

## Nanoconfinement Crystallization of Frustrated Alkyl Groups: Crossover of Mesophase to Crystalline Structure

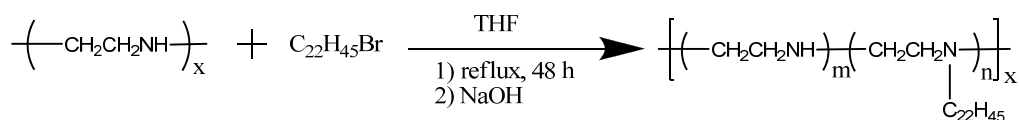
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### Electronic Supplementary Information

**Synthesis of PEI22C comblike polymer:** The mixture of 1 g (0.023 mol EI unit) sample of branched poly(ethyleneimine) and an equivalent amount of *n*-eicosyl bromide was heated under reflux in 100 mL of tetrahydrofuran for 48 h. An equivalent amount of sodium hydroxide, dissolved in methanol, was then added, and the solution was heated under reflux for another 24 h. After cooling to room temperature, NaBr was filtered off, and the solvent was removed. The product was rinsed alternatively with deionized water and acetone three times, and then dried in vacuum overnight. <sup>1</sup>H NMR was used to confirm the molecular structure of PEI22C, and substitution degree of 44% along the PEI molecules can be obtained. The preparation route of PEI22C was shown in Scheme 1.



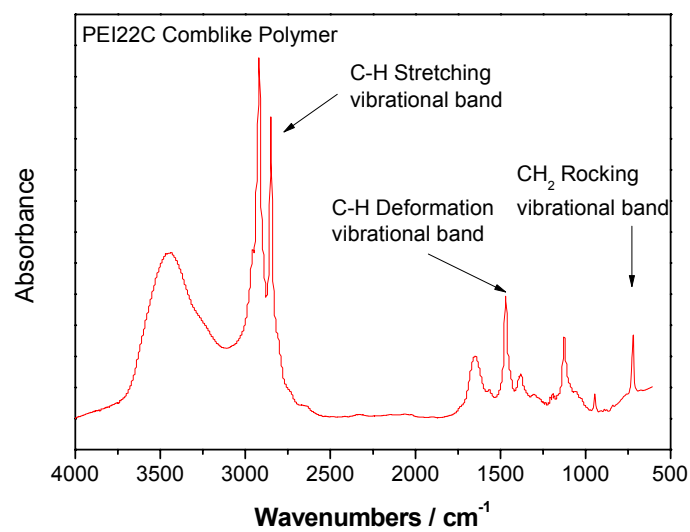
**Scheme 1.** The preparation route of PEI22C comblike polymers.

**Differential scanning calorimetry (DSC):** DSC Diamond (Perkin Elmer Instruments), calibrated with indium, was used to study the thermal behavior of PEI22C. Specimens of 3-5 mg were encapsulated in aluminum pans and heated at a rate of 10 °C/min from -60 °C to 100 °C, and kept at 100 °C for 5min, subsequently cooled to -60 °C at a rate of 10 °C /min and kept at -60 °C for 5 min. The samples were heated again at a rate of 10 °C /min from -60 °C to 100 °C. The second DSC thermograms were recorded.

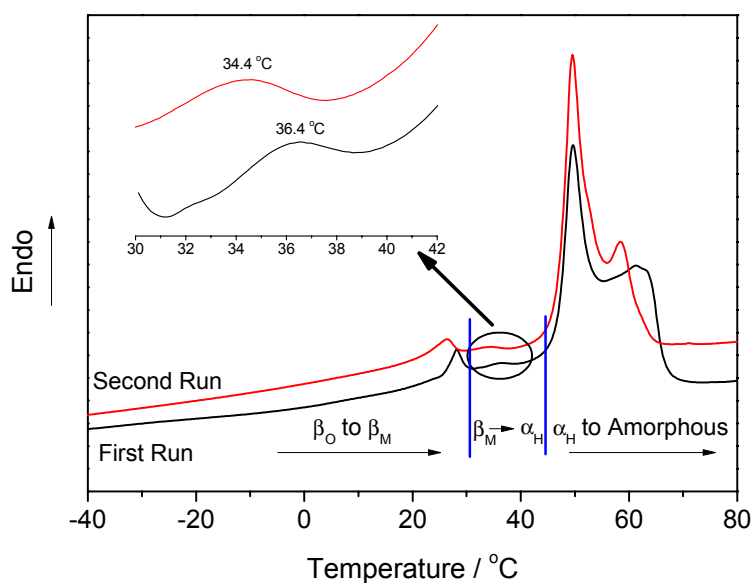
**Variable temperature wide-angle X-ray diffraction (WAXD):** Variable-temperature wide-angle X-ray diffraction patterns were recorded with a Bruker D8 Advance X-ray diffractometer (Bruker, Germany), operated at 40 kV and 40 mA (Nickel-filtered Cu K $\alpha$  radiation with wavelength of  $\lambda=0.154$  nm) in reflection mode. Data were recorded from 0 °C to 75 °C at 10 °C intervals and the 2-theta scanning range was from 15 to 30°. The measurement conditions were: target, Cu; voltage, 40 kV; current, 30 mA; divergence slit, 2 mm; anti-scatter slit, 0.6 mm; receiving slit, 0.1 mm; monochromator; detector slit, 0.1 mm. The step size was 0.02, and the dwell time at each step was 3 s. Approximately 150 mg samples were weighed into the sample holder, taking care not to introduce a preferential orientation of crystals.

