Dendritic Core-Shell Macromolecules Soluble in Supercritical Carbon Dioxide

Victor Martinez,[†] Stefan Mecking*,[†] Thierry Tassaing,[‡] Marcel Besnard,[‡] Sandy Moisan,[§]
François Cansell,[§] Cyril Aymonier*,[§]

[†] Department of Chemistry, Konstanz University, Universitätsstr. 10, 78457 Konstanz, Germany,

[‡] LPCM, CNRS-UMR 5803, Université Bordeaux 1, 351 cours de la Libération, 33405 Talence Cedex, France,

[§] ICMCB, CNRS-UPR 9048, Université Bordeaux 1, 87 avenue Albert Schweitzer, 33608 Pessac Cedex, France

Supporting Information

Materials:

All the experiments were performed under inert conditions. THF and toluene were dried over Na and used fresh distilled. Hyperbranched polyethyleneimine (PEI) with a DB around 60%¹ and a molecular weight around 5 kD were supplied as a water solution². Prior to use water was evaporated under vacuum at 80°C for several hours. 2H,2H,3H,3H-perfluoroundecaonic acid was purchased from Fluorolabs and Poly(hexafluoropropylene oxide) monocarboxylic acid, chloro terminated from Aldrich. The monocarbonyl acid terminated polydimethylsiloxane and the 3,6,9,12-tetraoxotridecanoic acid were synthesized as described in the literature.^{3,4} Other reagents were commercially available and used without any further purification.

Typical procedure for the synthesis of unimolecular micelles with a hydrophobic shell:

PEI-NHCOCH₂CH₂C₈F₁₇, 1. The 2H,2H,3H,3H-perfluoroundecaonic acid (1.06g, 2.16mmol) dissolved in THF (10mL) is added slowly to a solution of carbonyldiimidazol (338mg, 2.09mmol) in THF (10mL). The reaction is stirred for 1h at room temperature. An argon stream is used to displace remaining CO₂. Then the mixture is transferred to a schlenk containing the hyperbranched polymer PEI (293mg, 2.09mmol terminal amino groups). The reaction is heated at 40°C over night. The solvent is reduced to 10mL and 50mL water are added. The white precipitate is isolated and washed with water several times. After drying under high vacuum, the product is obtained as a white powder (480mg, 83% yield). ¹H NMR (C₆F₆) δppm: 2.4-3.6 (m, NCH₂CH₂N and R_fCH₂CH₂CO). ¹³C NMR (C₆F₆) δppm: 27.2 (R_fCH₂CH₂CO), 29.0 (R_fCH₂CH₂CO), 39 (NCH₂CH₂NHCO), 50-55 (NCH₂CH₂N), from 107 to 125 (CF₂), 173.5 (CH₂CONHCH₂). IR: N-H stretch 3306 cm⁻¹, C=O 1653 cm⁻¹, N-H bend 1559 cm⁻¹ and secondary amines 1451 cm⁻¹, C-F 1205 and 1149 cm⁻¹.

PEI-NHCOCF₂[OCF₂CF(CF₃)]_nCF₂Cl, 2. ¹H NMR (C₂D₂Cl₄) δppm: 2.4-3.6 (m, NCH₂CH₂N). IR: N-H stretch 3294 cm⁻¹, C=O 1689 cm⁻¹, N-H bend 1549 and secondary amines 1454 cm⁻¹, C-F 1259-1133 cm⁻¹.

PEI-NHCOCH₂CH₂SiH₃, 4. ¹H NMR (CDCl₃) δppm: 0.83 (t, 3H, CH₃), 1.22 (m, 24H, CH₂), 1.57 (m, 2H, COCH₂CH₂), 2.11 (m, 2H, COCH₂CH₂), 2.4-2.8 (m, NCH₂CH₂N), 3.22 (m, CONHCH₂CH₂N), 3.6 (m, NH). ¹³C NMR (CDCl₃) δppm: 14.3 (CH₃), 22.9, 29.6, 29.9 and 32.1 (CH₂), 26.2 (COCH₂CH₂), 36.7 (COCH₂CH₂), 33 and 38 (CONHCH₂CH₂N), 47.4, 49.0, 52.8 and 53.7 (NCH₂CH₂N), 174.0 (CH₂CONHCH₂). IR: C=O 1645 cm⁻¹.

DAB-NHCOCH₂CH₂C₈F₁₇, 6. ¹H NMR (C₆F₆) δppm: 2.4-3.6 (m, NCH₂CH₂N and R_fCH₂CH₂CO). ¹³C NMR (C₆F₆) δppm: 27.2 (R_fCH₂CH₂CO), 29.0 (R_fCH₂CH₂CO), 39 (NCH₂CH₂NHCO), 50-55 (NCH₂CH₂N), 107-125 (CF₂), 171.7 (CH₂CONHCH₂). IR: N-H stretch 3303 cm⁻¹, C=O 1650 cm⁻¹, N-H bend 1563 cm⁻¹, C-F 1204, 1149 and 1112 cm⁻¹.

