

Supporting informations

Behavior of wormlike micellar solutions formed without any additives from semi-fluorinated quaternary ammonium salts

Gennifer Padoan,^{a,b} Elisabeth Taffin de Givenchy,^a Alessandro Zaggia,^b Sonia Amigoni,^a Thierry Darmanin,^a Lino Conte^b and Frédéric Guittard,^{a,}*

^a Université de Nice – Sophia Antipolis & CNRS, Laboratoire de Physique de la Matière Condensée, UMR 7336, Parc Valrose, 06108 Nice Cedex 2, France

^b Department of Chemical Processes of Engineering, University of Padua, Via Marzolo 9, 35131, Padua, Italy

*guittard@unice.fr

I- Chemical characterizations of the synthesized products

Tertiary Amines (A_{n,m})

A_{8,1}

Yield 95 %

spectral data: MS *m/z* (rel. ab. %): 521 ([M]⁺, 5 %); 506 ([M-CH₃]⁺, 20 %), 88 ([M-CF₃(CF₂)₇, -CH₂]⁺, 10 %), 58 ([M-CF₃(CF₂)₈CHOHCH₂]⁺, 100 %);

¹H NMR (CD₃OD): δ = 2.39 (m, CH₂(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH₂(c), 2H); 2.29 (t, CH₃(d), 6H); 4.2 (d, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.9 (m, CF₂(f), 2F); -121.6 (m, CF₂(g,h), 4F).

A_{8,2}

Yield 84 %

spectral data: MS *m/z* (rel. ab. %): 549 ([M]⁺●, 3 %), 116 ([M-CF₃(CF₂)₇, -CH₂]⁺, 30 %), 86 ([M-CF₃(CF₂)₈CHOHCH₂]⁺, 100 %), 69 [CF₃]⁺ 15 %;

¹H NMR (CD₃OD): δ = 2.18(m, CH₂(a), 1H); 2.49 (m, CH₂(a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH₂(c,d), 6H); 1.04 (t, CH₃(e), 6H); 4.1 (d-d,OH(f), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F);-122.8 (m, CF₂(e), 2F);-121.9 (m, CF₂(f), 2F); -121.6 (m, CF₂(g,h), 4F).

A_{6,1}

Yield 94 %

spectral data: MS *m/z* (rel. ab. %): 421 ([M]⁺●, 5 %); 406 ([M-CH₃]⁺, 20 %), 88 ([M-CF₃(CF₂)₇, -CH₂]⁺, 100 %), 58 ([M-CF₃(CF₂)₈CHOHCH₂]⁺, 100 %);

¹H NMR (CD₃OD): δ = 2.39 (m, CH₂(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH₂(c), 2H); 2.29 (t, CH₃(d), 6H); 4.2 (d, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F);-122.8 (m, CF₂(e), 2F);-121.8 (m, CF₂(f), 2F).

A_{6,2}

Yield 89 %

spectral data: MS *m/z* (rel. ab. %): 449 ([M]⁺●, 5 %); 116 ([M-CF₃(CF₂)₇, -CH₂]⁺, 30 %), 86 ([M-CF₃(CF₂)₈CHOHCH₂]⁺, 100 %);

¹H NMR (CD₃OD): δ = 2.18 (m, CH₂ (a), 1H); 2.49 (m, CH₂ (a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH₂(c,d), 6H); 1.04 (t, CH₃(e), 6H); 4.1 (d-d, OH(f), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂ (b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂ (d), 2F);-122.8 (m, CF₂ (e), 2F);-121.8 (m, CF₂ (f), 2F).

A_{4,1}

Yield 93 %

spectral data: MS *m/z* (rel. ab. %): 321 ([M]⁺●, 5 %); 306 ([M-CH₃]⁺, 20 %), 88 ([M-CF₃(CF₂)₇, -CH₂]⁺, 100 %), 58 ([M-CF₃(CF₂)₈CHOHCH₂]⁺, 100 %);

¹H NMR (CD₃OD): δ = 2.39 (m, CH₂(a), 2H); 2.6 (m, CH(b), 1H); 2.49 (d, CH₂(c), 2H); 2.29 (t, CH₃(d), 6H); 4.2 (d, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F);-122.8 (m, CF₂(e), 2F);-121.8 (m, CF₂(f), 2F).

A_{4,2}

Yield 80 %

spectral data: MS *m/z* (rel. ab. %): 349 ([M]⁺•, 10 %), 116 ([M-CF₃(CF₂)₇, -CH₂]⁺, 30 %), 86 ([M-CF₃(CF₂)₈CH₂OHCH₂]⁺, 100 %);

¹H NMR (CD₃OD): δ = 2.18 (m, CH₂(a), 1H); 2.49 (m, CH₂(a), 1H); 4.2 (d-d, CH(b), 1H); 2.49 (m, CH₂(c,d), 6H); 1.04 (t, CH₃(e), 6H); 4.1 (d-d, OH(f), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F).

Quaternary ammonium salts (F_nH_m)

F₈H₁

Yield 91 % from A_{8,1}

¹H NMR (CD₃OD): δ = 2.24 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.51 (t, CH₂(c), 2H); 3.26 (m, CH₃(d), 9H); 4.7 (m, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F).

