

## Supporting Information

### **Synthesis of Conjugated Rod-Coil Block Copolymers by RuPhos Pd-catalyzed Suzuki-Miyaura Catalyst-Transfer Polycondensation: Initiation from Coil-Type Polymers**

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## Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Radical inhibitors were removed from monomers (styrene, methyl acrylate, and methyl methacrylate) before use by running them through a basic aluminum oxide plug. All solvents and monomers were degassed by argon bubbling for 10 minutes before using on polymerization.

## General analytical information

<sup>1</sup>H NMR spectra were recorded with a JEOL Resonance ECZ600R (600 MHz) spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, parts per million (ppm) downfield from TMS. Size exclusion chromatography (SEC) was performed at 35 °C using Shodex LF-804 columns eluted with tetrahydrofuran in a Waters 1515 pump, a Waters 2414 refractive index detector, and a Waters 2489 UV detector. Number average molecular weights ( $M_n$ ) and weight average molecular weights ( $M_w$ ) were calculated relative to linear polystyrene standards. Dispersity ( $\mathcal{D}$ ) values are reported as the quotient of  $M_w/M_n$ . IR spectra were recorded with a Thermo Scientific Nicolet iS50 FTIR spectrometer. Photopolymerization was performed using a THORLABS M405L3-C1 as a light source. Differential scanning calorimetry (DSC) was carried out under N<sub>2</sub> gas at a scan rate of 10 °C/min with DSC 200 F3 Maia from NETZSCH.

## Procedure for the preparation of 5-bromo-4-*n*-hexylthien-2-yl-MIDA-boronate (M1)

**M1** was prepared by the slightly modified procedure from the previous literature.<sup>34</sup> In summary, to a round-bottom flask equipped with a magnetic stir bar, (5-bromo-4-hexylthiophen-2-yl)boronic acid (2.0 g, 6.87 mmol),<sup>51</sup> *N*-methyliminodiacetic acid (3.0 g, 20.6 mmol), DMSO (5 ml), and benzene (45 ml) were added. The reaction mixture was heated with a Dean-Stark trap for 15 h at 110 °C.<sup>52</sup> The crude reaction mixture was concentrated under reduced pressure and then diluted with chloroform, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated again under reduced pressure. The reaction mixture was then purified by silica gel column chromatography using ethyl acetate/hexane (v/v = 1/3) as an eluent. The product was further purified by repeated recrystallization from cold hexane.

## Procedure for the preparation of 5-bromo-4-(2-ethylhexyl)thien-2-yl-MIDA-boronate (M2)

**M2** was prepared by the slightly modified procedure from the previous literature.<sup>34</sup> In summary, to a round-bottom flask equipped with a magnetic stir bar, (5-bromo-4-(2-ethylhexyl)thien-2-yl)boronic acid (2.0 g, 6.87 mmol),<sup>51</sup> *N*-methyliminodiacetic acid (3.0 g, 20.6 mmol), DMSO (5 ml), and benzene (45 ml) were added. The reaction mixture was heated with a Dean-Stark trap for 15 h at 110 °C.<sup>52</sup> The crude reaction mixture was concentrated under reduced pressure and then diluted with chloroform, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated again under reduced pressure. The reaction mixture was then purified by silica gel column chromatography using ethyl acetate/hexane (v/v = 1/3) as an eluent. The product was further purified by repeated recrystallization from cold hexane.

## Procedure for the preparation of 1-iodo-4-((prop-2-ynyl)oxy)methyl)benzene (A1)

The monomer was prepared by the previously reported synthetic method.<sup>53</sup> <sup>1</sup>H NMR spectrum of **A1** was matched with that reported in the literature.<sup>53</sup>

#### **Procedure for the polymerization of styrene via normal ATRP (PS-Br)<sup>37,38</sup>**

Ethyl  $\alpha$ -bromoisobutyrate (EBiB) (74  $\mu$ l, 0.5 mmol), CuBr (0.071 g, 0.5 mmol), PMDETA (0.10 ml, 0.5 mmol), styrene (2.8 ml, 25 mmol), and anisole (2.8 ml) were added to a 20 ml vial. The mixture was degassed by purging with argon for 10 minutes. The vial was then sealed with Teflon tape and Parafilm and reacted at 90 °C for 4 h. The crude reaction mixture was diluted in chloroform and passed through neutral alumina to remove the residual catalyst. The mixture was concentrated and precipitated into MeOH to give PS as a white solid. The molecular weight ( $M_n = 2.5$  kg/mol) and dispersity ( $\mathcal{D} = 1.05$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

#### **Procedure for the polymerization of methyl acrylate via photo-ATRP (PMA-Br)<sup>46</sup>**

Ethyl  $\alpha$ -bromoisobutyrate (EBiB) (49  $\mu$ l, 0.33 mmol), CuBr<sub>2</sub> (0.0011 g, 0.0049 mmol), Me<sub>6</sub>TREN (7  $\mu$ l, 0.0264 mmol), methyl acrylate (6 ml, 66 mmol), and DMSO (6 ml) were added to a 50 ml round bottom flask. The mixture was degassed by purging with argon for 10 minutes and irradiated with a 405 nm LED on a stir plate. The polymerization was left to stir for 12 minutes before turning off the light and opening the flask to air. The crude reaction mixture was diluted in chloroform and passed through neutral alumina to remove the residual catalyst. The organic layer was washed with brine three times, dried with MgSO<sub>4</sub>, concentrated, and precipitated into MeOH/H<sub>2</sub>O (v/v = 1:1) to give PMA as a sticky solid. The molecular weight ( $M_n = 5.5$  kg/mol) and dispersity ( $\mathcal{D} = 1.17$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

#### **Procedure for the preparation of high molecular weight PMA-Br via photo-ATRP<sup>46</sup>**

Ethyl  $\alpha$ -bromoisobutyrate (EBiB) (44  $\mu$ l, 0.3 mmol), CuBr<sub>2</sub> (0.0013 g, 0.006 mmol), Me<sub>6</sub>TREN (9.6  $\mu$ l, 0.036 mmol), methyl acrylate (5.4 ml, 60 mmol), and DMSO (5.4 ml) were added to a 50 ml round bottom flask. The mixture was degassed by purging with argon for 10 minutes and irradiated with a 405 nm LED on a stir plate. The polymerization was left to stir for 1 hour before turning off the light and opening the flask to air. The crude reaction mixture was diluted in chloroform and passed through neutral alumina to remove the residual catalyst. The organic mixture was concentrated and precipitated into MeOH/H<sub>2</sub>O (v/v = 1:1) to give PMA as a sticky solid. The molecular weight ( $M_n = 13.6$  kg/mol) and dispersity ( $\mathcal{D} = 1.04$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

#### **Procedure for the polymerization of methyl methacrylate via photo-ATRP (PMMA-Br)<sup>47</sup>**

Ethyl  $\alpha$ -bromoisobutyrate (EBiB) (73  $\mu$ l, 0.5 mmol), CuBr<sub>2</sub> (0.0044 g, 0.12 mmol), Me<sub>6</sub>TREN (32  $\mu$ l, 0.12 mmol), methyl methacrylate (10 ml, 100 mmol), and DMSO (10 ml) were added to a 50 ml round bottom flask. The mixture was degassed by purging with argon for 10 minutes and irradiated with a 405 nm LED on a stir plate. The polymerization was left to stir for 1 hour before turning off the light and opening the flask to air. The crude reaction mixture was diluted in chloroform and passed through neutral alumina to remove the residual catalyst. The organic layer was washed with brine three times, dried with MgSO<sub>4</sub>, concentrated, and precipitated into cold hexane to give PMMA as a white solid. The molecular weight ( $M_n = 4.8$  kg/mol) and dispersity ( $\mathcal{D} = 1.26$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

### Procedure for the preparation of high molecular weight PMMA-Br via photo-ATRP<sup>47</sup>

Ethyl  $\alpha$ -bromophenylacetate (EBPA) (122  $\mu$ l, 0.7 mmol), CuBr<sub>2</sub> (0.0031 g, 0.014 mmol), Me<sub>6</sub>TREN (22  $\mu$ l, 0.084 mmol), methyl methacrylate (15 ml, 140 mmol), and DMSO (15 ml) were added to a 50 ml round bottom flask. The mixture was degassed by purging with argon for 15 minutes and irradiated with a 405 nm LED on a stir plate. The polymerization was left to stir for 5 hours before turning off the light and opening the flask to air. The crude reaction mixture was diluted in chloroform and passed through neutral alumina to remove the residual catalyst. The mixture was concentrated and precipitated into MeOH to give PMMA as a white solid. The molecular weight ( $M_n = 14.1$  kg/mol) and dispersity ( $\mathcal{D} = 1.12$ ) of the polymer were obtained by SEC eluting with THF (using PS standard).

### General procedure for azidation of bromide end-group of ATRP polymers<sup>37,38</sup>

Bromide end-functionalized polymer (1 equiv) and NaN<sub>3</sub> (20 equiv) were added to a round bottom flask. The flask was evacuated and backfilled with argon three times, and degassed DMF was added until a clear solution was observed. The mixture was heated at 40 °C overnight. The reaction mixture was concentrated under vacuum, diluted with CHCl<sub>3</sub>, and purified by precipitation into MeOH/H<sub>2</sub>O (v/v = 1:1) for PMA and MeOH for PS and PMMA, respectively.

### General procedure for Click coupling reactions of PS-N<sub>3</sub>, PMA-N<sub>3</sub>, and PMMA-N<sub>3</sub> with 1-iodo-4-((prop-2-ynyl)oxy)methyl)benzene (A1)<sup>37,38</sup>

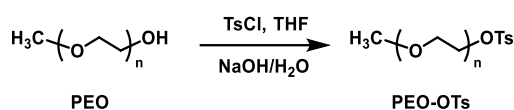
Azide end-functionalized polymer (1 equiv), CuI (3 equiv), PMDETA (3 equiv), and alkyne monomer **A1** (3 equiv) were added to a round bottom flask. The flask was evacuated and backfilled with argon three times, and degassed THF was added until a clear solution was observed. The mixture was heated at 50 °C overnight. The crude reaction mixture was diluted in chloroform and passed through neutral alumina to remove the residual catalyst. The reaction mixture was concentrated and precipitated into MeOH/H<sub>2</sub>O (v/v = 1:1) for PMA and MeOH for PS and PMMA, respectively.