PEI-NHCO-*p*-(C₆H₄)-OCH₂CH₂CH₂Si(Me)₂[(-OSi(Me)₂)_nCH₂CH₂SiMe₃], 3. Allyl bromide (8.5mL, 96.3mmol) were added to solution of *p*-hydroxybenzylbenzoate (20g, 87.6mmol) and potassium carbonate (12g, 87.6mmol) in acetone 100mL. Reaction was refluxed for 7h. Volatiles were removed under vacuum. The residual solid was dissolved into 50mL CH₂Cl₂. The organic layer was washed with basic and neutral water, dried over Na₂SO₄ and filtered. After solvent evaporation, an oil was obtained. Purification was achieved through a silica-gel column using CH₂Cl₂-hexane 1:1 as eluent. Product was obtained as a white solid. ¹H NMR (CDCl₃) δppm: 4.60 (d, 2H, OCH₂-allyl), 5.34 (s, 2H, COOCH₂Ph), 5.40 (m, 1H, CH₂=CHCH₂O), 6.02 (m, 2H, CH₂=CHCH₂O), 6.94 (d, 2H, ArH), 7.39 (m, 5H, COO-Ph) and 8.04 (d, 2H, ArH). ¹³C NMR (CDCl₃) δppm: 68.1 (COOCH₂Ph), 70.6 (OCH₂Allyl), 116.0 (CH₂=CHCH₂O), 134.3 (CH₂=CHCH₂O), 164.1, 119.9, 129.8 and 124.4 (OArCOO), 138.0, 129.8 and 133.5 (COOCH₂Ph), 167.9 (C=O). IR: C=O 1710cm⁻¹. This polydimethylsiloxane hydride-terminated (12.5g, 40eq), *p*-allyloxybenzylbenzoate (4.2g, 16mmol) vinyltrimethylsilane (3.7mL, 24mmol) and toluene 5mL were introduced into a rota-flo flask. After purging with argon, cyclovinyldimethylsiloxan-platinum complex (18μL catalyst PC085) was added and the reaction mixture was heated at 40°C for 4 days (Si-H 2125 cm⁻¹ IR band was disappeared). Volatiles were removed under vacuum. The monoester product was isolated by a silica gel column chromatography with CH₂Cl₂-pentane 1:20 as eluent. Isolated product 5.3g, yield 33%. ¹H NMR (CDCl₃) δppm: -0.02 (s, 9H, CH₂Si(CH₃)₃), 0.00 (s, 6H, CH₂Si(CH₃)₂O), 0.08 (m, 54H, OSi(CH₂)₂O), 0.41 (d, 4H, SiCH₂CH₂Si), 0.66 (m, 2H, SiCH₂CH₂CH₂), 1.84 (m, 2H, SiCH₂CH₂CH₂), 3.97 (t, 2H, CH₂CH₂CH₂O), 5.34 (s, 2H, COOCH₂Ph), 6.94 (d, 2H, ArH), 7.39 (m, 5H, COO-Ph) and 8.04 (d, 2H, ArH). ¹³C NMR (CDCl₃) δppm: -2.2 (Si(CH₃)₃), -0.5 (SiCH₂CH₂Si(CH₃)₂), 0.1 (OCH₂CH₂CH₂Si(CH₃)₂), 1.1 (OSi(CH₃)₂), 8.0 (Me₃SiCH₂CH₂Si), 10.2 (Me₃SiCH₂CH₂Si), 14.2 (OCH₂CH₂CH₂Si), 23.1 (OCH₂CH₂CH₂Si), 70.7 (OCH₂CH₂CH₂Si), 68.1 (COOCH₂Ph), 164.1, 119.9, 129.8 and 124.4 (OArCOO), 138.0, 129.8 and 133.5 (COOCH₂Ph), 167.9 (C=O). IR: C=O 1710cm⁻¹, Si-O 1165, 1025 and 789cm⁻¹. In a round bottom flask this monoester and Pd/C (10%, 500mg) were purged with argon. Then degassed EtOH 16mL, THF 86mL and cyclohexene (0.4mL, 3.7mmol) were added. The reaction was stirred at reflux during 4 days. After filtration over celite, solvent was removed yielding a colourless oil. The white precipitate formed by addition of water was isolated and washed several times with water. Purification through a silica-gel column with THF yields the deprotected acid. Isolated product 3.9g yield 74%. ¹H NMR (CDCl₃) δppm: -0.02 (s, 9H, CH₂Si(CH₃)₃), 0.00 (s, 6H, CH₂Si(CH₃)₂O), 0.08 (m, 54H, OSi(CH₂)₂O), 0.41 (d, 4H, SiCH₂CH₂Si), 0.66 (m, 2H, SiCH₂CH₂CH₂), 1.84 (m, 2H, SiCH₂CH₂CH₂), 3.97 (t, 2H, CH₂CH₂CH₂O), 6.94 (d, 2H, ArH), and 8.04 (d, 2H, ArH). ¹³C NMR (CDCl₃) δppm: -2.2 (Si(CH₃)₃), -0.5 (SiCH₂CH₂Si(CH₃)₂), 0.1 (OCH₂CH₂CH₂Si(CH₃)₂), 1.1 (OSi(CH₃)₂), 8.0 (Me₃SiCH₂CH₂Si), 10.2 (Me₃SiCH₂CH₂Si), 14.2 (OCH₂CH₂CH₂Si), 23.1 (OCH₂CH₂CH₂Si), 70.7 (OCH₂CH₂CH₂Si), 163.7, 114.2, 132.3 and 121.3 (OArCOO), 171.3 (C=O). IR: C=O 1696cm⁻¹, Si-O 1165, 1025 and 789cm⁻¹. carbonyldiimidazol (338mg, 2.09mmol) was added slowly to a solution of the above obtained PDMS monocarbonyl acid-terminated (1851mg, 2.16mmol) in 20mL THF. The reaction evolution was observed through CO₂ formation. After stirring at room temperature during 2h, the solution was degassed by an argon stream. PEI (293mg, 2.09mmol primary amines) was dissolved into 20mL THF at 40°C and added to the reaction mixture. Reaction was allowed to stir at 50°C over night. 50mL water were added to induce a complete product precipitation. Upon cooling to room temperature, solvent was removed. The white precipitate was dissolved in toluene and washed with water. Then solvent was evaporated to give a white solid. After cleaning with a methanol solution saturated in K₂CO₃ and pure methanol, the solid was dried under vacuum. Isolated product 1897mg, yield 90%. ¹H NMR (CDCl₃) δppm: -0.02 (s, 9H, CH₂Si(CH₃)₃), 0.00 (s, 6H, CH₂Si(CH₃)₂O), 0.08 (m, 54H, OSi(CH₂)₂O), 0.41 (d, 4H, SiCH₂CH₂Si), 0.66 (m, 2H, SiCH₂CH₂CH₂), 1.84 (m, 2H, SiCH₂CH₂CH₂), 2.4-2.8 (m, NCH₂CH₂N), 3.22 (m, CONCH₂CH₂N), 3.97 (t, 2H, CH₂CH₂CH₂O), 6.94 (d, 2H, ArH), and 8.04 (d, 2H, ArH). ¹³C NMR (CDCl₃) δppm: -2.2 (Si(CH₃)₃), -0.5 (SiCH₂CH₂Si(CH₃)₂), 0.1 (CH₂CH₂CH₂Si(CH₃)₂), 1.1 (OSi(CH₃)₂), 8.0 (Me₃SiCH₂CH₂Si), 10.2 (Me₃SiCH₂CH₂Si), 14.2 (OCH₂CH₂CH₂Si), 23.1 (OCH₂CH₂CH₂Si), 39 (CONHCH₂CH₂N), 47, 49, 52 and 54 (NCH₂CH₂N), 70.5 (OCH₂CH₂CH₂Si), 161.5, 114.0, 128.9 and 126.5 (OArCOO), 161.5 (ArCONHCH₂). IR: C=O 1696cm⁻¹, Si-O 1165, 1025 and 789cm⁻¹. Anal. Calcd. for C₁₃₁₀H₃₀₁₆N₁₁₆O₃₄₈Si₃₁₃: C, 45.27; H, 8.57; N, 4.67. Found: C, 46.29; H, 8.83; N, 5.62.

