Electronic Supplementary Information

Morphology Control Enables Thickness-insensitive Efficient Nonfullerene Polymer Solar Cells

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1. J-V curves of annealed devices as a function of thickness

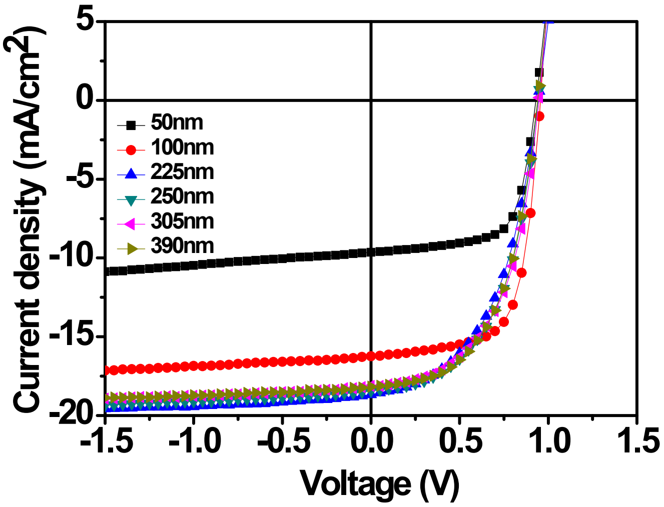


Figure S1 J-V characteristics of annealed PBDB-T: IT-M (1:1) solar cells with different active layer thicknesses.

Table S1. Optimized device performance data for as-cast and annealed treatment PBDB-T/IT-M (1:1) based solar cells with increasing active layer thickness. Devices were measured under AM 1.5 G, 100 mW/cm^2 illumination.

Conditions	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE^a (%)	Thickness (nm)
As-cast	0.945±0.01	9.63±0.25	0.67±0.02	5.88±0.19(6.13)	45
	0.950±0.01	15.89±0.20	0.63±0.03	9.30±0.17(9.60)	108
	0.957±0.01	16.97±0.17	0.47±0.05	7.37±0.18(7.65)	205
	0.924±0.01	16.60±0.16	0.44±0.02	6.52±0.12(6.73)	240
	0.924±0.01	16.06±0.15	0.44±0.03	6.43±0.11(6.57)	320
	0.921±0.01	14.97±0.11	0..41±0.01	5.56±0.11(5.71)	395
Annealed	0.930±0.01	9.90±0.23	0.68±0.01	6.17±0.06(6.28)	50
	0.961±0.01	16.69±0.13	0.70±0.02	11.34±0.12(11.50)	100
	0.940±0.01	18.17±0.20	0.54±0.03	9.21±0.13(9.35)	225
	0.948±0.01	18.13±0.17	0.54±0.03	9.09±0.22(9.37)	250
	0.943±0.01	18.44±0.15	0.53±0.01	9.03±0.25(9.32)	305
	0.942±0.01	18.66±0.12	0.51±0.02	8.73±0.16(8.90)	390

[a] The reported data are the average PCEs from ten devices.

Figure S2 Effect of annealing time on the PCE of PBDB-T: IT-M based thick-film PSCs (~250nm)