F₈H₂

Yield 88 % from A_{8,2}

¹H NMR (CD₃OD): δ = 2.46 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.52 (m, CH₂(c,d), 6H); 3.14 (s, CH₃(e), 3H); 4.7 (m, CH(f), 1H); 1.37 (t, CH₃(g), 6H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.9 (m, CF₂(f), 2F); -121.6 (m, CF₂(g,h), 4F).

F₆H₁

Yield 94 % from A_{6,1}

¹H NMR (CD₃OD): δ = 2.24 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.51 (t, CH₂(c), 2H); 3.26 (m, CH₃(d), 9H); 4.7 (m, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.8 (m, CF₂(f), 2F).

F₆H₂

Yield 89 % from A_{6,2}

¹H NMR (CD₃OD): δ = 2.46 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.52 (m, CH₂(c,d), 6H); 3.14 (s, CH₃(e), 3H); 4.7 (m, CH(f), 1H); 1.37 (t, CH₃(g), 6H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F); -122.8 (m, CF₂(e), 2F); -121.8 (m, CF₂(f), 2F).

F₄H₁

Yield 93 % from A_{4,1}

¹H NMR (CD₃OD): δ = 2.24 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.51 (t, CH₂(c), 2H); 3.26 (m, CH₃(d), 9H); 4.7 (m, OH(e), 1H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F).

F₄H₂

Yield 73 % from A_{4,2}

¹H NMR (CD₃OD): δ = 2.46 (m, CH₂(a), 2H); 4.6 (m, CH(b), 1H); 3.52 (m, CH₂(c,d), 6H); 3.14 (s, CH₃(e), 3H); 4.7 (m, CH(f), 1H); 1.37 (t, CH₃(g), 6H).

¹⁹F NMR (CD₃OD): δ = -80.9 (t, CF₃(a), 3F); -111.7 (m, CF₂CH₂(b), 2F); -126.2 (m, CF₂(c), 2F); -123.3 (m, CF₂(d), 2F).

II- Surfactant properties

The surface tensions of the aqueous solutions of the fluorinated surfactants were measured using a Kruss K100 tensiometer by the Wilhelmy plate technique [N.R. Pallas, B.A. Pethica, Colloids Surf. 36 (1989) 369]. All of the measurements were performed at 25 °C

Table 1 : surface tension at the critical micellar concentration γ_{cmc} and cmc measured for the synthesized surfactants

<i>surfactants</i>	γ_{cmc} [mN/m]	cmc [mmol/L]
F ₈ H ₁	15.7	0.840
F ₆ H ₁	16.6	1.280
F ₄ H ₁	19	1.470
F ₈ H ₂	17.5	0.756
F ₆ H ₂	20.2	1.200
F ₄ H ₂	22.9	1.360

III- DLS measurments

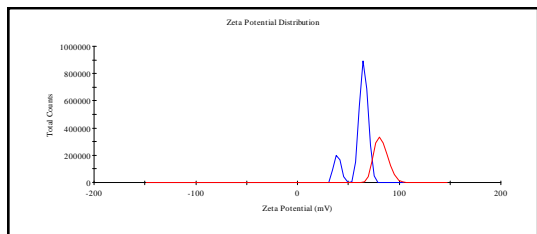


Figure 1. Zeta potential for F_8H_1 . Red at $C_1=20\text{xcmc}$, blue F_8H_1 at $C_2=30\text{xcmc}$

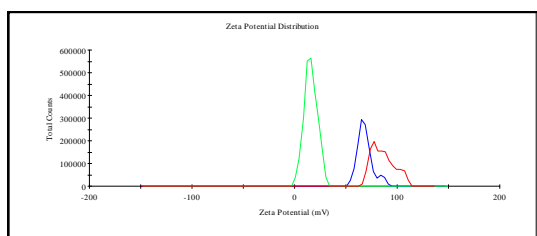


Figure 2. Zeta potential for F_8H_2 . Red at $C_1=20\text{xcmc}$, blue F_8H_2 at $C_2=30\text{xcmc}$, green F_8H_2 at $C_3=40\text{xcmc}$.

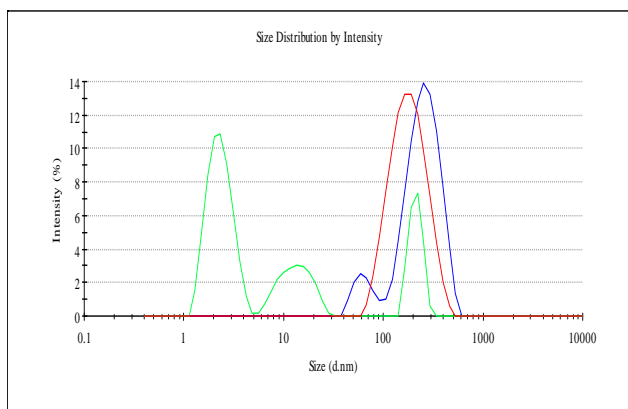


Figure 3. Variation in diameter as a function of fluorinated chain. Blue line for F_8H_1 , green line for F_6H_1 , red line for F_4H_1 .