### General procedure for block copolymerization of M1 with coil-type macroinitiators

To a round bottom flask equipped with a magnetic stir bar, macroinitiator (0.008 mmol), RuPhos Pd G3 precatalyst (0.0088 mmol), RuPhos (0.0528 mmol), and K<sub>3</sub>PO<sub>4</sub> (1.2 mmol) were added. The flask was evacuated and backfilled with argon three times. After that, THF (2 ml) and H<sub>2</sub>O (0.72 ml) degassed with argon were added to the flask. The mixture was heated and stirred at 50 °C for 1 h to prepare the externally initiated catalyst. After that, **M1** (0.2 mmol when [monomer]/[initiator] = 25) in degassed THF (17 ml) was added to the flask, and polymerization was left to stir at 45 °C for 15–28 h depending on [M]/[I] ratios. The polymerization was quenched with 6N HCl (5 ml) for **P2** or 5N NH<sub>4</sub>Cl solution (5 ml) for **P5** and **P6**. The crude reaction mixture was diluted with CHCl<sub>3</sub> and washed with brine. The organic layer was concentrated under reduced pressure and purified by precipitation into MeOH. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum. Reaction conditions with various [M]/[I] ratios are summarized below.

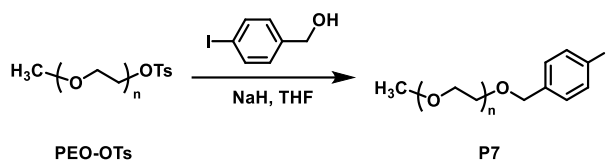
[M]/[I]	Macroinitiator (mmol)	RuPhos Pd G3 precatalyst (mmol)	RuPhos (mmol)	K <sub>3</sub> PO <sub>4</sub> (mmol)	THF (ml) for catalyst preparation	H <sub>2</sub> O (ml) for catalyst preparation	<b>M1</b> in THF (mmol/ml)
25	0.008	0.0088	0.0528	1.2	2	0.72	0.2/17
50	0.004	0.0044	0.0264	1.2	2	0.72	0.2/17
75	0.0027	0.0029	0.0178	1.2	2	0.72	0.2/17

### Procedure for the preparation of PEO-OTs



PEO-OTs was prepared by the procedure from the previous literature.<sup>S4</sup> To a round-bottom flask equipped with a magnetic stir bar, sodium hydroxide (1.8g, 45 mmol), water (15ml) and polyethylene glycol (3g, 1.5 mmol) were added. *p*-Toluenesulfonyl chloride (2.9g, 45 mmol) dissolved in THF (15 ml) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was allowed to stir for 3 hours at 0 °C and then for 24 hours at room temperature. The crude reaction mixture was diluted in dichloromethane, washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure to give PEO-OTs as a white solid.

### Procedure for the preparation of PEO macroinitiator (P7) from PEO-OTs



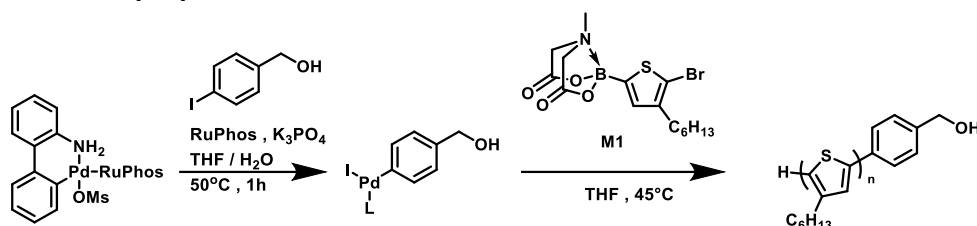
To a round bottom flask equipped with a magnetic bar, sodium hydride (0.08g, 3.34 mmol) and THF (11ml) were sequentially added. 4-iodobenzyl alcohol (0.65g, 2.78 mmol) dissolved in THF (9 ml) was added to the reaction mixture at 0 °C and allowed to stir for 30 minutes at room temperature. After that, PEO-OTs (0.6g, 0.28 mmol) dissolved in THF (7 ml) was added dropwise at 0 °C and then stirred at room temperature overnight. The crude reaction mixture was diluted in dichloromethane, washed with brine, dried over anhydrous MgSO<sub>4</sub>, concentrated under reduced pressure and precipitated into diethyl ether to give PEO macroinitiator as a white solid.

### Procedure for block copolymerization of M1 with P7

To a 20 ml vial equipped with a magnetic stir bar, RuPhos Pd G3 precatalyst (0.0052 mmol), **P7** (0.004 mmol), RuPhos (0.0312 mmol), and K<sub>3</sub>PO<sub>4</sub> (1.2 mmol) were added. The flask was evacuated and backfilled with argon three times. THF (2 ml) and H<sub>2</sub>O (0.72 ml) degassed with argon were then added. The mixture was heated and stirred at 50 °C for 1 h to prepare the externally initiated catalyst. **M2** (0.2 mmol where **[M2]/[P7]** = 50) in degassed THF (17 ml) was then added to the flask, and polymerization was left to stir at 45 °C for 16 hours before quenched with 6N HCl (5 ml). The crude reaction mixture was diluted with CHCl<sub>3</sub> and washed with brine. The organic layer was concentrated under reduced pressure and precipitated into methanol to afford a violet solid. The precipitate was collected by filtration, washed with methanol, and dried under vacuum. The molecular weight (*M<sub>n</sub>* = 10.0 kg/mol) and dispersity (*D* = 1.10) of the polymer were obtained by SEC eluting with THF (using polystyrene standard). The reaction condition with **[M2]/[P7]** ratio of 75 is summarized below.

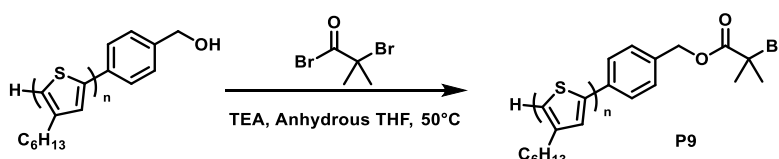
[M]/[I]	Macroinitiator (mmol)	RuPhos Pd G3 precatalyst (mmol)	RuPhos (mmol)	K <sub>3</sub> PO <sub>4</sub> (mmol)	THF (ml) for catalyst preparation	H <sub>2</sub> O (ml) for catalyst preparation	<b>M1</b> in THF (mmol/ml)
75	0.0027	0.0035	0.0208	1.2	2	0.72	0.2/17

### Procedure for the preparation of P3HT-OH via SCTP



To a round bottom flask equipped with a magnetic stir bar, RuPhos Pd G3 precatalyst (0.067 mmol), 4-iodobenzyl alcohol (0.067 mmol), RuPhos (0.1 mmol), and K<sub>3</sub>PO<sub>4</sub> (6 mmol) were added. The flask was evacuated and backfilled with argon three times. After that, THF (10 ml) and H<sub>2</sub>O (3.6 ml) degassed with argon were added to the flask. The mixture was heated and stirred at 50 °C for 1 h to prepare the externally initiated catalyst. **M1** (1 mmol) in degassed THF (85 ml) was then added to the flask, and polymerization was left to stir at 45 °C for 15 h before quenched by 6N HCl (25 ml). The crude reaction mixture was diluted with CHCl<sub>3</sub>, washed with brine. The organic layer was concentrated under reduced pressure and purified by precipitation into MeOH. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum to afford P3HT-OH as a violet solid. The molecular weight ( $M_n = 3.3$  kg/mol) and the dispersity ( $D = 1.11$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

### Procedure for the preparation of P3HT macroinitiator (P9) from P3HT-OH

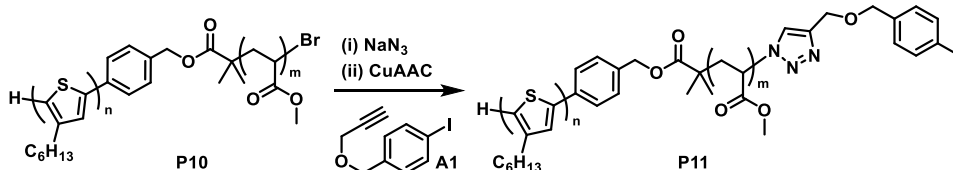


**P9** was prepared by the slightly modified procedure from the previous literature.<sup>23</sup> In summary, to a 20 ml vial equipped with a magnetic stir bar, P3HT-OH (0.05 mmol), anhydrous THF (2 ml), triethylamine (1 mmol) and 2-bromoisobutyryl bromide (1 mmol) were added. The mixture was degassed by purging with argon for 10 minutes and heated at 50 °C overnight. The crude reaction mixture was diluted in chloroform and washed with brine three times. The organic layer was concentrated and precipitated into MeOH to afford **P9** as a violet solid. The molecular weight ( $M_n = 3.3$  kg/mol) and the dispersity ( $D = 1.12$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

### Procedure for the preparation of P3HT-*b*-PMA (P10) from P3HT macroinitiator (P9) via normal-ATRP<sup>50</sup>

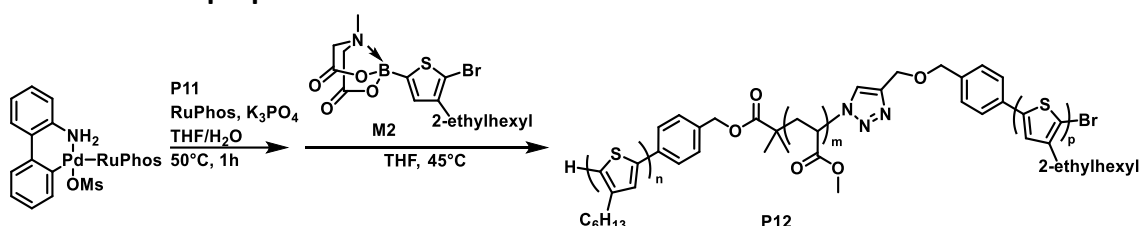
To a 4 ml vial equipped with a magnetic stir bar, P3HT macroinitiator (**P9**, 0.046 mmol), CuBr (0.046 mmol), PMDETA (0.046 mmol) were added. The vial was evacuated and backfilled with argon three times. Toluene (1.25 ml) and methyl acrylate (1.25 ml) degassed by purging with argon for 10 minutes in a separate vial were added to the vial containing the mixture. After that, the vial was sealed with Teflon tape and Parafilm and stirred at 90 °C for 1 hour. The crude reaction mixture was diluted with CHCl<sub>3</sub> and washed with brine. The organic layer was concentrated under reduced pressure and purified by precipitation into MeOH. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum. The molecular weight ( $M_n = 4.7$  kg/mol) and dispersity ( $D = 1.19$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

## Procedure for the preparation of macroinitiator **P11** from **P10** via end-group azidation and sequential Click reaction with **A1**



P3HT-*b*-PMA-Br (**P10**) (0.027 mmol) and  $\text{NaN}_3$  (0.83 mmol) were added to a 20 ml vial. The vial was evacuated and backfilled with argon three times, and THF (2 ml) and DMF (1 ml) degassed with argon were added. The reaction mixture was stirred at 40 °C overnight. After the reaction, the crude reaction mixture was concentrated under vacuum, diluted with  $\text{CHCl}_3$ , and purified by precipitation into methanol. Subsequently, azide-end functionalized P3HT-*b*-PMA- $\text{N}_3$  (1 equiv), alkyne **A1** (4 equiv), CuI (4 equiv), and PMDETA (4 equiv) were added to a 4 ml vial. The vial was evacuated and backfilled with argon three times, and THF (1 ml) degassed with argon was added. The reaction mixture was stirred at 50 °C overnight. After the reaction, the crude reaction mixture was diluted in chloroform and washed with brine three times. The organic layer was concentrated and precipitated into MeOH. The molecular weight ( $M_n = 4.8$  kg/mol) and dispersity ( $D = 1.19$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard).

