Supporting Information for:

“Host-Guest” Interaction between Cyclohexasilane and Amphiphilic Macromolecules

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General Considerations

All experiments with cyclohexasilane were carried out in a dry nitrogen atmosphere using a glovebox. Deuterated benzene, diethyl sebacate, and poly(ethylene glycol) dimethyl ether with a molecular weight of 500 g/mol (all from Aldrich) were sparged with nitrogen, dried over 4Å molecular sieves, and stored under nitrogen. Sebacic acid, poly(ethylene glycol) with a molecular weight of 600 g/mol, and $LiAlH_4$ (1.0M in diethyl ether) were purchased from Aldrich and used as received. Diethyl ether and hexane were passed through alumina columns and then soaked in 4Å molecular sieves for several days before usage. ^{1}H NMR spectra were recorded using Joel ECA 400 MHz NMR spectroscopy at 400 MHz and at 22.5°C. The spectra were indirectly referenced to TMS using residual solvent signals as internal standards. FTIR spectra were collected using a Thermo Scientific Nicolet 8700 spectrometer with a resolution of 4 cm^{-1}. The average molecular weights and polydispersity index (PDI) were determined by GPC using a Waters 515 HPLC pump with an Ultrahydrogel™ 500 7.8 × 300 mm Column (Waters) and a Waters 2410 refractive index detector. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL/min; 200 µL of a 5 mg/mL THF solution were injected for each sample. All samples were filtered before running through a 0.45 µm THFE filter (Nalgene). A molecular weight calibration curve was generated with polystyrene standards of low polydispersity (Polymer Laboratories, USA).

Synthesis of the Amphiphilic Invertible Polyester

The polyester was synthesized according to technique described in our previous work.[1] Briefly, a three-necked flask fitted with a nitrogen inlet, a thermometer, and a Dean-Stark trap with a reflux condenser was charged with 60.0 g (0.1 mol) of poly(ethylene glycol)-600, 20.2 g (0.1 mol) of sebacic acid, and 250 mL of toluene. The Dean-Stark trap was filled with toluene. The reactive mixture was agitated and heated to dissolve sebacic acid completely. Then 0.1 mL of 75% sulfuric acid was added to catalyze the polycondensation reaction. The mixture was refluxed under nitrogen for about 20 h. To neutralize H_2SO_4, 0.175 mL of a NaOH solution (40%) was added, and the mixture was stirred at room temperature for 12 h. Sodium sulfate that formed was separated by centrifugation. Toluene was removed under reduced pressure. Polymer was dried under vacuum at 60 °C for at least 24 h. The structure of the synthesized polyesters was confirmed by means of FTIR spectroscopy. The following absorption bands were found in its spectrum: a very intensive band at 1095 cm^{-1}, which belongs to valence oscillations of C-O bonds in the PEG fragments; an intense absorption band at 1730 cm^{-1}, indicating the presence of ester carbonyl groups (C=O); and absorption bands at 2860 cm^{-1} and 1460 cm^{-1} correspond to the valence and deformation oscillations of $-(CH_2)_n-$ groups, respectively. In a ^{1}H NMR spectrum ($CDCl_3$), peaks appeared at 3.64 ppm (m, ≈50H, PEG fragments) and 1.30 ppm (m, 8H, $(CH_2)_4$), which were in agreement with those of PEG and sebacic acid. At 4.22 ppm, a triplet peak that can be attributed to the methylene protons of the acylated PEG end unit was observed (t, 4H, $COOC\mathit{H}_2CH_2O$). The spectrum shows a triplet peak at 2.32 ppm and a pentet peak at 1.61 ppm corresponding to the methylene groups in an α- and β-position in relation to the carbonyl groups in sebacic acid moieties (4H, $CH_2C\mathit{H}_2COO$ and 4H, $C\mathit{H}_2CH_2COO$, corresponding). The weight average molecular weight of the polyester was 7000 g/mol, PDI 1.24.