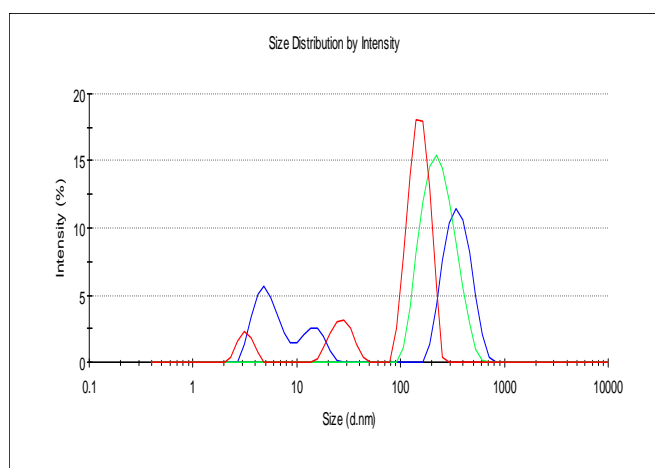


Figure 4. Variation in diameter as function of the fluorinated chain. Blue line for F_8H_2 , Red line for F_6H_2 , green line for F_4H_2 .

IV-Rheological curves

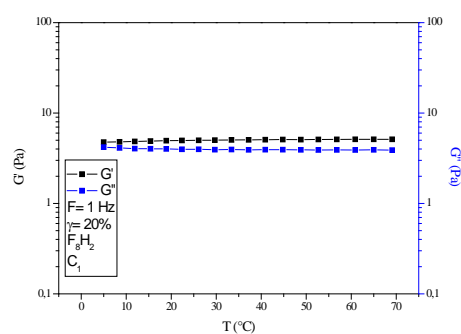


Figure 5. Storage and loss modulus at $C_1=20\text{xcmc}$ as function of temperature for F_8H_2

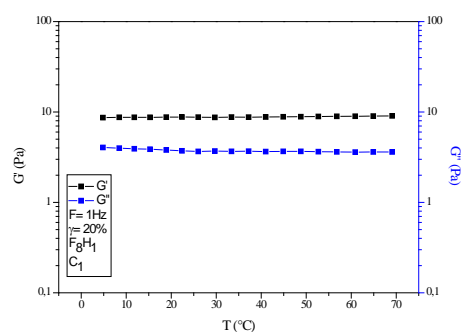


Figure 6. Storage and loss modulus at $C_1=20\text{xcmc}$ as function of temperature for F_8H_1 .

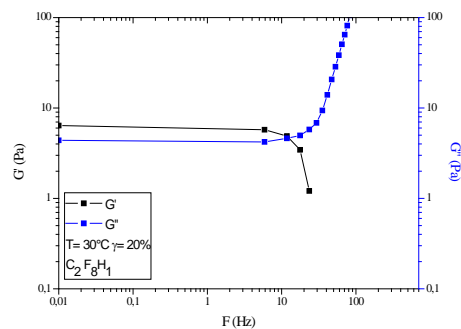


Figure 7. G' and G'' as function of frequency for F_8H_2 at $C_2=30xcmc$

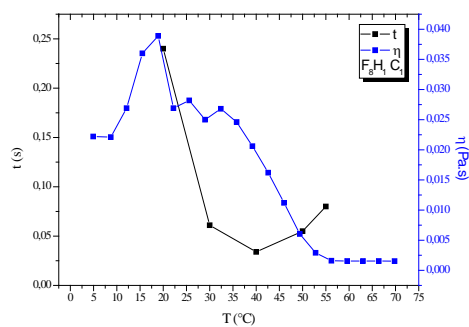


Figure 8. Correlation between viscosity and relaxation time for F_8H_1 at $C_2=30xcmc$

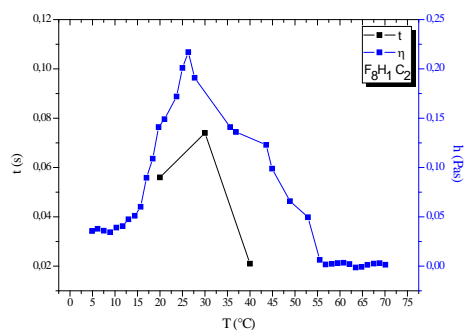


Figure 8. Correlation between viscosity and relaxation time for F_8H_1 at $C_1=20xcmc$

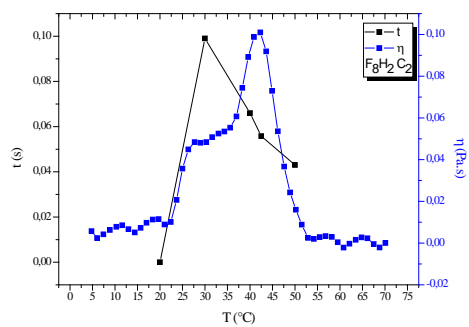


Figure 9. Correlation between viscosity and relaxation time for F_8H_2 at $C_2=30xcmc$