

Supporting Information

**Microphase Separation Promoted Crystallization in
All-Conjugated Poly(3-alkylthiophene) Diblock Copolymers
with High Crystallinity and Carrier Mobility**

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Feature S1.

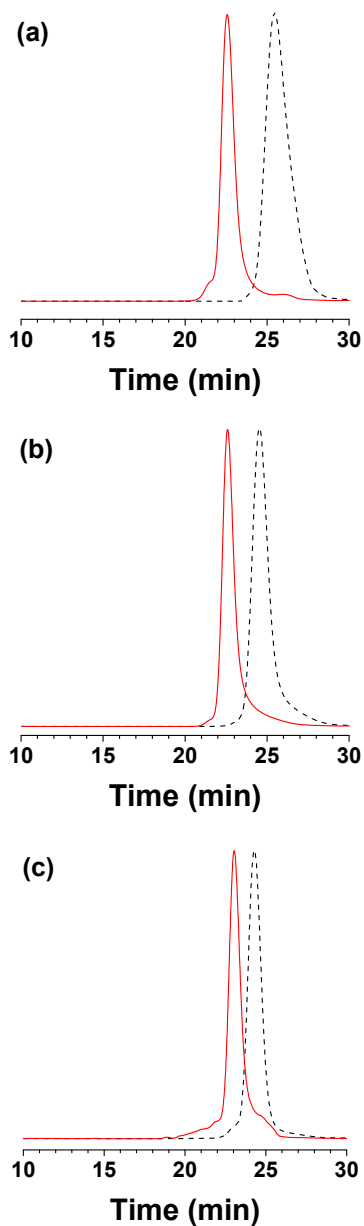


Fig. S1 GPC profiles of P3BT-*b*-P3DDT diblock copoly(3-alkylthiophene)s. Dashed lines represent the GPC profiles of P3BT synthesized in the first step and solid lines show the GPC profiles of the final products of P3BT-*b*-P3DDTs with the monomers' feed molar ratios of (a) 1:2, (b) 1:1, and (c) 2:1 after the second-stage polymerization.

Feature S2.

