Crystallization of Polylactides Examined by Vibrational Circular Dichroism of Intra- and Inter-Chain Chiral Interactions

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Supporting information

1. Material preparation

Figure S1 Synthetic routes of PDLA by ring-opening polymerization using benzyl alcohol as an initiator.

Figure S2 ^{1}H NMR spectrum (500 MHz) of PDLA. The measurement was carried out using deuterated dichloromethane as a solvent at 25 ^{o}C.

Figure S3 GPC curve for PDLA synthesized through ring-opening polymerization; at which a sharp peak can be clearly identified but with a smaller hump appearing at shorter elution time. Yet, even with this dual population, the polydispersity is approximately 1.2, suggesting that the molecular weight distribution should be narrow enough with the least effect of polydispersity on crystallization.

2. Sample Preparation.

3. Crystallization α phase for PDLA

Figure S4 One-dimensional WAXD profiles of PDLA cold-crystallized at (a) 80 ℃; (b) 82.5 ℃; (c) 85 ℃; (d) 87.5 ℃, giving characteristic peaks for α phase occurred at reflections of 2θ around 14.9^{o}, 16.6^{o}, 18.9^{o}, 22.6^{o} that

correspond to the reflections planes of (010), (200)/(110), (203) and (210), respectively.

4. Time-resolved VCD analysis for relative crystallinity at various temperature

Figure S5 Time evolution of the VCD and corresponding FTIR absorption spectra of C=O stretching for PDLA cold-crystallized at (a) 80.0 ℃; (c) 82.5 ℃; (e) 85 ℃; (g) 87.5 ℃, and C-O-C vibrations at (b) 80.0 ℃; (d) 82.5 ℃; (f) 85 ℃; (h) 87.5 ℃.

5. DSC analysis for relative crystallinity at various temperature

Figure S6 DSC thermograms of exothermic curves for PDLA isothermally crystallized at (a), (b) 87.5 ºC; (c), (d) 85 ºC; (e), (f) 82.5 ºC; (g), (h) 80 ºC with first and second rounds of the measurements for the examination of the reproducible results.

6. Time-resolved FTIR and WAXD analysis for relative crystallinity at 80ºC

Figure S7 Time evolution of (a) FTIR absorption spectra in the region 770 - 970 cm^{-1} and (b) WAXD patterns of cold-crystallized PDLA at 80 °C.

7. FTIR deconvolution for the calculation of relative crystallinity at 80ºC

Figure S8 FTIR spectra for PDLA cold-crystallized at 80 ℃ for (a) 1 min, (b) 2 min, (c) 3 min, (d) 4 min, (e) 5 min, and (f) 6 min after curve fitting.

8. VCD analysis for relative crystallinity at various temperature

Figure S9 Time evolution of the amplitudes of split-type Cotton effect of C=O stretching and C-O-C vibrations in VCD corresponding to the variations of the intra-chain and inter-chain chiral interactions for PDLA cold-crystallized at (a) 82.5 ℃; (b) 85 ℃; (c) 87.5 ℃. The dash blue line in (a) and (b) shows the intrinsic signal for intra-chain chiral interactions before amplification by crystallization.

1. Material preparation

The molecular weight and polydispersity of the synthesized polylactides were determined by ^{1}H NMR (**Figure S2**) and GPC **(Figure S3)** analysis, respectively. **Figures S2** shows the ^{1}H-NMR spectra of PDLA with (500MHz, $CDCl_3$): δ = 7.30-7.40 (C, 5H, ArH), 5.15 (B, 1H, $CH(CH_3)$), 1.54 (A, 3H, $CH(CH_3)$, indicating the successful fabrication of aimed polymers. The molecular weight of PDLA were calculated to be 36000 g/mol based on the peak area ratio of peak B (repeating unit) and peak C (benzyl end group).

