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Supporting Information

Revealing Temperature-Dependent Polymer Aggregation in Solution with Small-Angle X-ray Scattering

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1. Figures

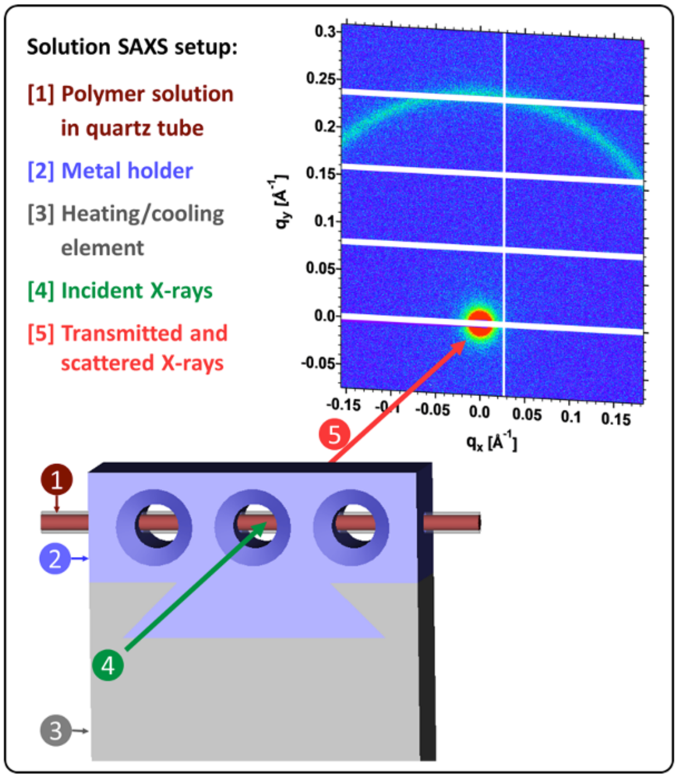

Figure S1 Schematic representation of solution SAXS setup. The setup allows performing SAXS measurements at three-different fresh slots to avoid beam damage.

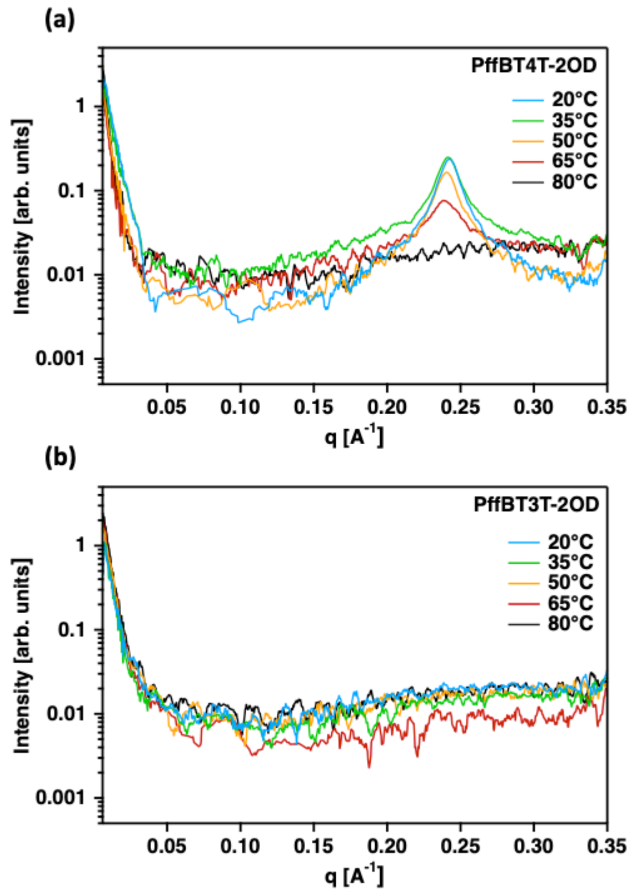

Figure S2 Background-subtracted solution small-angle X-ray scattering (SAXS) profiles for PffBT4T-2OD and PffBT3T-2OD in a solvent mixture of oDCB: CB [1:1] at different temperatures in (a) and (b), respectively. At $q > 0.02$Å^{-1} intensity values were smoothed with 10 point moving average to reduce the noise.

