲) and copoly(**2**) (●); concentrations of copolymers given in moles of constitutional repeating units per litre according to graphic representations of formulae given above

^1H NMR spectra were broadened (compare Figs. 2(a) and (b)). In case of the water-soluble copoly(**1**) and copoly(**2**), integration of the NMR signals in D_2O of the alkyl chain was not proportional to the corresponding number of protons due to side-chain aggregation of the polysoaps[8] (Fig. 2(b)). In the IR spectra characteristic signals of polysulfones[5] at wave numbers ν/cm^{-1} = 1294 (ν_{as}, —SO_2—) and 1118 (ν_s, —SO_2—) were observed. In agreement, the sulfur analysis indicates a 1:1 mol/mol composition of the olefin/SO_2 copolymers (see formulae of copoly(**1**), copoly(**2**) and copoly(**3**), Tab. 2).

Because the molecular weights could not be determined using gel-permeation chromatography (GPC) due to adsorption of the polymer onto the column material, end-group analysis was attempted. CN-groups of the initiator AIBN could neither be detected in the ^{13}C NMR spectra (no signal at δ (in ppm) 115–125) nor in the IR spectra (no signal at ν/cm^{-1} = 2260–2240 (ν, —CN)). As ultraviolet spectroscopy is much more sensitive, end-group analysis was attempted using the naphthyl-labelled azoinitiator **4** for polymerization. However, even at high polymer concentration, no naphthyl end group could be detected, suggesting spontaneous copolymerization. This was verified by the reaction of the monomer with SO_2 in the absence of initiator which

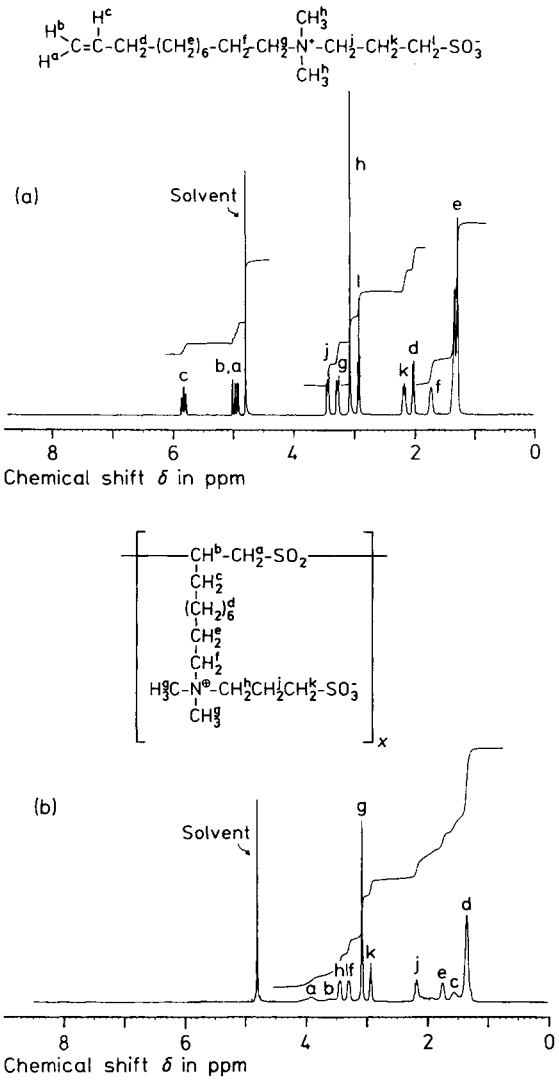


Fig. 2. ^{1}H NMR spectra of monomer **1** (a) and copoly(**1**) (b) in D_2O at room temperature

afforded comparable yields of polymer. For copoly(**1**) and copoly(**2**), the average yield of purified polymer was 37% and 39%, respectively, for copoly(**3**) the yield was substantially lower (3%) (Tab. 2). We attribute this to side reactions during the polymerization caused by the ether- and secondary alcohol moiety of monomer **3**.

All three copolymers copoly(**1**)–copoly(**3**) are hygroscopic solids. Thermogravimetry shows decomposition above 150 °C, in agreement with literature on the thermostability of olefin/SO_2 copolymers[5]. Differential scanning calorimetry (DSC) studies showed no thermal transition within −100 °C and +130 °C, as reported for other polyzwitterions[8,12].

