Supporting Information

Pressure Induced Crystallization in situ Simultaneous SAXS/WAXS Investigations on Structure Transitions

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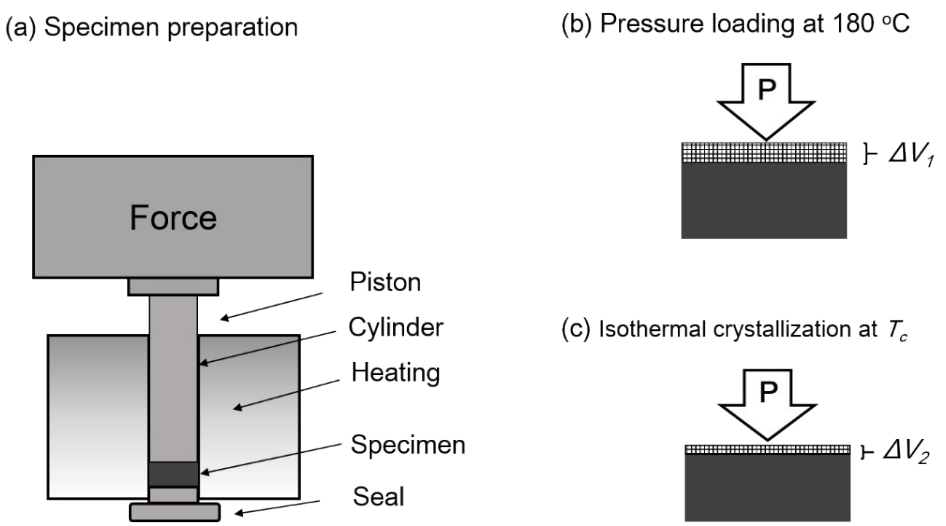
As shown in **Scheme S1** (a), PLLA pellets were loaded in the cylinder of PVT100 (SWO Polymer-technik GmbH). After completely melted, cooled to 180 °C and loaded a pressure (P_c). Then cooled to a temperature (T_c) for isothermal crystallization. As loading P_c, the melt would be compressed and flow, leading to a decrease of the volume ΔV_1. This process would resulted in a weak shear flow on chains, and orient chain segments. During crystallization, the volume modulus of the crystallizing specimen increased with time. Pressure deformed specimen and made the amorphous chains and crystal blocks sliding, until the volume modulus of the crystallizing specimen equals to the pressure loaded. During crystallization, the decrease of volume is ΔV_2. It is the result from crystallization ΔV_c, deformation ΔV_o, and decrease of the free volume ΔV_f.



Scheme S1 Schematic illustrations of (a) specimen preparation, (b) loading pressure leads to a decrease of volume ΔV_1, (c) a small decrease of volume ΔV_2 is produced during isothermal process.

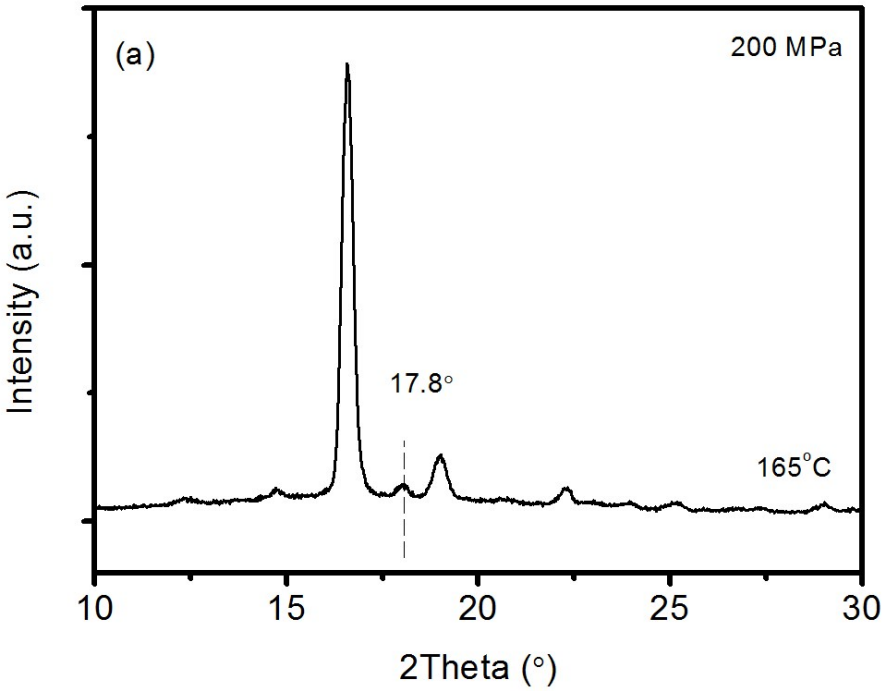


Figure S1 WAXS profiles of PLLA samples prepared at 200 MPa at T_c of (a) 165 °C.