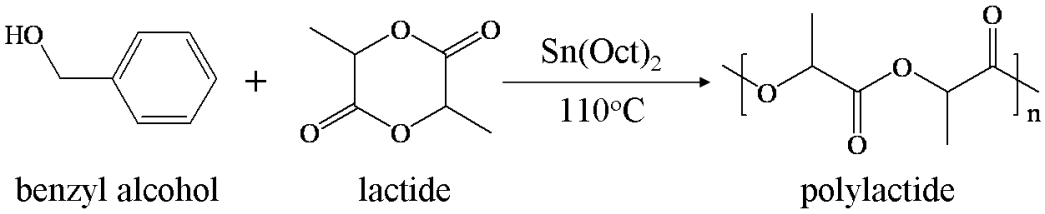

Figure S1. Synthetic routes of PDLA by ring-opening polymerization using benzyl alcohol as an initiator.

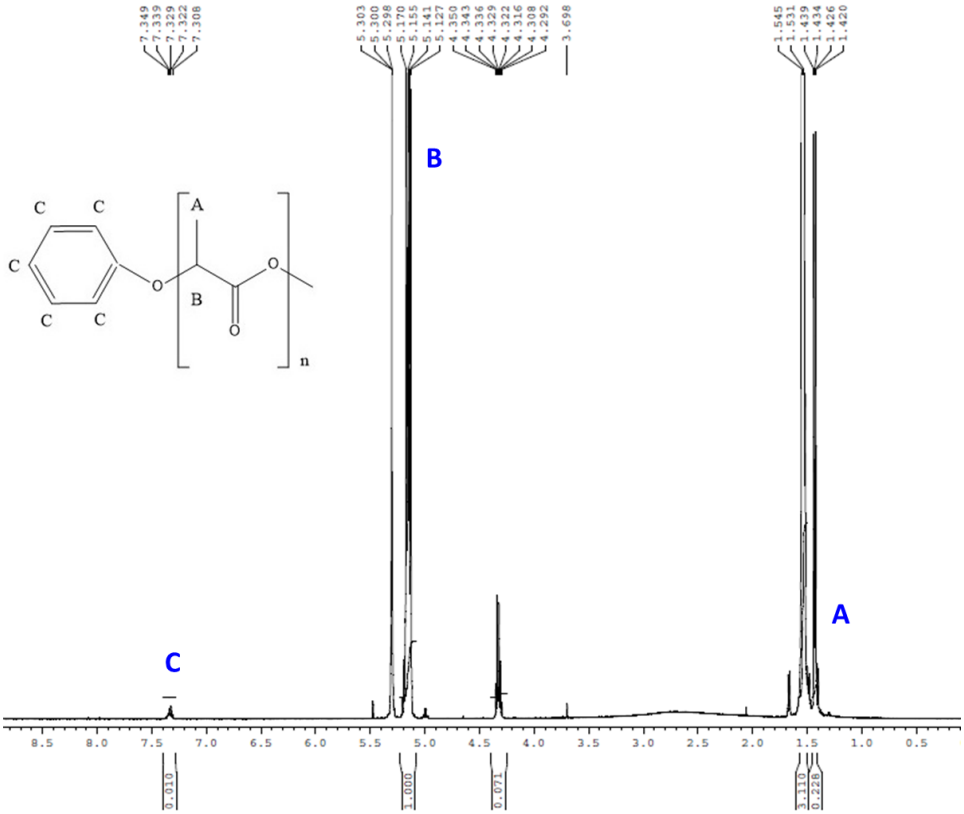

Figure S2. ^{1}H NMR spectrum (500 MHz) of PDLA. The measurement was carried out using deuterated dichloromethane as a solvent at 25 °C.

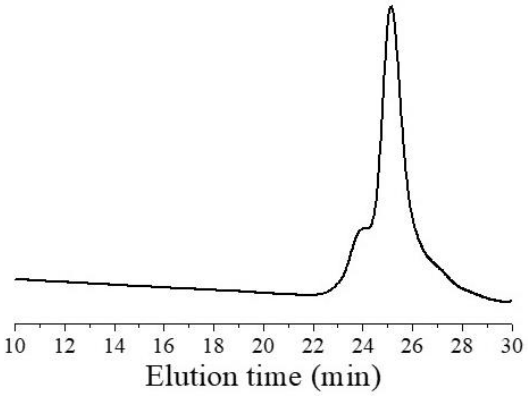

Figure S3. GPC curve for PDLA synthesized through ring-opening polymerization; at which a sharp peak can be clearly identified but with a smaller hump appearing at shorter elution time. Yet, even with this dual population, the polydispersity is approximately 1.2, suggesting that the molecular weight distribution should be narrow enough with the least effect of polydispersity on crystallization.