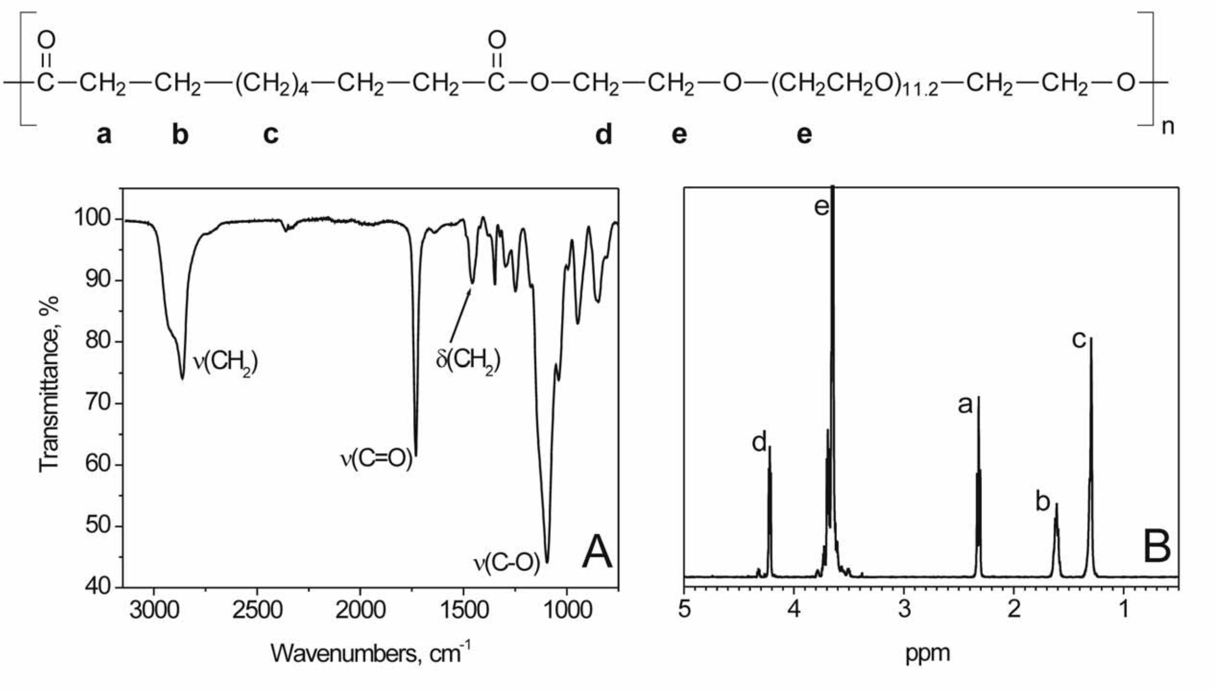

Figure 1S. FTIR (A) and ^{1}H NMR (B) spectra of the polyester. The letters on ^{1}H NMR spectra correspond to letters on the polyester structural scheme.

The polycondensation of dicarboxylic acids with diols is known to be an equilibrium process; therefore, the water evolved during the reaction must be continuously removed from the reactive mixture to shift the equilibrium toward the desired polyester formation. Hence, the acylation of PEG-600 by sebacic acid has been carried out in toluene as an azeotrope former; a Dean-Stark trap has been used to remove water. The reaction has been performed in the presence of catalytic amounts of sulfuric acid (1.25 mol %). The progress of the reaction has been monitored by the amount of water released during polycondensation. The chemical structure of the synthesized polyester was confirmed by FTIR and ^{1}H NMR spectroscopy (**Fig. 1S**).

Synthesis of cyclohexasilane

A colorless slurry of $[PEDETA(SiH_2Cl)]_2[Si_6Cl_{14}]$ (55.4g, 43.18mmol) in diethyl ether (200 mL) was reduced by dropwise addition of $LiAlH_4$ (175mL, 1.0M in diethyl ether) over the course of 1.5 h.[2,3] The reaction mixture was stirred an additional 4 h and then filtered through a glass frit. Solvent was removed from the filtrate *in vacuo* giving white waxy solid due to freezing of Si_6H_{12}. This residue was extracted twice with dry hexane (20 mL and 10 mL) leaving a very viscous liquid comprising PEDETA coordinated LiCl, $AlCl_3$ and trace unreacted $LiAlH_4$. The two hexane solutions were combined and the solvent removed *in vacuo*. This crude Si_6H_{12} was purified via vacuum distillation (35-38°C / 180-160 mTorr) giving 5.7 g Si_6H_{12} as a colorless liquid at a yield of 73.3% based upon $[PEDETA(SiH_2Cl)]_2[Si_6Cl_{14}]$. NMR characterization of Si_6H_{12} was consistent with literature report,[4] while preliminary elemental analysis by X-ray fluorescence spectroscopy indicates an aluminum chloride byproduct impurity of 0.5 ± 0.1 wt.%.

Interaction between cyclohexasilane and the amphiphilic invertible polyester

An appropriate amount of the polyester (5, 50 or 160 μg) or diethyl sebacate (5 or 50 μg) or poly(ethylene glycol) dimethyl ether (5 or 50 μg) was dissolved in 0.8 mL of benzene-d6 under gentle agitation. The solutions were left for at least 16 h to equilibrate at 22.5°C. Cyclohexasilane (5 or 50 μg) was added, the mixture was allowed to equilibrate for another 16 h to form a corresponding adduct (complex) and then

^{1}H NMR spectra were recorded. Shifts of signals in ^{1}H NMR spectra of the adducts (complexes) were determined by comparing their spectra with the spectra of each initial substance alone dissolved in benzene-d_6 at the same concentration.

References

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