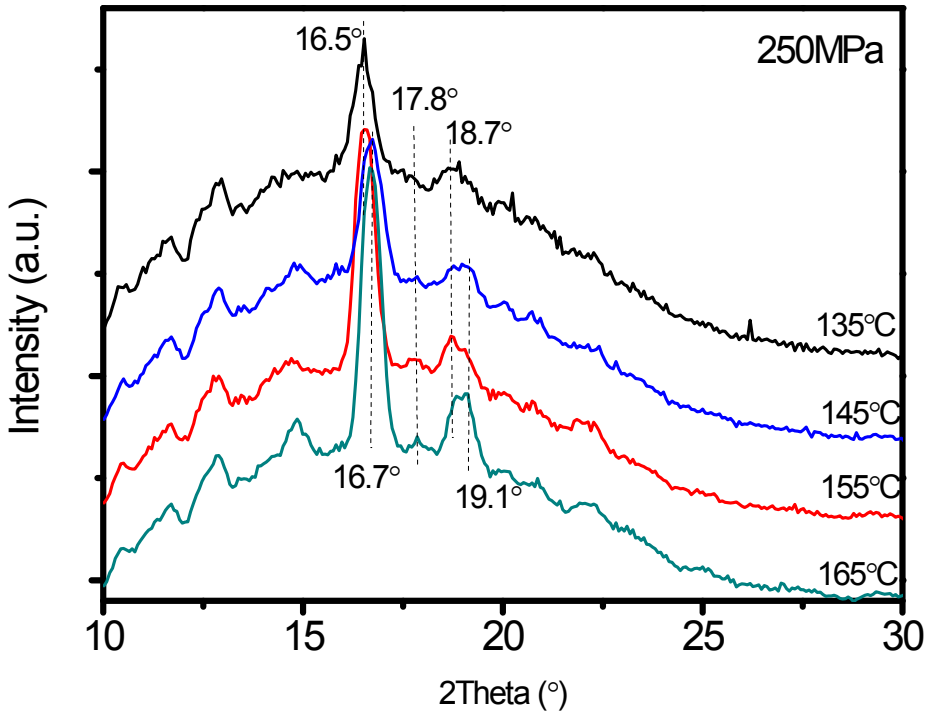


Figure S2 WAXS profiles of PLLA samples isothermally crystallized at 250 MPa.

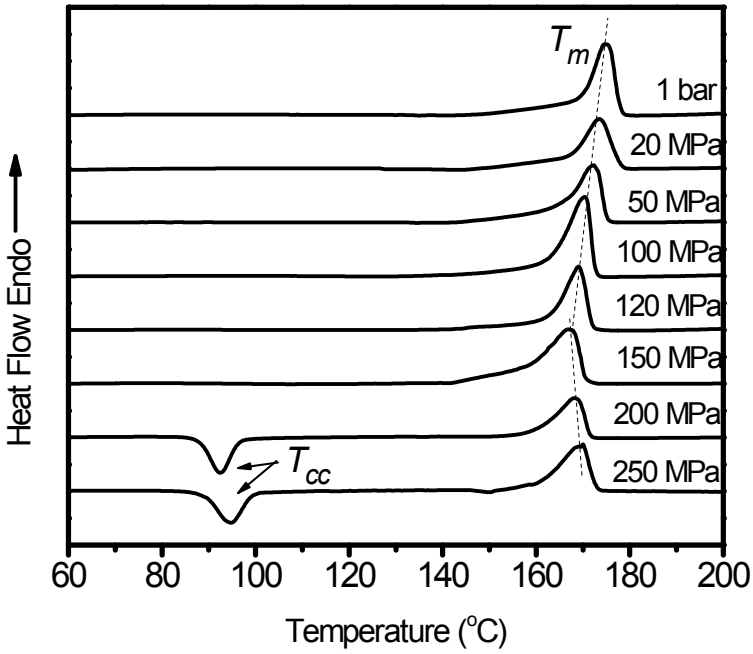


Figure S3 DSC heating traces of PLLA samples that crystallized at 145 °C at various pressures, T_m and T_{cc} represent the melting temperature and the cold crystallization temperature, respectively.