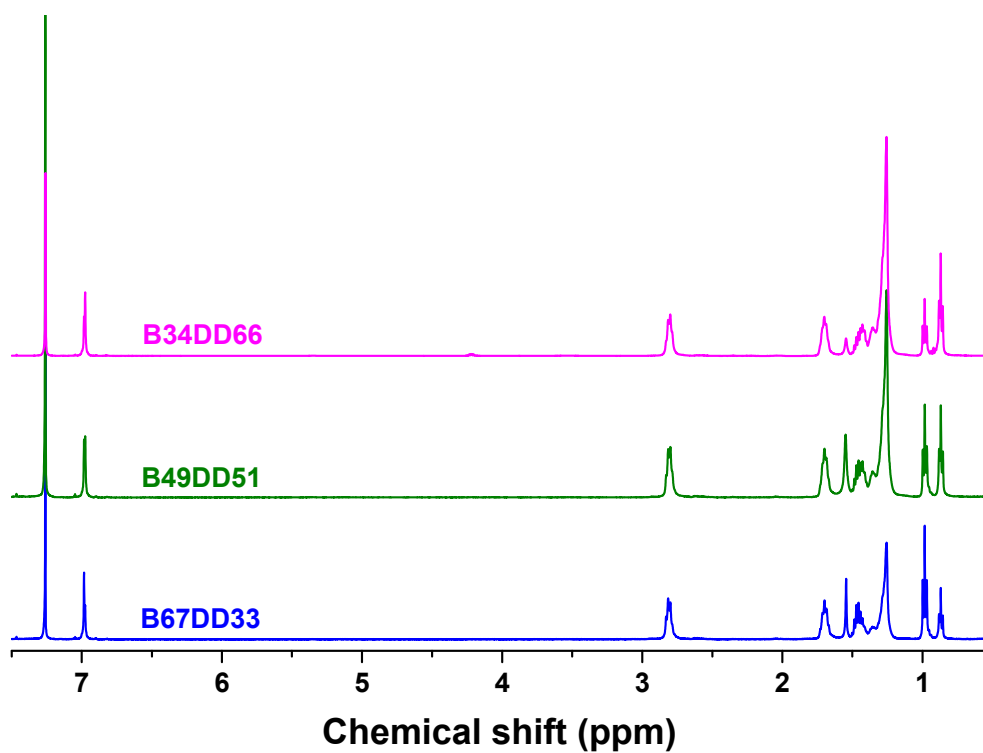


Fig. S2 ¹H NMR spectra of poly(3-butylthiophene)-*b*-poly(3-dodecylthiophene) (P3BT-*b*-P3DDT) with block ratios of 34:66 (B34DD66), 49:51 (B49DD51) and 67:33 (B67DD33).

Feature S3.

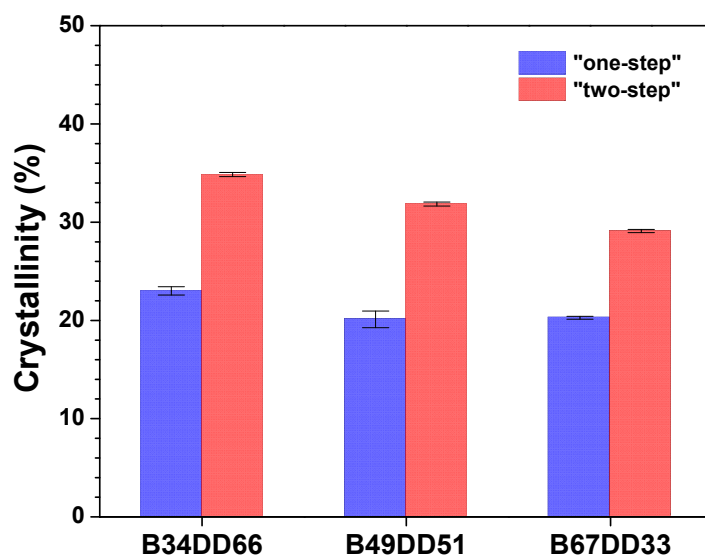


Fig. S3 Degrees of the crystallization of B34DD66, B49DD51, and B67DD33 after the "one-step" or "two-step" thermal treatment.

Feature S4.

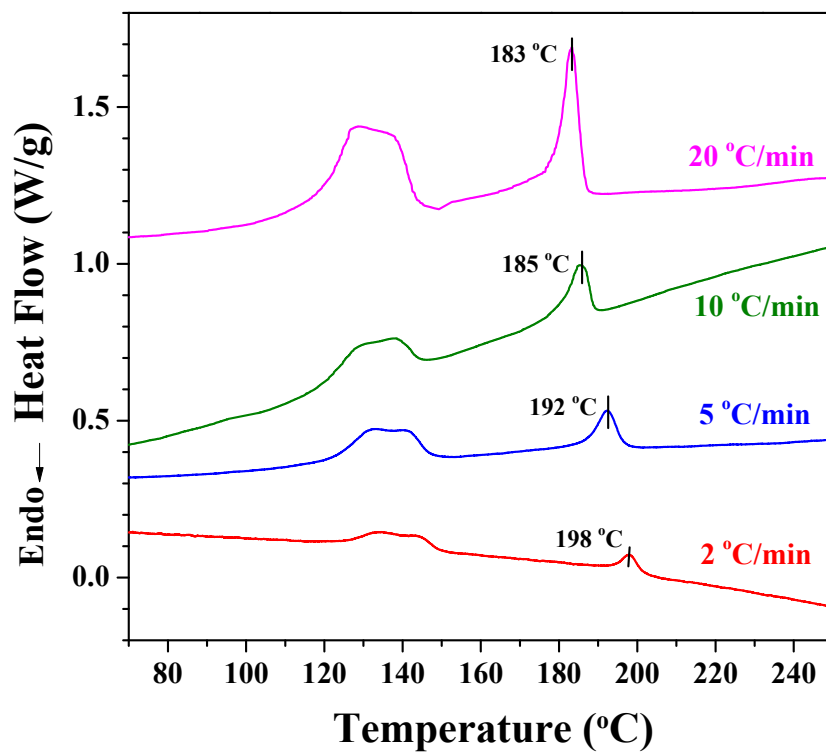


Fig. S4 DSC cooling scans of B34DD66 at different cooling rates. The crystallization temperatures of the P3BT block are marked in the Figure.

