Supporting Information

Synthesis and characterization of [Poly(3-dodecylthiophene)]_2 Poly(methyl methacrylate) Miktoarm Star Copolymer

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1. **Thermal properties of P3DDT$_2$PMMAs.** The thermal properties of P3DDT$_2$PMMAs were measured by using Perkin-Elmer DSC 4000. Calibration was conducted with indium, and all the thermograms were recorded under a nitrogen atmosphere at a scan rate of 10 °C/min.

![Image of DSC thermograms](image.jpg)

**Figure S1.** (a) 2nd heating DSC thermograms of miktoarm star copolymers and P3DDT$_2$-PMMA with $w_{P3DDT}=0.76$ (previously prepared at Ref 1, $M_n, P3DDT = 6,400$) at a heating rate of 10 °C/min. The glass transition temperature of PMMA is obscured due to main chain melting of P3DDT. (b) Degree of crystallinity of P3DDT$_2$PMMAs as a function of $w_{P3DDT}$. Degree of crystallinity was calculated by heat of fusion ($\Delta H_m$) from the DSC thermograms divided by that of an ideal P3DDT crystal ($\Delta H^\circ = 52$ J/g).²
2. Additional $^1$H NMRs.

Figure S2. $^1$H NMR spectra for $\omega$-azidopropyl-P3DDT.

Figure S3. $^1$H NMR spectra for Azido-terminated PMMA and PMMA-$\equiv_2$ with $M_n = 3,300$ g/mol. The inset clearly shows the shift of proton peak adjacent to phenyl group before and after click reaction.
3. Synthesis of P3DDT₂PMMA using the previous reported method.³

The scheme for the synthesis of P3DDT₂PMMA using the previous reported method³ is shown in the left panel of Figure S4.

**Monoethynyl-terminated Poly(3-dodecylthiophene) (P3DDT≡)** 2. Fully H/Br-terminated poly(3-dodecylthiophene) was synthesized according to the literature.⁴ Tris(dibenzylideneacetone)dipalladium(0) (Pd₂(dba)₃) (0.0018 g, 0.00197 mmol), bis(tri-tert-butylphosphine)palladium(0) (Pd(P(t-Bu)₃)₂) (0.0028 g, 0.00548 mmol), and fully H/Br-terminated P3DDT (0.162 g, 0.0342 mmol) were introduced into a reactor under nitrogen purging. Then, anhydrous THF (20 ml) was added. Finally, ethynyltributylstannane (0.3 ml, 1.04 mmol) was added. The solution was stirred at room temperature. After keeping overnight, it was precipitated into methanol and dried under vacuum to yield the product.³¹H NMR (CDCl₃, 400MHz): δ 6.98 (s, 1H), 3.52(s, 1H), 2.80 (t, 2H), 1.70-1.30 (m, 20H), 0.91 (t, 3H); Mn (¹H NMR): 4,750; PDI (SEC): 1.17.

**PMMA terminated with two azido group (PMMA-(N₃)₂)** 4. Diphenyl ethylene (DPE) (1 mL, 5.66 mmol) was reacted with sec-BuLi (1.3 M solution in cyclohexane, 3.8 mL, 4.94 mmol) in 30.0 mL of purified THF at 0 °C for 1 h. LiCl (0.06 g, 0.142 mmol) was dried at 170 °C overnight under high-vacuum, and 30 mL of purified THF was distilled. After LiCl was fully dissolved in THF, temperature was decreased to –78 °C followed by slow injection of prepared initiator (3.49 mL, 0.495 mmol) into the solution. After methyl methacrylate (1.75 g, 17.5 mmol) was introduced and polymerized for 0.5 h, the living PMMA anion solution was injected slowly into tris(bromomethyl)benzene (1.5 g, 4.20 mmol) in THF solution. This mixture was stirred at –78 °C for 2 h, and then solution temperature was increased to –30 °C. After 12 h, reaction was terminated by adding 1 mL of anhydrous 2-propanol. This solution was precipitated into methanol. Reprecipitation with methanol was conducted two times. After drying in vacuum, prepared polymer (0.8 g) and NaN₃(0.075 g) were added into a reactor. Then, anhydrous DMF (20 ml) was added. The solution was stirred at 60 °C for 24 h and precipitated twice into a mixture of methanol and distilled water to yield PMMA-(N₃)₂ ¹H NMR (CDCl₃, 400MHz): δ 7.25-6.90 (m, aromatic H), 4.35 (s, 4H), 3.63-
3.48 (m, 3H), 2.47, 2.76 (m, 2H), 2.30 (m, H), 1.79 (m, 2H), 1.01 (m, 2H), 0.83 (s, 3H), 0.55(m, 6H); Mₙ (SEC): 3,500; PDI: 1.11.

