Structured Growth from Sheaf-like Nuclei to Highly Asymmetric Morphology in Poly(nonamethylene terephthalate)

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Supporting Information

Experimental section

Materials

Poly(nonamethylene terephthalate) (PNT), an arylate polyester with nine methylene groups between two terephthalates in one repeat unit, was synthesized in laboratory from appropriate glycol (1,9-nonanediol) and dimethyl terephthalate using 0.1% butyl titanate as catalyst via two-step polymerization, using synthesis procedures already reported in earlier studies.[41] The first step was the transesterification followed by the polycondensation process. Synthesized PNT product was purified for at least two times after synthesis. The weight-average molecular weight (Mw) of the synthesized PNT as determined by GPC (Waters) using polystyrene as a standard were 28,280 g/mol with polydispersity index (PDI) = 1.44. From DSC characterization, PNT has T_g = -2^{o}C and T_m = 92^{o}C. Detailed characterization results (NMR/IR for structures, DSC for T_g, Tm and GPC for Mw) for synthesized PNT polymer are attached in Supporting Information **Figures S1** to **S4**.

Polymer samples for POM characterization in controlled-thickness films were prepared by drip-casting of PNT solutions (4 wt.%) and dried films were crystallized at selected temperature (at fixed T_c=85^{o}C after melting at T_{max}=110^{o}C or 120^{o}C for 2 min); slightly thicker specimens for SEM characterization were prepared by direct melt-crystallization by heating a suitable quantity of PNT material to T_{max}=110^{o}C (or 120^{o}C) and quenched to T_c=85^{o}C till full crystallinity. Crystallization at 85^{o}C has been proved for developing known ring-band forms of two types (Type-I and Type-II), and it has been proven earlier that both Type-1 and Type-II coexist in any Tc showing different relative fractions.[39,40] From earlier studies, it is easily distinguishable between the Type-I and Type-II ring bands of PNT spherulites. Interior lamellar assembly and top-surface relief patterns of Type-I band was the main objective of this study; thus, SEM characterization was focused on only the Type-I band. Crystallized PNT films were fractured by marking on glass substrate using a diamond knife to guide the fracture line. The fractured surfaces of the crystallized PNT samples were to be examined using SEM.

Apparatus and procedures

Polarized-light optical microscopy (POM, Nikon Optiphot-2). Optical microscopy was used for revealing birefringence banding patterns of Type-1 vs. Type-II. In addition, early-stage nucleation and nuclei morphology were in-situ monitored by placing samples on isothermally controlled hot-stage at 75 or 85^{o}C. Microscope is equipped with a digital camera Nikon Digital Sight (DS-U1) and hot stage with temperature programmer (Linkam THMS-600 with T95 temperature programmer), was used to characterize the optical transparency and crystalline morphology.

Scanning electron microscopy (SEM). Interior lamellar assembly morphologies of PNT samples was characterized using scanning electron microscopy (SEM, FEI Quanta 400F). Fractured surfaces of bulk samples were examined and characterized using scanning electron microscopy (FEI Quanta-400F, SEM) for revealing lamellar structure in the fracture and top free surface. Samples in bulk forms were fractured across the thickness direction. They were then coated with gold vapor deposition using vacuum sputtering prior to SEM characterization. 10 mA gold sputtering was performed under a vacuum condition for 300 seconds (5 minutes) using Auto Fine Coaters JFC-1600 from JEOL, USA. The thickness of the gold coating on the sample is no more than 100 nm. The polymer has a relatively low melting point that results in some inevitable charging issues. However, we managed to capture considerable high-resolution images to show the detail lamellar assembly in PNT banded spherulites.

Atomic-force microscopy (AFM). AFM investigations were made in intermittent tapping mode of AFM (diCaliber, Veeco Co., Santa Barbara, USA) with a silicon-tip (f = 70 kHz, r = 10 nm). The largest scan range was 150 μm × 150 μm, which could be further zoomed in to 5 μm × 5 μm for larger magnifications on selected areas of interest.