2. Sample preparation

PDLA samples are first melted at 200 °C in DSC under nitrogen atmosphere to erase the thermal history, and then rapidly cooled at 150 °C/min to room temperature to obtain the vitrified state. Such obtained vitrified samples were used for isothermal crystallization experiments at 80 °C, 82.5 °C, 85 °C, and 87.5 °C for systematic comparisons of the cold-crystallized PDLA using VCD, DSC, WAXD and FTIR.

3. Crystallization phase for PDLA

The crystallization behaviours for PLLA and PDLA are different. While the crystallization phase for PLLA is related to the crystallization temperature, giving a less ordered α-phase and an ordered α-phase at low and high crystallization temperature respectively, PDLA is consistently an ordered α-phase (**Figure S4**).

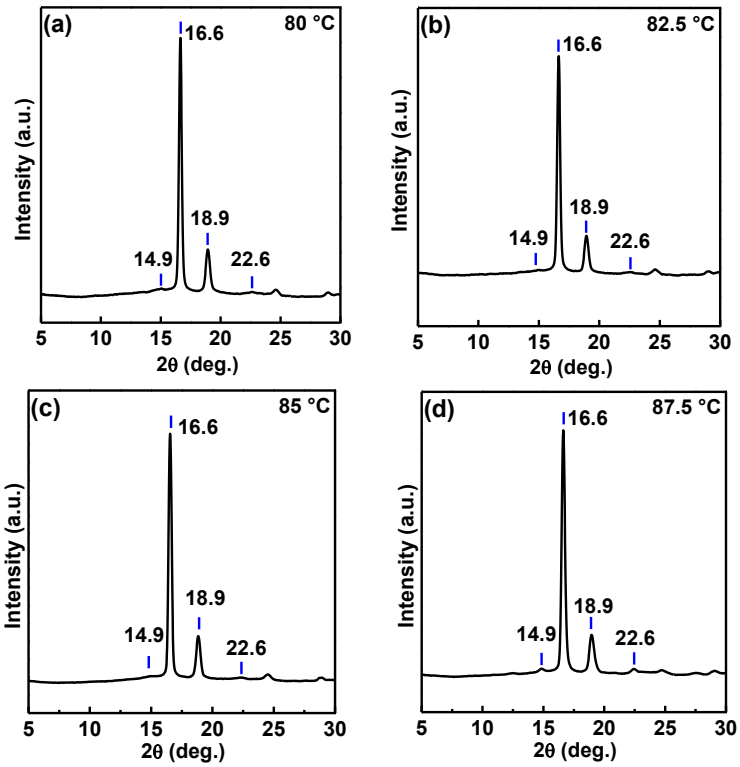

Figure S4. One-dimensional WAXD profiles of PDLA cold-crystallized at (a) 80 ℃; (b) 82.5 ℃; (c) 85 ℃; (d) 87.5 ℃, giving characteristic peaks for α phase occurred at reflections of 2θ around 14.9º, 16.6º, 18.9º, 22.6º that correspond to the reflections planes of (010), (200)/(110), (203) and (210), respectively.

