Supporting Information

Cylinder-to-Gyroid Phase Transition in Rod-Coil Diblock Copolymer

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Synthesis of Silane-Terminated Poly(3-dodecylthiophene), 1.

Bromine-terminated poly(3-dodecylthiophene) (1.0 equiv)[1], 4-(trimethylsilane-ethynyl)phenylboronic acid pinacol ester (1.5 equiv) and tetrakis(triphenyl-phosphine)palladium(0) [$Pd(PPh_3)_4$] (1 mol %) were added into a degassed mixture of THF and 2 M potassium carbonate aqueous solution (3:2 in volume). The mixture was stirred and refluxed at 80-90 ^oC for 48 h under the atmosphere of nitrogen. After cooling, the mixture was poured into the stirred mixture of methanol and deionized water (10:1). A crude solid was obtained by filtration. The solid was redissolved in $CHCl_3$, washed with water several times to remove total alkali solution, dried over anhydrous $MgSO_4$, and evaporated. The residue was precipitated in methanol several times to obtain silane-terminated P3DDT.

Synthesis of Alkyne-Terminated Poly(3-dodecylthiophene), 2.

Silane-terminated P3DDT (0.5 g) was dissolved in dry THF (250 ml), and then cooled to 0 ^oC under nitrogen. After addition of tetrabutylammonium fluoride (TBAF) (1.0 M, 1 mL) to the solution, the mixture was stirred for 30 min at 0 ^oC. The crude polymer was precipitated in methanol several times to obtain alkye-terminated P3DDT.

Synthesis of Azido-Terminated Poly(methyl methacrylate), 3.

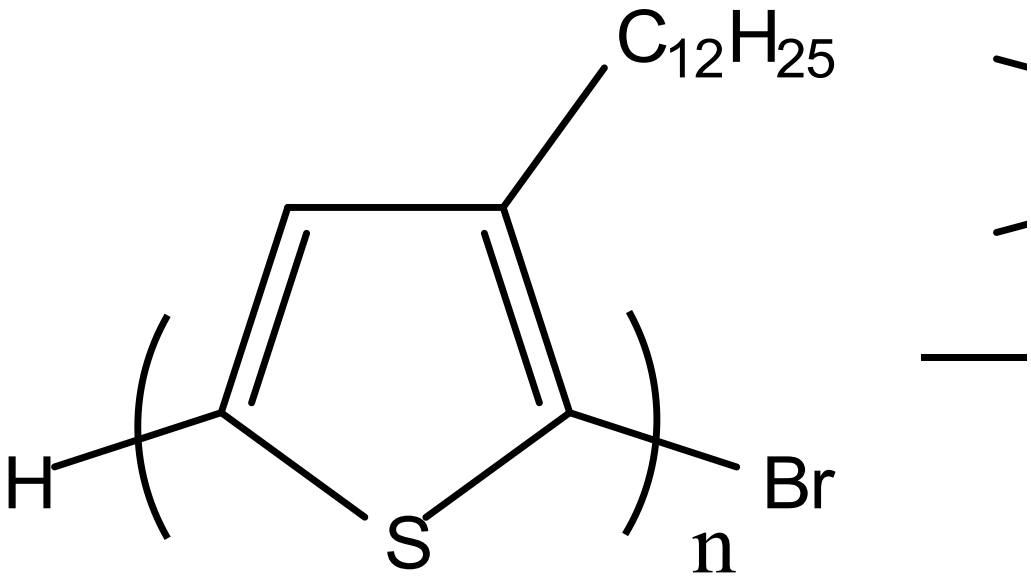
The detailed of synthesis of azido-terminated PMMA was described in our previous work.[2,3] Briefly, anionic polymerization was carried out in an oxygen-free and moisture-free glass reactor under a nitrogen atmosphere. LiCl (1.1 g, 25.87 mmol), THF (250 mL) and DPE (0.55 mL, 3.10 mmol) were successively placed in a Schlenk

flask, and the mixture was cooled to -78 °C. Then, *sec*-BuLi (1.99 mL, 2.59 mmol) was injected to initiate the DPE. After 15 min, MMA (10 mL, 92.90 mmol) was added, and the reaction was allowed to proceed at -78 °C for 30 min. The PMMA anion solution was introduced dropwisely into a *α,α′*-dibromo-*p*-xylene (6.83 g, 25.9 mmol) solution. After 30 min, the reaction mixture was terminated with methanol. The corresponding polymer was purified over a basic alumina column to remove LiCl and precipitated twice in hexane to produce a white solid.

