(Supporting Information)

Two-Dimensional Folded Chain Crystals of a Synthetic Polymer in a Langmuir-Blodgett Film

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Experimental Section

Materials. The polymer samples used in this study were an isotactic poly(methyl methacrylate) (\textit{it}-PMMA) with the number average molecular weight of 175,700, a polydispersity index of 1.21, and an mm content of 98%, and a syndiotactic PMMA (\textit{st}-PMMA) with the number average molecular weight of 178,700, a polydispersity index of 1.16, and an rr content of 79%. These polymers were purchased from Polymer Source (Montreal, Canada) and used without further purification. Highly purified chloroform (Infinity Pure, Wako Chemicals, Osaka, Japan) was used as the solvent for the spreading solutions without further purification. Water purified by a Milli-Q system was used as the subphase for the Langmuir-Blodgett (LB) investigations.

LB Film Preparations and Surface Pressure-Area Curve Measurements. The polymers were spread from solutions having a polymer concentration of around $1 \times 10^{-4}$ g/mL in chloroform onto a water surface at 25 °C in a commercial LB trough (FSD-50, USI, Japan), compressed to a prescribed pressure at the rate of $4.1 \times 10^{-2}$ nm$^2$-repeating unit (ru)$^\dagger$ min$^{-1}$ or $8.2 \times 10^{-4}$ nm$^2$-ru$^{-1}$ min$^{-1}$ and
deposited onto a freshly cleaved mica by pulling it out of the water at the rate of 4.2 mm/min while compressing the monolayer at that pressure (the vertical dipping method). The samples obtained in a dilute state (surface pressure = 0 mN/m) were deposited by stopping the moving barrier. In the dilute state, the monolayer on the water surface was not necessarily homogeneous, thus the monolayer was usually deposited on mica at several areas by stepwise compressing the area, then the areas of the mica where the polymer was properly deposited were observed by AFM. The surface pressure-area curves were measured at a compression rate of $4.1 \times 10^{-2}$ nm$^2$·ru$^{-1}$·min$^{-1}$ using filter paper as a Wilhelmy plate.

**AFM Observations.** AFM observations were done using a commercial AFM (NanoScopeIV / multimode AFM unit, Veeco Instruments, Santa Barbara, USA) in air in the tapping mode. Standard silicon cantilevers (PointProbe, NCH, NanoWorld, Neuchâtel, Switzerland) and super-sharp cantilevers (SSS-NCH) were used for the usual and high-magnification observations, respectively. The typical settings of the AFM for the high-magnification observations were as follows: a drive amplitude of 1.4-1.5 V, a set point of 1.1-1.2 V, and a scan rate of 2-2.5 Hz. The AFM observation was done under laboratory conditions at the relative humidity of 50-85%. The AFM images are shown without any image processing except flattening.
Figure S-1. (a) High magnification AFM height and phase images of it-PMMA. The sample was deposited on mica at 10 mN/m, then annealed at 50 °C for 12 h in air. The compression rate was 8.2 x 10^{-4} \text{nm}^2 \cdot \text{ru}^{-1} \cdot \text{min}^{-1}. (b) A zoomed phase image of the area indicated in a. Schematic representation of a possible chain conformation is also shown in b (right) as a black line.

The deposited film further crystallized at relatively low temperatures. After annealing the sample at 50 °C, the crystallinity was improved; the amount of vague areas between the long lamelllas was reduced and the outline of the small crystals between the lamelllas became clearer. Although in most areas, the chain foldings were not perfectly visible, but in some areas, regular chain foldings were clearly observed as shown in (b).