

Supporting information for

**Tuning Polymorphism, Molecular Orientation and Crystallinity in
P(NDI2OD-T2) Thin Films Informed by Hansen Solubility Analysis**

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Table S1. Hansen solubility parameters of P(NDI2OD-T2), side chain, and backbone of P(NDI2OD-T2) and of four solvents.^{1,2}

| | δ_D (MPa ^{1/2}) | δ_P (MPa ^{1/2}) | δ_H (MPa ^{1/2}) |
|-------------------------|----------------------------------|----------------------------------|----------------------------------|
| P(NDI2OD-T2) | 18.0 | 2.2 | 3.5 |
| P(NDI2OD-T2) side chain | 15.9 | 0.1 | 0.1 |
| P(NDI2OD-T2) backbone | 23.0 | 5.1 | 7.1 |
| CF | 17.8 | 3.1 | 5.7 |
| CB | 19 | 4.3 | 2 |
| MeTHF | 16.9 | 5 | 4.3 |
| CN | 20.5 | 4.8 | 2.5 |

Table S2. Crystallographic and optical fingerprints of P(NDI2OD-T2) polymorphs identified from GIWAXS and UV-vis.

| Features | Face-on form I- α | Face-on form I- β | Edge-on form II | End-on form III | End-on form I |
|-----------------------|-----------------------------|--------------------------------------|--------------------------------------|---------------------------------------|---|
| GIWAXS: Lamellar | $\chi = 90^\circ$ | $\chi = 90^\circ$ | $\chi = 0^\circ$ | Tilted lamellar $\approx 70-74^\circ$ | Tilted lamellar |
| GIWAXS: π - π | Arcing of π - π | Streak of π - π | No clear of π - π | No clear of π - π | No clear of π - π |
| GIWAXS: Backbone | $\chi = 0^\circ$ | $\chi = 0^\circ$ | $\chi = 0^\circ$ | $\chi = 90^\circ$ | Tilted backbone |
| GIWAXS: Registry | Backbone and π - π | Lamellar and π - π | Lamellar and backbone | Lamellar and backbone | - |
| UV-vis | Single broad peak at 700 nm | Two shoulders peak at 650 and 700 nm | Two shoulders peak at 650 and 700 nm | Two shoulders peak at 650 and 700 nm | Single broad peak at 700 nm with lower oscillation strength |

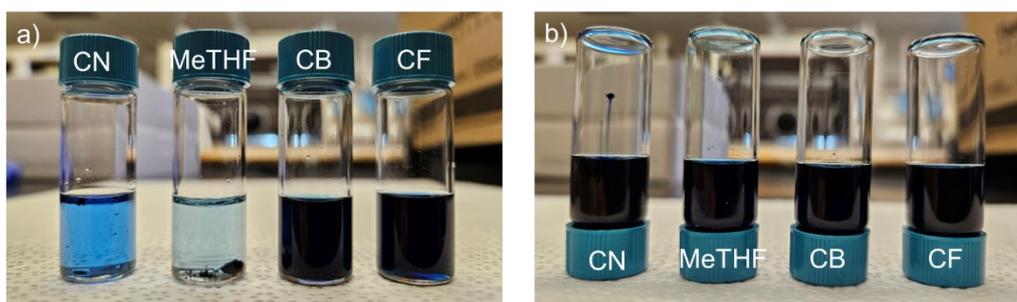


Figure S1. Solubility test of 1mg/mL P(NDI2OD-T2) solutions in different solvents: a) all solvents at room temperature. b) 130 °C in CN solvent, 100 °C in MeTHF solvent, and room temperature in CB and CF solvents.