The bromine end-terminated PMMA (8.0 g, 2.20 mmol) was dissolved in DMF (200 mL), followed by adding excess sodium azide (0.72 g, 11.02 mmol). The reaction mixture was stirred overnight at 60 °C. The polymer was purified over a basic alumina column to remove the remaining NaN_3 and salts. The polymer was then precipitated twice in hexane, yielding a white solid.

Synthesis of Poly(3-dodecylthiophene)-*block*-Poly(methyl methacrylate) (P3DDT-*b*-PMMA), 4.

The azido-terminated PMMA (1.0 equiv), the alkyne-terminated P3DDT (2.0 equiv), and CuBr (0.4 equiv) were first placed in the Schlenk flask. The flask was evacuated and backfilled with dry nitrogen for three times. THF to make 2 wt % of polymer solution was added. PMDTA (0.5 equiv) was then introduced, and the reaction was stirred at 40 °C. The completion of the reaction was monitored by GPC until the intensity of the peak associated with the elution of block copolymer no longer increased in size. The polymer was precipitated in hexane several times to remove the excess homo P3DDT. The residue was precipitated in methanol several times to obtain desired block copolymer.



Scheme S1. Synthetic routes of P3DDT-*b*-PMMA rod-coil block copolymer via "click" chemistry.

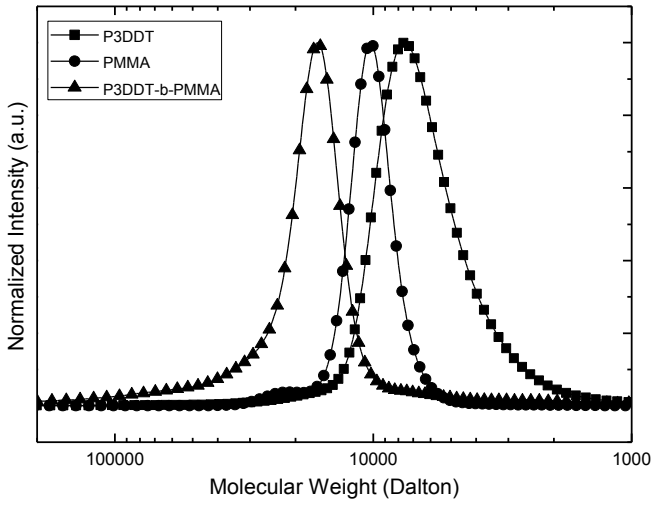


Figure S1. GPC traces of end-functionalized homopolymers of P3DDT (square) and PMMA (circle), and their corresponding block copolymer (triangle) after "click" reaction.

Table S1. Molecular Characterization of P3DDT, PMMA and P3DDT-*b*-PMMA Block Copolymer

Polymer	M_w[a] (kDa) P3DDT	M_w[a] (kDa) PMMA	PDI[b]	f_{PMMA}[c]
P3DDT	7.29	-	1.12	0
P3DDT-*b*-PMMA	7.29	15.18	1.11	0.652

[a]Absolute weight average molecular weight (M_w) of P3DDT and PMMA segments of the copolymer were determined via GPC incorporated with the light scattering. [b]The polydispersity of all polymers were evaluated by conventional GPC. [c]PMMA coil volume fraction (f_{PMMA}) was calculated by using absolute molecular weight and their density of P3DDT (1.07 g/cm^3)[4] and PMMA (1.19 g/cm^3)[5].