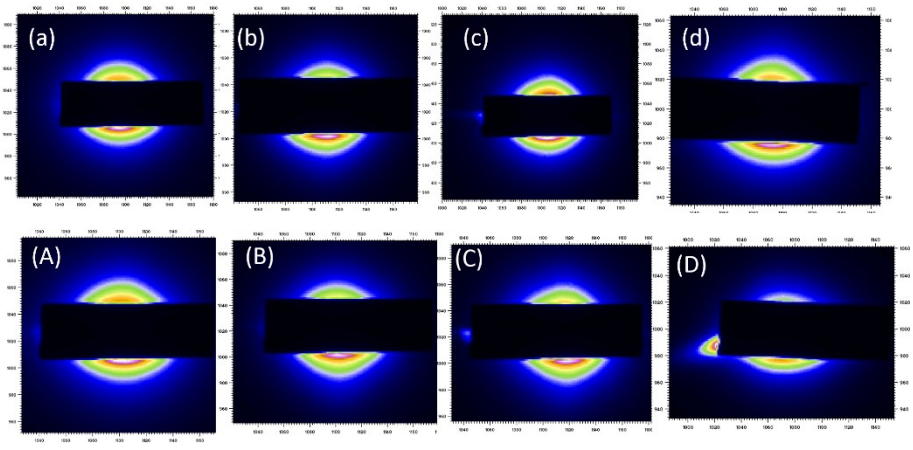


Figure S4 2D SAXS patterns of PLLA prepared at 145 °C (a, b, c, d) and 165 °C (A, B, C, D) at (a, A) 1 bar, (b, B) 50 MPa, (c, C) 100 MPa and 200 MPa (d, D).

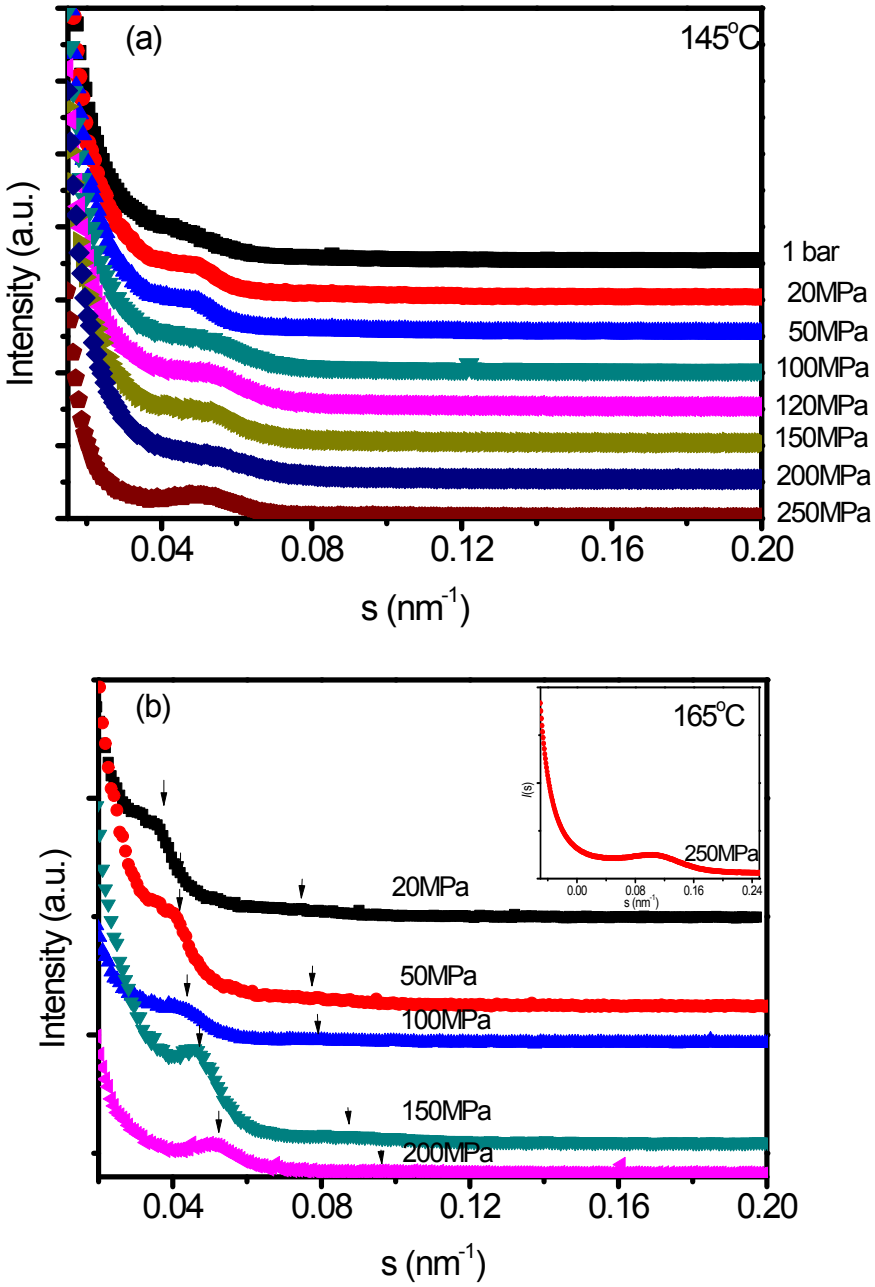


Figure S5 SAXS profiles of samples prepared at T_c of (a) 145 °C and (b) 165 at various pressure.