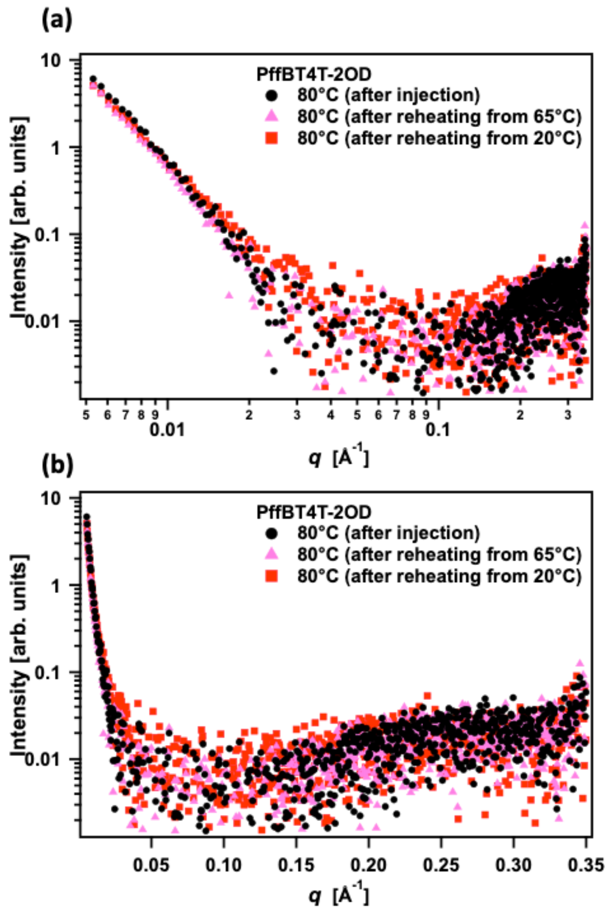

Figure S3 Background-subtracted solution small-angle X-ray scattering (SAXS) profiles for PffBT4T-2OD in a solvent mixture of oDCB: CB [1:1] at 80 ^{o}C after injection (black) and after reheating from RT (red); (a) log-log plot, and (b) log-linear plot.