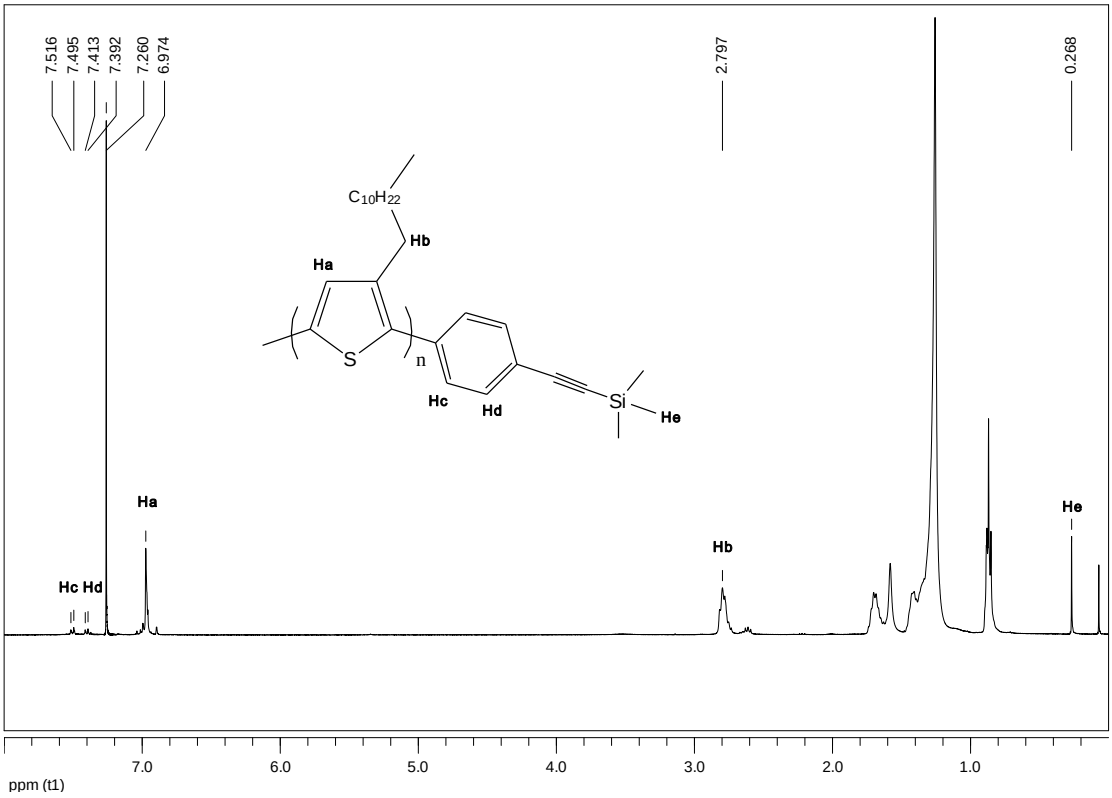


Figure S2. ^{1}H NMR spectrum of polymer 1.

