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Supporting information for Crystallization Kinetics of semiconducting Poly(2,5-bis(3-alkylthiophen-2-yl)-thieno-[3,2-b]thiophene) (PBTTT) from its Different Liquid Phases

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EXPERIMENTAL SECTION

Materials

Poly(2,5-bis(3-alkylthiophen-2-yl)-thieno-[3,2-b]thiophene), PBTTT-C_{12} (M_w = 65,000; Đ = 2.5), thin-films were deposited from 20 µL from 20 mg/mL solutions in chlorobenzene at 90 ºC after 1h of stirring at 1000 rpm during 60 s.

Fast Scanning Chip Calorimetry (FSC)

FSC Experiments were performed on a Mettler-Toledo Flash DSC 2+ device. The equipment is connected to a Huber TC-100 intracooler, permitting scans of up to 40,000 ºC/s. The MultiSTAR UFS1 (24×24×0.6 mm3) chip sensors were conditioned and corrected prior to use according to the Flash DSC 2+ specifications. Measurements were carried out under a nitrogen atmosphere with a constant 80 mL/min flow rate. The STARe software was used to analyze the data. The thermal protocols essentially consisted in recording heat flow rates during the heating of the sample crystallized at a given temperature for different times.

Atomic Force Microscopy (AFM)

A dimension ICON with a Nanoscope V controller (Bruker) AFM was used to image the samples. A Peak-Force Tapping mode using ScanAsyst-Air tips by Bruker (nominal tip radius of 2 nm, nominal frequency of 70 kHz, nominal spring constant = 0.4 N/m) was used to obtain the images. A PBTTT thin-film was deposited from a 20 mg/mL solution on the back side of the chip with a glucose cover on the reference cell, which was removed after deposition with water. The sample was heated above the smectic-to-isotropic transition (T_{LC}), and after melting it was rapidly cooled (at 4000 ºC/s) to the crystallization temperature (T_c). Subsequently, the sample was kept at T_c for 48h, it was rapidly cooled to a temperature below the glassy state,

T_g, and rapidly heated to room temperature and then measured by AFM.

Polarized Light Optical Microscope (PLOM)

Experiments were performed on a polarized light optical microscope, Olympus BX51 (Olympus, Tokyo, Japan), with an Olympus SC50 digital camera coupled to the microscope. The PLOM was equipped with a Linkam-15 TP-91 hot stage Linkam, Tadworth, U.K, connected to a liquid nitrogen cooling system that was used to observe the morphology of the sample. Samples were prepared by heating a small fraction of the polymer powder from 25 ºC to a T_{LC}+ 30 ºC to at 20 ºC/min

Grazing Incidence Wide Angle X-Ray Scattering (GIWAXS)

GIWAXS measurements were performed at the BL11 NCD-SWEET at ALBA Synchrotron Radiation Facility (Barcelona, Spain). The incident X-ray beam energy was set to 12.4 eV using a channel cut Si (1 1 1) monochromator. 2D GIWAXS patterns were corrected as a function of the components of the scattering vector (q). 2D GIWAXS patterns were corrected as a function of the components of the scattering vector. The angle of incidence α_i was set between 0.1º and 0.2º to ensure surface sensitivity. Data are expressed as a function of the scattering vector, which was calibrated using Cr_2O_3, obtaining a sample-to-detector distance of 145.6 mm. The scattering patterns were recorded using a Rayonix LX255-HS area detector, which consists of a pixel array of 1920 × 5760 pixels (H × V) with a pixel size of 44 × 44 μm^2. All the measurements were performed under N_2 atmosphere to minimize the damage of the films. PBTTT thin-films were deposited from a 20 mg/mL solution on to Si wafers by spin-coating the sample. Acquisition time was 0.5 s.

In the in-situ GIWAXS experiment, GIWAXS patterns were collected wile heating up the samples from 30 to 300 ºC at 20 ºC/min under N_2 atmosphere.