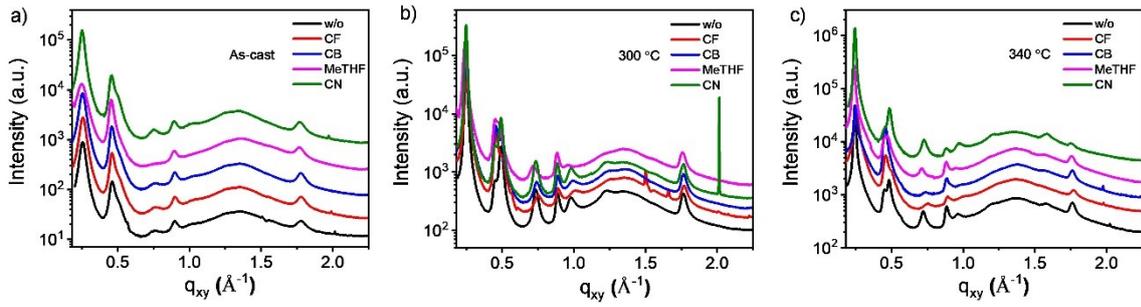


Figure S2. 1D line profiles of films without and with SVA along the IP direction a) as-cast films, b) 300 °C films, c) 340 °C films.

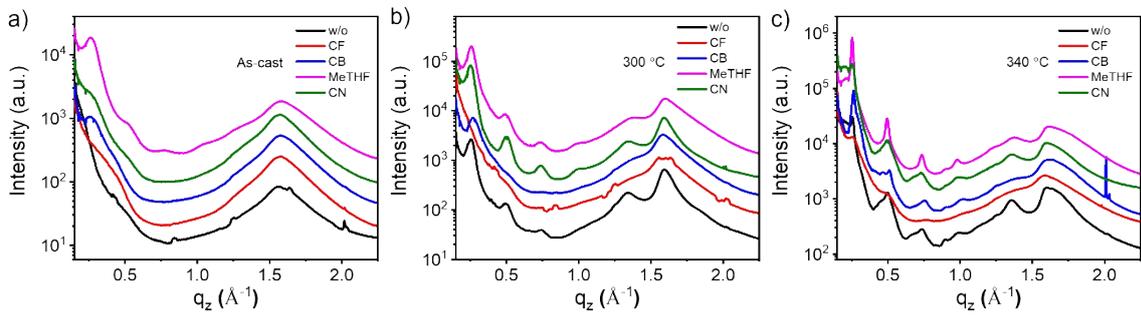


Figure S3. 1D line profiles along OOP direction of films without and with SVA: a) as-cast films + SVA, b) 300 °C films + SVA, c) 340 °C films + SVA.