Tab. 2. Yield and sulfur content of olefin/SO_2 copolymers copoly(1), copoly(2) and copoly(3)

Polymer	Yield after purification in %	Sulfur content calculated for 1 : 1 mol/mol copolymers in %	Sulfur content found in %
copoly(1)	37	15,79	16,68
copoly(2)	39	13,63	14,27
copoly(3)	3	13,10	15,03

Polymer properties in aqueous solution

In case of the polymers copoly(1) and copoly(2), the surfactant side groups are attached to the polymer backbone via the end of the hydrophobic tail, in case of copoly(3) the surfactant side groups are attached to the polymer backbone via the hydrophilic head. In agreement with such polymer geometries, copoly(1) and copoly(2) are water-soluble, but copoly(3) is not[7,8]. However, copoly(3) is soluble in methanol/water (volume ratio 1 : 1) mixtures. Thus, the solubility in polar protic solvents is much improved compared to analogously built acrylic surfactants[8]. This behaviour is attributed to the elongated polysulfone backbone $\text{-}(\text{-}CH_2\text{—}CHR\text{—}SO_2\text{-})_x$ instead of $\text{-}(\text{-}CH_2\text{—}CHR\text{-})_x$, enabling a more advantageous arrangement of the surfactant side groups in polar solvents.

The surface activity of copoly(1) and copoly(2) is illustrated in Fig. 1b. Both polymers show a slightly increased depression of surface tension γ at low concentrations, but a much lower depression of γ at moderate and high concentrations, compared to their monomers. Furthermore, the depression of γ with $\log_{10}$ (concentration) exhibits neither a break nor a plateau value indicative of a cmc. This behaviour at the air-water interface is characteristic for polysoaps, and has been attributed to intramolecular aggregation of the hydrophobic groups in the polymers[3].

Both copoly(1) and copoly(2) are capable of solubilizing hydrophobic molecules such as pyrene. As the fine structure of the fluorescence spectrum of pyrene is sensitive to the polarity of its local environment[13], it provides information on the onset of formation of hydrophobic pockets and on the polar quality of such pockets. In general, the intensity ratio of the emission bands at 372 nm (band I) and at 383 nm (band III) is used in the so-called "py-scale"[13,14].

Characteristically for low-molecular-weight surfactants in water[13], the intensity ratio I/III decreases with increasing concentration, until the cmc is reached, in order to level in a final plateau as observed for monomers **1** and **2** (Fig. 3). For copoly(1) and copoly(2), however, the intensity ratio I/III is nearly constant, indicating the presence of hydrophobic pockets down to high dilutions (Fig. 3). This points to an intramolecular aggregation of the surfactant groups in the polymers and the non-existence of a cmc, in agreement with the surface tension studies. Hence, copoly(1) and copoly(2) behave as classical polysoaps.

Studying the fluorescence of the pyrene probe in more detail, a noteworthy feature are the rather high intensity ratios I/III obtained for the polymers, compared to the

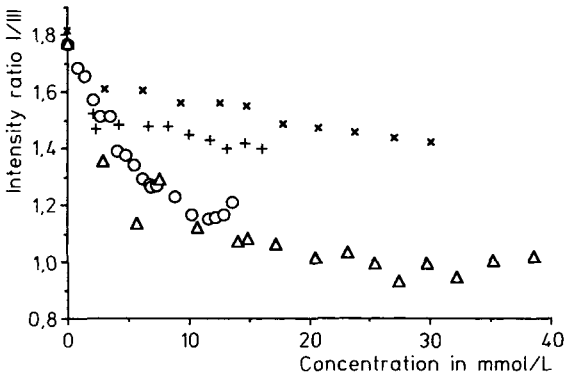


Fig. 3. Intensity ratio I/III of bands I and III of pyrene fluorescence in an aqueous solution of surfactant monomer **1** (△), **2** (○) and the corresponding olefin/SO_2 copolymers copoly(**1**) (×) and copoly(**2**) (+) at 25 °C (pyrene concentration ca. $3 \cdot 10^{-7}$ mol/L; concentrations of copolymers given in moles of constitutional repeating units per litre according to graphic representations of formulae given above

plateau value of the monomers above cmc (Fig. 3). This implies that the hydrophobic pockets provided by the polysoaps are much less polar than the ones provided by the monomeric surfactants. Such a behaviour has been reported previously[8] and was attributed to the (partial) immobilization of the terminal hydrophobic parts of the surfactant monomers by the polymer backbone, which are the most mobile and thus most efficiently solubilizing parts of the soaps.

Conclusion

Olefinic zwitterionic surfactants and SO_2 copolymerize spontaneously in water. Although less rigid, the general geometric requirements for water solubility of the copolymers correspond to those of acrylic polymer analogues. Only copolymers in which the surfactant side chains are bound to the polymer backbone via the hydrophobic tails are water-soluble. Such copolymers behave like classical polysoaps concerning surface activity and solubilization capability.