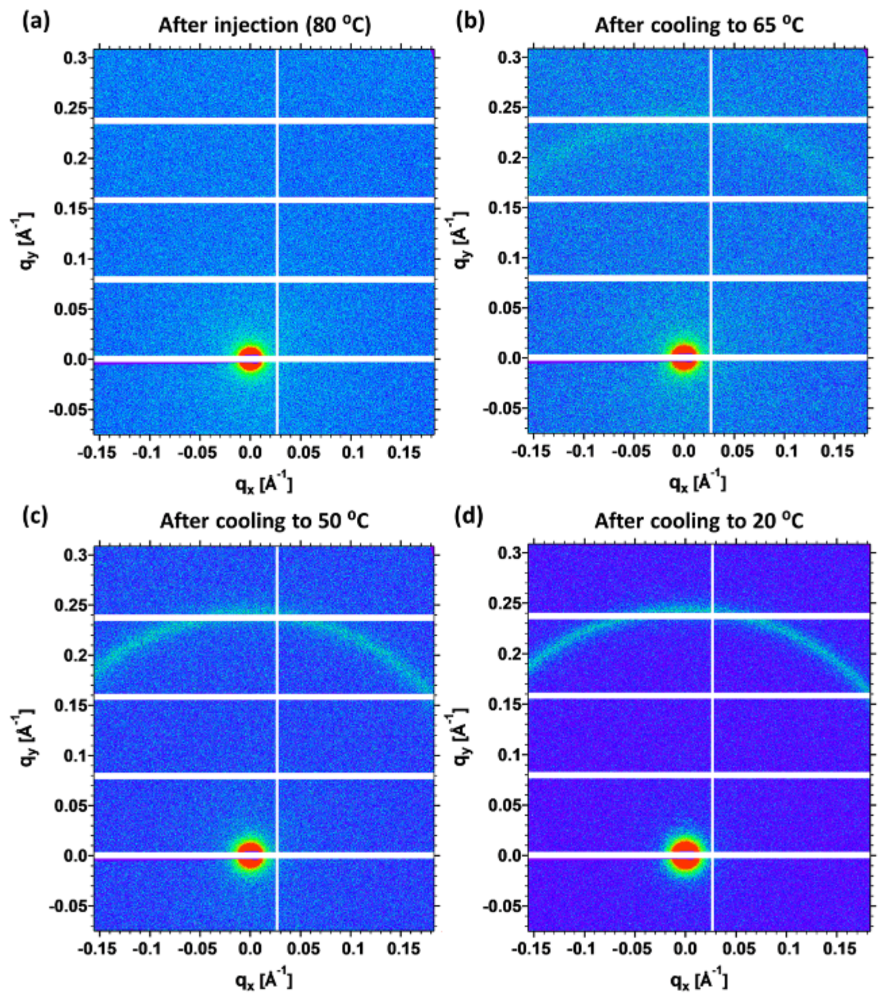

Figure S4 Solution small-angle X-ray scattering (SAXS) images for PffBT4T-2OD solution in a solvent mixture of 1,2-Dichlorobenzene (oDCB): Chlorobenzene (CB) [1:1] at different temperatures; (a) 80 ^{o}C, (b) 65 ^{o}C, (c) 50 ^{o}C, and (d) 20 ^{o}C. The solution was injected into capillary at 80 ^{o}C and cooled down to 20 ^{o}C with data acquired during cooling.

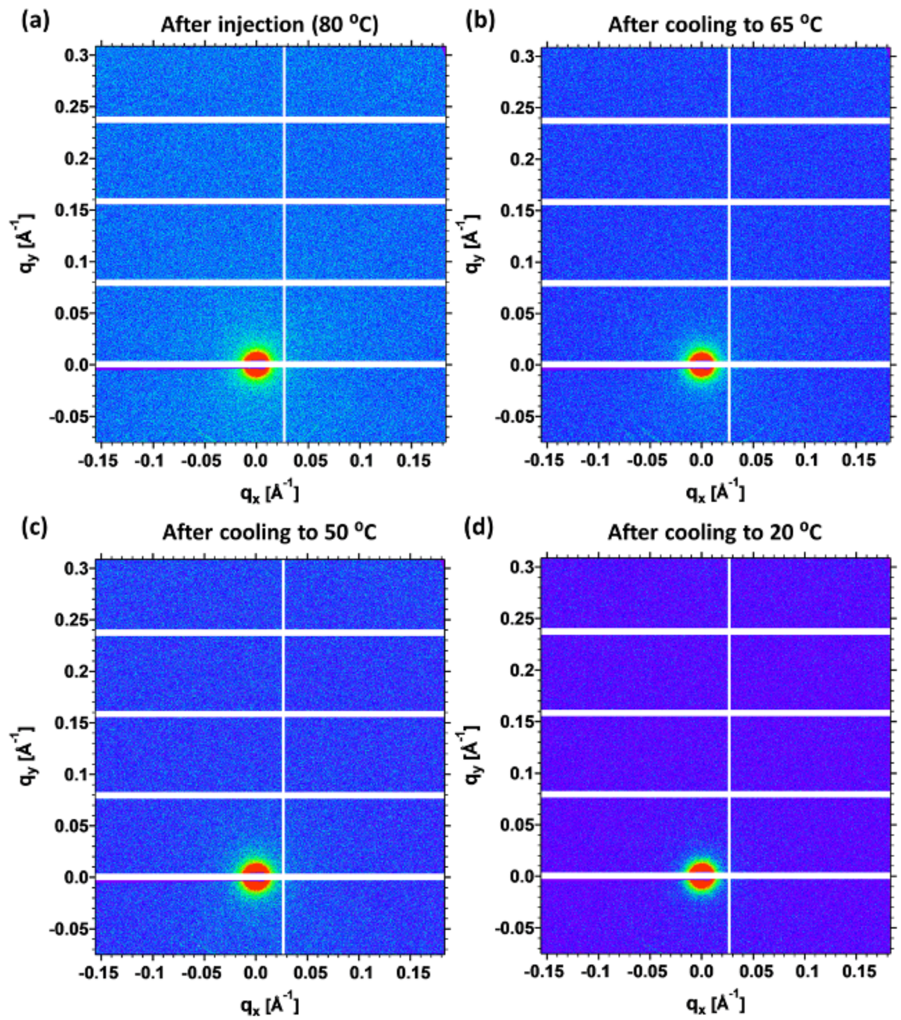

Figure S5 Solution small-angle X-ray scattering (SAXS) images for PffBT3T-2OD solution in a solvent mixture of oDCB: CB [1:1] at different temperatures; (a) 80 ^{o}C, (b) 65 ^{o}C, (c) 50 ^{o}C, and (d) 20 ^{o}C. The solution was injected into capillary tube at 80 ^{o}C and cooled down to 20 ^{o}C with data acquired during cooling.