**Variable temperature small-angle X-ray scattering (SAXS):** Variable-temperature small-angle X-ray scattering experiments were carried out at the beamline BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). The high brilliance of synchrotron sources enabled time resolved experiments with a high signal/noise ratio. The wavelength of the radiation source was 0.124 nm. The SAXS pattern was collected by a MAR CCD (MAR-USA) detector, which had a resolution of 2048×2048 pixels with pixel size of 79×79  $\mu\text{m}^2$ . The sample to detector distance was 3117.4 mm, which was calibrated by a biophysical standard (bull collagen). After background scattering subtraction and correction for X-ray absorption and sample thickness, the 2D SAXS patterns were converted to 1-dimensional data.

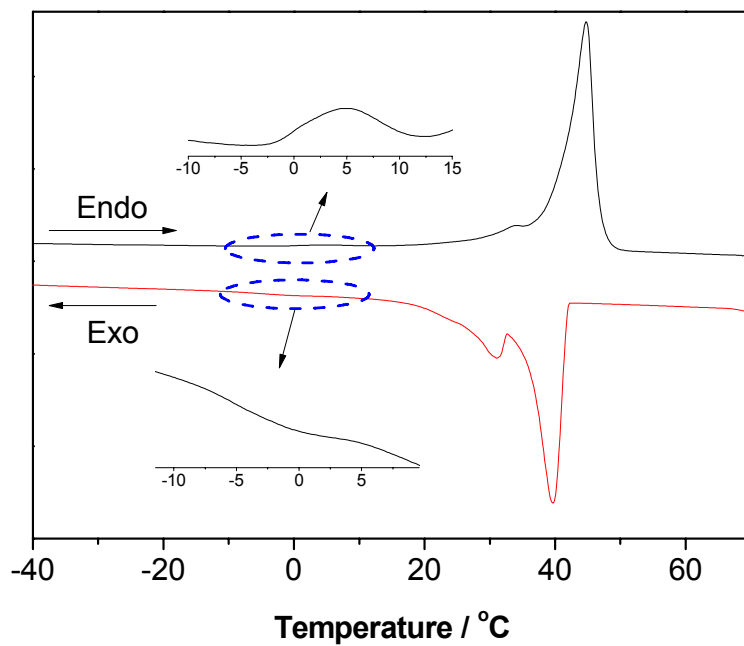
**High-resolution temperature-dependent FT-IR spectroscopy:** The PEI22C sample was mixed with KBr powders, and then pressed into a thin pellet. FT-IR spectra measurements were performed on a Perkin Elmer 100 spectrometer equipped with a temperature-variable cell, and the obtained spectra were processed by a PE spectra program. The cell was kept in vacuum, and liquid nitrogen was used as coolant. A resolution of  $1\text{ cm}^{-1}$  was chosen and 100 scans were accumulated. Infrared spectra were recorded as temperatures ranging between  $-70\text{ }^{\circ}\text{C}$  to  $80\text{ }^{\circ}\text{C}$  during heating process. At every temperature point, the samples were equilibrated for 3-5 minutes before measurements.



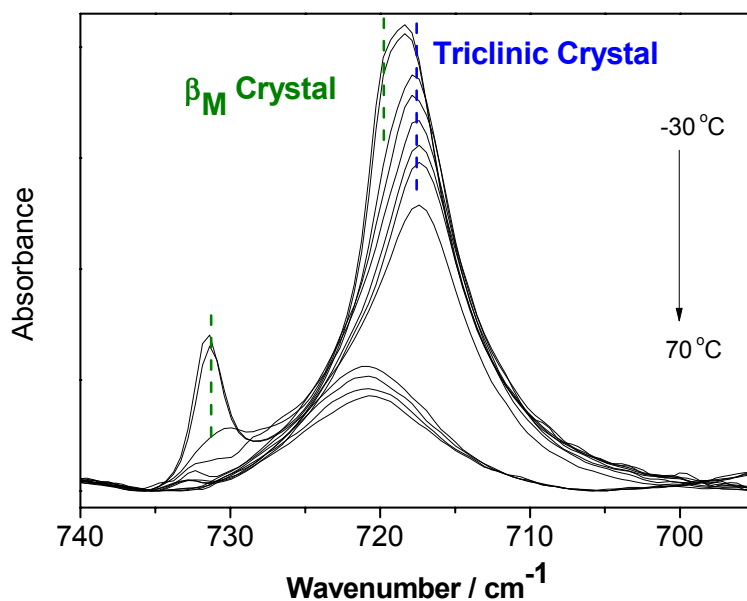
**Fig. S1** The structural composition of PEI22C comblike polymer characterized by FT-IR spectroscopy. As shown in the above band assignments, the C22 alkyl groups had been successfully grafted on the flexible PEI molecules.



**Fig. S2** DSC melting thermal diagrams for PEI22C sample at the heating rate of 10 °C/min. The enlarged section marked by black circle shows the obviously endothermic behaviors (indicated by arrow) in the first and second heating processes, which is characteristic of the transition of monoclinic to orthorhombic phase. It is the first time to observe the phase transition of mesophase (hexagonal) to crystalline structure (monoclinic and orthorhombic phase) in the nanocrystalline domains formed by frustrated C22 alkyl groups.



**Fig. S3** DSC melting thermograms for *n*-docosane at the scanning rate of 10 °C/min in the heating/cooling runs.



**Fig. S4** High-resolution variable temperature FT-IR spectra of *n*-docosane recorded from -30 to 70 °C at 1 cm<sup>-1</sup> resolution. Monoclinic and triclinic phase structure can be observed at the lower temperature, and with temperature increasing, the formation of hexagonal phase can be found in the microscopic viewpoint. Different from the hexagonally packed mesophase formed by the frustrated C22 alkyl groups in PEI22C, the formation and vanish of metastable hexagonal phase of *n*-docosane is transient, and quickly enter into amorphous state.