Results

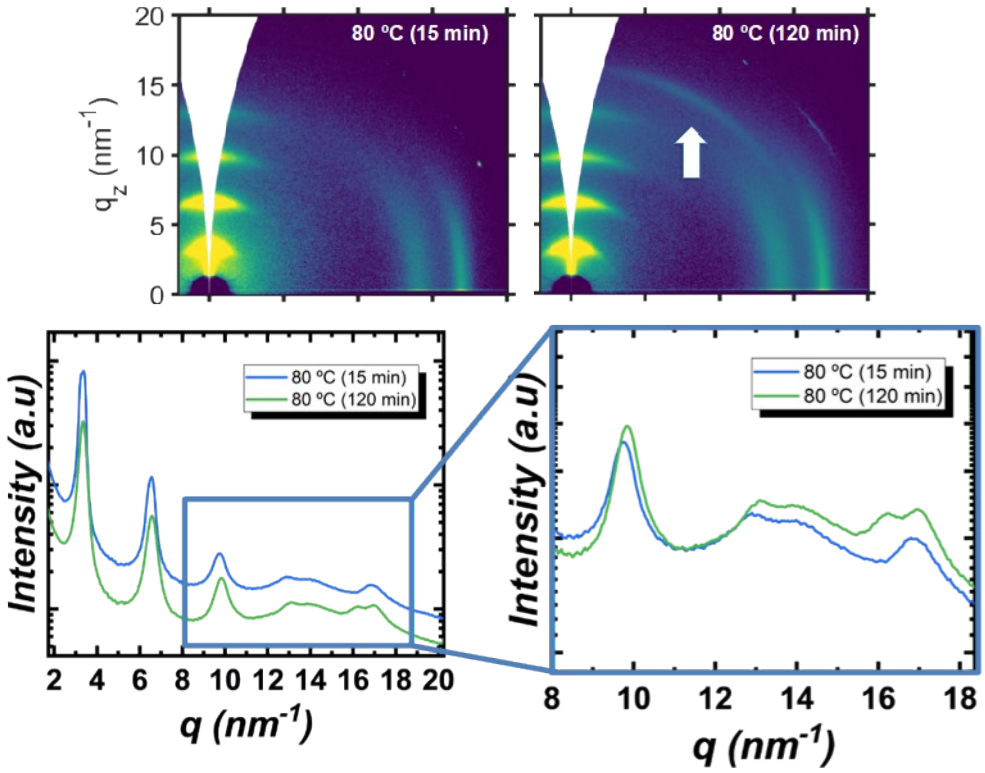

Figure S1. GIWAXS patterns for PBTTT films annealed at 80 ºC for 15 min and 120 min).