Feature S5.

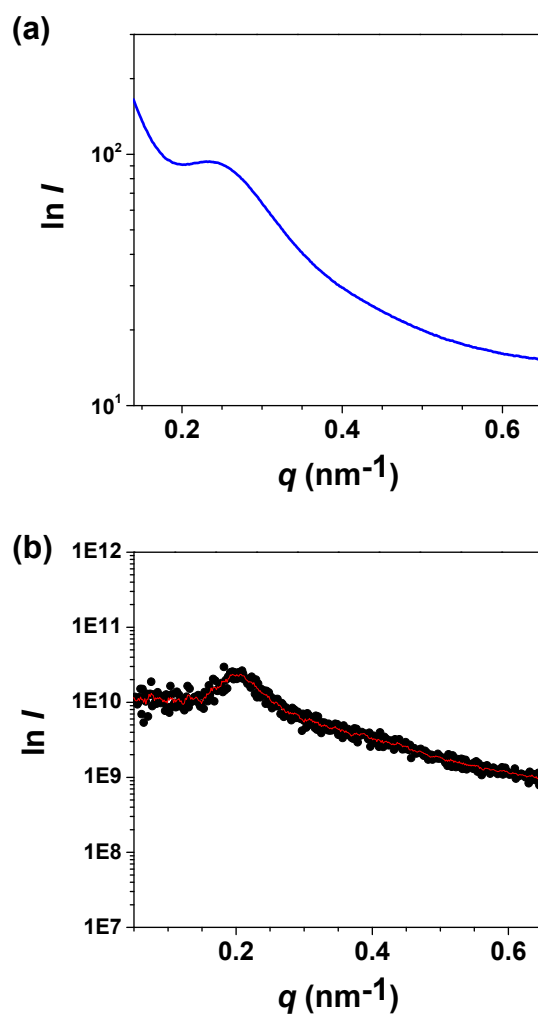


Fig. S5 (a) SAXS profile of B34DD66 after the “two-step” annealing, and (b) Fourier transform of the AFM phase image of B34DD66 after the “two-step” annealing.

Feature S6.

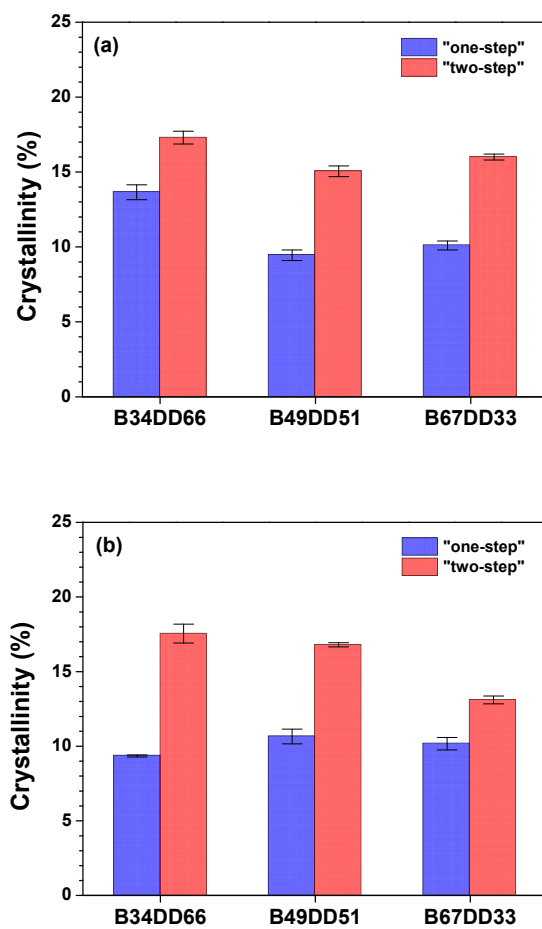


Fig. S6 Degrees of the crystallization of (a) P3BT block and (b) P3DDT block in B34DD66, B49DD51 and B67DD33 after the "one-step" or "two-step" thermal treatment.