## Procedure for the preparation of **P12** from **P11** via SCTP



To a 20 ml vial equipped with a magnetic stir bar, RuPhos Pd G3 precatalyst (0.0052 mmol), **P11** (0.004 mmol), RuPhos (0.0312 mmol), and  $\text{K}_3\text{PO}_4$  (0.6 mmol) were added. The flask was evacuated and backfilled with argon three times. THF (1 ml) and  $\text{H}_2\text{O}$  (0.36 ml) degassed with argon were then added. The mixture was heated and stirred at 50 °C for 2 h to prepare the externally initiated catalyst. **M2** (0.1 mmol where  $[\text{M2}]/[\text{P11}] = 25$ ) in degassed THF (8.5 ml) was then added to the flask, and polymerization was left to stir at 45 °C for 15 hours before quenched with 5N  $\text{NH}_4\text{Cl}$  (2.5 ml). The crude reaction mixture was diluted with  $\text{CHCl}_3$  and washed with brine. The organic layer was concentrated under reduced pressure and precipitated into methanol to afford a violet solid. The precipitate was collected by filtration, washed with methanol, and dried under vacuum. The molecular weight ( $M_n = 11.5$  kg/mol) and dispersity ( $D = 1.20$ ) of the polymer were obtained by SEC eluting with THF (using polystyrene standard). The reaction condition with  $[\text{M2}]/[\text{P11}]$  ratio of 50 is summarized below.

[M]/[I]	Macroinitiator (mmol)	RuPhos Pd G3 precatalyst (mmol)	RuPhos (mmol)	$\text{K}_3\text{PO}_4$ (mmol)	THF (ml) for catalyst preparation	$\text{H}_2\text{O}$ (ml) for catalyst preparation	<b>M2</b> in THF (mmol/ml)	Reaction time (1 <sup>st</sup> step/2 <sup>nd</sup> step) (h)
50	0.002	0.0026	0.0156	0.6	1	0.36	0.1/8.5	1.5/20

Figure S1. IR spectrum and SEC traces of PS-N<sub>3</sub> and PS macroinitiator (P1)

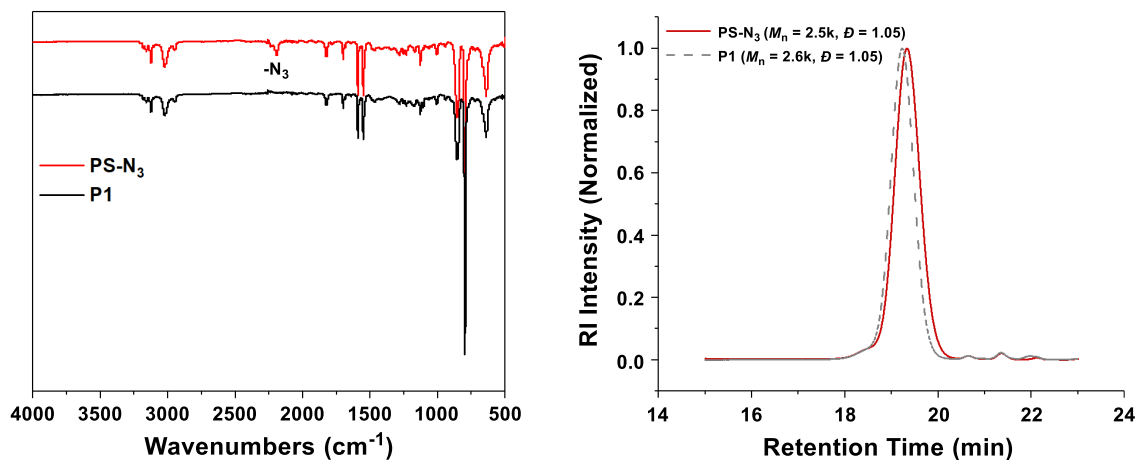


Figure S2. <sup>1</sup>H NMR spectrum and SEC traces of PS-*b*-P3HT (P2). SEC traces were monitored by RI and UV (450 nm) detectors (Table1, entries 1–3)

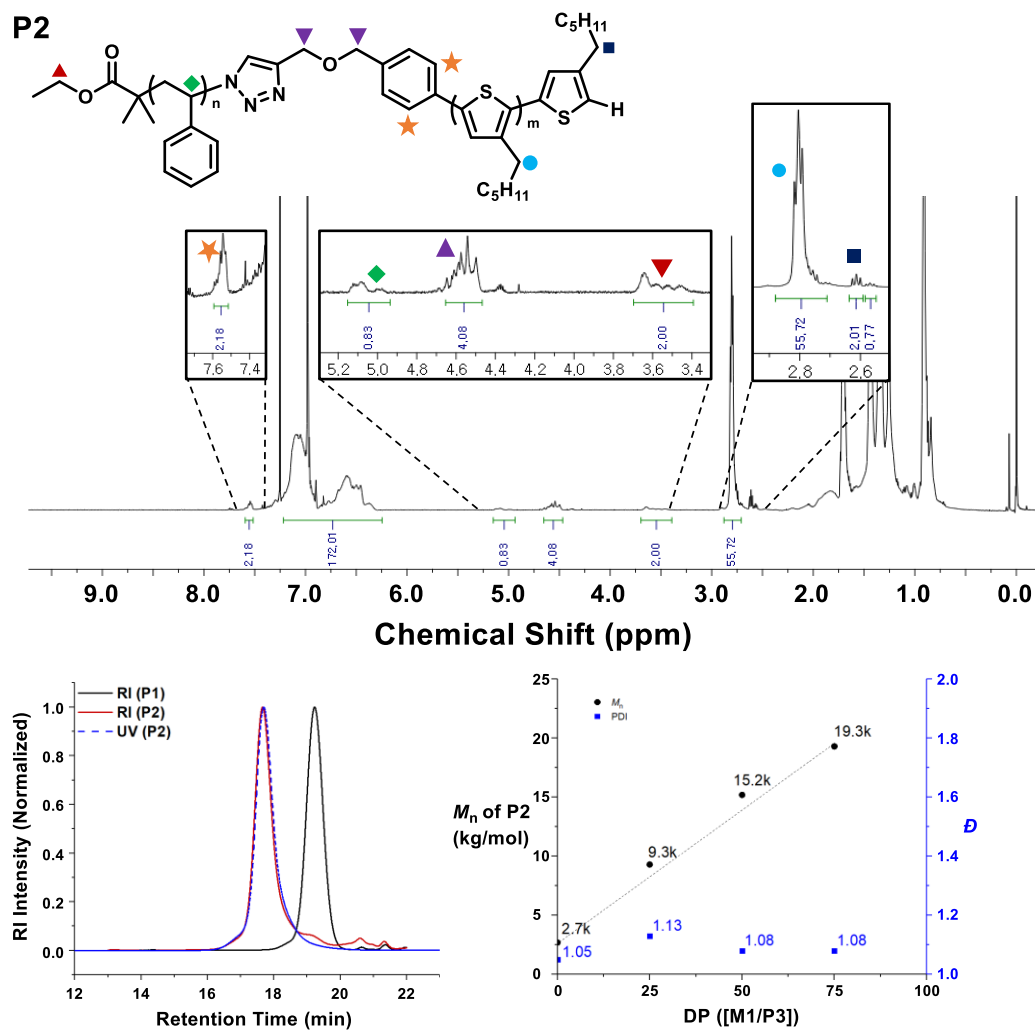
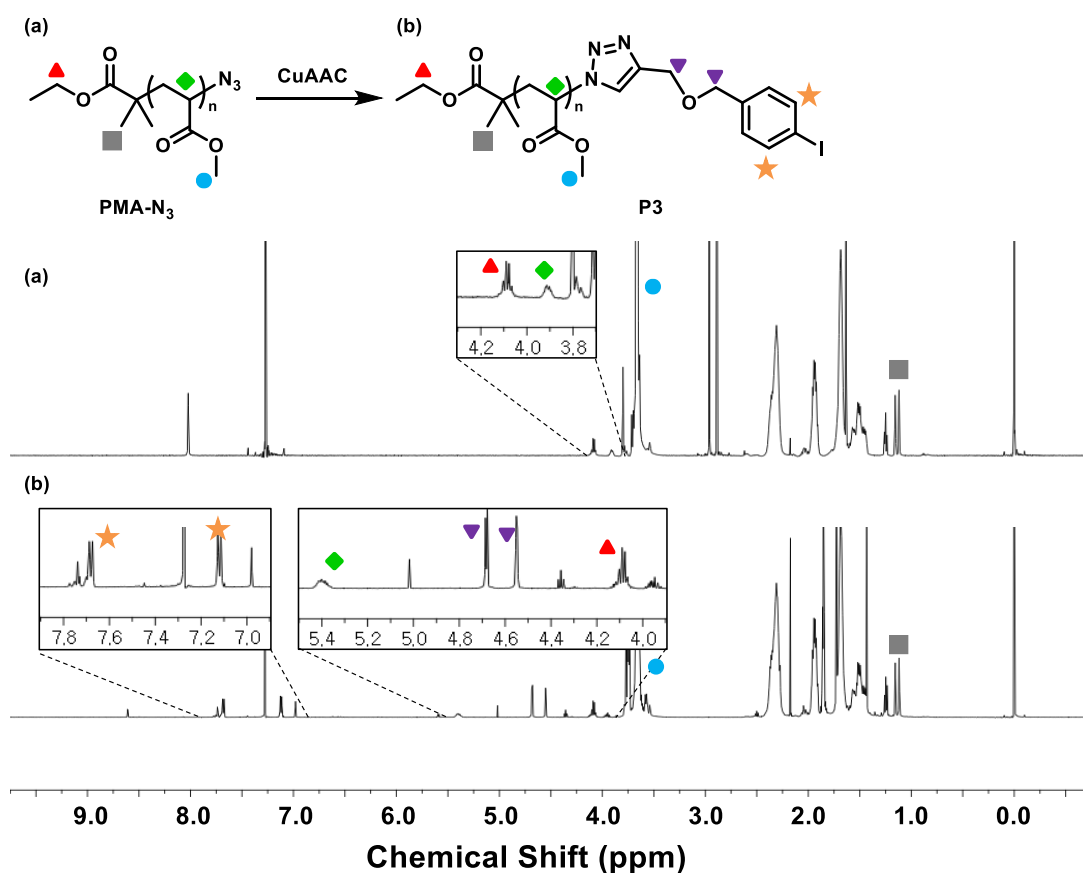


Figure S3.  $^1\text{H}$  NMR and IR spectra and SEC traces of PMA- $\text{N}_3$  and PMA macroinitiator (P3).