Experimental part

Materials

Acetonitrile and triethylamine: they were dried over molecular sieves (3 Å). Petroleum ether was distilled prior to use, boiling range 40 °C–70 °C. Water was purified by a Milli Q water purification system (resistance 18 MΩ). Flash chromatography was performed on Silicagel (Baker, 230 mesh).

N,N-Dimethyl-10-undecenyl 1-amine: 30,5 g (0,13 mol) of 11-bromo-1-undecene, 50 mL (0,4 mol) of 7,9 molar aqueous dimethylamine and 5,4 g (0,135 mol) of NaOH in 150 mL of ethanol are stirred for 4 days under N_2 at 70 °C. The solvent is removed. The residue is suspended in acetone, filtered, the filtrate evaporated and distilled in vacuo ($bp_{0,5\ mbar}$ = 82–83 °C). Yield: 20,9 g (81%), colourless liquid, refractive index n_D^{25} = 1,4401.

3-[*N,N*-Dimethyl-*N*-10-undecenyl)ammonio]propane-1-sulfonate (**1**): 18,6 g (94 mmol) of *N,N*-dimethyl-10-undecenylamine and 11,5 g (94 mmol) of 1,3-propanesultone (Aldrich) in 250 mL of acetonitrile are refluxed for 5 days under N_2. On cooling, the crude product crystallizes;

it is recrystallized repeatedly from acetonitrile. Yield: 19,3 g (64%) hygroscopic colourless powder, mp = 132 °C

$C_{16}H_{33}NO_3S$ 319,51	Calc.	C 60,15	H 10,41	N 4,38	S 10,04
	Found	C 60,16	H 7,95	N 4,42	S 10,30

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) = 1,2–1,4 (m; 14H, —$(CH_2)_7$—), 1,67 (m; 2H, —CH_2—C—N^+—), 2,01 (m; 2H, C=C—CH_2—), 2,18 (m; 2H, —N^+—C—CH_2—C—SO_3), 2,86 (t; 2H, —CH_2—SO_3), 3,16 (s; 6H, —$N^+(CH_3)_2$), 3,24 (m; 2H, —CH_2—N^+), 3,64 (m; 2H, —N^+—CH_2—C—C—SO_3), 4,85–4,50 (m; 2H, CH_2=C—), 5,78 (m; 1H, C=CH—C).

N-methyl-*N'*-(10-undecenoyl)piperazine: 4 g (0,04 mol) of 1-methylpiperazine and 7,1 g (0,039 mol) of 10-undecenoic acid are refluxed in 100 mL of toluene for 3 days. The reaction mixture is then washed 3 times with aqueous 2 molar NaOH and 3 times with water. Toluene is removed and the remaining oil is filtered over a silica gel column (eluent: $CHCl_3/CH_3OH$, volume ratio 10:1). Yield: 7,7 g (77%), colourless oil, refractive index n_D^{20} = 1,4848.

3-[*N*-Methyl-*N'*-(10-undecenoyl)piperazino]-1-propanesulfonate (**2**): 7,2 g (0,027 mol) of *N*-methyl-*N'*-(10-undecenoyl)piperazine and 3,2 g (0,026 mol) of 1,3-propanesultone (Aldrich) in 80 mL of acetonitrile are refluxed under N_2 for 3 days. The crude product precipitating from the reaction mixture is recrystallized from ethanol. Yield: 8,2 g (79%) hygroscopic colourless powder; mp = 193 °C (under decomposition)

$C_{19}H_{36}N_2O_4S \times H_2O$ 388,46 + 18,01	Calc.	C 56,09	H 9,42	N 6,89	S 7,89
	Found	C 56,29	H 9,49	N 6,93	S 7,83

^{1}H NMR (400 MHz, CD_3OD): δ (in ppm) = 1,3–1,5 (m; 10H, —$(CH_2)_5$—), 1,6–1,7 (m; 2H, CH_2—C—CO), 2,06–2,08 (m; 2H, C=C—CH_2), 2,24–2,31 (m; 2H, CH_2—C—SO_3), 2,46–2,50 (t; 2H, CH_2—CO), 2,91–2,95 (t; 2H, CH_2—SO_3), 3,25 (s; 3H, N^+—CH_3), 3,52–3,56 (m; 2 + 2H, CO—$N(CH_2)_2$, cis/trans conformers), 3,59–3,70 (m; 2H, N^+—CH_2—C—C—SO_3), 3,86–4,11 (m; 2 + 2H, $(CH_2)_2N^+$, cis/trans conformers), 4,83–5,04 (m; 2H, CH_2=C—), 5,79–5,89 (m; 1H, C=CH).

