Supporting Information

## RapidSolvo-MicrowaveAnnealingforOptimizingOrderedNanostructuresandCrystallizationofRegioregularPolythiophene-BasedBlockCopolymers†

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■ Crystalline characteristics of P3DDT in P3DDT-b-PLA (0.48) thin films

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- TEM images and corresponding FFT images of P3DDT-b-PLA (0.24) thin
  S2 films. The images represent the degree of ordering according to annealing methods: (a) As-spuncast, (b) thermal annealing followed by fast-quenching,
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- GISAXS in-plane plot of P3DDT-*b*-PLA (0.24) thin film prepared by thermal annealing (fast-quenched and slowly-cooled) and solvo-microwave annealing.
- GIWAXS (a) out of plane and (b) in-plane plots of P3DDT-b-PLA (0.48) thin
  S7 films prepared by thermal annealing (fast-quenched and slowly-cooled) and solvo-microwave annealing



Fig. S1 SEC traces of P3DDT-alkyne, P3DDT-b-PLA (0.48) and P3DDT-b-PLA (0.24)



**Fig. S2** TEM images and corresponding FFT images of P3DDT-*b*-PLA (0.24) thin films. The images represent the degree of ordering according to annealing methods: (a) As-spuncast, (b) thermal annealing followed by fast-quenching, (c) thermal annealing followed by slow cooling and (d) solvo-microwave annealing. P3DDT domains appear dark due to  $RuO_4$  vapor staining. The scale bars are 100 nm.



**Fig. S3** TEM images of solvent annealed thin films : (a) P3DDT-*b*-PLA (0.48) and (b) P3DDT-*b*-PLA (0.24)



**Fig. S4** TEM images of P3DDT-*b*-PLA (0.24) thin film prepared by solvo-microwave annealing with different temperatures and times. The scale bars are 100 nm.



**Fig. S5** 2D GISAXS images of P3DDT-*b*-PLA (0.48) thin films prepared by (a) thermal annealing (fast-quenching), (b) thermal annealing (slow-cooling) and (c) solvo-microwave annealing.



**Fig. S6** GISAXS in-plane plot of P3DDT-*b*-PLA (0.24) thin film prepared by thermal annealing (fast-quenched and slowly-cooled) and solvo-microwave annealing.



**Fig. S7** GIWAXS (a) out of plane and (b) in-plane plots of P3DDT-*b*-PLA (0.48) thin films prepared by thermal annealing (fast-quenched and slowly-cooled) and solvo-microwave annealing

Table S1. Crystalline characteristics of P3DDT in P3DDT-b-PLA (0.48) thin films

Polymer	Annealing method	FWHM <sub>(200)</sub> (Å <sup>-1</sup> )	FWHM <sub>(010)</sub> (Å <sup>-1</sup> )	L <sub>c(200)</sub> (Å)	$L_{c(010)}(Å)$	g <sub>(010)</sub> (%)
P3DDT- <i>b</i> - PLA(0.48)	Thermal (fast-quenching)	0.041	0.551	147	10	24
	Thermal (slow-cooling)	0.027	0.113	209	49	11
	Solvo- microwave	0.031	0.103	183	55	10