The end-group fidelity of low  $M_n$  P3 (5.6k) is estimated by  $\blacklozenge/\blacktriangle$  ratio (>95%).  
 The end-group fidelity of high  $M_n$  P3 (13.8k) is estimated by  $\star/\blacksquare$  ratio (80%).

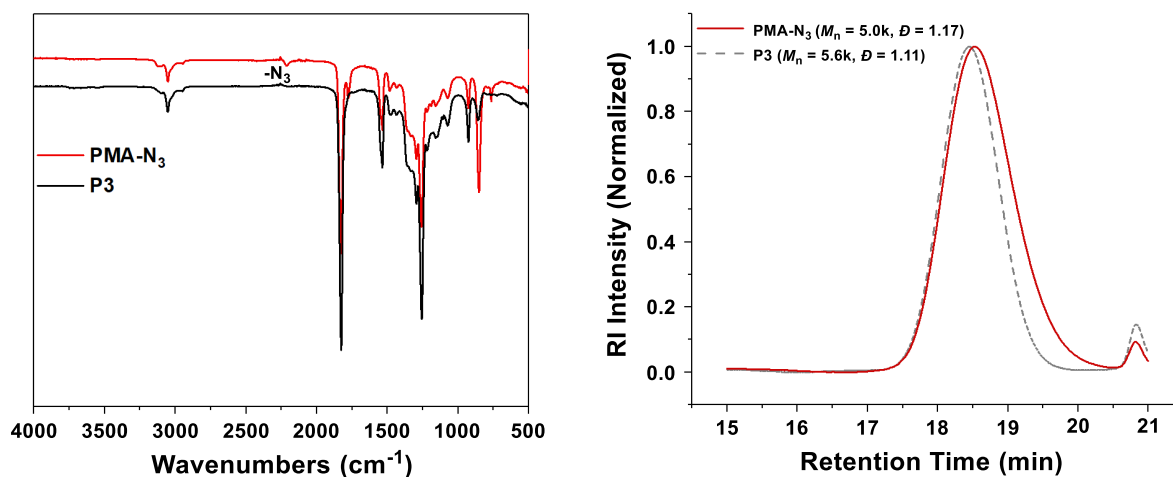


Figure S4.  $^1\text{H}$  NMR spectrum and SEC traces of PMA-*b*-P3HT (P4; Table2, entries 1–3)

P4

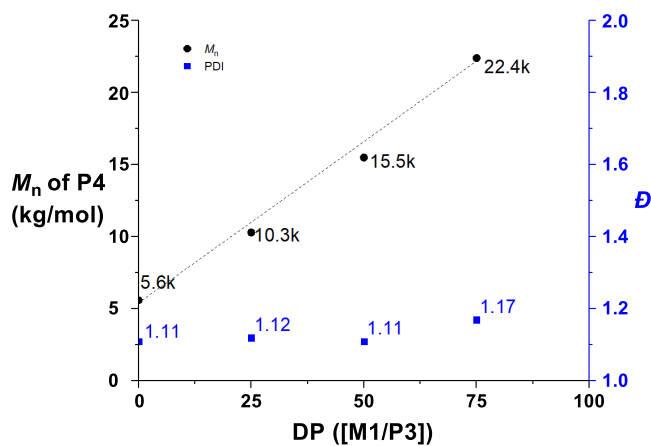
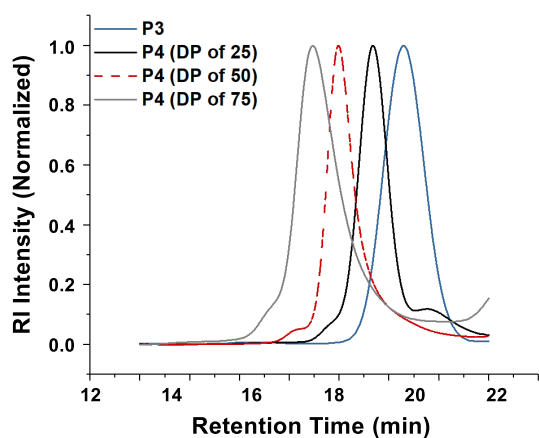
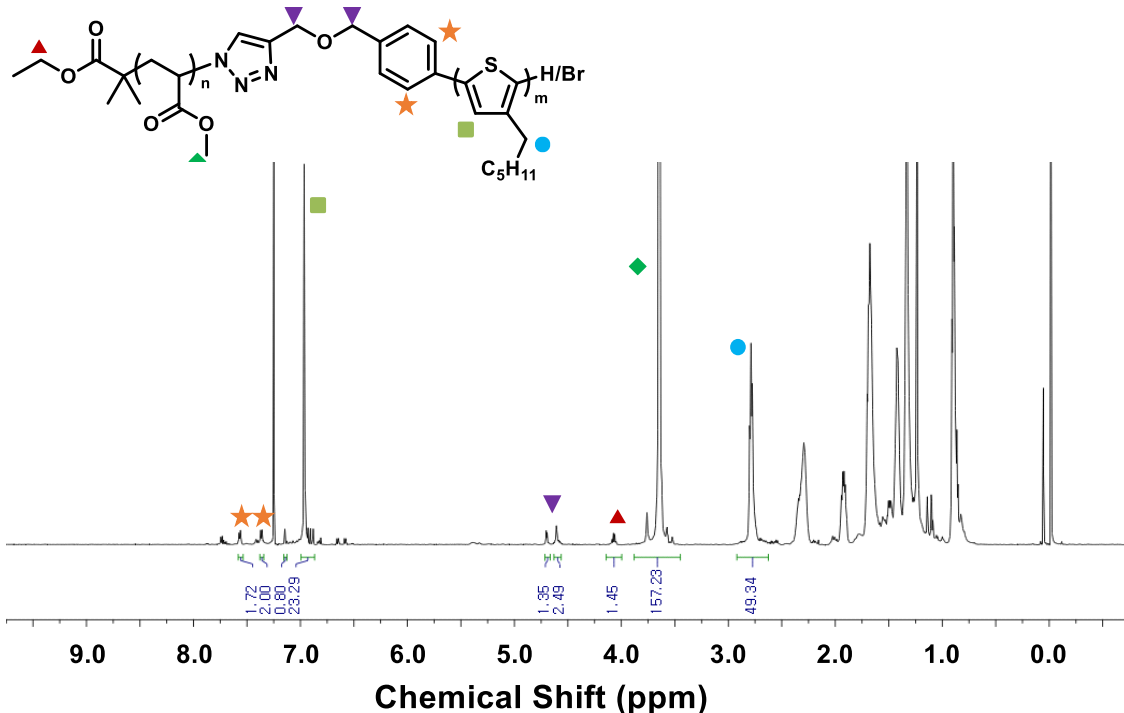
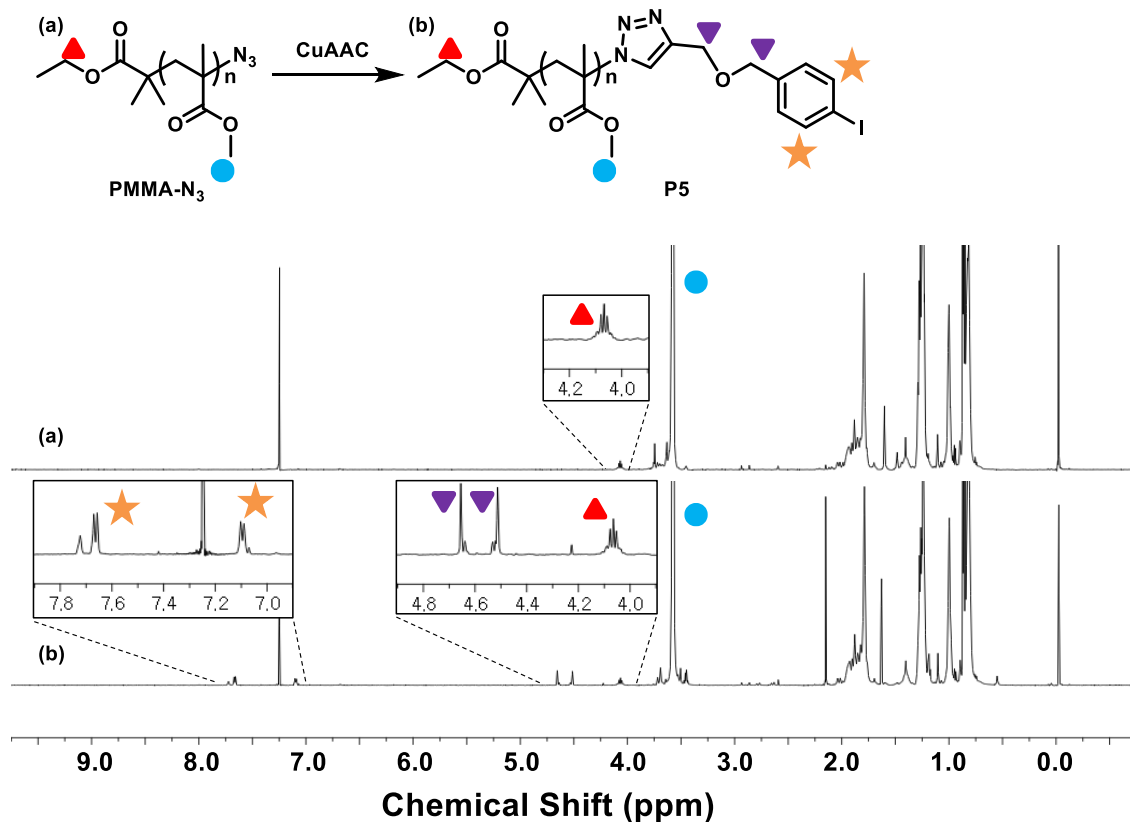


Figure S5. <sup>1</sup>H NMR and IR spectra and SEC traces of PMMA-N<sub>3</sub> and PMMA macroinitiator (P5)



The end-group fidelity of low  $M_n$  P5 (4.8k) was estimated by ★/▲ ratio (80%).  
 The end-group fidelity of high  $M_n$  P5 (14.2k) was estimated by ★/▲ ratio (70%).