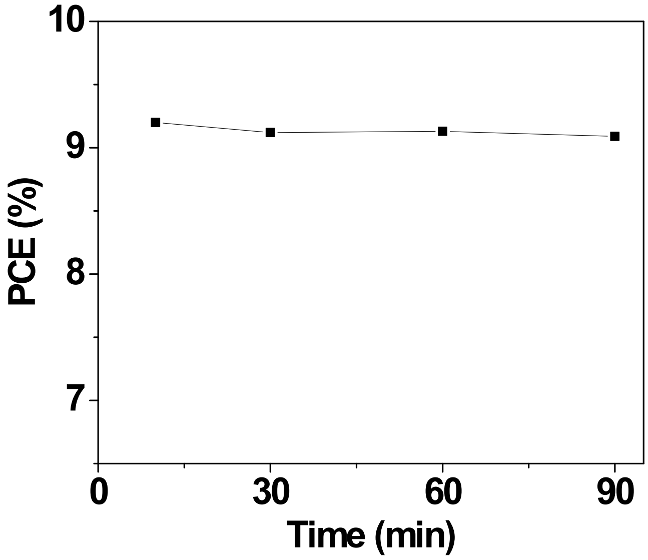
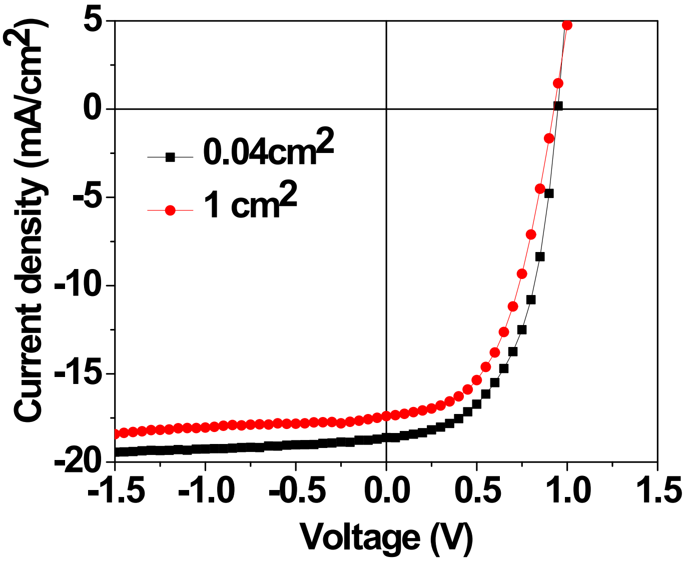


Table S2 Photovoltaic properties of the thick-film PSCs based on PBDB-T: IT-M (~250nm) with different annealing times. The annealing temperature is kept at 100 °C.

Time (min)	V_{oc} (V)	J_{sc} (mA/cm2)	FF	PCE[a] (%)	Thickness (nm)
10	0.952±0.01	17.90±0.25	0.54±0.02	9.08±0.10(9.20)	249
30	0.942±0.01	18.09±0.20	0.53±0.03	9.00±0.08(9.12)	254
60	0.950±0.01	18.12±0.17	0.52±0.05	9.04±0.07(9.13)	252
90	0.944±0.01	18.50±0.26	0.51±0.02	8.91±0.07(9.09)	247

[a] The reported data are the average PCEs from ten devices.

Figure S3 J-V characteristics of annealed thick-film PBDB-T: IT-M (1:1) solar cells (250 nm) with a device area of ~0.04 cm^2 and 1.00 cm^2.