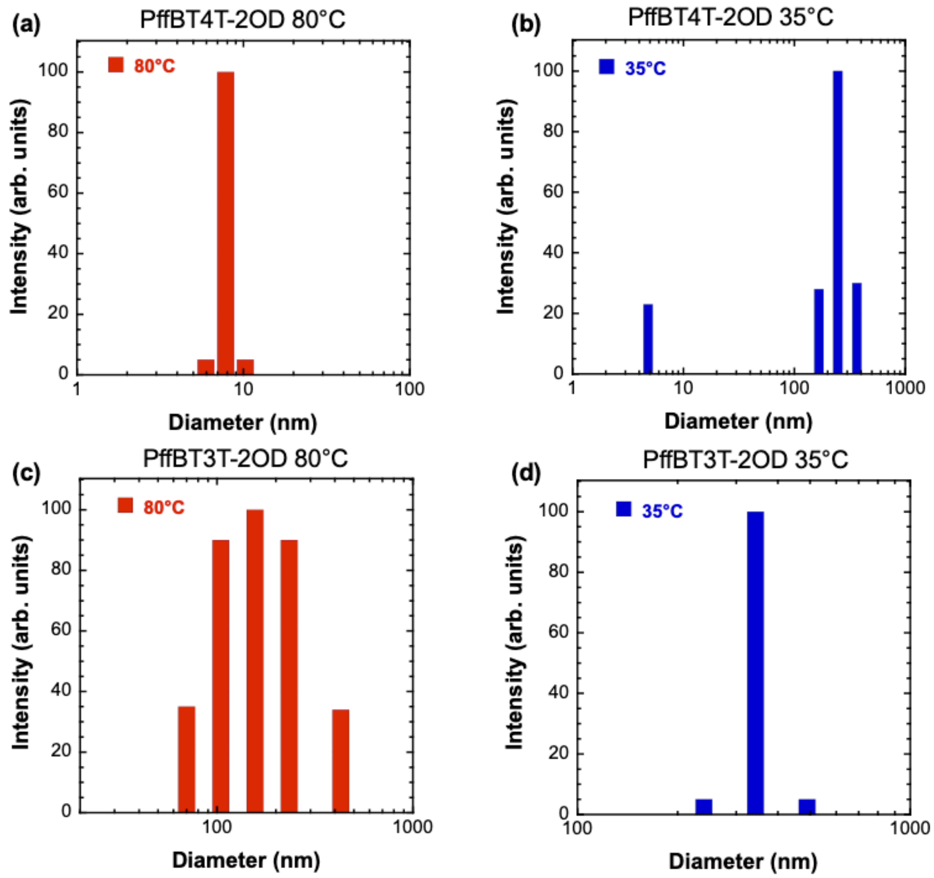

Figure S6 Particle size distribution histograms from DLS measurements for PffBT4T-2OD (a-b) and PffBT3T-2OD (c-d) at 80 °C and 35 °C.