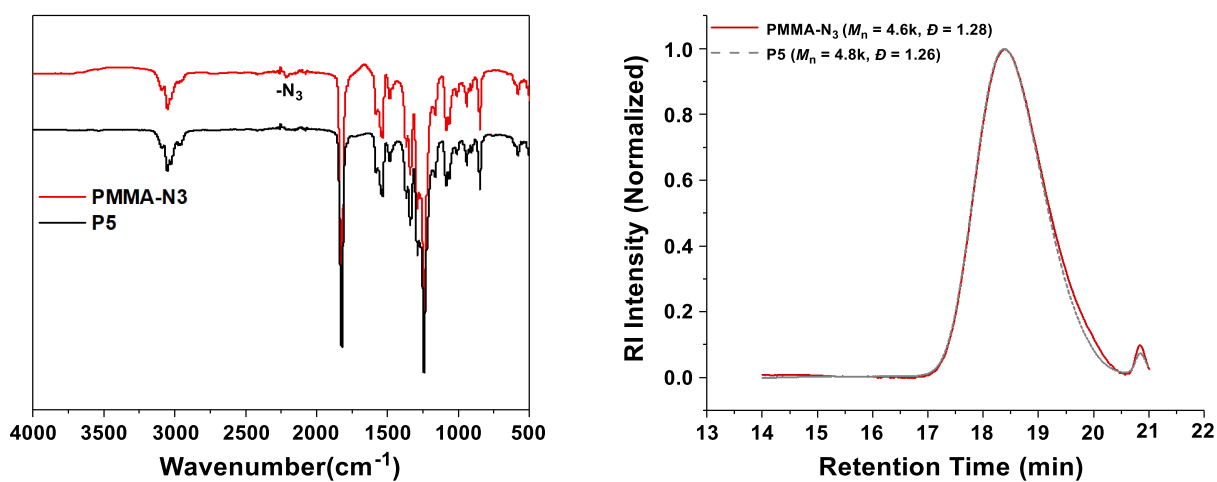


Figure S6.  $^1\text{H}$  NMR spectrum and SEC traces of PMMA-*b*-P3HT (P6; Table2, entries 4 and 5)

P6

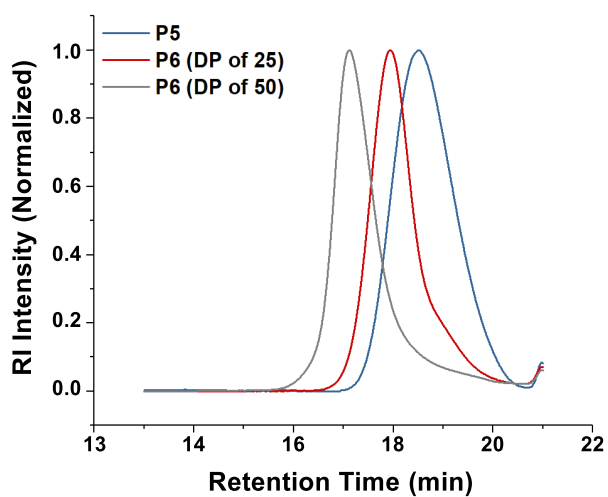
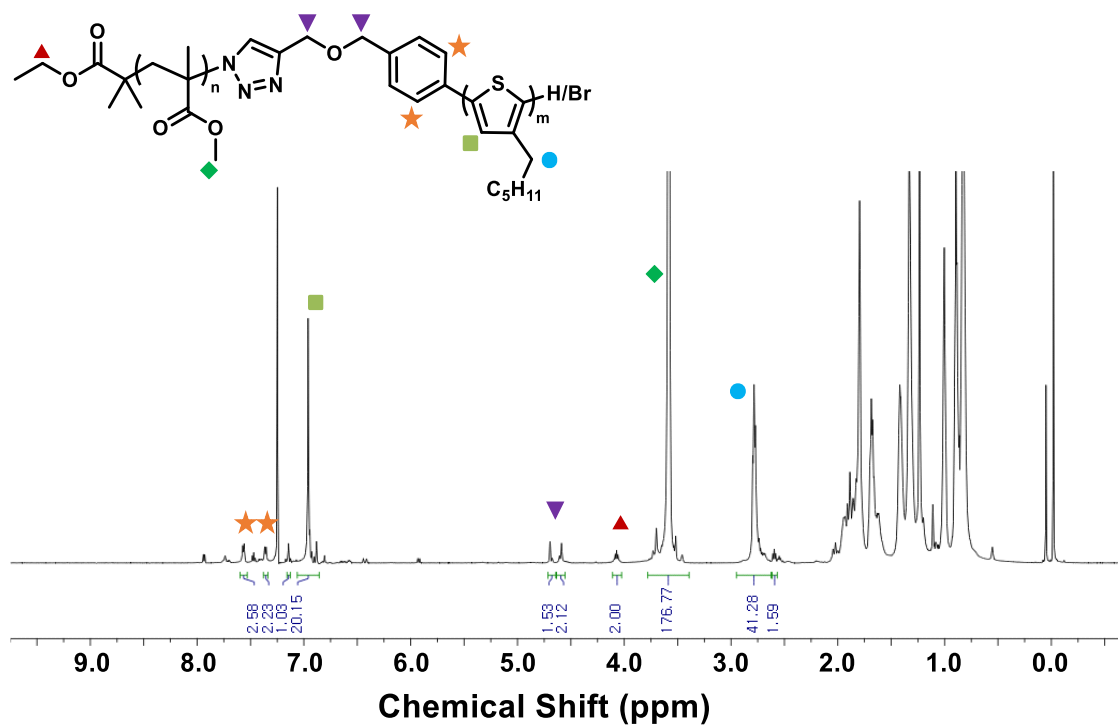


Figure S7. SEC RI traces of high molecular weight PMA (P3) and PMMA (P5) macroinitiators and SEC RI and UV-vis traces of their corresponding diblock copolymers, PMA-*b*-P3HT (P4) and PMMA-*b*-P3HT (P6) (Table2, entries 6–8).

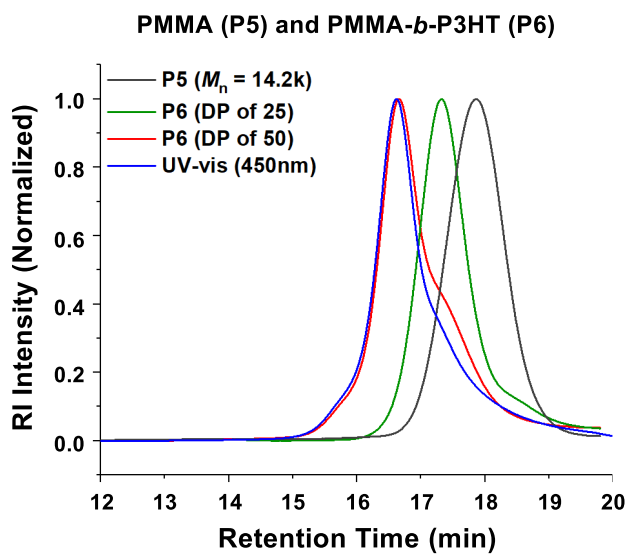
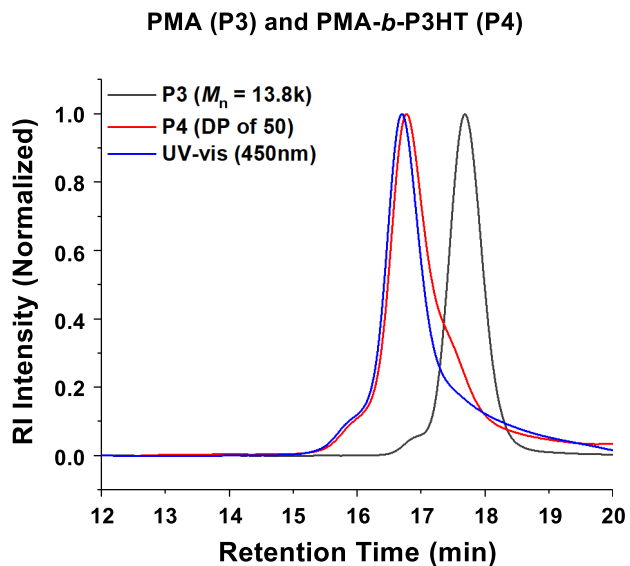


Figure S8.  $^1\text{H}$  NMR spectrum and SEC trace of PEO macroinitiator (P7)

P7

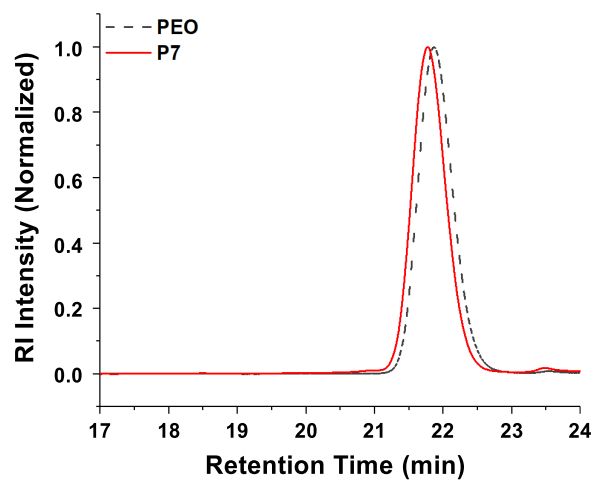
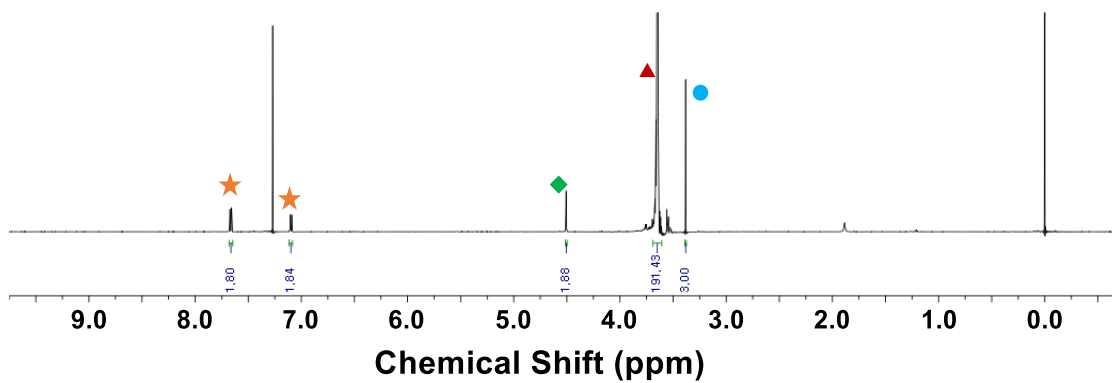
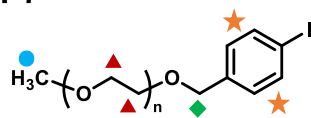