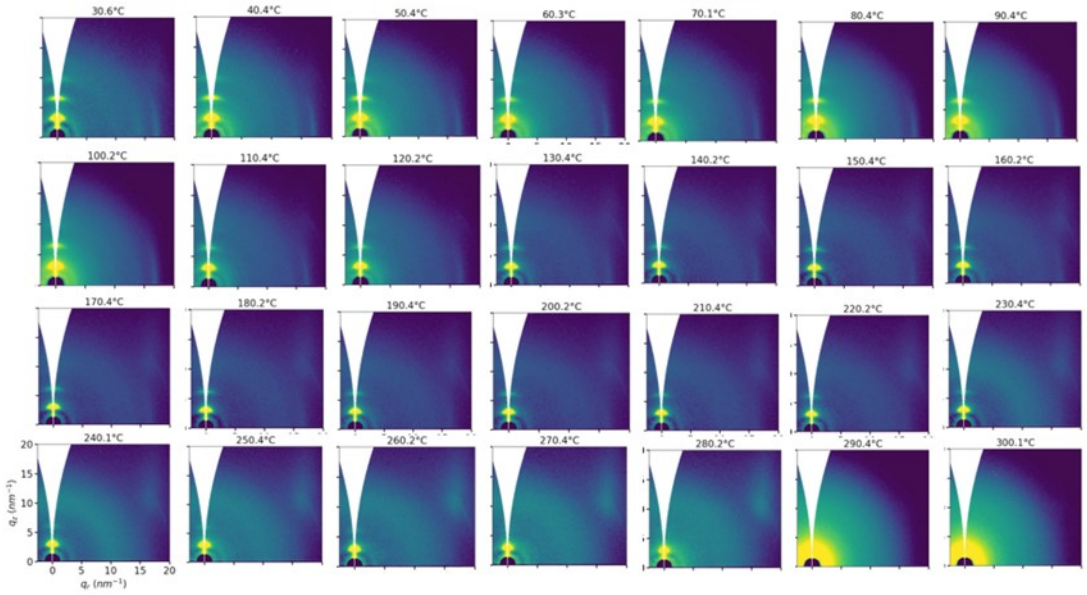

Figure S2. *In situ* GIWAXS patterns for PBTTT films acquired during heating from 30 ºC to 300 ºC

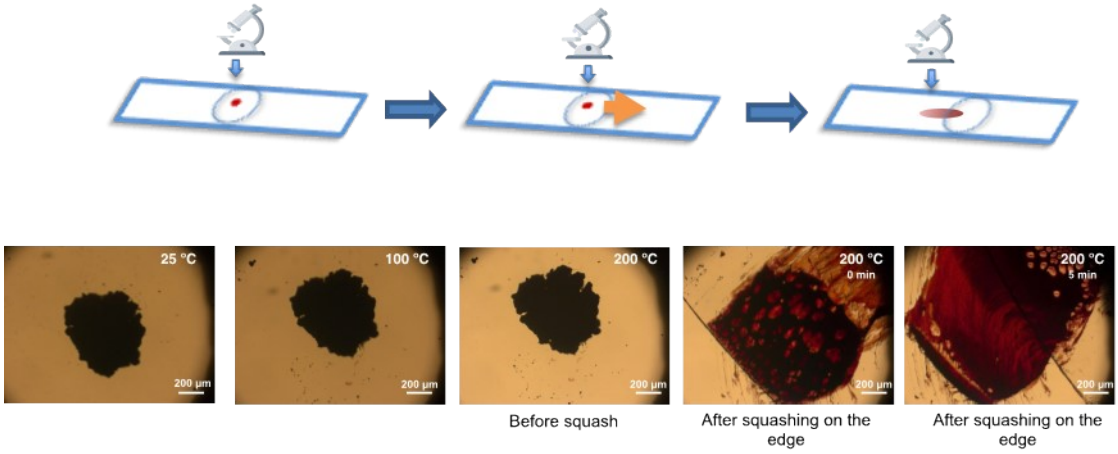

Figure S3. Optical microscopy images of a small piece of PBTTT acquired at the indicated temperatures. The images on the right hand side clearly show that PBTTT is a liquid at 200 ºC.