2. Space-charge-limited-current measurements

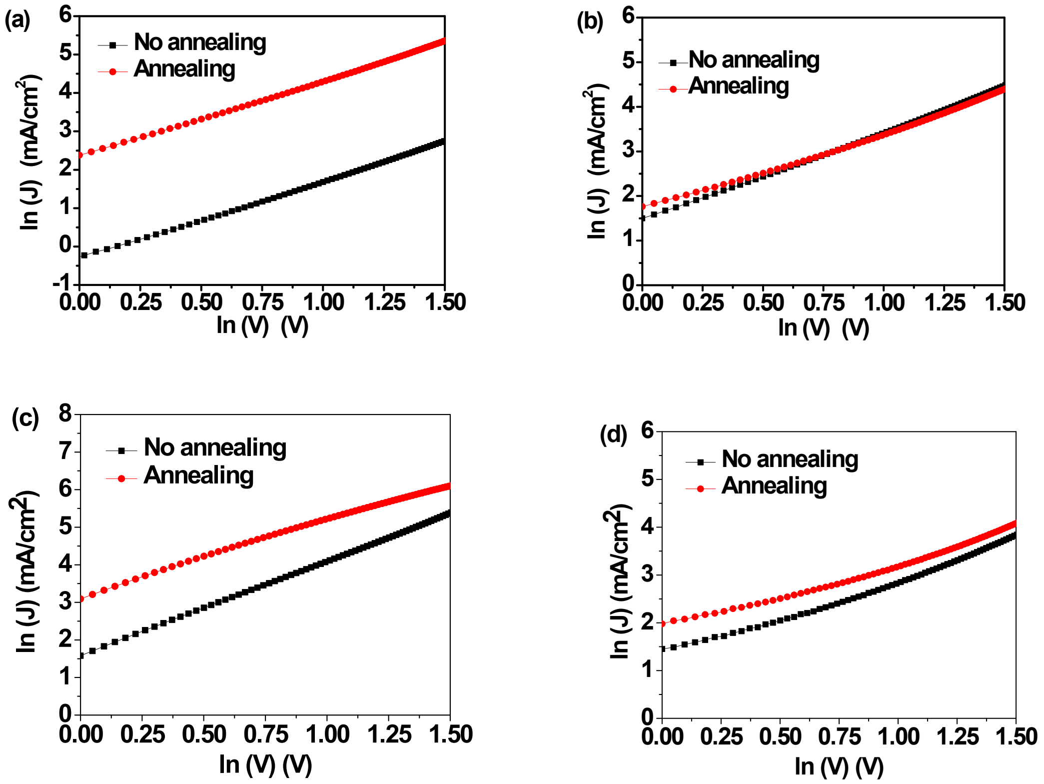


Figure S4 Plots used for the calculation of electron and hole mobilities of PBDB-T:IT-M blends and the pure materials for both as-cast and annealed conditions. Electron-only current for the pure IT-M is shown in (a) and the PBDB-T:IT-M blend is shown in (b). Hole-only currents for pure PBDB-T (c) and the PBDB-T:IT-M based devices in (d).

3. AFM phase images

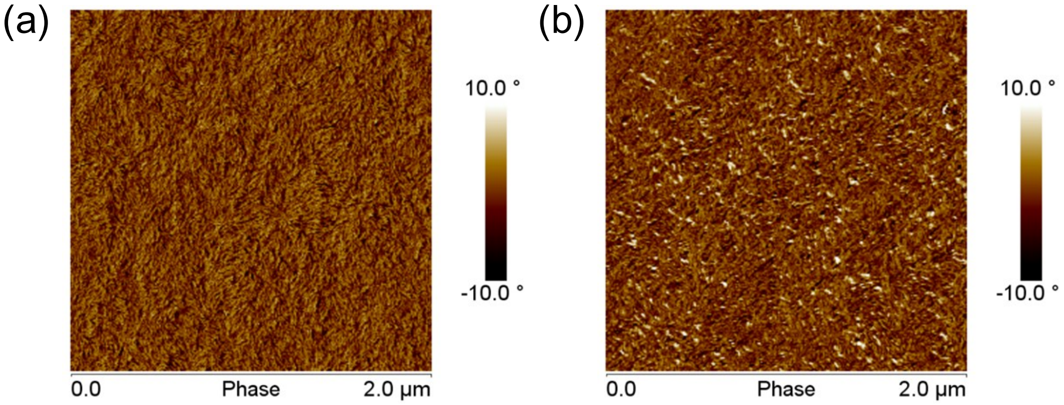


Figure S5 Tapping mode AFM phase images of (a) as-cast and (b) annealed thick-films. The size of the AFM image is 2μm × 2 μm.

4. TEM images

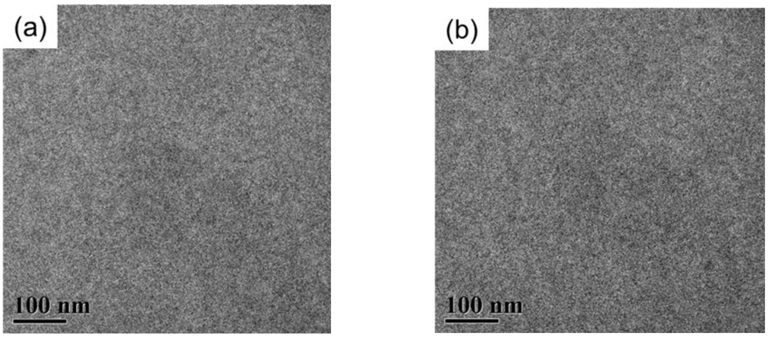


Figure S6 TEM images of PBDB-T/IT-M based thick-films (250 nm) processed by chlorobenzene with 1% DIO additive: (a) annealed and (b) as-cast.