4. Time-resolved VCD analysis for relative crystallinity at various temperature

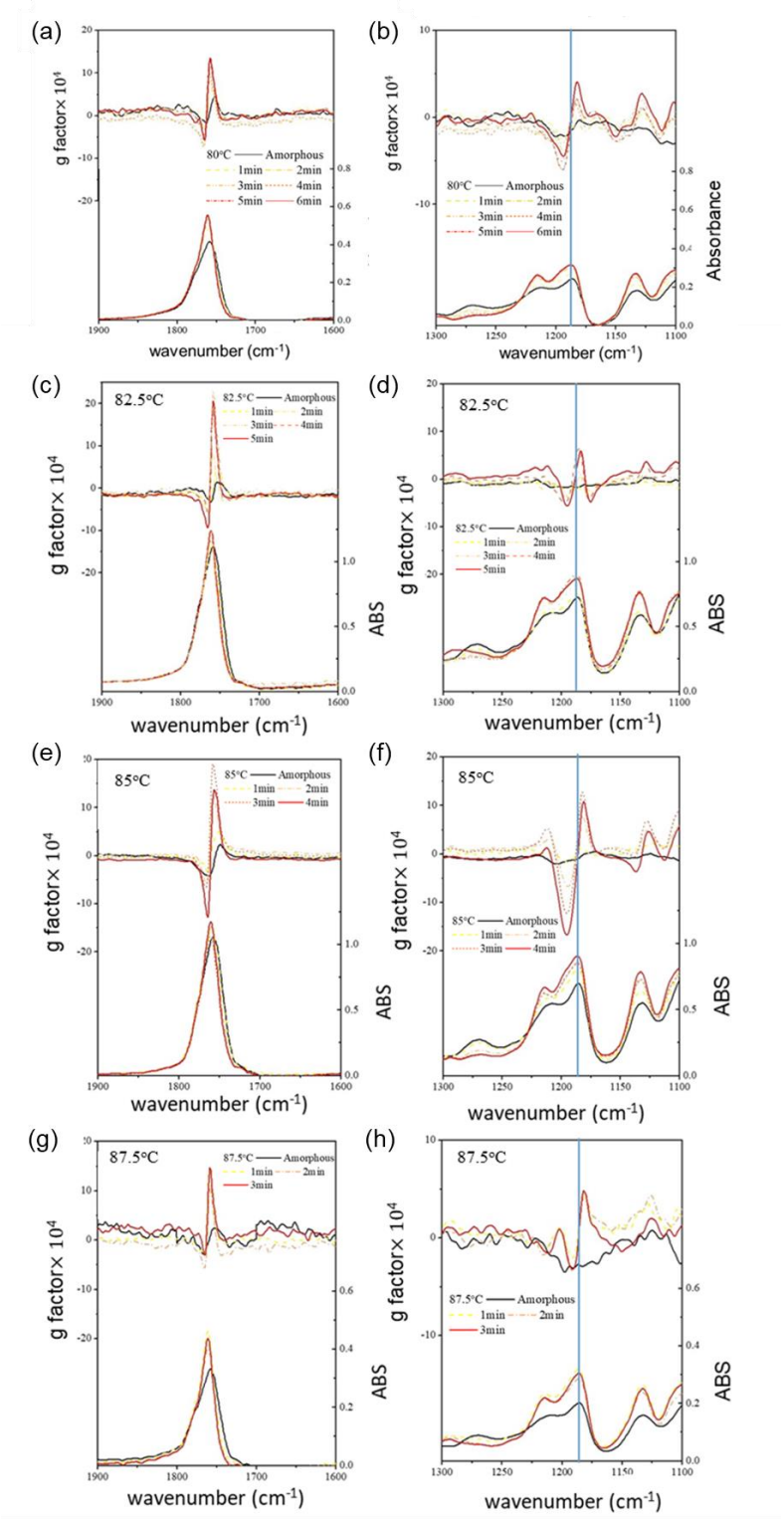

Figure S5. Time evolution of the VCD and corresponding FTIR absorption spectra of C=O stretching for PDLA cold-crystallized at (a) 80.0 ℃; (c) 82.5 ℃; (e) 85 ℃; (g) 87.5 ℃, and C-O-C vibrations at (b) 80.0 ℃; (d) 82.5 ℃; (f) 85 ℃; (h) 87.5 ℃.