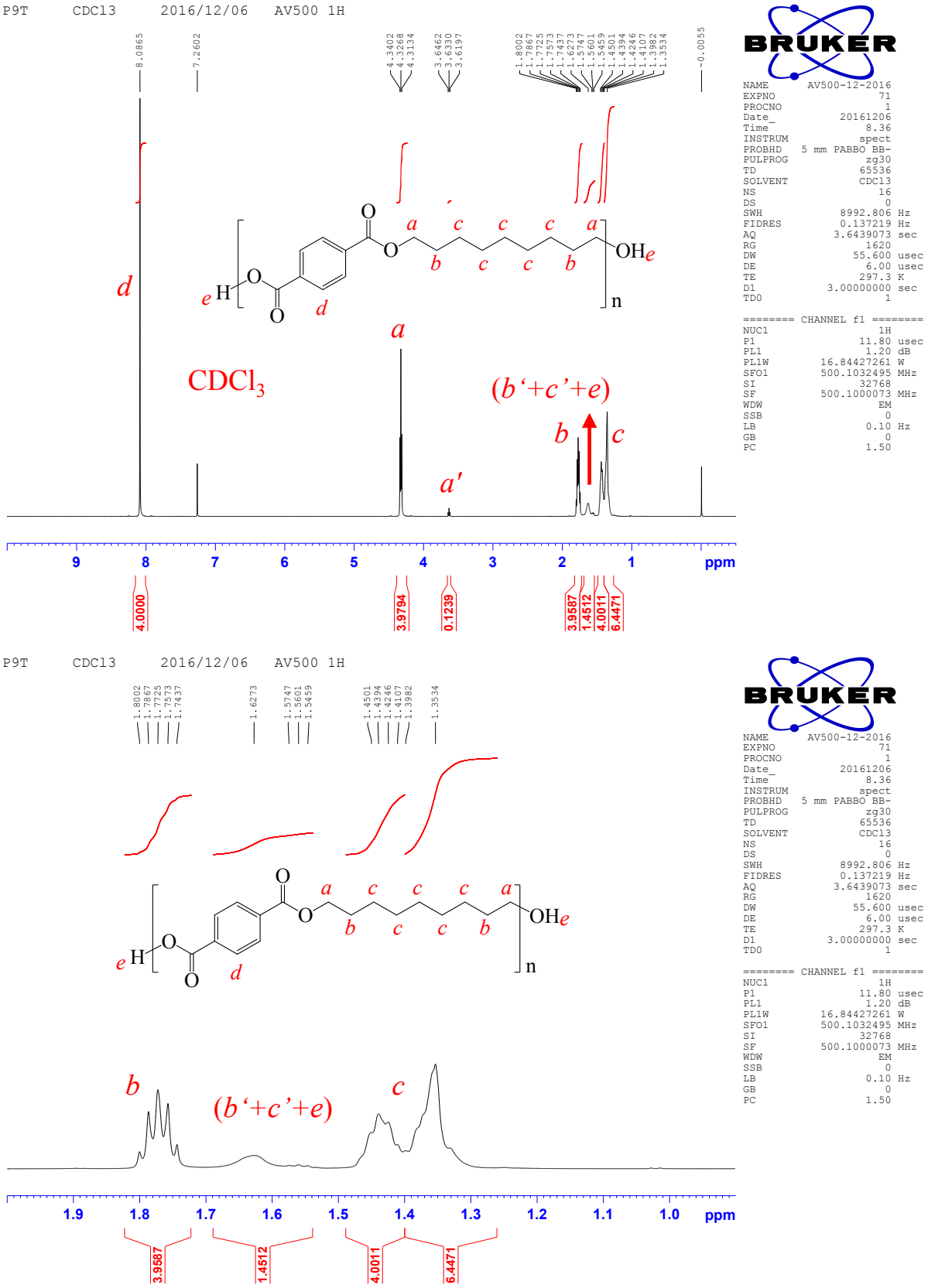


Figure S-1. ^{1}H NMR spectra of synthesized PNT.