**P3DDT₂PMMA.** 2 (0.15 g, 0.0303 mmol, 2.5 equiv), PMMA-(N₃)₂ 4 (0.042 g, 0.0121 mmol, 1 equiv), and CuBr (0.018 g, 0.125 mmol) were introduced in a Schlenk flask. The flask was degassed thoroughly and backfilled twice with argon. After anhydrous THF (30 ml) was added, nitrogen-purged N,N',N",N"'-pentamethyldiethylamine (PMDETA) (0.025 ml, 0.120 mmol) was injected slowly. The reactor was stirred for 24 h at room temperature. After the solution was diluted with THF and passed through short neutral alumina column to remove the catalyst, it was precipitated in methanol, filtered, and dried under vacuum to yield crude product.

**Figure S4.** Left: Synthetic scheme used to prepare P3DDT₂PMMA according to the previous report.³ Right: SEC traces of 2 (P3DDT-≡), 4 (PMMA-(N₃)₂), and crude product after the click reaction between 2 and 4.
Click reaction between 2 and 4 was conducted to prepare P3DDT$_2$PMMA. An excess amount of monoethynyl-functionalized P3DDT 2 (2.5 equiv relative to PMMA-(N$_3$)$_2$) was used to ensure the complete formation of miktoarm star copolymer. However, form SEC traces as shown in the right panel of Figure S4, a large amount of undesired P3DDT-$b$-PMMA was formed after click reaction, although P3DDT$_2$PMMA was synthesized.

Steric hindrance is important factor in synthesizing complex polymer architecture. Hanisch et al.\textsuperscript{5} synthesized ABC miktoarm star copolymers using click reaction between azido-terminated A polymer and B-$b$-C diblock copolymer having alkyne group at the block junction. They successfully synthesized ABC miktoarm star copolymer when overall molecular weight was smaller than 25,000 g/mol. However, synthesis of ABC miktoarm star copolymer with higher molecular weight was not successful because the alkyne group at the center of the B-$b$-C diblock copolymer is less amenable. Luo et al.\textsuperscript{6} synthesized graft copolymer using click reaction between azide groups on main chain and alkyne groups at star copolymers. However, the graft efficiency is lower than 63.9% due to the steric hindrance.

This suggests that a click reaction using monoethynyl-terminated poly(3-dodecylthiophene) might not be efficient for synthesis of complex block copolymer architecture such as miktoarm star copolymer due to steric hindrance around reactive groups because of long dodecyl side group.
4. WAXS profiles for P3DDT$_2$PMMAs.

![WAXS profiles for P3DDT$_2$PMMAs](image)

**Figure S5.** WAXS profiles at room temperature for three different P3DDT$_2$PMMAs and $\omega$-azidopropyl-P3DDT after thermal annealing at 160 °C for 24 h.
5. SAXS and TEM image of P3DDT$_2$PMMA with various values of $w_{\text{P3DDT}}$

![Graph and TEM image](image)

**Figure S6.** SAXS profile measured at room temperature and (b) TEM image of P3DDT$_2$PMMA-M1 with $w_{\text{P3DDT}} = 0.33$.

Figure S7 gives SAXS profile measured at room temperature and TEM image of P3DDT$_2$PMMA-M3 with $w_{\text{P3DDT}} = 0.59$. In TEM image, line and dot patterns are clearly seen in the whole area, suggesting that this block copolymer has cylindrical microdomains. Interestingly, SAXS profile does not clearly show $\sqrt{3} q^*$ (or $\sqrt{7} q^*$) peak, while this peak is expected for hexagonally packed cylindrical microdomains (for instance, see Figure 5 in the main manuscript as well as Figures S8 and S9). This might be attributed to the fact that the weight fraction ($w_{\text{P3DDT}} = 0.59$) in P3DDT$_2$PMMA-M3 would be close to the phase boundary between lamellar and cylinder microdomains. However, only a single first order peak $q^*$ was observed, as seen in the inset of Figure S7(a), meaning that this block copolymer has one type of microdomain, not mixed microdomains. Therefore, we conclude that P3DDT$_2$PMMA-M3 shows cylindrical microdomains, although a good ordering of the cylindrical microdomains in hexagonal packing is not achieved.
Figure S7. SAXS profile measured at room temperature (inset is an enlarged SAXS profile) and (b) TEM image (inset is a high magnified image) of P3DDT\textsubscript{2}PMMA-M3 with $w_{\text{P3DDT}} = 0.59$.

Figure S8. SAXS profile measured at room temperature and (b) TEM image of P3DDT\textsubscript{2}PMMA-M4 with $w_{\text{P3DDT}} = 0.69$
Figure S9. SAXS profile measured at 160 °C for P3DDT2PMMA-M5 with \( w_{P3DDT} = 0.76 \).

References