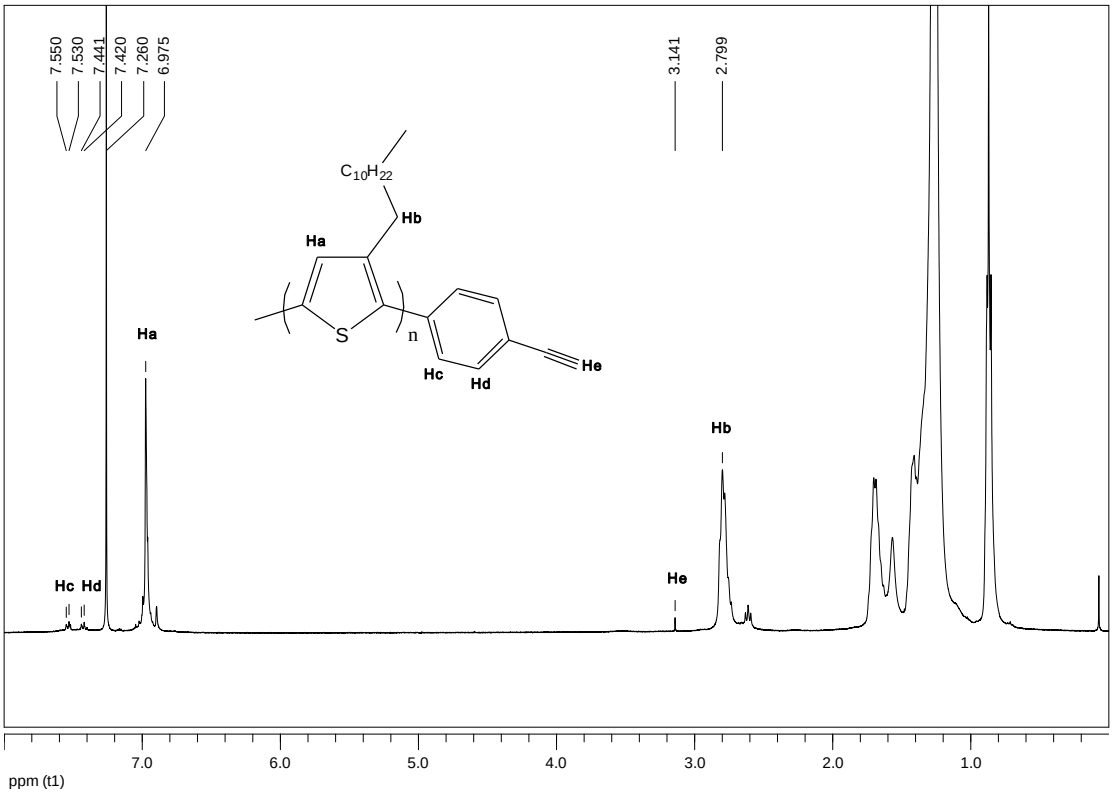


Figure S3. ^{1}H NMR spectrum of polymer 2.

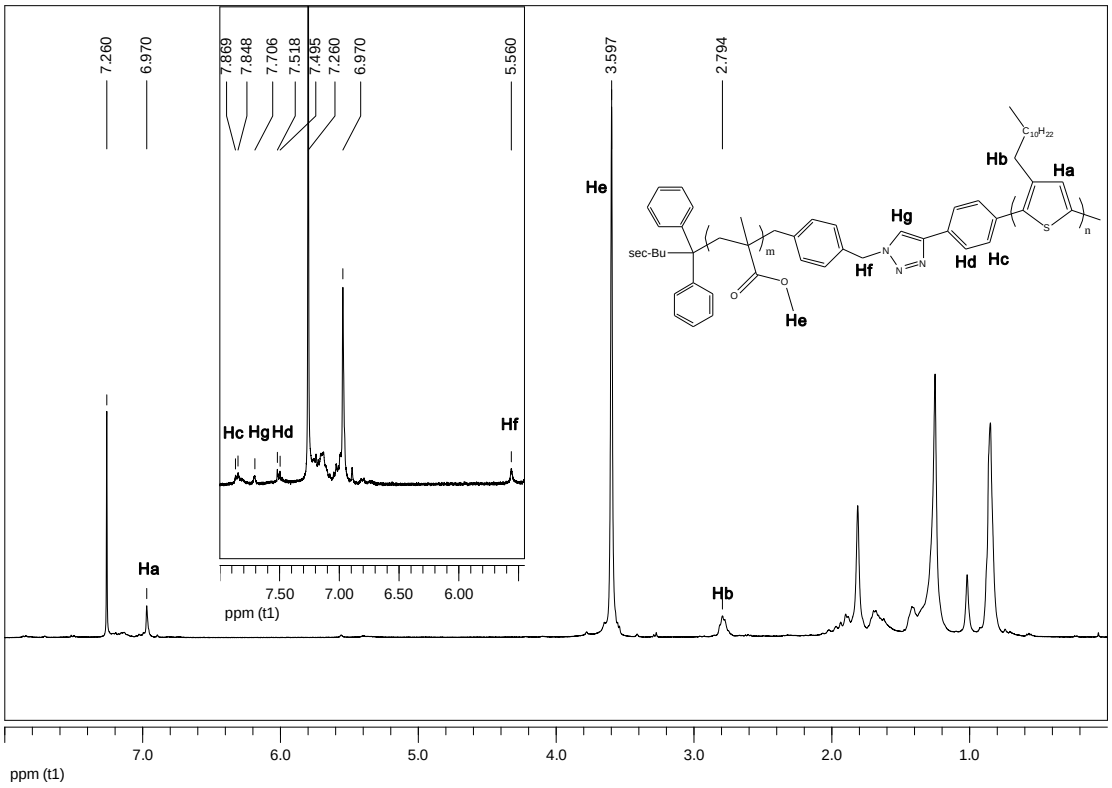


Figure S4. ^{1}H NMR spectrum of polymer 4.