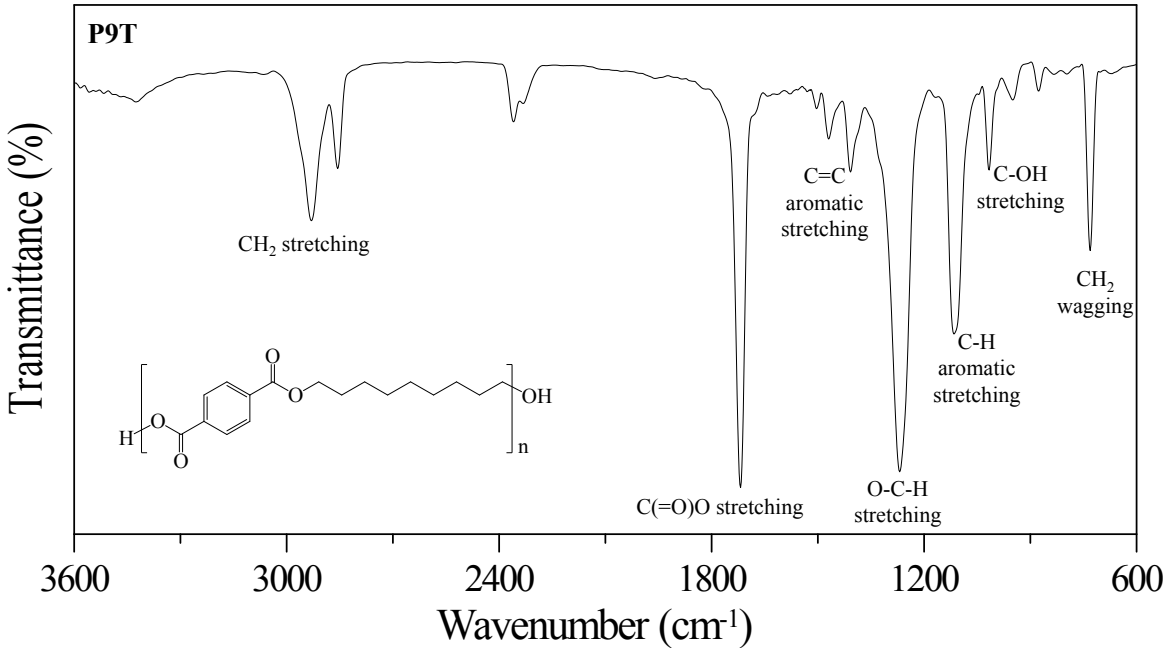
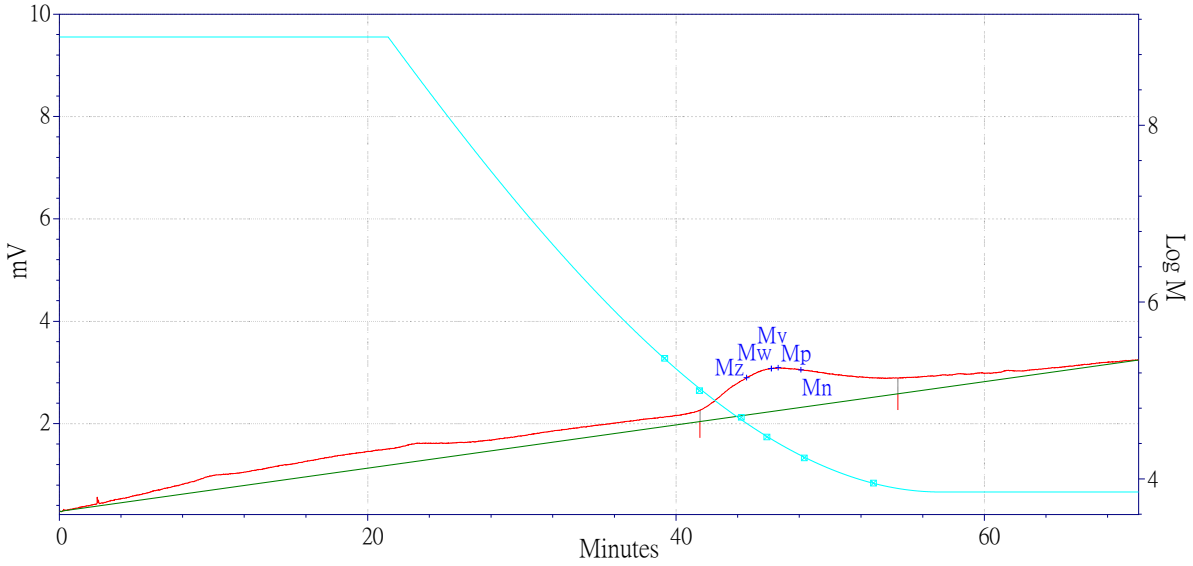