5. DSC analysis for relative crystallinity at various temperature

For systematic comparisons of the cold-crystallized PDLA, isothermal crystallization experiments were carried out at 80 ℃, 82.5 ℃, 85 ℃, and 87.5 ℃ from vitrified state; note that the maximum crystallization temperature is approximately at 110 ℃. Also, the enthalpy responses of aimed crystallization event traced by DSC will not be able to be clearly resolved once the crystallization temperature is over 87.5 ℃ due to the fast crystallization rate whilst the crystallization might not be occurred at lower crystallization temperature.

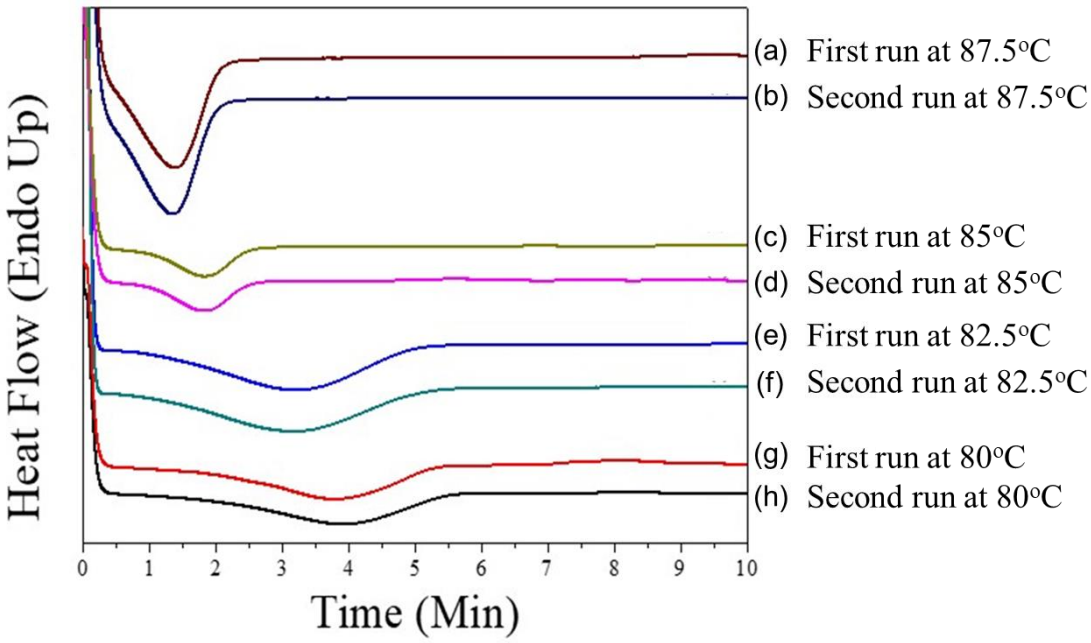

Figure S6. DSC thermogram of exothermic curves for PDLA isothermally crystallized at (a), (b) 87.5 ºC; (c), (d) 85 ºC; (e), (f) 82.5 ºC; (g), (h) 80ºC with first and second rounds of the measurements for the examination of the reproducible results.