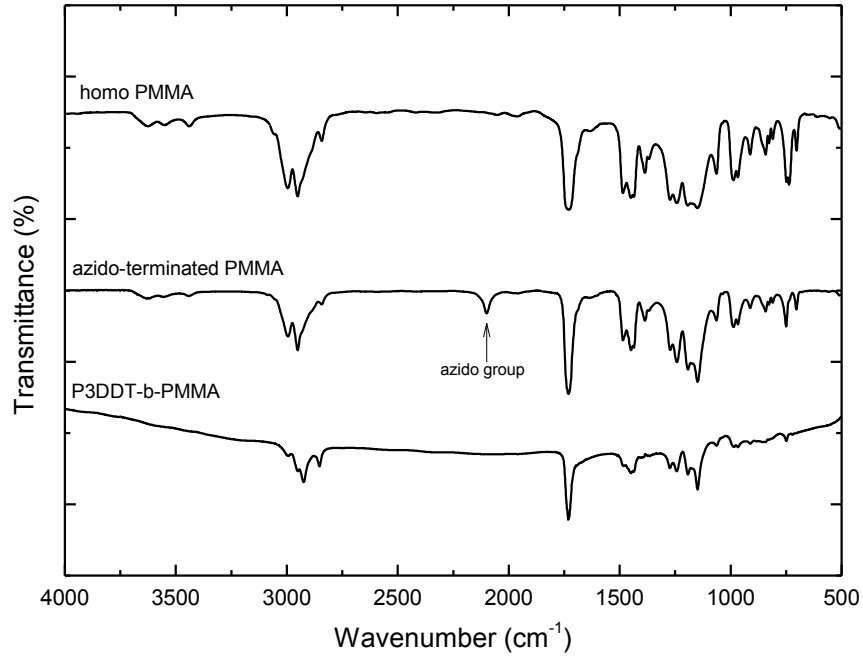


Figure S5. FTIR spectra of homo PMMA, azido-terminated PMMA and block copolymer.