Figure S9.  $^1\text{H}$  NMR spectrum and SEC trace of PEO-*b*-P3HT (P8; Table3, entries 1 and 2)

P8 (DP of 75)

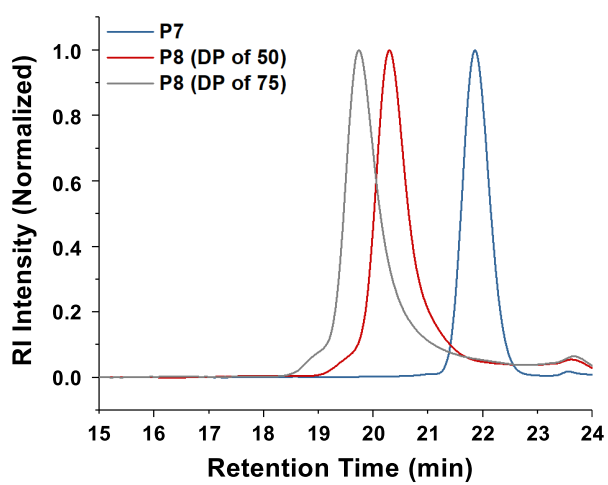
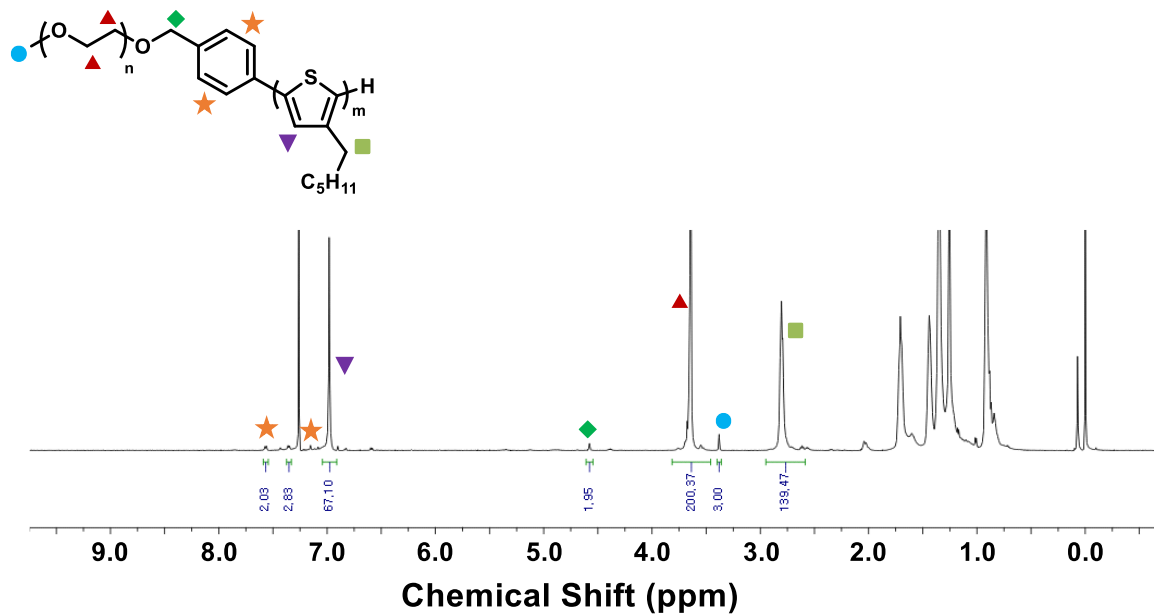
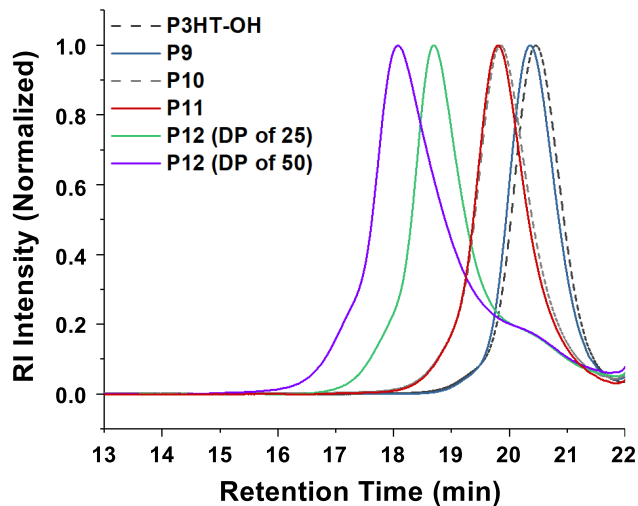
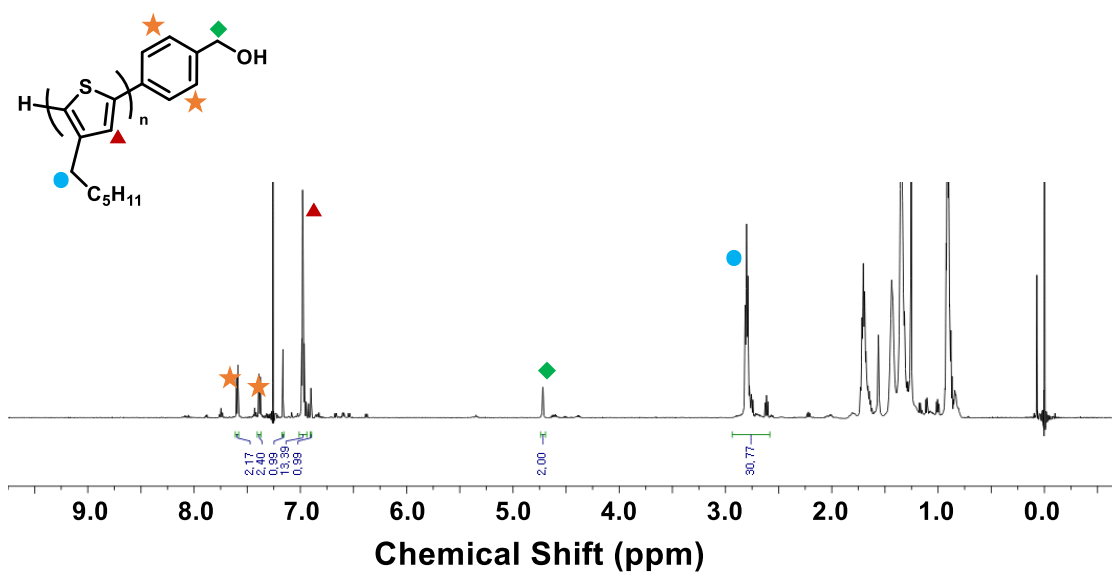


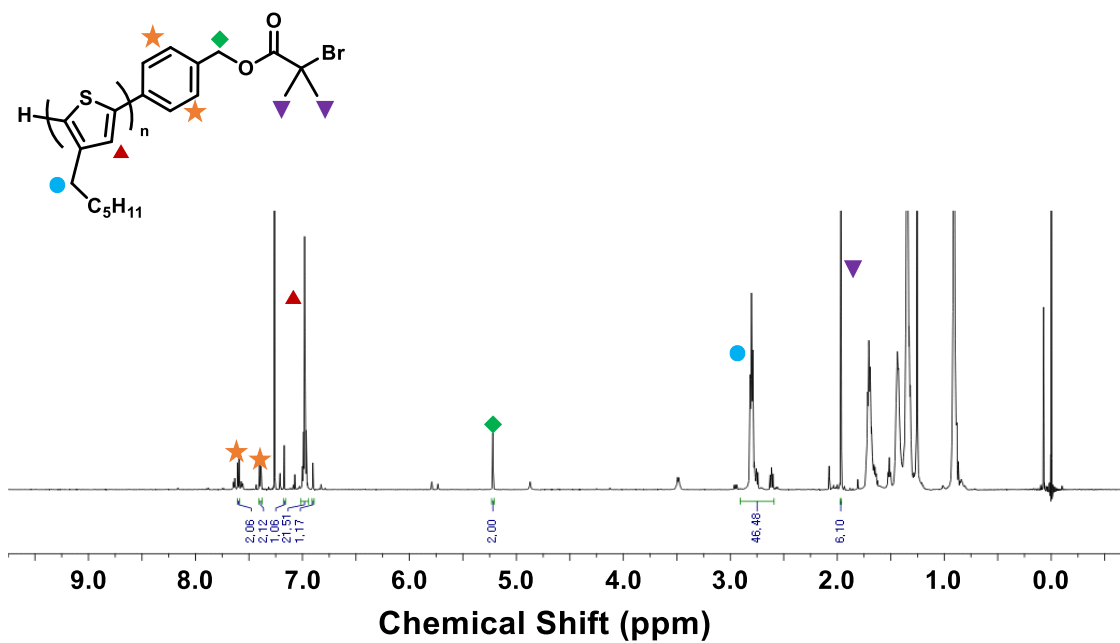
Figure S10.  $^1\text{H}$  NMR spectra and SEC traces of P3HT-OH, P3HT macroinitiator for ATRP (P9), P3HT-*b*-PMA-Br (P10), P3HT-*b*-PMA macroinitiator for SCTP (P11), and P3HT-*b*-PMA-*b*-P3EHT (P12)