Table S1.

Table S1 Summary of mobility extracted from the J - V curves of P3BDDT according to the Mott-Gurney equation, and their crystallinity after the “one-step” thermal treatment, respectively.

polymer	Mobility μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Crystallinity (%)
B67DD33	$2.9 \pm 0.1 \times 10^{-3}$	20.3 ± 0.2
B49DD51	$1.8 \pm 0.1 \times 10^{-3}$	20.1 ± 0.8
B34DD66	$2.5 \pm 0.2 \times 10^{-3}$	23.0 ± 0.4

Table S2.

Table S2 List of parameters for the calculation of crystalline size of P3BT blocks in B34DD66.

	T_m (°C)	T_m^0 (°C)	$\Delta\gamma$ (10^{-7} J/cm ²)	ΔH_c (J/cm ³)
P3BT block	235	321 ¹	235.2 ²	131.5 ²

References

1. V. Causin, C. Marega, A. Marigo, L. Valentini and M. Kenny, *Macromolecules* 2005, **38**, 409.
2. S. Malik and A. K. Nandi, *J. Polym. Sci. B-Polym. Phys.*, 2002, **40**, 2073.

Feature S7.

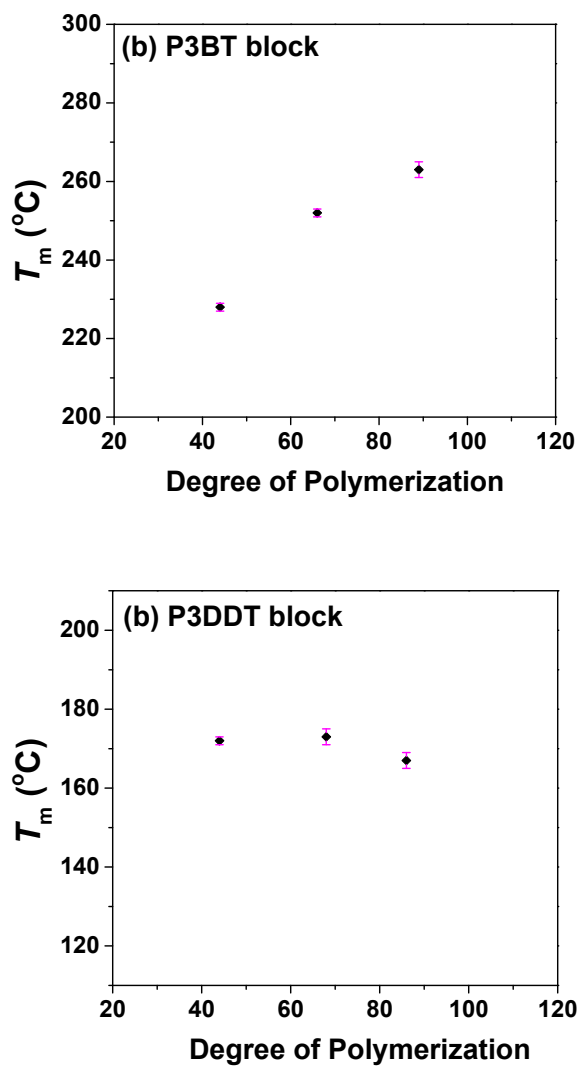


Fig. S7 Melting temperature of (a) P3BT block and (b) P3DDT block within all P3BDDT block copolymers as a function of the degrees of polymerization of the blocks, respectively.