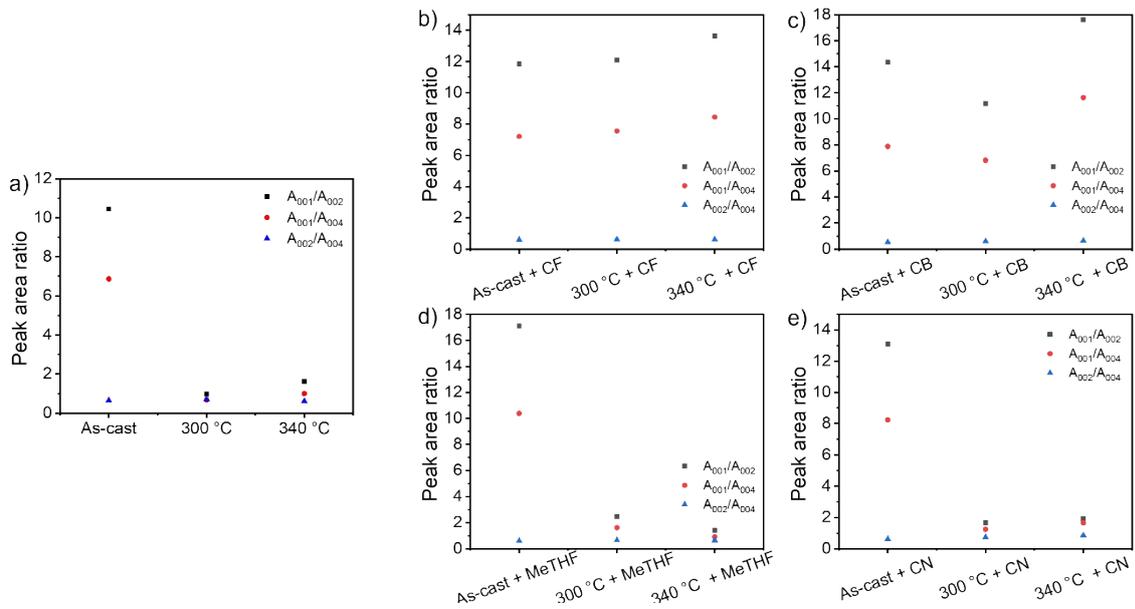


Figure S4. Peak area ratio quantification for P(NDI2OD-T2) films under TA and TA + SVA treatments.

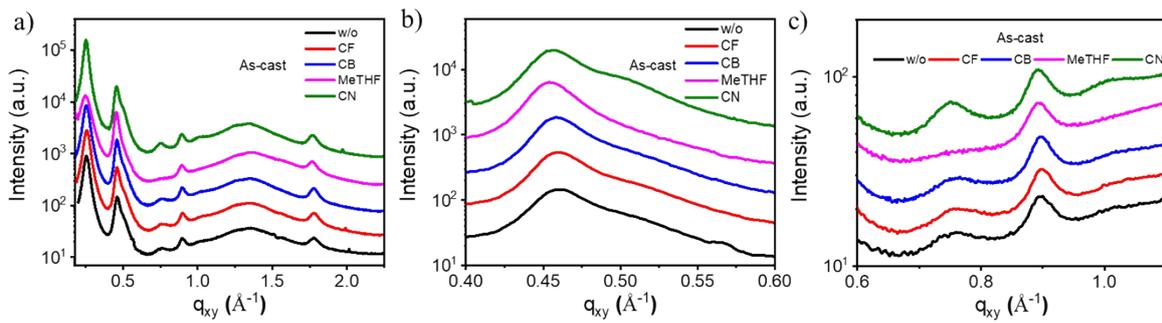


Figure S5. 1D line profiles along IP direction extracted for as-cast P(NDI2OD-T2) films under SVA treatment: a) full region; b) selected region at composite of (200) and (001) peaks; c) selected region at (300) and (002) peaks.