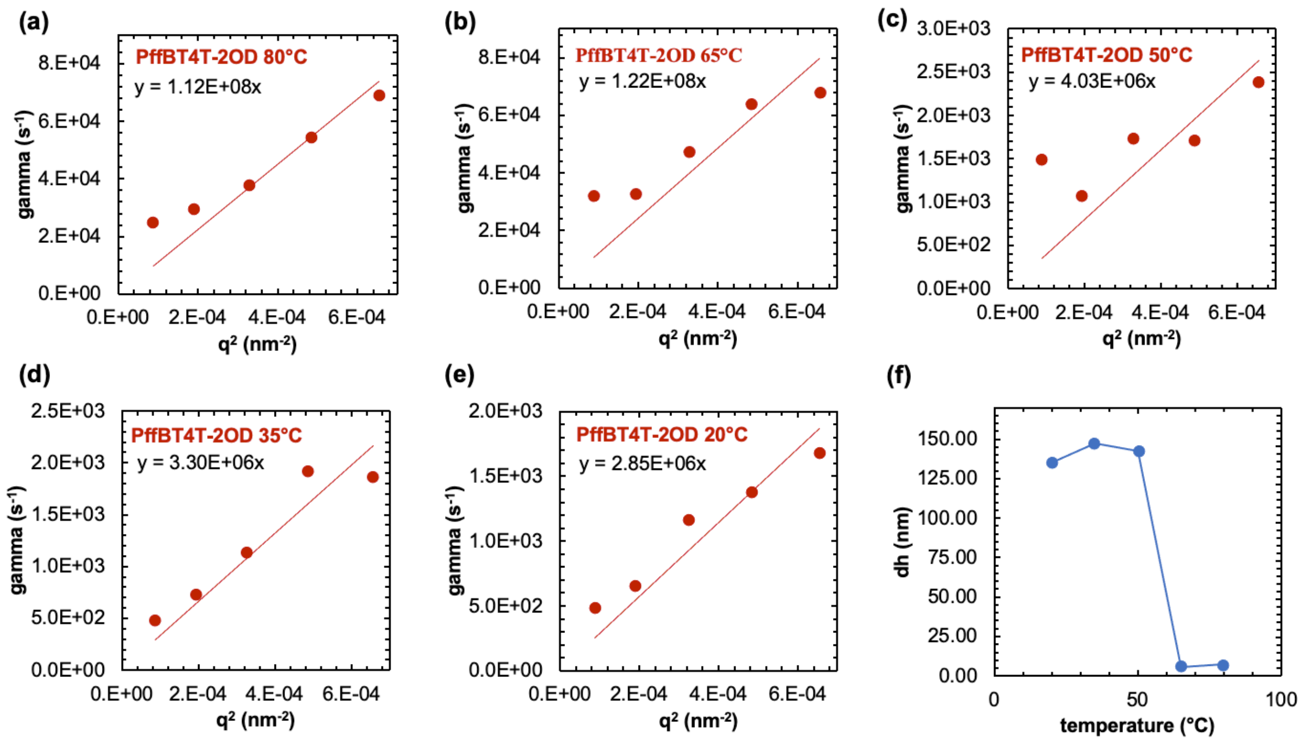

Figure S7 (a-e) Plots of the dominant Gamma value against the scattering vector squared from DLS measurements of PffBT4T-2OD polymer solution as it was cooled. (f) shows the resulting hydrodynamic diameters calculated with stokes Einstein relationship using the translational diffusion coefficient gained from linear regression analysis of Gamma vs q^{2-}.

