

SUPPORTING INFORMATION

The Role of Solvent Additive on Polymer Crystallinity During Supercritical Fluid Deposition

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1. Critical Properties for the n-pentane:acetone System

Figure S1 is constructed based on the available critical data for the n-pentane:acetone system.¹ As acetone concentration increases, the critical temperature and pressure increases, reaching $T_C = 507.6$ K and $P_C = 4.67$ MPa for the system containing only acetone.

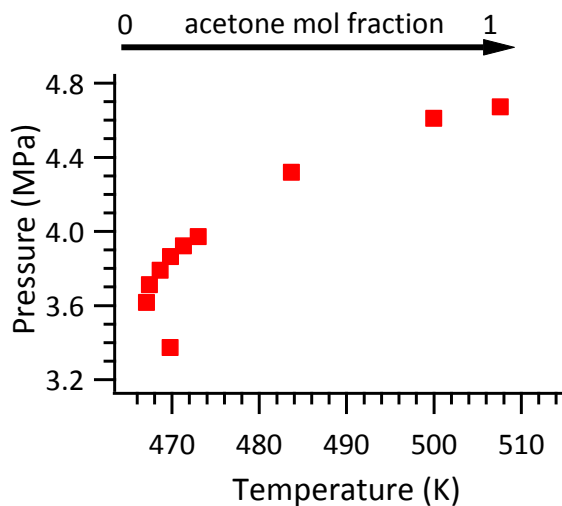


Figure S1. Critical coordinates of n-pentane:acetone solutions as a function of mole fraction of acetone.

2. Grazing Incidence Wide Angle X-Ray Scattering Results

Figure S2 displays the observed scattering pattern from films grown at several different pressures from n-pentane:acetone solutions. The GIWAXS patterns are consistent with the α -form of *i*PP for all samples. Specifically, the diagnostic peaks of the α -form, $(110)_\alpha$, $(130)_\alpha$, $(040)_\alpha$, $(111)_\alpha$, $(131)_\alpha$, and $(041)_\alpha$ are observed.²⁻⁴ Moreover, the intensity of the diagnostic peaks decreases for all *i*PP films as the pressure is increased.

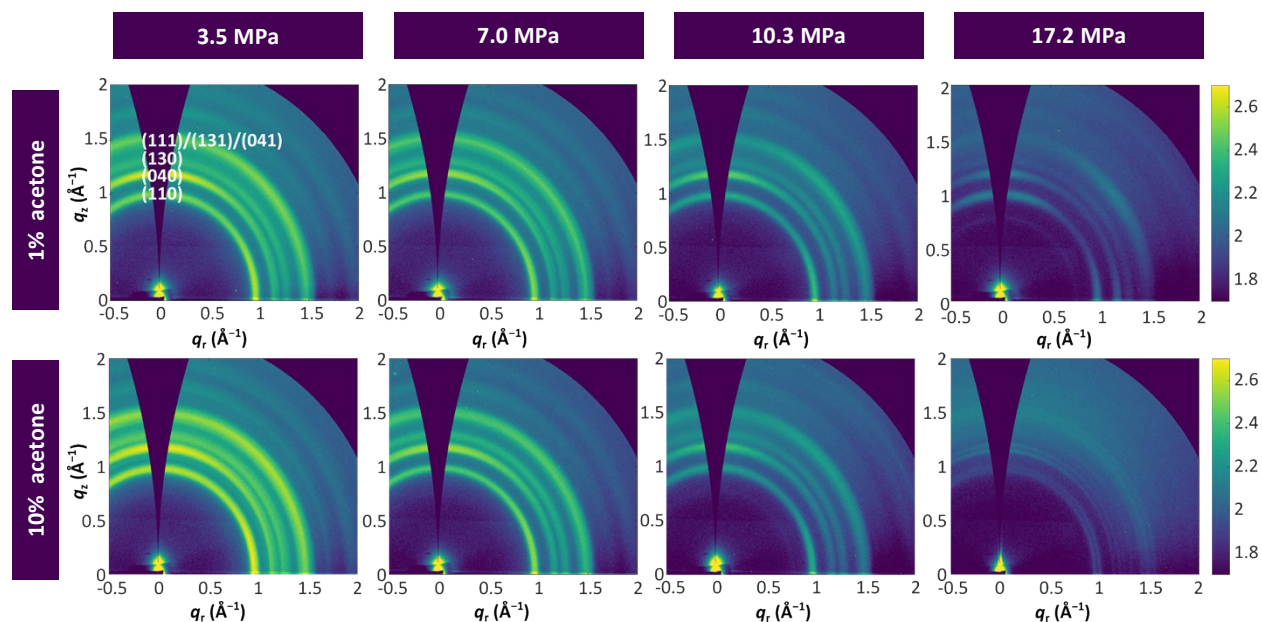


Figure S2. GIWAXS patterns of *i*PP films grown in pressurized n-pentane:acetone solutions at different pressures. Intensity is plotted on a log scale.

3. Molecular Weight Measurement via High-temperature Size Exclusion Chromatography

The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of as-received *i*PP sample was compared with *i*PP samples collected via gravimetric analysis from supercritical n-pentane:acetone solutions. The molecular weight measurements were performed via size exclusion chromatography (SEC) and the results are provided in Table S.1. Based on the results, there is no consistent trend between *i*PP films crystallinity degree and polymer molecular weight.