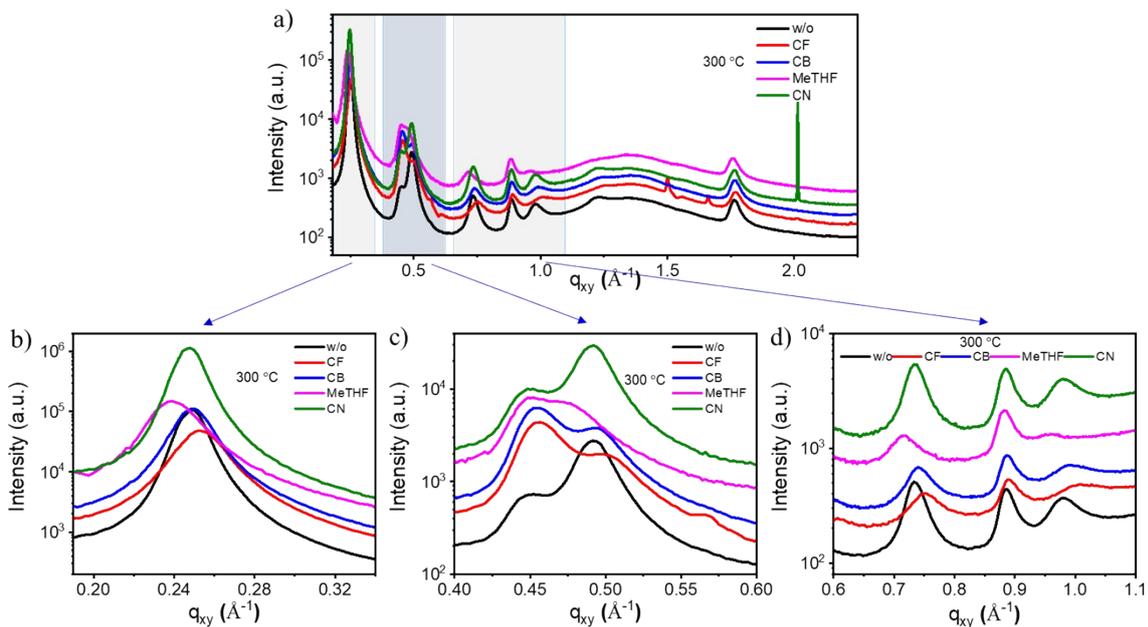


Figure S6. 1D line profiles along IP direction extracted for 300 °C P(NDI2OD-T2) films under SVA treatment: a) full region; b) selected region at (100) peak; c) selected region at composite of (200) and (001) peaks; d) selected region at (300) and (002) peaks.