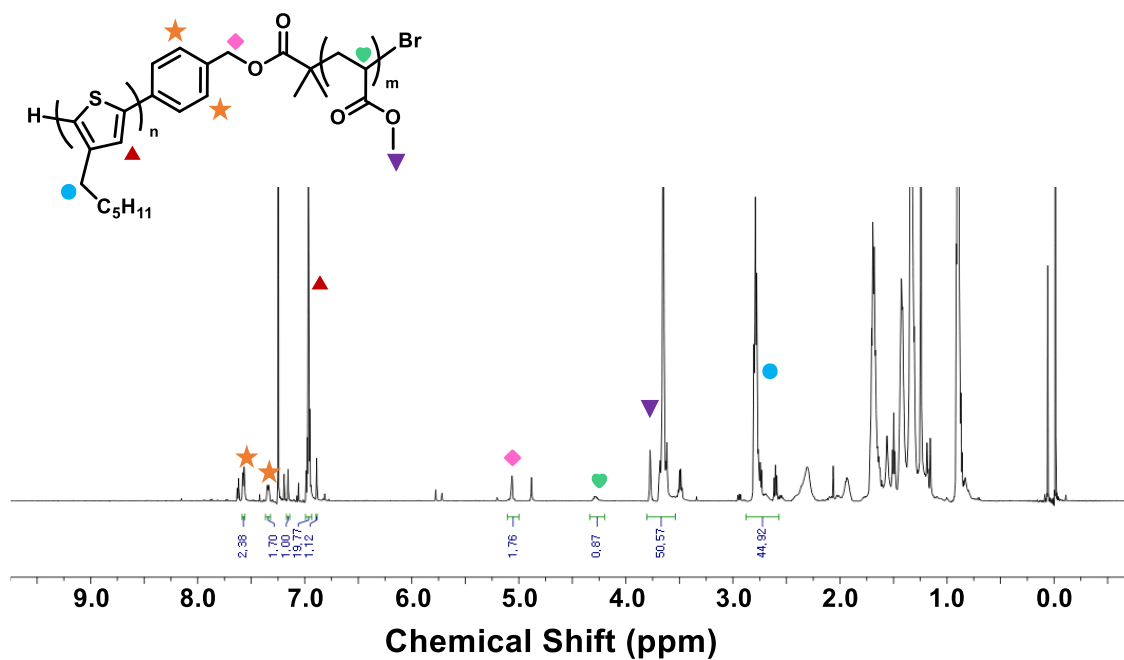
### P3HT-OH



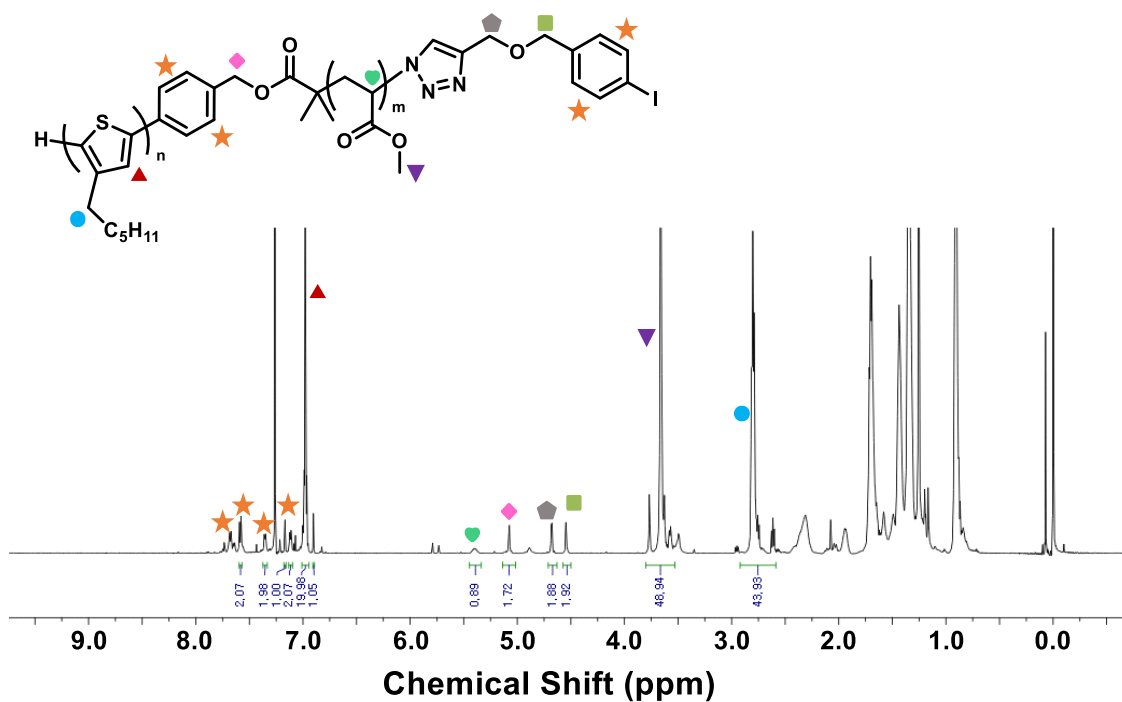
P9



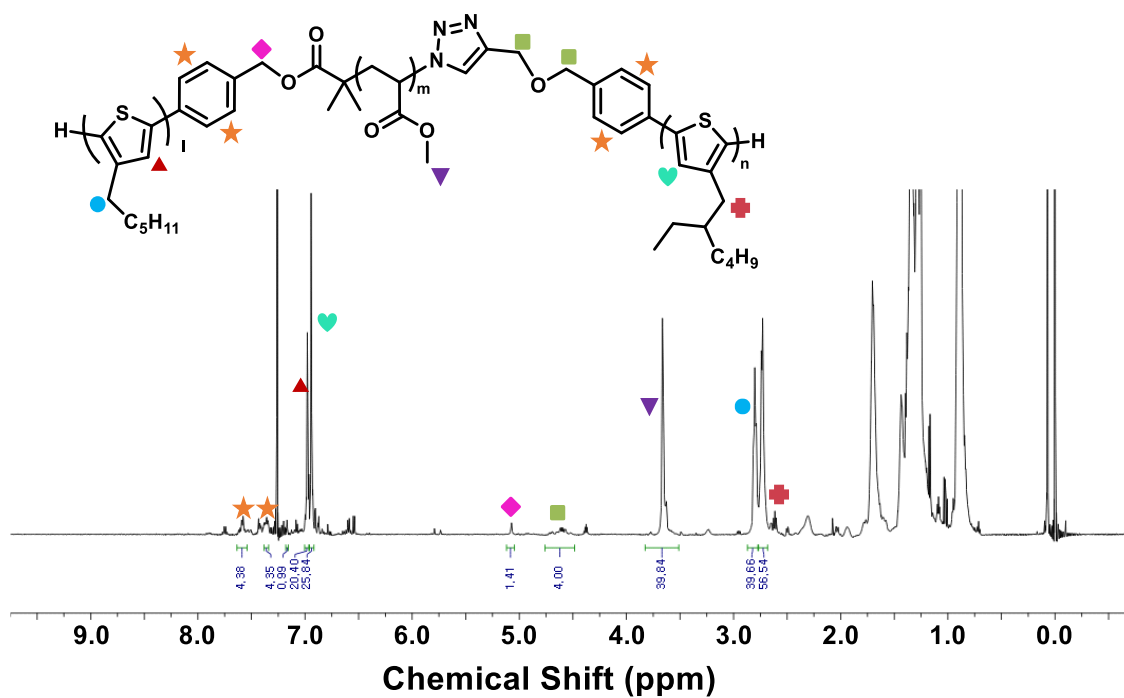
P10



**P11**



**P12 (DP of 25)**



P12 (DP of 50)