Table S.1. The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) of as-received *i*PP sample and *i*PP samples collected via gravimetric analysis from supercritical n-pentane:acetone solutions at 418 K (423 K in case of n-pentane:acetone) at different pressures via size exclusion chromatography.

| Sample | M_n (kDa) | M_w (kDa) | PDI |
|--|-------------|-------------|-----|
| <i>i</i>PP, as received | 120 | 4,730 | 39 |
| <i>i</i>PP in n-pentane, 3.5 MPa | 130 | 6,410 | 49 |
| <i>i</i>PP in n-pentane, 7.0 MPa | 137 | 7,610 | 55 |
| <i>i</i>PP in n-pentane, 10.3 MPa | 131 | 7,000 | 53 |
| <i>i</i>PP in n-pentane, 17.2 MPa | 134 | 6,090 | 45 |
| <i>i</i>PP in n-pentane + 1% acetone, 10.3 MPa | 127 | 5,307 | 42 |
| <i>i</i>PP in n-pentane + 10% acetone, 10.3 MPa | 140 | 4,950 | 35 |

4. Polarized Optical Microscopy Image of iPP Film

Figure S3 displays a POM image of an *i*PP films grown at 10.3 MPa. The ring-like structures observed in this image are observed in all films grown at high pressures. We interpret them as reflective of Rayleigh-Bénard convection cells present in the fluid during deposition. The estimated Rayleigh number is $\sim 10^{11}$ indicating that the flow regime is turbulent, in agreement with our interpretation of ring-like morphologies.

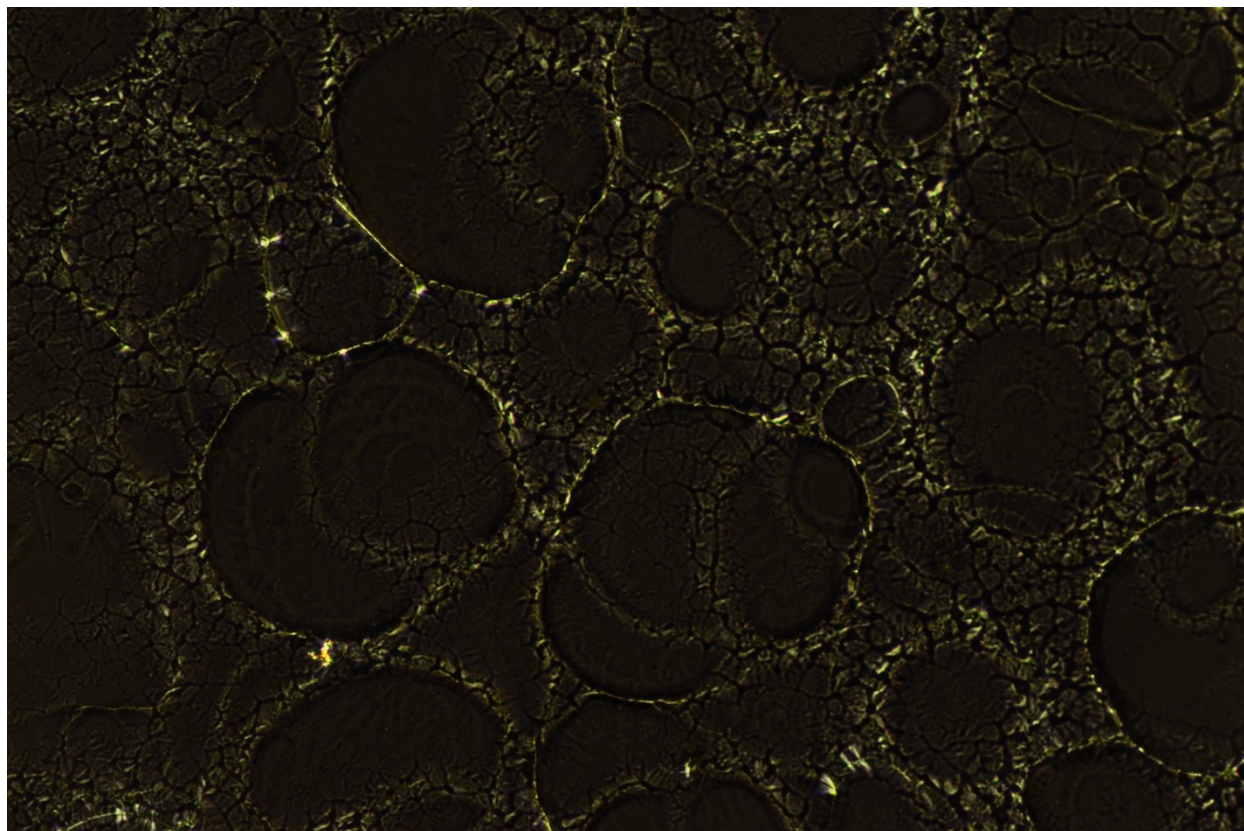


Figure S3. Polarized optical microscopy image (x10) of *i*PP film grown in supercritical n-pentane at 10.3 MPa in the presence of 10% acetone.

5. References

1. Hajjar, R. F.; Cherry, R. H.; Kay, W. B., Critical properties of the vapor—liquid equilibria of the binary system acetone—n-pentane. *Fluid Phase Equilibria* **1986**, 25 (2), 137-146.
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