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Effect of CO_2 on the Crystallization of Poly(Lactic Acid) Homo-Crystallites via Influencing Crystal Structure of Stereocomplex Crystallites

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Figure S1 displays the POM photos of the sample crystallized at 120 °C under 6 MPa CO_2 after 160 °C isothermal crystallization for 2 h. As shown in Figure S1(a), only SC spherulites formed at 160 °C. After 4 min, the observation area is filled up with spherulites which process low brightness. Then, some spherulites with high brightness formed.

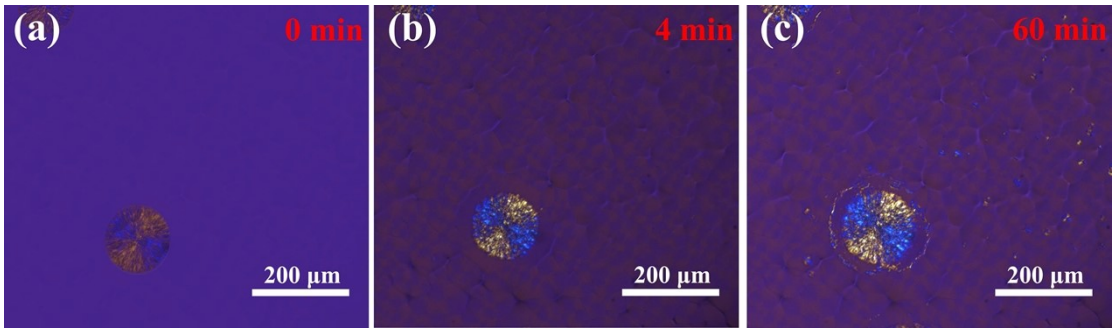

Figure S1 HP-POM photos of PLLA/PDLA crystallizes at T_{c2} (120 °C) under 6 MPa for (a) 0 min, (b) 4 min and (c) 60 min. PDLA/PLLA first crystallizes at T_{c1} (160 °C) for 2 h.

To distinguish the HC and SC, the samples in Figure S1 are heated to 180 °C, and the results are shown in Figure S2. As shown, when heated to about 151 °C, the spherulites with high brightness all disappear, and the spherulites with low brightness still exist at about 180 °C. It should be noted that the melting temperature of samples would be reduced under CO_2 due to the plasticization effect of CO_2. Thus, the disappearance of spherulites with high brightness results from the melting of HC, and spherulites with low brightness should be SC.

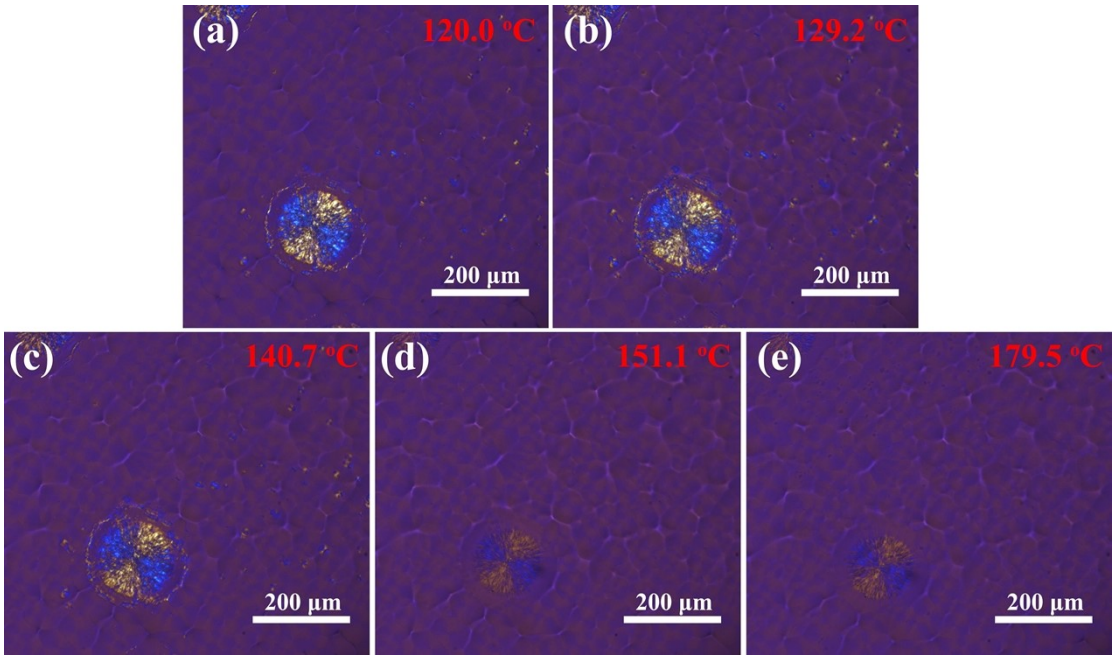

Figure S2 HP-POM photos of PDLA/PLLA crystals during heating process after crystallization at T_{c1} (160 °C) for 2 h and then T_{c2} (120 °C) for 1 h under 6 MPa. The temperature is (a) 120.0 °C, (b) 129.2 °C, (c) 140.7 °C, (d) 151.1 °C and (e) 179.5 °C.