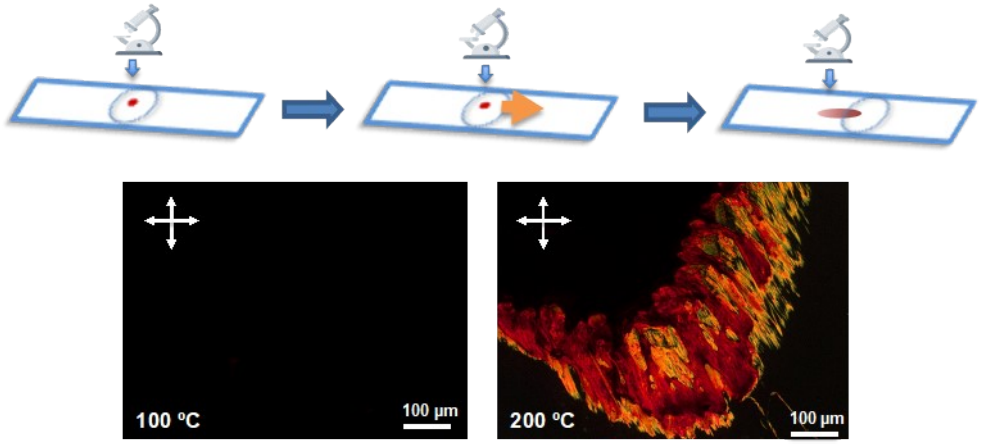

Figure S4. Optical microscopy images of a small piece of PBTTT acquired at the temperatures indicated. The images on the right hand side clearly show that PBTTT is a birefringent liquid at 200 ºC.

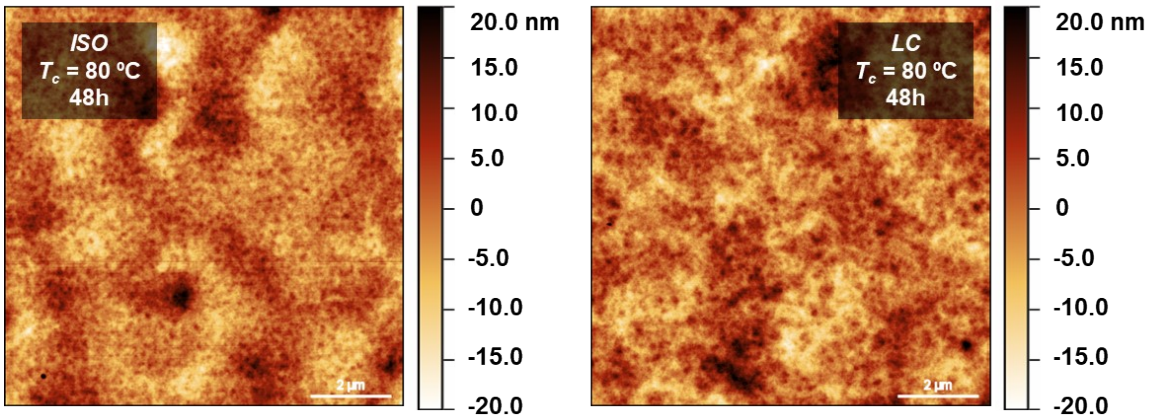

Figure S5. A) AFM-height images of PBTTT crystallized at $T_c =$ 80 °C to form a ribbon phase after 48h (ISO state) . B) AFM-height images of PBTTT crystallized at $T_c =$ 80 °C to form a terraced phase after 48h (LC state).

Atomic Force Microscopy (AFM) characterization of the thin films were conducted after applying the thermal protocols described above. **Figure S5A** and **Figure S5B** confirm the different solid-state morphologies of resulting films, the ribbon phase in **Figure S5A** and the terraced phase **Figure S5B** (we must emphasize here the difficulty of acquiring high-quality AFM images on thin film cast directly onto the FSC chip-sensors employed for FSC).