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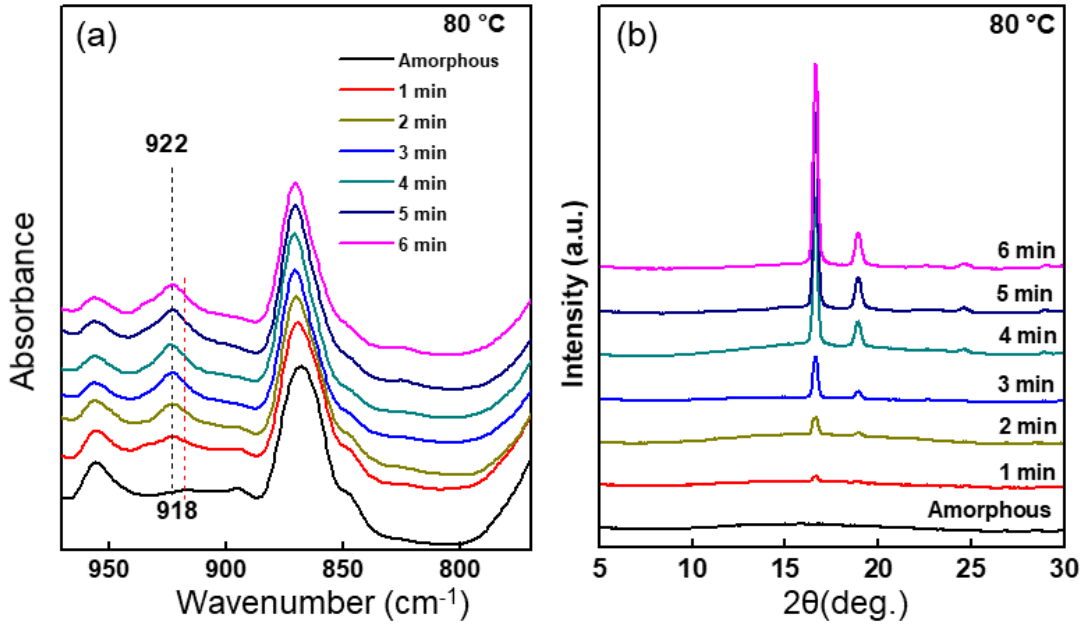
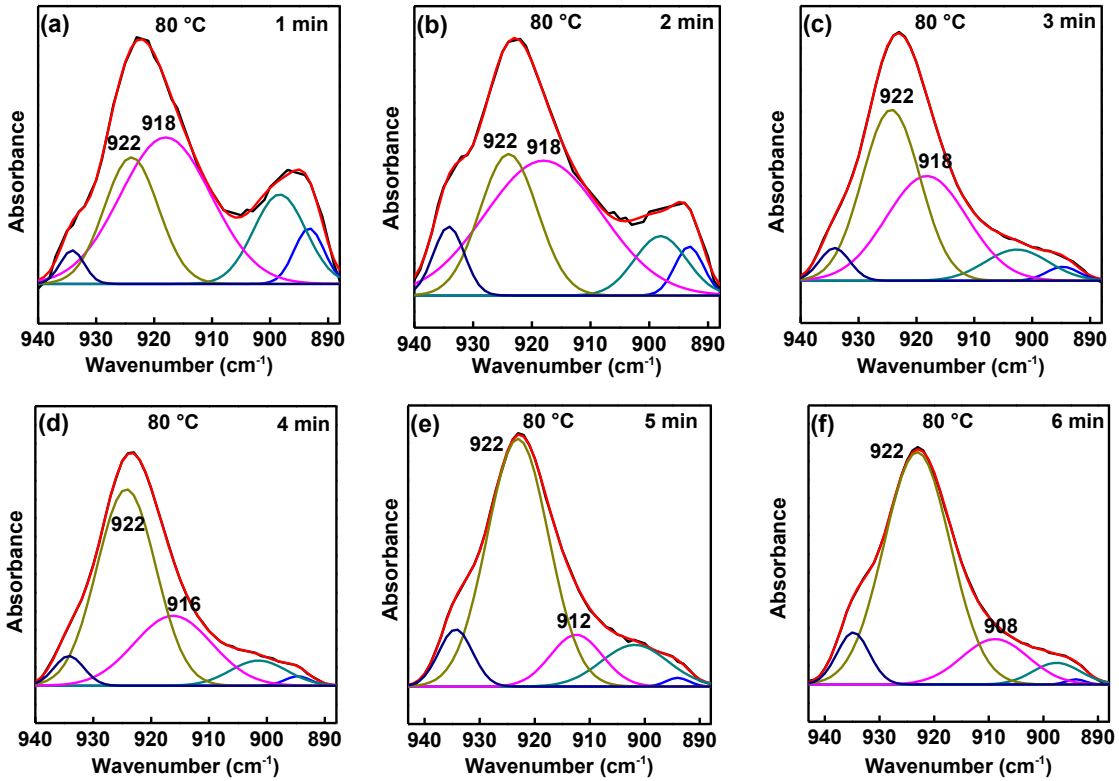


Figure S7. Time evolution of (a) FTIR absorption spectra in the region 770 - 970 cm^{-1} and (b) WAXD patterns of cold-crystallized PDLA at 80 °C.