5. 1 D GIWAXS profiles

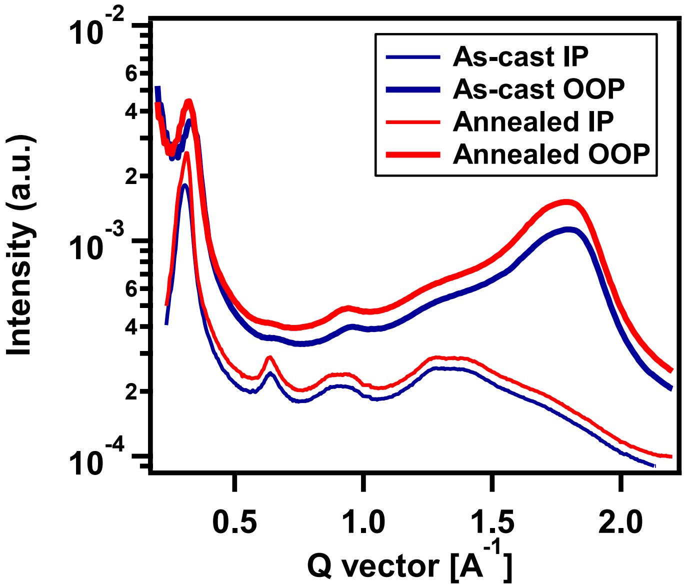


Figure S7 In-plane and out-of-plane 1D profiles of as-cast and annealed thick-films.

6. Schematic illustrations of molecular ordering

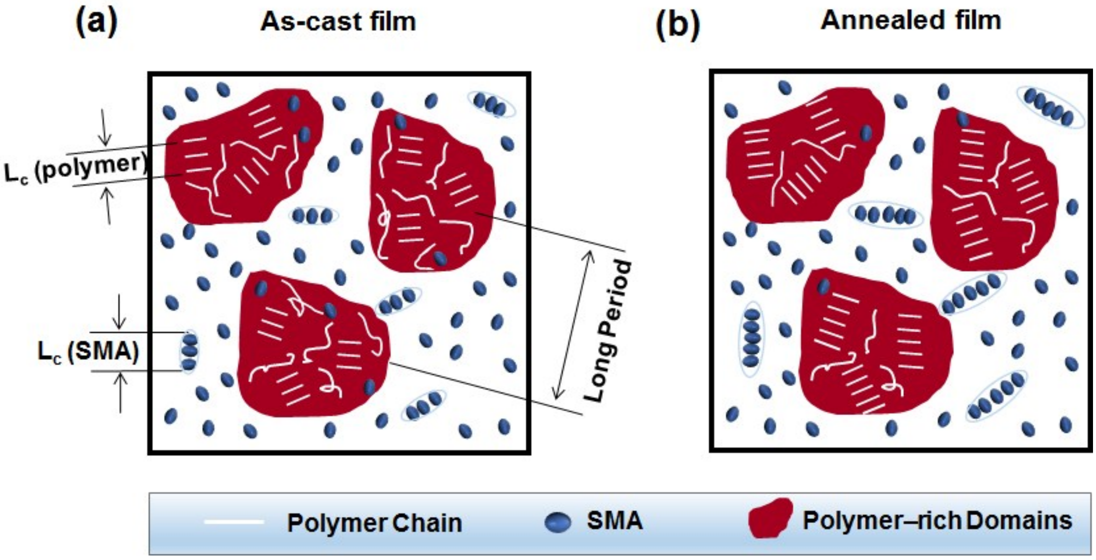


Figure S8. Schematic illustration of molecular packing of polymer and SMA in the PBDB-T:IT-M blends: (a) as-cast films; (b) annealed films.

