Lamellar Architecture and Crystalline Transformation in Supramolecular Complexes of Highly-branched Polyethyleneimine-Octadecanoic Acid

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Experimental Section

Materials. PEI(average Mw = 55000g/mol; 50% aqueous solution, purchased from ACROS) and OA(Grade 1, obtained from Sigma) were used as received. Carbon tetrachloride (CTC) and tetrahydrofuran (THF) (analysis grade) were distilled before use.

Preparation of the complexes. OA was dissolved in CTC to obtain 1%(wt/v) solution, and PEI was diluted to 1%(wt/v) solution with deionized water. The solutions were mixed and refluxed at 75 °C for 48 hours under quick stirring with the protection of nitrogen gas. CTC was evaporated at 75°C till the pre-complex precipitated. The precipitate was filtered after cooling and dried in vacuum at 50 °C for two days. The dried pre-product were dissolved in THF, and refluxed at 68 °C for 8 hours under stirring with the protection of nitrogen gas. The solution was first evaporated at 70 °C and further dried at 50 °C in vacuum for 8 hours, and finally the solid complexes were obtained.

Differential scanning calorimetry (DSC). A DSC 822e differential scanning calorimeter was utilized for DSC analysis. The samples were firstly melted at 100 °C for 5 minutes then quenched in liquid nitrogen, subsequently heated at the speed of 20 °C /min from -70 °C to +120 °C (first scan). Then, the samples were cooled at the speed of -10 °C /min from +120 °C to -70 °C (second scan), and followed by heating at the speed of 20 °C /min from -70 °C to +120 °C (third scan).

Temperature-variable FT-IR spectroscopy. Pure OA or PEI(OA)$_{1.03}$ was powdered together with KBr and pressed into pellets. The FT-IR measurements were performed on a Bruker EQUINOX 55 spectrometer equipped with a temperature-variable cell and obtained spectra were processed by the Bruker OPUS program. The cell was kept in vacuum, and liquid nitrogen was used as coolant. A resolution of 4 cm^{-1} was chosen and 32 scans were accumulated. For pure OA, the sample was first cooled to -125 °C, and then spectra were collected from -125 °C to +75 °C at a heating rate of about 2 °C /min. The spectra collecting for temperature decreasing process of pure OA was done from 60 °C to -121 °C. The temperature of the heating process of PEI(OA)$_{1.03}$ was from -163 °C to +77 °C, and that of the cooling process was from +77 °C to -160 °C.

Small-angle X-ray scattering. SAXS measurements were performed at room temperature (ca. 25 °C). The power for the X-ray scattering was 200mA, 40kV. The X-ray source is an 18Kw rotating anode Cu target. The incident X-ray beam was monochromated by pyrolytic graphite, and a set of three pinhole inherent collimated small-angle X-ray cameras can be avoided. The sizes of the first and second pinholes are 0.3 and 0.2mm, respectively, and the size of the guard pinhole before the sample is 0.25mm. All data were corrected by the background (dark current and empty beam scattering) and the sensitivity of each pixel of the area detector. The area scattering pattern has been rapidly averaged to increase the efficiency of data collection, compared with one-dimensional linear detector. Data were acquired and processed on a Dell-personal computer. The intensity profile was output as the plot of the scattering intensity (I) vs the scattering angle (2θ).

Transmission electron microscopy. The negative staining technique was used for TEM studies. A drop of sample solution was allowed to settle on a carbon precoated grid for 30 seconds. Excess sample was wicked away with filter paper and a drop of 1% uranyl acetate solution was then allowed to contact the sample for 3-5 minutes. The samples were submitted for TEM observation after the solution got dried. TEM measurement was performed on a TECHI transmission electron microscope. The accelerating voltages was 120 kV. Image analysis was performed with a commercially available software package (SISanalySIS® and AdobePhotoshop 6®).

