Electronic Supporting Information

Thermoreversible formation and negative thermal expansion of supramacromolecular assemblies of unimolecular micelles in solution.

Agustín S. Picco, Basit Yameen, Omar Azzaroni and Marcelo Ceolín

Experimental Section

Materials and methods

Hyperbranched polyethylenimine (Mn ~ 10,000 by GPC, PDI ~ 2.5, degree of branching ~ 60%), palmitic acid (99%) and 1,1´-carbonyldiimidazole (97%) were obtained from Sigma-Aldrich,Schnelldrof, Germany. 1H-NMR was performed on a Bruker Spectrospin 250 MHz NMR spectrometer (Fallanden, Switzerland).

Amidation of hyperbranched polyethylenimine (HPEI)

The amidation of hyperbranched polyethylenimine (HPEI) was carried out in accordance with the experimental protocol described by Stiriba and-corkers[1]. Briefly, 79.77 g (0.493 mole) of 1,1´-carbonyldiimidazole was slowly added to the solution of 126.2 g (0.492 mole) of palmitic acid in 705 mL of chloroform. The solution was stirred at room temperature for 1 h. Then, a solution of 40g of hyperbranched PEI in 200 mL of chloroform was added to it. The reaction mixture was stirred at room temperature for 4 h followed by overnight reaction at 50 °C. After cooling down to room temperature the reaction mixture was washed three times with aq. NaCl solution. The organic phase was dried over anhydrous sodium sulfate. After filtration and removal of volatiles, the residue was kept overnight at 40 °C under vacuum. ^{1}H-NMR (CDCl3): δ = 3.64-1.92 (br, -CH2-*CH2*-NHCO-,-CH2-C*H2*NCO-, -N-*CH2*-*CH2*-N-, -HN-CO-*CH2*-CH2 (CH2)12-CH3), 1.50 (br, -HN-CO-CH2-*CH2*-(CH2)12-CH3),1.18 (br, -HN-CO-CH_2-CH_2-(CH_2)$_{12}$-CH_3), 0.81 (t, -HN-CO-CH_2-CH_2-(CH_2)$_{12}$-CH_3).

Small-Angle X-ray Scattering (SAXS) Characterization

SAXS experiments were performed either using the D02B-SAXS1 beamline of the Laboratorio Nacional de Luz Sincrotron (Campinas, Brazil), or using a SAXSess-MC2 compact Kratky Camera (Anton-Paar, GmbH, Austria). For the synchrotron experiments, the sample-to-detector distance was kept to 415 mm and the x-ray wavelength was set to 0.1488 nm. Sample temperature was kept to 22 °C using a circulating water bath. Two parallel micas were used as windows defining a 1mm optical path sample chamber. For the laboratory experiments the wavelength was 0.15417 nm (Cu K-α) and the sample was placed in a 1 mm diameter quartz capillary. Temperature was controlled using a Peltier thermal element. For all the experiments the concentration of HPEI-C16 was 10 g/L and the solvent was toluene. Each spectrum was corrected for beam attenuation and time integrated photon flux following normal procedures, and the corresponding solvent scattering was subtracted from each spectrum before analysis.

The instrumental resolution was determined to be 0.05 nm^{-1} from the average linewidth obtained from the diffraction pattern of a polycrystalline sample of silver behenate. The sample linewidth from the amphiphilic hyperbranched samples was determined from $\Gamma^2_{exp} = \Gamma^2_{HBP} + \Gamma^2_{inst}$, where the term Γ corresponds to the crystallographic linewidth and subscripts *exp*, *HBP* and *inst* refer to experimental, “true” and instrumental contributions to the linewidth, respectively.

Excess electron density profile for HPEI-C16

To fit the excess electron density it was assumed that the aliphatic chains could be anchored not only at the external surface of the polyethyleneimine core but also at any reactive nitrogen inside the core. Clearly, the number of anchoring points inside the core increases with the distance from the micelle centre following a quadratic law. Then, the excess electron density Δρ for HPEI-C16 can be written as:

$$\Delta\varrho(r) = \Delta\varrho_c + (\Delta\varrho_s - \Delta\varrho_c)(\frac{r}{R_c})^2$$

Where, $\Delta\rho_c$, $\Delta\rho_s$ and R_c are the excess electron density of the core, the shell and the radius of the core, respectively.

The values obtained for the fitted parameters were

Parameter	Units	Mean value	Fitting error
$\Delta\rho_c$	a.u.	0.127	0.003
$\Delta\rho_s$	a.u.	0.016	0.004
R_c	nm	1.34	0.03

References

1 Liu, H.; Chen, Y.; Zhu, D.; Shen, Z.; Stiriba, S.-E., *React. Funct. Polym.* **2007**, *67*, 383-396.