7. Miscibility data

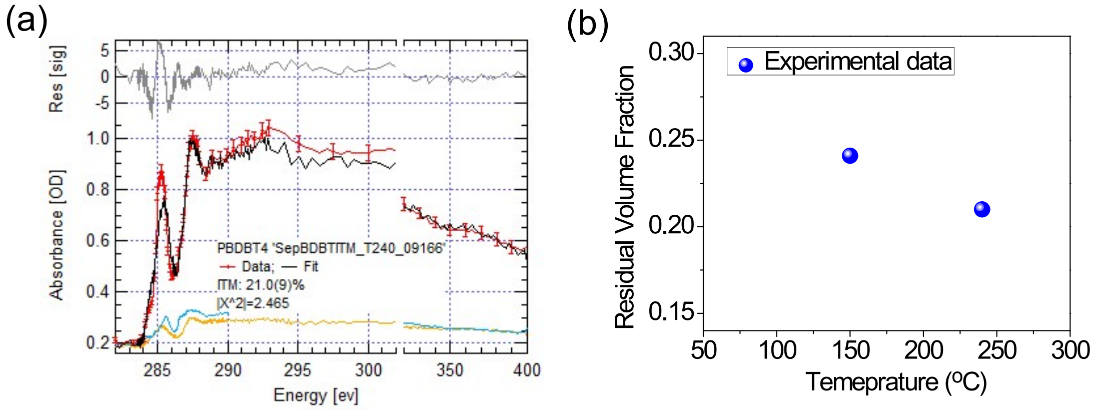


Figure S9. (a) Miscibility fit of the PBDB-T:IT-M blend (1:1,wt/wt) after solvent vapor annealing and subsequent isothermal annealing at 240 °C for three days; the details of this procedure can be found in a previous report by Collins et al.[1] (b) Plot of the residual volume fraction of IT-M in the amorphous polymer matrix as a function of temperature. Since the polymer is essentially amorphous (no melting peak from DSC thermograms), this residual volume fraction is related to the binodal composition in a partially miscible blend, and indicates reduced miscibility at higher temperature. We thus consider this system to be a LCST system based on common thermodynamics descriptions of polymer solutions[2].

References

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Appendix

R-SoXS Data Analysis[S6]

Lorentz correcting is a nice way of getting the PSD-equivalent of the system is applied according to previously established protocols, which were discussed at length in our recent perspectives [S1,S2]. To summarize briefly from these papers: Under the assumption of a globally isotropic 3-dimensional morphology, without the assumption of any specific form factor for the phases such as sphere, cylinder, or lamellae, the multiplicative Lorentz correction factor for structure factors should be proportional to q^2 as described by Stribeck[S3]. We note that this method yields reasonable comparisons between identical material systems. This factor is not always appropriate for analyzing R-SoXS data from BHJ films, as phase separation may result in features that are comparable to or larger than the sample thickness, so this correction should indeed not be blindly applied to all scattering features. In our prior works[S4-S7], the power spectral density (PSD) of the AFM data agrees very well with the Lorentz-corrected R-SoXS data. Such agreement[S8-S10] has also been previously seen between PSD of EF-TEM data and Lorentz-corrected R-SoXS data when both exhibited bimodal size distributions firmly establishing the scattering features seen in Lorentz-corrected data as representative of complicated multi-length scale BHJ morphologies. Lastly, it has been shown for SAXS data and simulated R-SoXS data that long periods of Lorentz-corrected profiles give the best agreement to real-space domain spacings when compared to similarly complex analysis methods. Overall, we think about scattering as representing the PSD (coming from microscopy) of a system (which is basically what Lorentz-correction is doing), so regardless of what the real "source" is, if there are peaks (or shoulders in uncorrected data) it is an indication of length scales in the system. The length scales don't always directly respond to domain sizes or spacings, just as a power spectral density peak doesn't correspond to a specific device-relevant distance. Comparative analysis of peak locations is totally fine, as long as the systems are the same family (i.e. comparing peaks from a system with very well defined form factor to one where structure factor might be dominating may bring problems). For more details, we suggest the readers refer to *Chapter 3* of Dr. Eliot Gann's Ph.D. Thesis[S11].

References

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