PEI-NHCOPEGMe, 5. Tetraethylenglycol monomethylether (2.08g, 0.01mol), potassium hydroxide (1.12g, 0.02mol) and potassium permanganate (3.16g, 0.02mol) in 100mL water are stirred at room temperature during 12h. The brown precipitate is filtered off and washed several times with water. After reduction of the aqueous volume to 50mL, the product is extracted with dichloromethane. The organic solution is dried over Na₂SO₄ and filtered. The solvent is evaporated yielding the 3,6,9,12-tetraoxatridecanoic acid as an oil (1.4g, 63% yield). This oil (1.22g, 5.5mmol) dissolved in THF (25mL) is added slowly to a solution of carbonyldiimidazol (842mg, 5.2mmol) in THF (25mL). The reaction is stirred for 1h at room temperature. An argon stream is used to displace remaining CO₂. Then the mixture is transferred to a schlenk containing the hyperbranched polymer PEI (745mg, 5.2mmol terminal amino groups). The reaction is heated at 40°C over night. The solvent is evaporated and the product is purified by dialysis in water (1.4g, 80% yield). ¹H NMR (CDCl₃) δppm: 2.4-2.8 (m, NCH₂CH₂N), 3.33 (s, 3H, OCH₃), 3.6 (m, 12H, OCH₂CH₂O), 3.94 (m, 2H, COCH₂O). ¹³C NMR (CDCl₃) δppm: 59.2 (CH₃), 70-72 (OCH₂CH₂O), 70 (COCH₂O), 38 (CONHCH₂CH₂N), 47, 49, 52 and 54 (NCH₂CH₂N), 170.3 (OCH₂CONHCH₂).