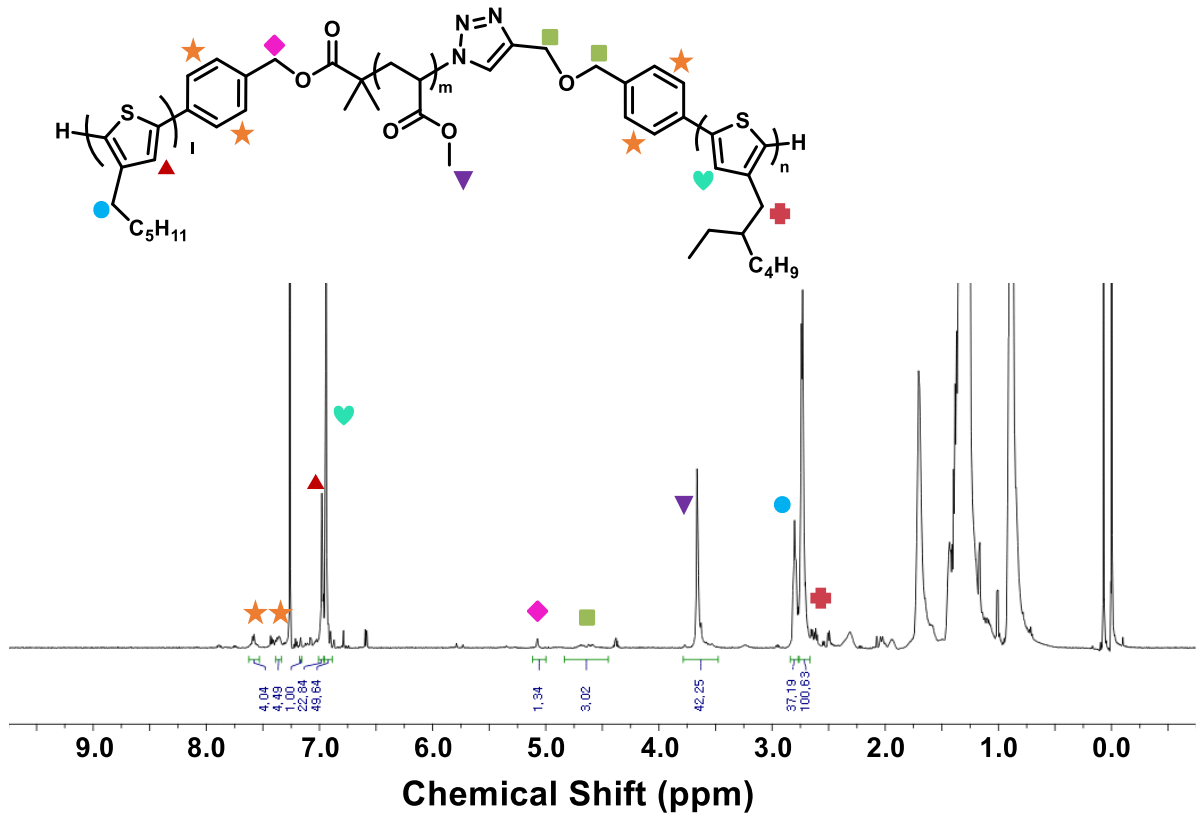
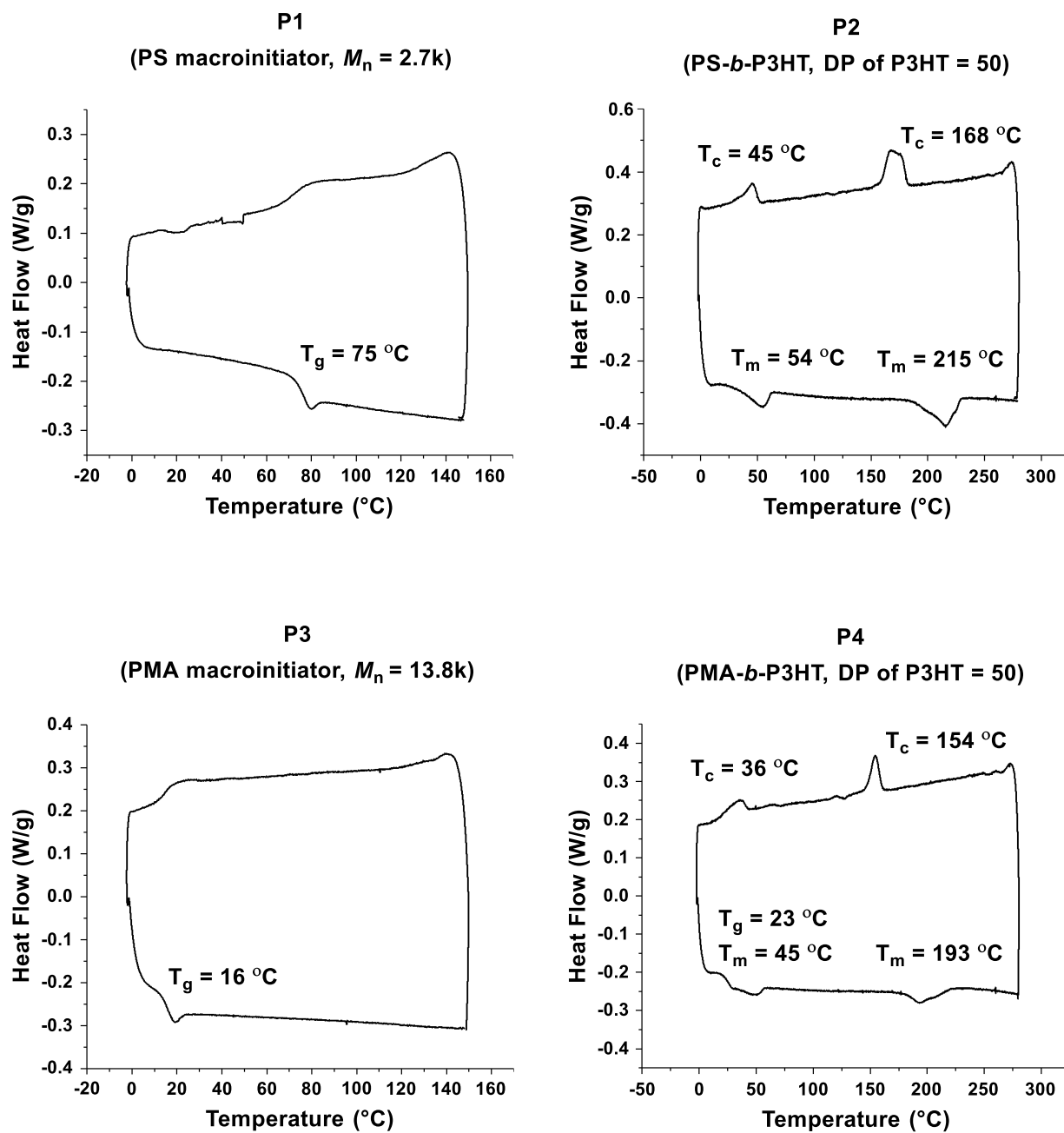
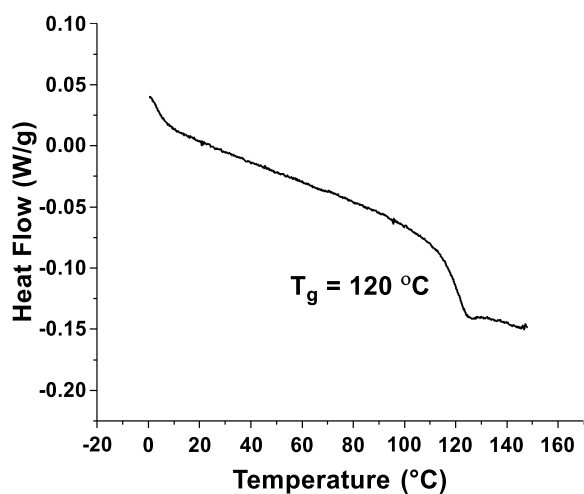


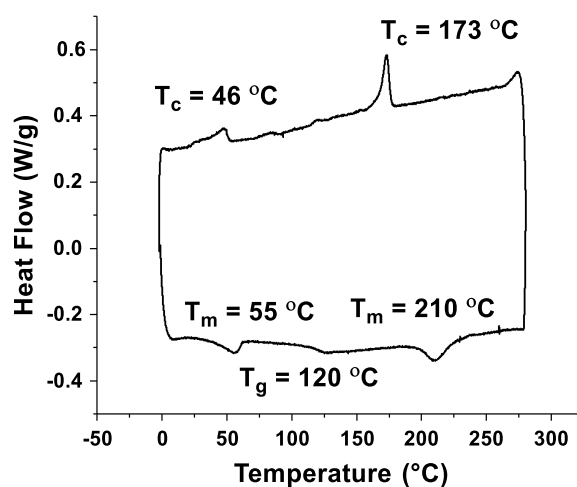
Figure S11. DSC thermograms of macroinitiators and block copolymers (1<sup>st</sup> cooling and 2<sup>nd</sup> heating cycles)



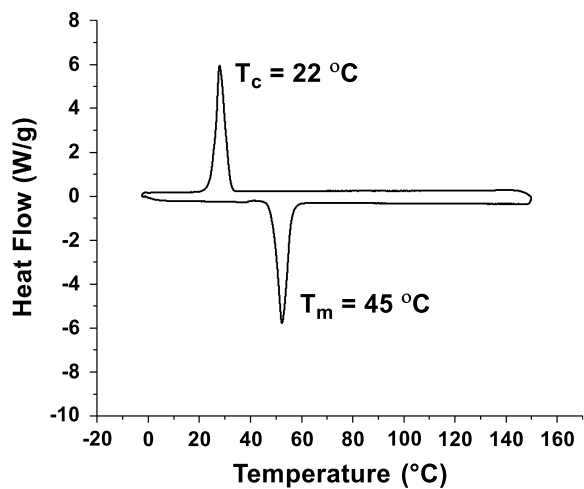
**P5**  
(PMMA macroinitiator,  $M_n = 14.2k$ )



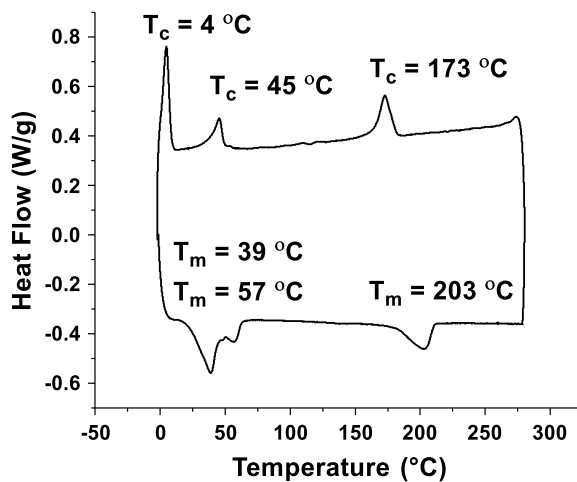
**P6**  
(PMMA-*b*-P3HT, DP of P3HT = 50)



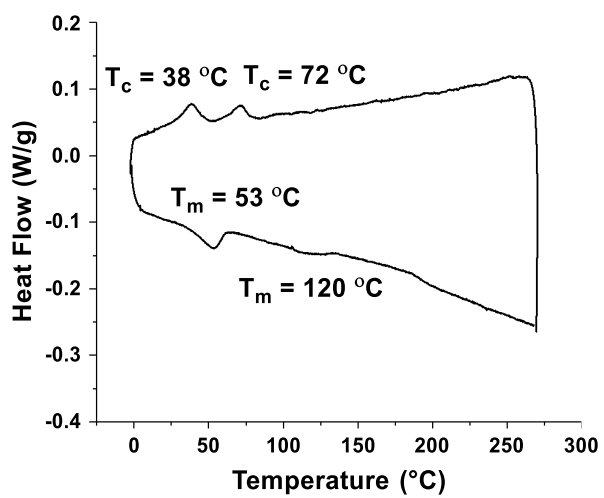
**P7**  
(PEO macroinitiator,  $M_n = 3.0k$ )



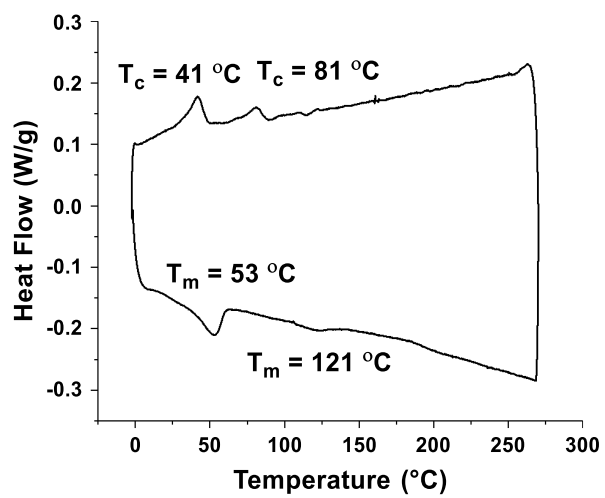
**P8**  
(PEO-*b*-P3HT, DP of P3HT = 50)



**P12**  
**(P3HT-*b*-PMA-*b*-P3EHT, DP of P3EHT = 25)**



**P12**  
**(P3HT-*b*-PMA-*b*-P3EHT, DP of P3EHT = 50)**



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