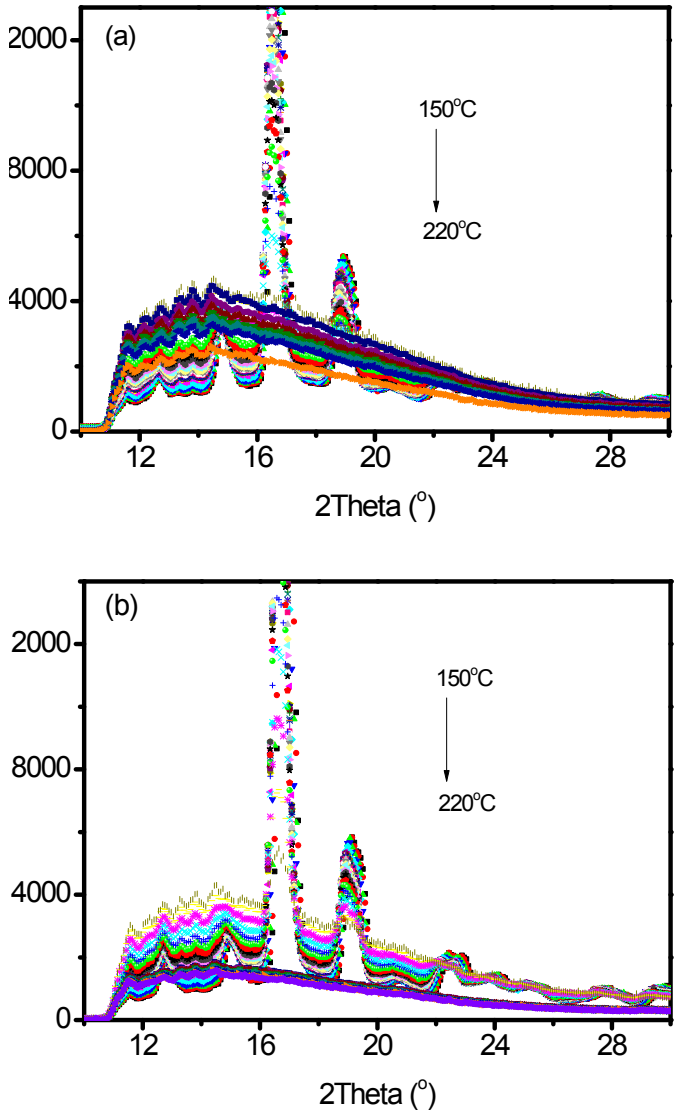


Figure S6 In situ WAXS profiles of samples prepared at T_c (a) 170 °C, (b) 180 °C at 200 MPa. Heating from 150 °C to 220 °C at 2°C/min, scanned 30s at the temperature every 3 °C.

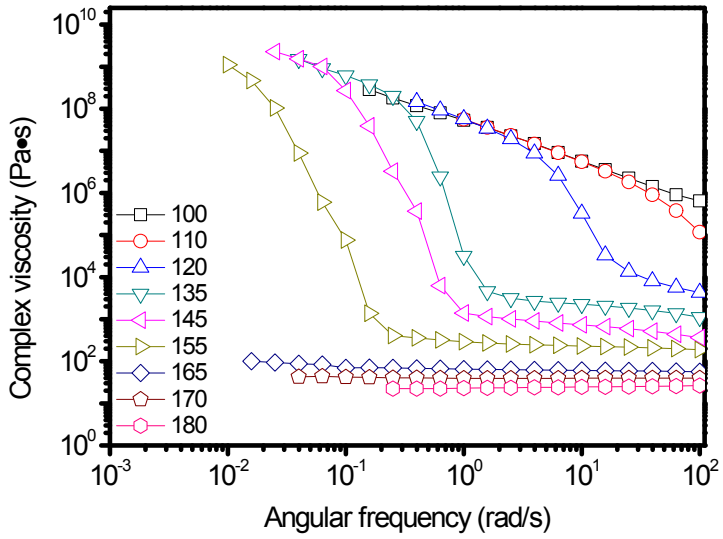


Figure S7 Complex viscosity of PLLA measured at various temperatures after completely melted.