Solubility measurements:

The infrared absorption experiments were performed using a homemade titanium optical cell⁵ withstanding high pressures up to 35 MPa and temperatures up to 250°C. A schematic view of the optical cell is shown in Figure S1. Optical access is given by the way of four cylindrical windows, two silicon windows for the infrared absorption measurements with a path length of 2.5 cm (which can be varied from 0.3 to 2.5 cm) and the two others sapphire windows for direct observation of the solution to insure that there is no demixing in the sample. The cell volume is 5.5 cm³ and the homogeneity is ensured with a magnetic stirrer disposed at the bottom of the cell. The sealing is obtained using the unsupported area principle. All windows are positioned on the flat surface of the Inconel plug with a 100 μm kapton foil placed between the window and the plug in order to compensate for imperfections at the two surfaces. Flat teflon seals are used to insure sealing between the plug and the cell body. The heating is performed with four cartridge heaters disposed in the body of the cell in which two thermocouples are placed. The first one is located close to one cartridge in order to achieve a good temperature regulation and the second one is kept close to the sample area, to measure the temperature with an accuracy of about ΔT ~ ±0.5°C. The cell is connected via a stainless steel capillary to a hydraulic pressurising system which allows to adjust the pressure up to 50 MPa with an absolute uncertainty of ±0.1 MPa with a relative error of ±0.3% (Figure S2).

Figure S1: a) Scheme of the high pressure high temperature cell; b) Experimental set-up

The infrared absorption measurements are performed with a Biorad interferometer (type FTS-60A). Single beam spectra recorded in the spectral range 400-6000 cm^{-1} with 2 cm^{-1} resolution are obtained by Fourier transformation of 50 accumulated interferograms. The spectra have been collected at two different constant temperatures, 40°C and 100°C, as a function of pressure, from 6 to 35 MPa. A typical infrared spectrum, as they appear after the removal of the CO_2 contribution, is displayed in Figure S2. Then, after identification of specific vibrational modes associated with functional groups of the solute, the integrated intensity of these characteristic infrared bands allows to determine the concentration of the solute in solution according to Beer-Lambert law, $A = \epsilon \cdot l \cdot c$ with A, sample absorbance without dimension; ϵ , molar extinction coefficient ($\text{L mol}^{-1} \text{cm}^{-1}$); l, optical path length (cm) and c, sample concentration (mol L^{-1}). In this study, a spectral domain is integrated to determine A which implies that ϵ is homogeneous to $\text{L mol}^{-1} \text{cm}^{-2}$. Therefore, the method of solubility determination that we adopted is the following: i) identification of a characteristic vibrational band; ii) determination of the molar extinction coefficient for the considered bands, by checking that a small quantity of the product is completely solubilized at 40°C and 35 MPa ($\rho = 0.9 \text{ g cm}^{-3}$) (see Table S1); iii) determination of the solubility with an important initial mass of product by integrating the selected bands.

Figure S2: Spectrum of PEI-NHCOCH₂CH₂C₈F₁₇, **1** (T=40°C, P=25 MPa).

Table S1. Molar Extinction Coefficients ($10^{-2} \text{ L mol}^{-1} \text{cm}^{-2}$) and corresponding region (cm^{-1})

Entry	Formula	Vibrational band	Molar Extinction Coefficients (region)
1	PEI -CO-C ₁₀ H ₄ F ₁₇	C-F C=O	1931 (1123-1163) 3891 (1634-1708)
2	PEI -CO- C ₁₀ ClF ₂₀ O ₃	C-F C=O	385 (943-1016) 800 (1655-1749)
3	PEI -CO-C ₃₁ H ₇₄ O ₈ Si ₉	Si-O-Si C-H	29490 (970-1152) 1547 (2943-2983)
4	PEI -CO-C ₁₀ H ₂₁	insoluble	
5	PEI -CO-C ₈ H ₁₇ O ₄	insoluble	
6	DAB-CO-C ₁₀ H ₄ F ₁₇	C-F C=O	1512 (1123-1163) 2731 (1634-1707)

(1) DB = 2D/(2D+L), D = dendritic units (tertiary amines), L = linear units (secondary amines).

(2) LUPASOL®PRODUCT RANGE, Preliminary Technical Information, BASF.

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