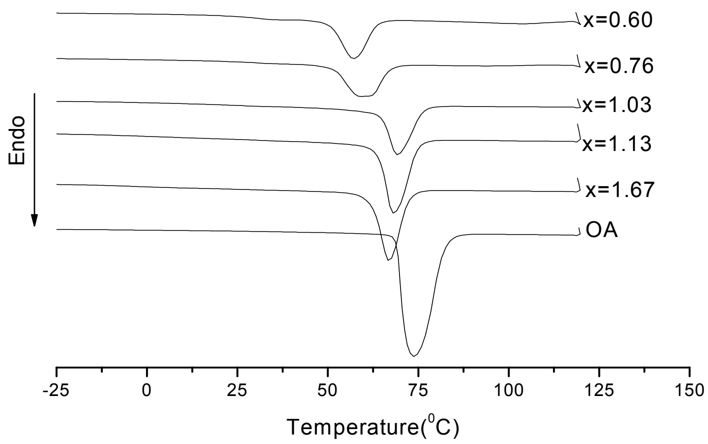

Figure S1. DSC curves of PEI(OA)x and pure OA. The melting temperatures and enthalpies of the complexes increase in the range of x = 0.60-1.03, but decrease in the range of x = 1.03-1.67.

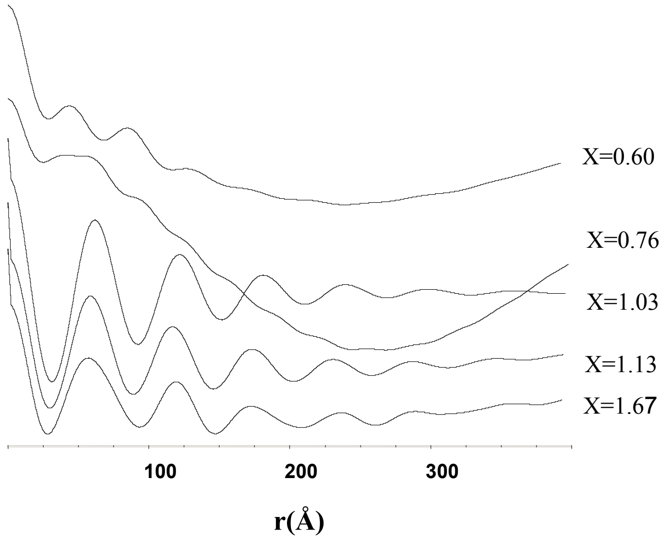

Figure S2. Long period profiles of PEI(OA)$_X$ complexes obtained by Fourier-transformation of the small-angle X-ray scattering. According to Strobl and Schneider, we can achieve the thickness of amorphous layers (La) and crystalline layers (Lc), and infer the packing models of the alkyl side chains.

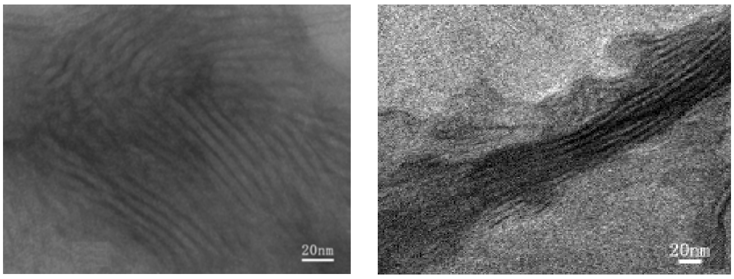

Figure S3. TEM images of PEI(OA)$_{1.03}$ (left) and PEI(OA)$_{1.13}$ (right) obtained using negative staining with uranyl acetate. A distinct feature is the observation of the considerably thinner dark layers, corresponding to the polar layer of PEI, the thicker light grey layers corresponding to the nopolar alkyl chains layer. TEM image clearly shows that PEI(OA)$_{1.03}$ and PEI(OA)$_{1.13}$ complexes have a well-ordered lamellar structure with a characteristic period of approximately 60.8 Å and 50.9 Å respectively, in good agreement with the SAXS results (62.5 Å and 50.9 Å,respectively). To enhance contrast, the complexes was stained with uranyl acetate(2% ethanol solution). Since the alkyl layers are highly crystalline, the uranyl acetate can only reach the polar backbone layers of PEI and the possible amorphous transition regions of the alkyl chains on the surface of the crystalline lamellae.