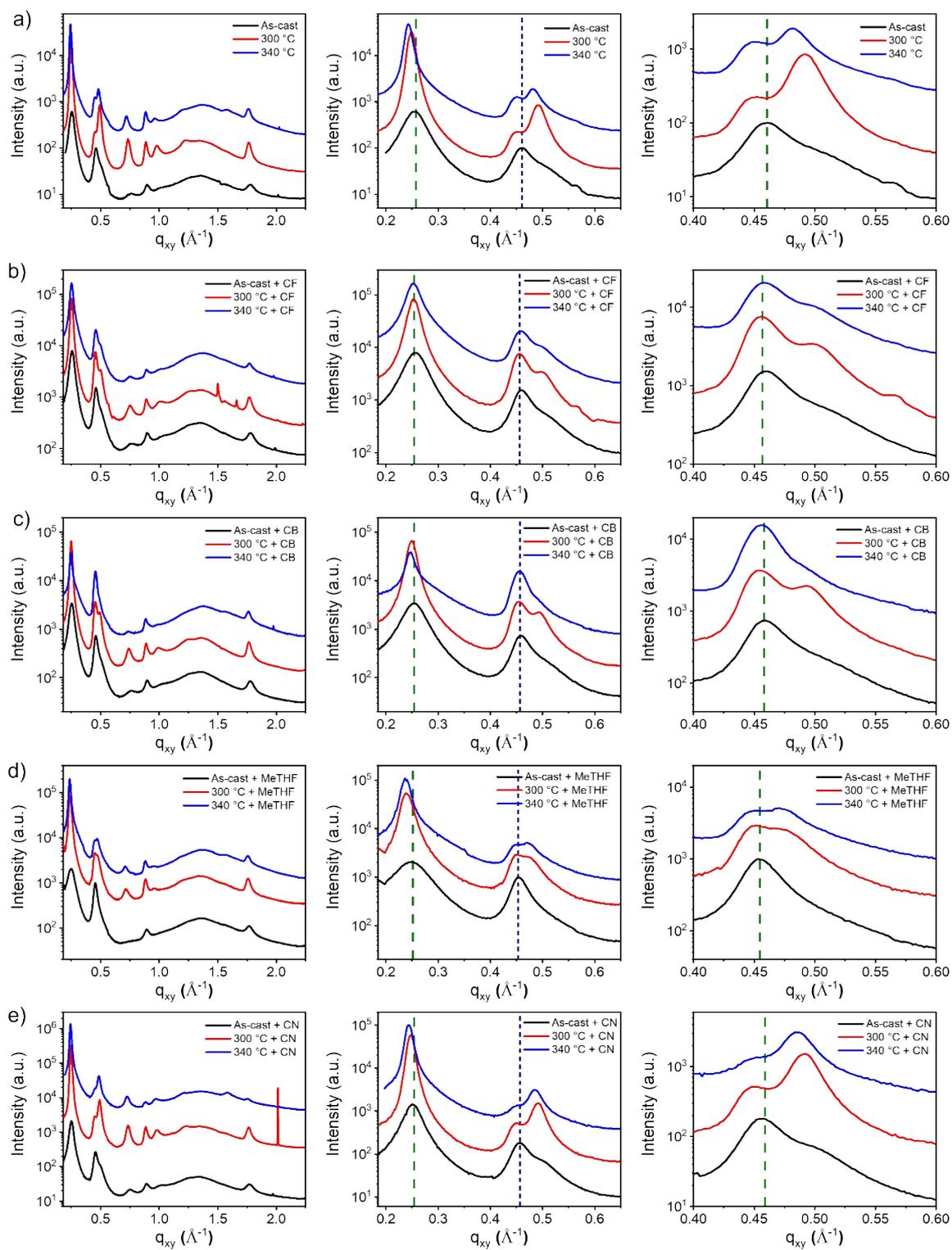


Figure S7. Full region and selected region of 1D line profiles along IP direction for: a) TA only films, b) TA + CF films, c) TA + CB films, d) TA + MeTHF films, e) TA + CN films.

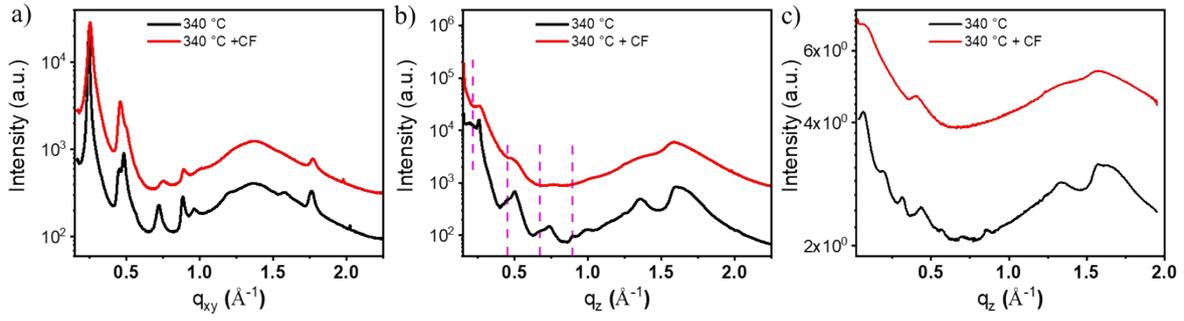


Figure S8. Comparison of 1D line profiles between 340 and 340 + CF: a-c) along IP direction, OOP direction and along $q_{xy} = 0.24 \text{ \AA}^{-1}$, respectively.