7. FTIR deconvolution for the calculation of relative crystallinity at 80oC

The FTIR absorption region from 890 to 940 cm^{-1} is sensitive to the structural regularization process; note that the bands in this region are attributed to the backbone stretching coupled with $–CH_3$ rocking. FTIR spectra of cold-crystallized PDLA at 80 °C was deconvoulated using the Grams software. A FTIR band at 918 cm^{-1} is required to fit the data properly for the samples crystallized within 4 minutes. The coexistence of band 918 cm^{-1} along with the 922 cm^{-1} band can be evidenced by the FTIR analysis for crystallization within 4 minutes, indicating the presence of both partially ordered texture from helical aggregation and crystalline phase. The relative crystallinity was calculated by the normalized integrated absorbance of 922 cm^{-1} band.



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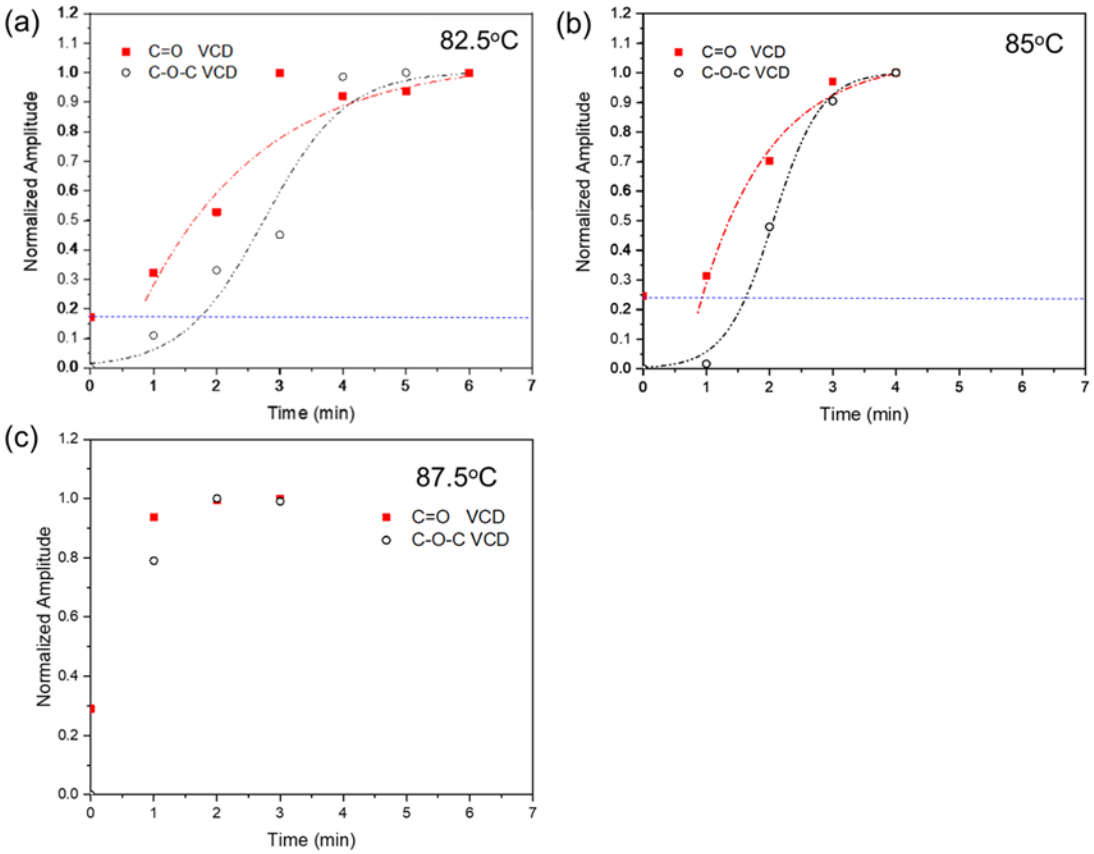
8. VCD analysis for relative crystallinity at various temperature



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