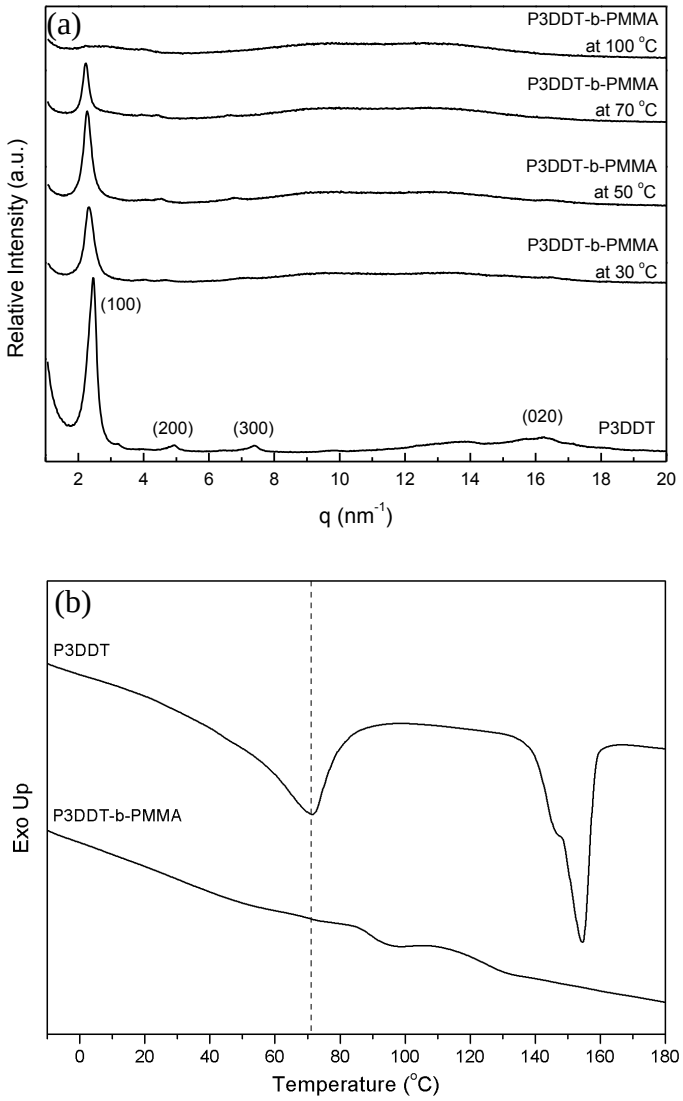


Figure S6. Study of crystallization of P3DDT-*b*-PMMA block copolymer with a 65.2% volume fraction of PMMA. (a) WAXS curves at different temperatures, the peaks around 2.33 nm^{-1} and 16.51 nm^{-1} are associated with (100) and (020) reflections, corresponding to the lattice spacing of 2.70 and 0.38 nm in P3DDT block at room temperature. With increasing temperature, the peaks of P3DDT crystallites were gradually diminished, and then completely disappeared above the melting temperature. (b) DSC thermograms of P3DDT homopolymer and P3DDT-*b*-PMMA block copolymer. The scan rate is 10°C/min. Melting temperature of block copolymer is around 97°C, which is much lower than that of P3DDT around 154°C.

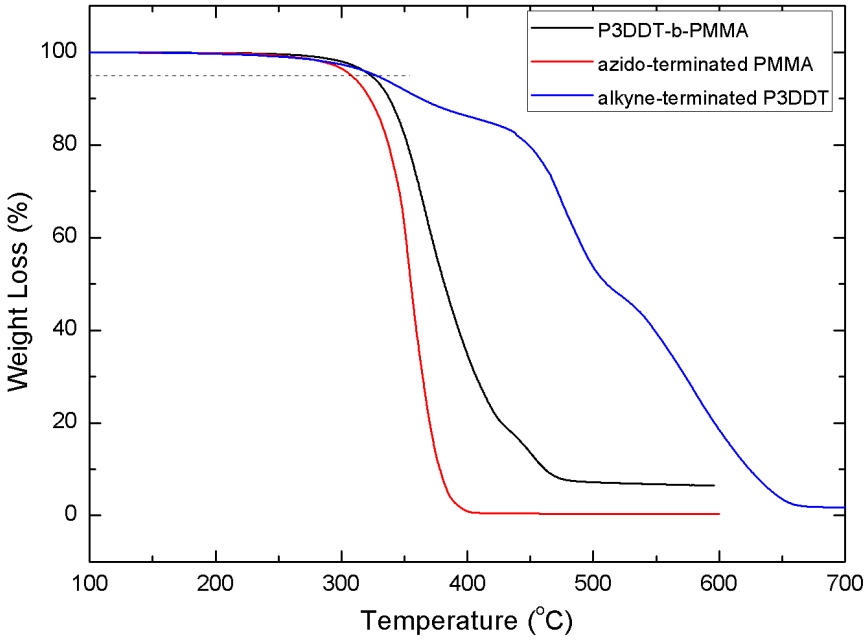


Figure S7. TGA thermographs of alkyne-terminated P3DDT, azido-terminated PMMA and their block copolymer.

References:

1. A. Yokoyama, R. Miyakoshi and T. Yokozawa, *Macromolecules*, 2004, **37**, 1169-1171.
2. C. C. Ho, Y. H. Lee, C. A. Dai, R. A. Segalman and W. F. Su, *Macromolecules*, 2009, **42**, 4208-4219.
3. C. C. Ho, C. A. Dai and W. F. Su, *J. App. Polym. Sci.*, 2009, **111**, 1571-1580.
4. K. Tashiro, K. Ono, Y. Minagawa, M. Kobayashi, T. Kawai and K. Yoshino, *J. Polym. Sci., Part B: Polym. Phys.*, 1991, **29**, 1223-1233.
5. J. A. Shetter, *J. Polym. Sci., Part B: Polym. Lett.*, 1963, **1**, 209–213.