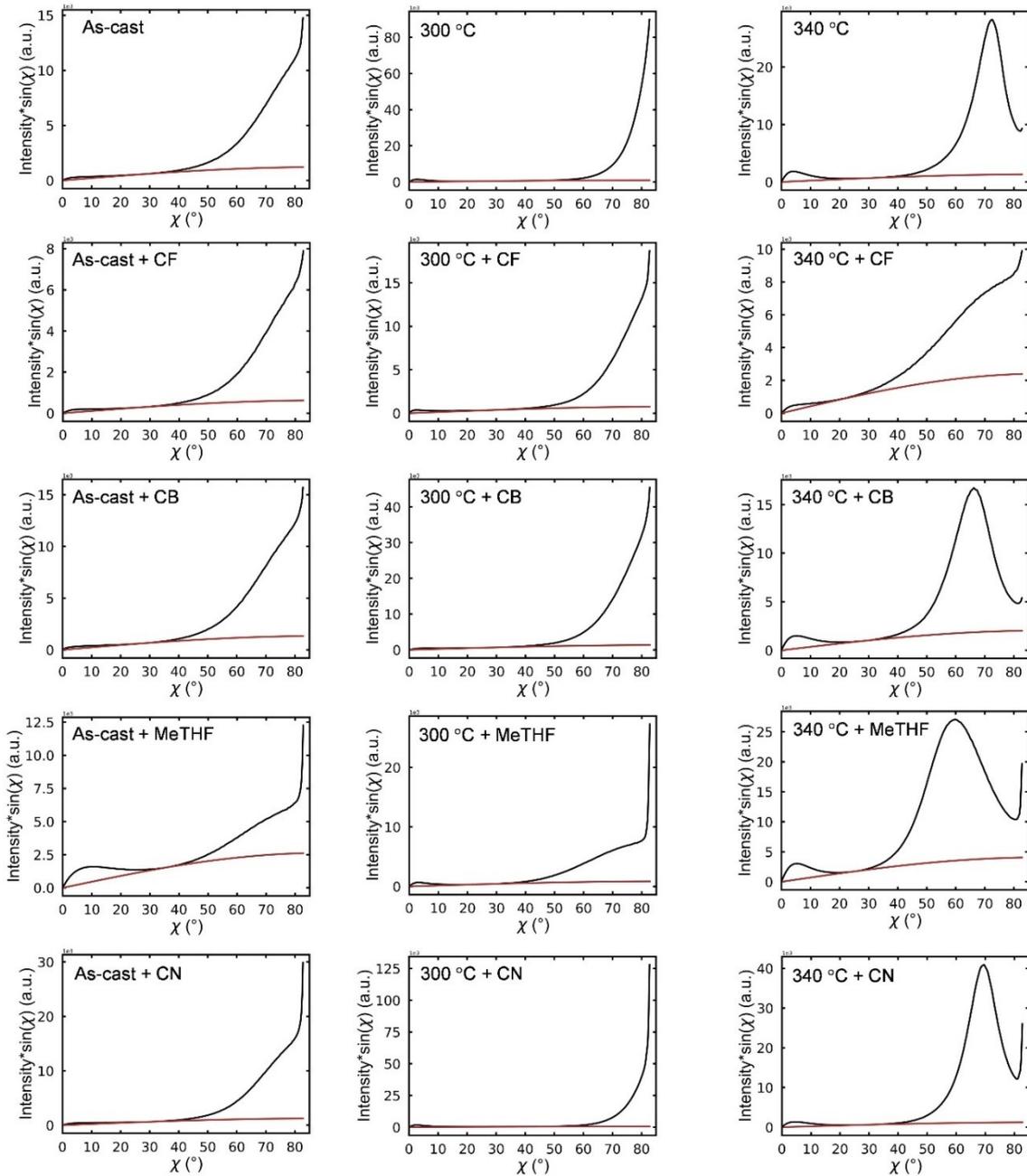


Figure S9. Corrected intensity pole figures for TA and TA + SVAs films.