Figure S3 displays the effect of CO_2 on the crystallization of HC introduced by SC. The crystallization temperature for SC is 150 °C. As shown, some HC formed after the crystallization SC under air (Figure S3(a)). For pure PLLA, the HC could not form at this high temperature, but the SC could act as heterogeneous nucleation sites to reduce the nucleation energy, thus the HC could crystallize at a low supercooling. With the introduction of CO_2, due to the decreasing supercooling, the HC could not form at 150 °C, but the SC could introduce HC at 120 °C. In accordance with Figure 5, the SC would form first at amorphous region, and the HC forms at the internal of SC.

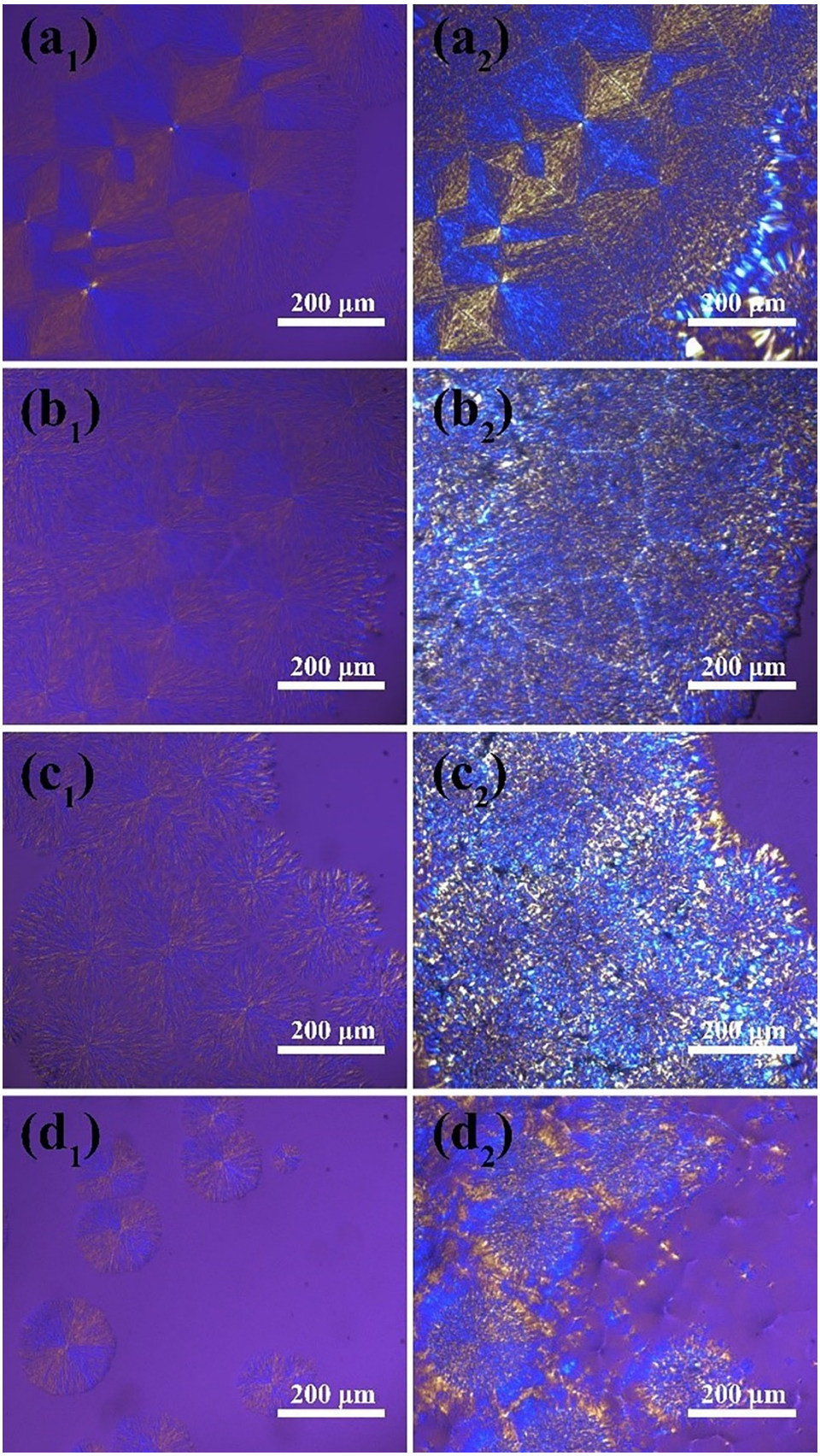

Figure S3 HP-POM photos of PDLA/PLLA after crystallization at T_{c1}(150 °C) for 2 h under (a_1) air, (b_1) 2 MPa, (c_1) 4 MPa and (d_1) 6 MPa CO_2, and then crystallization at T_{c2} (120 °C) for 1 h under (a_2) air, (b_2) 2 MPa, (c_2) 4 MPa and (d_2) 6 MPa CO_2.