Allyl 3-(*N*-decyl-*N*-methyl)amino-2-hydroxypropyl ether: 10,4 g (0,06 mol) of decylmethylamine and 6,92 g (0,06 mol) of allyl 2,3-epoxypropyl ether (Fluka) are refluxed in 50 mL of dry tetrahydrofurane (THF) for 1 day. The THF is removed and the residue purified by flash-chromatography (eluent: $CHCl_3/CH_3OH$, volume ratio 10:1). Yield: 12,5 g (72%), colourless liquid, refractive index n_D^{22} = 1,4552.

3-(*N*-Decyl-*N*-methyl-*N*-(3-allyloxy-2-hydroxypropyl)ammonio-1-propanesulfonate (**3**): 8,4 g (29,5 mmol) of allyl 3-(*N*-decyl-*N*-methyl)amino-2-hydroxypropyl ether and 3,6 g of 1,3-propanesultone in 250 mL of dry acetonitrile are refluxed for 3 days under nitrogen. The solvent is removed and the residue purified by flash-chromatography (eluent: $CHCl_3/CH_3OH$, volume ratio 10:1). Yield: 10,8 g (90%), hygroscopic colourless oil, refractive index n_D^{20} = 1,4912.

$C_{20}H_{41}NO_5S \times H_2O$ 407,61 + 18,01	Calc.	C 56,44	H 10,18	N 3,29	S 7,53
	Found	C 56,43	H 10,37	N 3,29	S 7,41

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) = 0,84 (t; 3H, CH_3—), 1,2–1,4 (m; 14H, —$(CH_2)_7$—), 1,70 (m; 2H, —CH_2—C—N^+—), 2,22 (m; 2H, —N^+—C—CH_2—C—SO_3), 2,94 (m; 2H, —CH_2—SO_3), 3,1–3,45 (m; 7H, —CH_2—$N^+(CH_3)$—, —CH_2—O—), 3,53 (m; 2H, —N^+—CH_2—C—C—SO_3), 3,69 (m; 2H, —N^+—CH_2—C(—O)—), 3,97 (d; —O—CH_2—C=C), 4,45 (m; 1H, —CH(—O)—), 5,1–5,3 (m; 2H, —C=CH_2), 5,83 (m; 1H, —CH=C).

2,2'-Azobis[2-(1-naphthyl)ethyl 2-methylpropionate]*) (**4**): 1,5 g (9 mmol) of 2,2'-azobis-(2-methylpropionitrile)**) and 2-(1-naphthyl)ethanol are dissolved in dry benzene. The solution

*) Systematic IUPAC name: 2,2'-dimethyl-2,2'-azo-2-(1-naphthyl)ethyl propionate.

**) Systematic IUPAC name: 2,2'-dimethyl-2,2'-azopropionitrile.

is cooled to 5 °C, saturated with HCl and stirred overnight. White crystals of the iminoester precipitate, which are filtered off and hydrolyzed with H_2O. The aqueous phases is extracted several times with petroleum ether. The combined extracts are concentrated to 10 mL and filtered over a short column of neutral Al_2O_3 (eluent: petroleum ether/ethylacetate (volume ratio 50:1). Yield: 770 mg (17%), colourless powder, mp = 114 °C (decomposition).

^{1}H NMR (400 MHz, $CDCl_3$): δ (in ppm) = 1,38 (s; 12H, $C(CH_3)_2$), 3,34–3,38 (t; 4H, COO—C—CH_2), 4,40–4,42 (t; 4H, COO—CH_2), 7,29–8,07 (m; 14H, naphthyl).

Copolymerization with SO_2 (typical procedure)

1,5 mmol of the monomers and about 5 mmol of SO_2 are dissolved in 25 mL of water. 1 mol-% of 2,2'-azoisobutyronitrile is added. The mixture is kept at 60 °C for 24 h. The polymers are purified by repeated precipitation in acetone and redissolution in water or, in case of copoly(**3**), in ethanol to yield colourless powder.

Methods

NMR spectra were recorded with a Bruker AC200 and a Bruker Aspect 3000. The sulfur content was analyzed according to Schöninger [15] and Fritz [16]. Thermogravimetry was performed on a Perkin-Elmer TGS-2 under nitrogen, with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC2. X-ray scattering was studied with a Siemens Kristalloflex diffractometer, using the Ni-filtered CuK_α-line (wavelength = 0,154 nm). Surface tensions were measured at 25 °C with a Lauda tensiometer. Fluorescence spectra were taken with a Spex spectrograph, excitation at 334 nm.

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