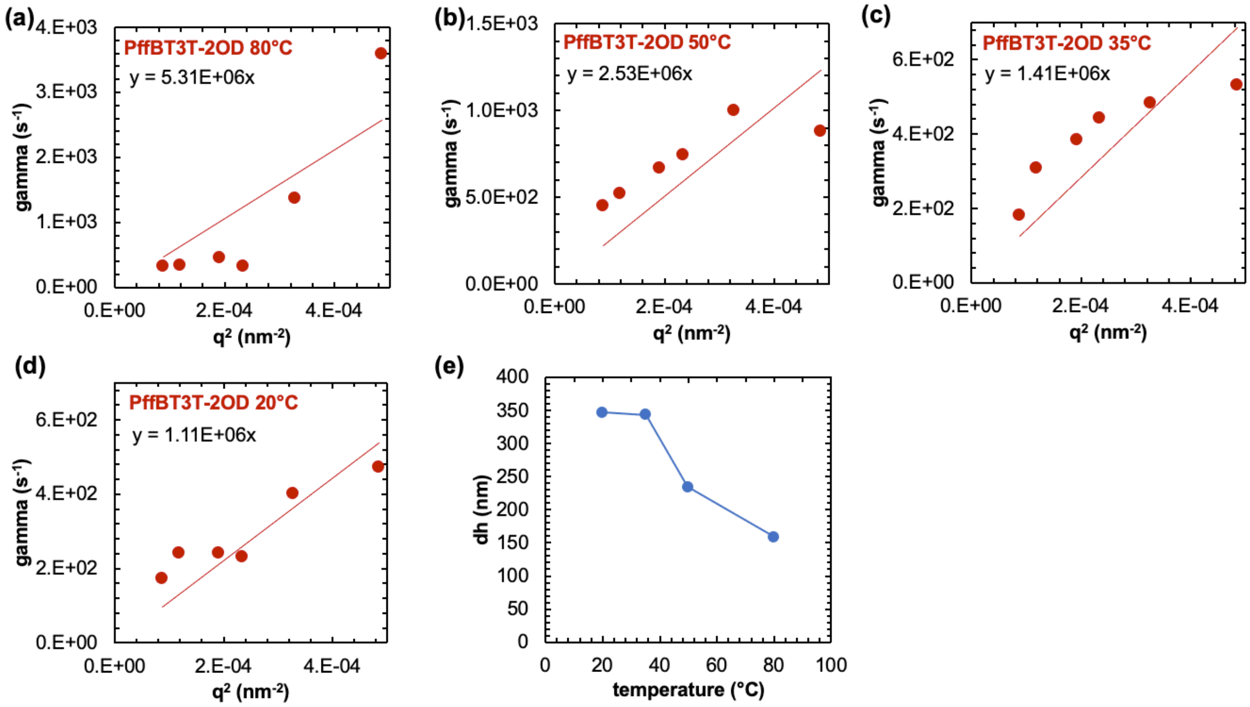

Figure S8 (a-d) Plots of the dominant Gamma value against the scattering vector squared from DLS measurements of PffBT3T-2OD polymer solution as it was cooled. The 65 °C dataset was omitted due to measurement error. (e) shows the resulting hydrodynamic diameters calculated with stokes Einstein relationship using the translational diffusion coefficient gained from linear regression analysis of Gamma vs q^{2-}.

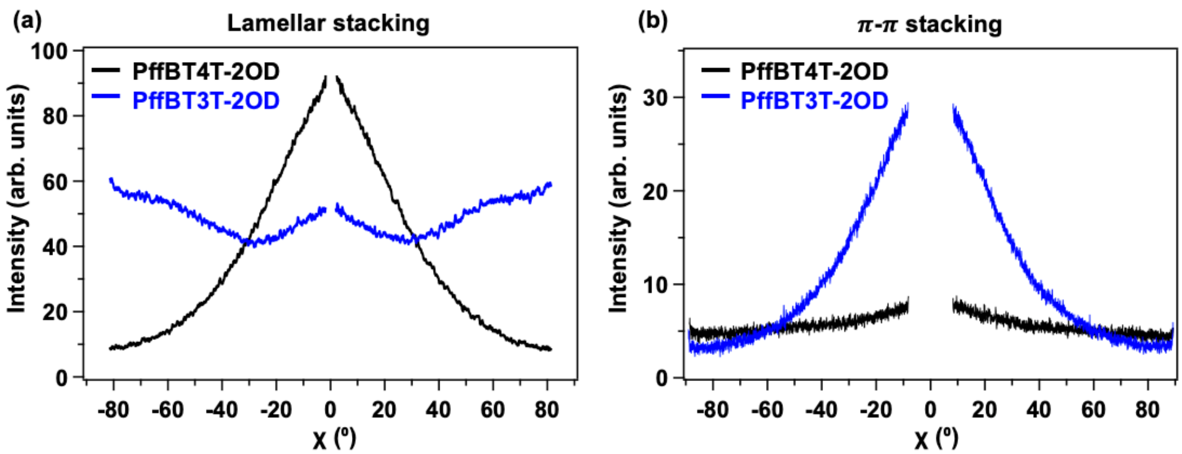

Figure S9 Pole figures of the (100) lamellar stacking peak in (a) and (010) π-π stacking peak in (b) for pristine films of PffBT4T-2OD [PffBT4T-2OD] (black) and PffBT3T-2OD (blue).

2. Equations

$$\boldsymbol{I(q) = G_i e^{\frac{q^2R_{g,i}^2}{3}} + e^{\frac{q^2R_{gco,i}^2}{3}} B_i \left\{\frac{\left(\mathrm{erf}\left(\frac{qR_{g,i}}{\sqrt{6}}\right)\right)^3}{q}\right\}^{P_i}} \quad (1)$$