With further decreasing SC crystallization temperature to 140 ^{o}C, the HC appears at 140 ^{o}C under air and CO_2 after the crystallization of SC due to the increasing supercooling. When temperature is decreased to 120 ^{o}C, the HC further crystallizes and full fills the internal of SC. Combination with Figure 5 to Figure S4, except for the 160 ^{o}C and air, the HC form between the SC lamella at all conditions, especially when CO_2 is introduced. It may be caused by the different kinetic of SC and HC under CO_2.

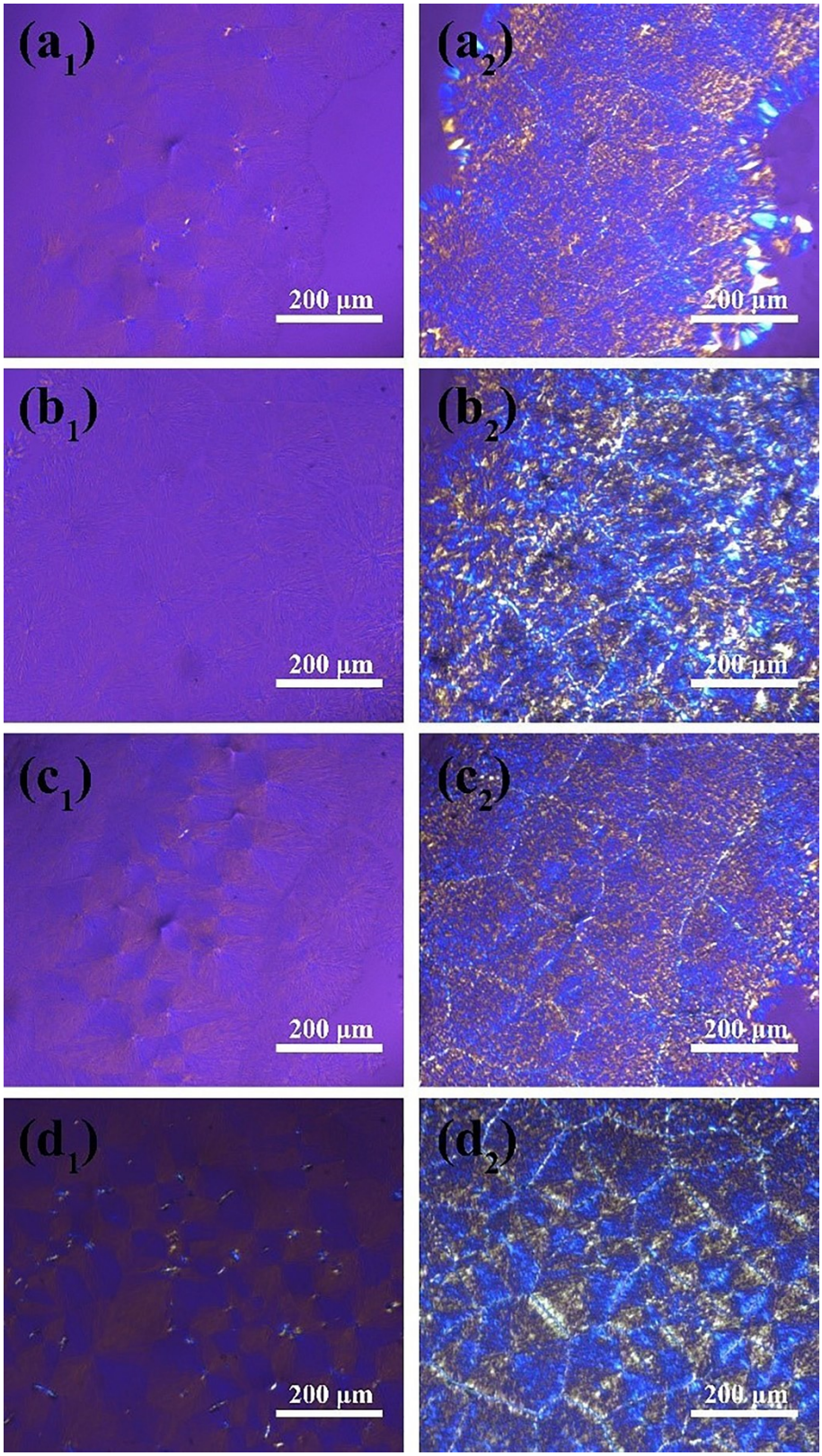

Figure S4 HP-POM photos of PDLA/PLLA after crystallization at T_{c1}(140 °C) for 2 h under (a_1) air, (b_1) 2 MPa, (c_1) 4 MPa and (d_1) 6 MPa CO_2, and then crystallization at T_{c2}(120 °C) for 1 h under (a_2) air, (b_2) 2 MPa, (c_2) 4 MPa and (d_2) 6 MPa CO_2.