Figure S-2. FTIR spectrum of synthesized PNT



Mn = 18 518 g/mol Mw = 28 280 Mz = 42 669 Mv = 28 280

Figure S-3. GPC graph of synthesized PNT

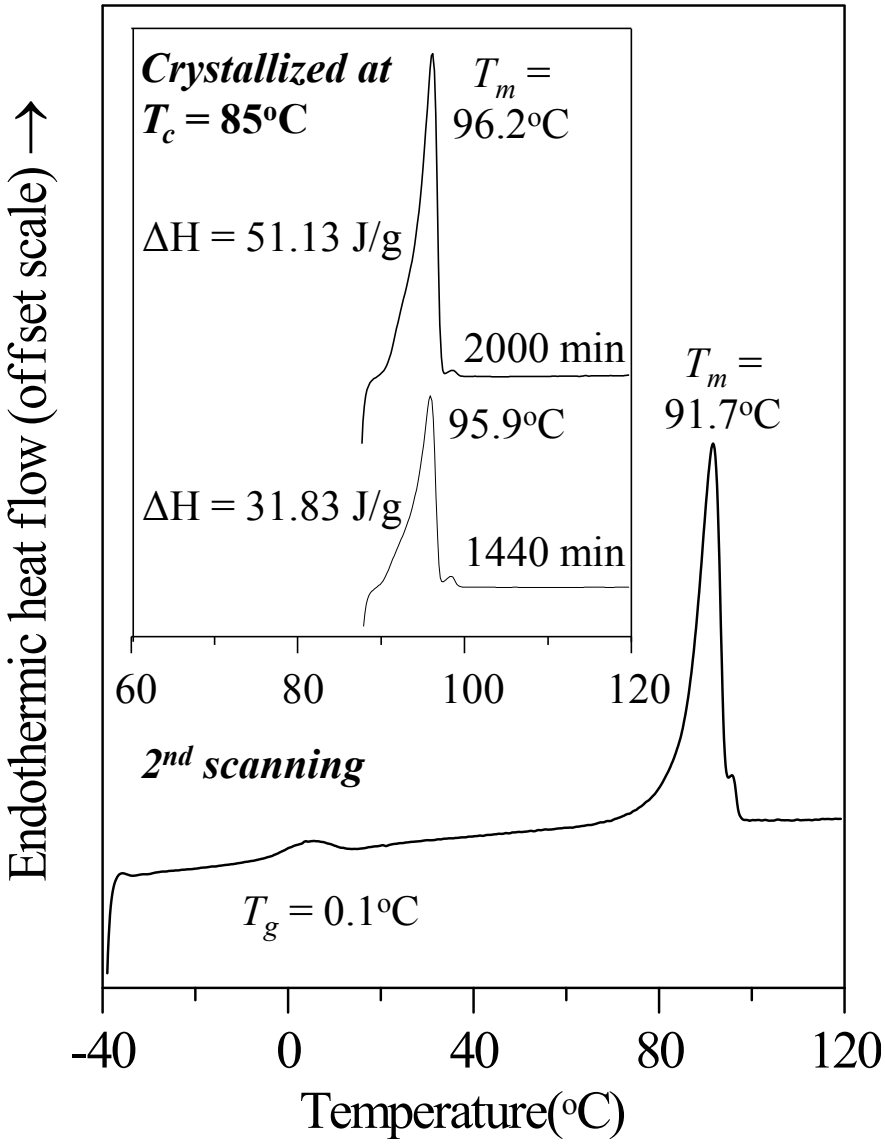


Figure S-4. DSC thermograms of synthesized PNT [second scanning at 10°C/min after melting at T_{max} = 120°C]. Insets showing scans after isothermal crystallization at 85°C for 1440 and 2000 minutes, respectively.