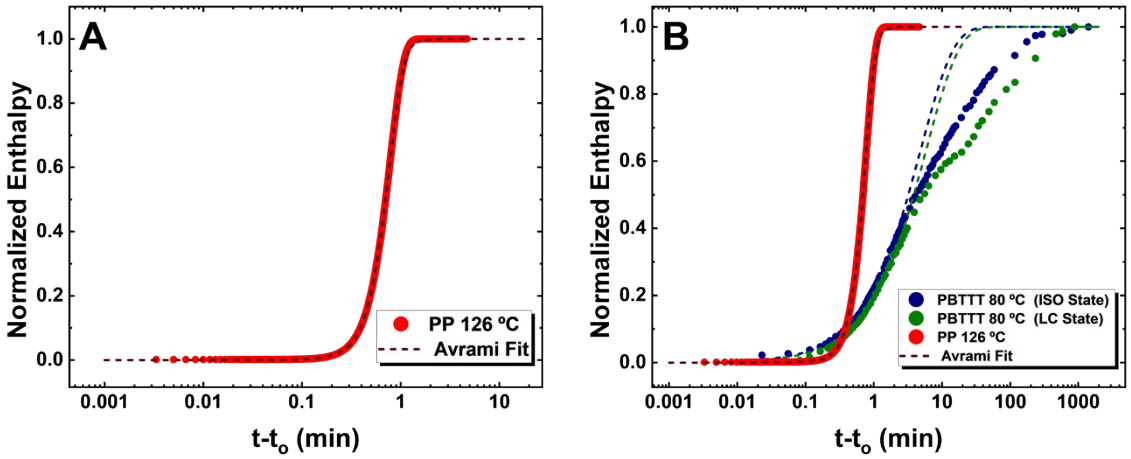

Figure S6. Crystallization kinetics A) Example of Polypropylene (PP) normative crystallization kinetics. B) Comparison of PP kinetics with the data obtained of PBTTT at T_c = 80 ºC.

Scheme S1. Diagram of crystallization from an ISO state and a LC state

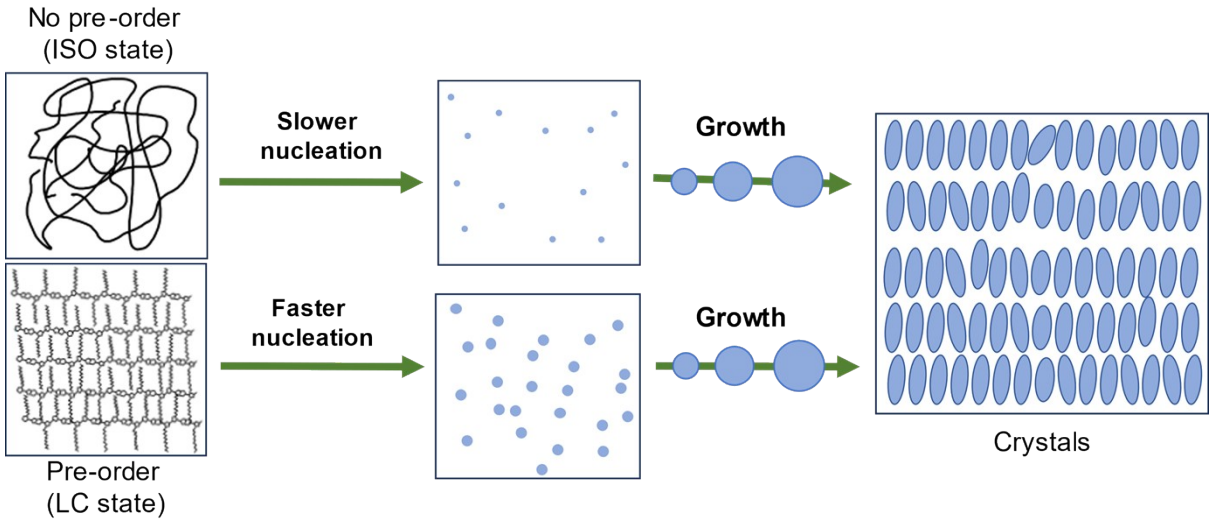

Table S1. Values obtained from applying the Avrami theory to the experimental data

T_c (°C)	State	$1/t_{20\%exp}$ (min^{-1})	$k^{1/n}$ (min^{-1})	Avrami index (n)
60	ISO	0.23	0.06	1.2
	LC	0.54	0.1	0.89
65	ISO	0.66	0.23	1.4
	LC	0.86	0.24	1.1
70	ISO	0.26	0.06	0.97
	LC	0.82	0.17	0.89
75	ISO	0.32	0.03	0.65
	LC	0.59	0.13	0.96
80	ISO	1.10	0.20	0.89
	LC	0.93	0.23	1.05
85	ISO	0.44	0.09	0.88
	LC	0.35	0.07	0.89
90	ISO	0.41	0.08	0.90
	LC	0.740	0.11	0.88