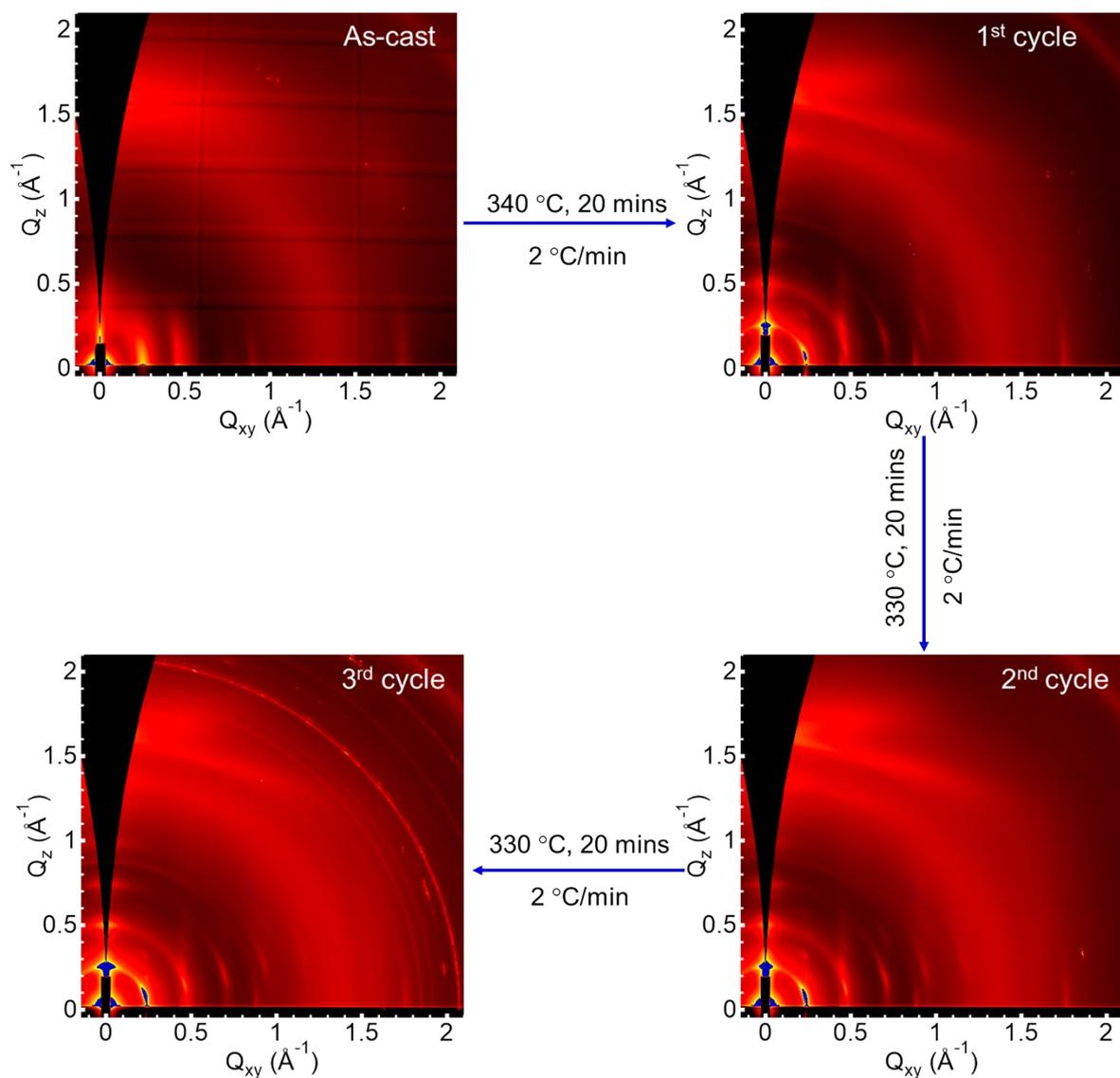


Figure S10. Thermal stability of end-on oriented form III after two thermal cycles of melting-annealing followed by slow cooling.

References

- 1 Zhao, K.; Zhang, Q.; Chen, L.; Zhang, T.; Han, Y. Nucleation and Growth of P(NDI2OD-T2) Nanowires via Side Chain Ordering and Backbone Planarization. *Macromolecules* 2021, **54**, 2143-2154.
- 2 Sung, Y.; Lee, W.; Lee, H.; Lee, J.-W.; Kim, B. J.; Yoo, S.; Jeong, S.; Kim, J.; Lee, J.-Y. Nanostructured Molecular Packing of Polymer Films Formed on Water Surfaces. *Nano Lett.* 2024, **24**, 7474-7482.