

Block copolymers containing organic semiconductor segments by RAFT polymerization

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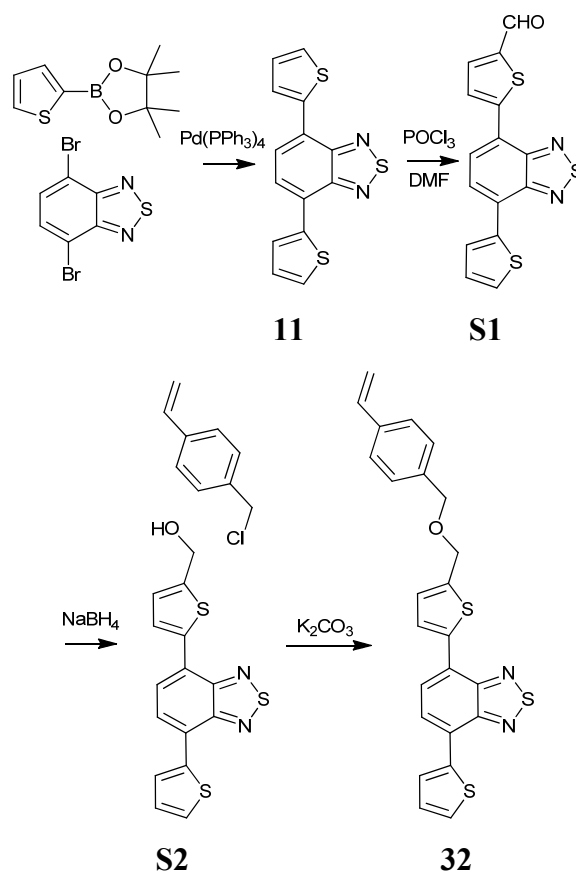
Supplementary Material

Radical polymerizations in the presence of thiophene model compounds

To test whether thiophene derivatives interfere with radical polymerization a series of control polymerizations of St, MA and MMA were conducted in the presence of thiophene and thiophene-containing compounds (**9-12**). The results are presented in Tables S1-S4. The addition of compounds **9-11** provided a lowering of molecular weight vs. the control and some retardation manifest as a reduced conversion of monomer to polymer. Moreover, analysis by GPC with diode array detection showed that some of the thiophene derivative was incorporated into the polymer. The effect was most profound with the acrylate (MA) and was small with MMA. This order correlates with the intrinsic activity of the corresponding propagating radicals.^{1,2} Compound **12** in which the 2- and 5-positions of the thiophene are substituted appeared to be substantially less reactive (some lowering of molecular weight was observed but no retardation).

Synthesis of benzobisthiadiazole monomer **32**

The synthesis of the benzobisthiadiazole (TBT) monomer was accomplished by the sequence of reactions shown in Scheme S1.



Scheme S1. Synthesis of benzobisthiadiazole monomer.

RAFT Polymerization of benzobisthiadiazole monomer **32**.

GPC traces of polymer formed in RAFT Polymerization of **32** with macro-RAFT agent **30** are shown in Figure S1. With observation at 528 nm, an absorption maxima for the perylene diimide chromophore, a peak with retention time 37.5 minutes is attributed to a low molecular weight by-product formed from the RAFT agent **30**. With observation at 400 nm, where there is no significant absorption by the perylene diimide chromophore but where the monomer absorbs strongly, this peak is not observed. The polymer peak appears similar for the two traces indicating that while the molecular weight distribution is bimodal both components have similar composition. UV spectra show that both components contain the perylene diimide chromophore. The peak with retention time 40 minutes is due to residual monomer.

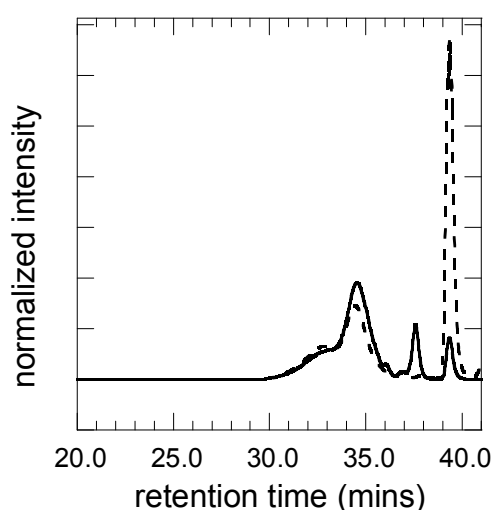


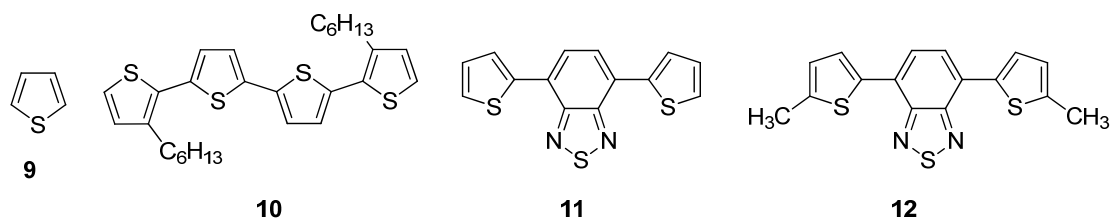
Figure S1. GPC traces for polymer formed in RAFT Polymerization of benzobisthiadiazole monomer **32** with macro-RAFT agent **30** (See Table 5); UV detection with observation wavelength 528 nm (—) or 400 nm (- - -)

Experimental

Thiophene (**9**), thiophen-2-ylboronic acid, (5-methylthiophen-2-yl)boronic acid, 4,7-dibromobenzo[*c*][1,2,5]thiadiazole and 3,3''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene (**10**) were obtained from Sigma-Aldrich and used as received.

4,7-bis(5-methylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**12**)

This compound was prepared by Suzuki-coupling with a procedure similar to similar to that described for compound **27** but using (5-methylthiophen-2-yl)boronic acid (1 g, 4.5 mmol) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (0.6g, 2.04 mmol). Recrystallization from hexane/dichloromethane gave 0.53g (90%) of red needle-like crystals. TLC (CHCl₃) *R_f* = 0.73. ¹H NMR (CDCl₃): δ 7.89 (d, 3J = 3.6 Hz, 2H; CH), 7.76 (s, 2H; CH), 6.85 (dd, 3J = 3.6 Hz, 4J = 1.1 Hz, 2H; CH), 2.58 (s, 6H; CH₃). UV (dichloromethane): λ_{max} (relative intensity) = 262 (0.53), 318 (1.00), 465 (0.49) nm. PL (λ_{ex} 466 nm, dichloromethane): λ_{max} = 604 nm. GC-MS: Found 328.1 Calculated for C₁₆H₁₂N₂S₃ 328.02. The spectral analysis was consistent with that reported.³



Radical polymerizations in the presence of thiophene model compounds

Prior to polymerisation the monomers was flash distilled. The monomer, dye, initiator (Vazo-88 or AIBN) and solvent (concentrations as indicated in Table S1-Table S3) were combined in an ampoule which was degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated in a constant-temperature oil bath for the stated time. Polymerisation was terminated by rapid cooling of the ampoule. A small sample of the reaction mixture was retained to determine the monomer conversion by ^1H NMR spectroscopy. The polymer solutions were evaporated under reduced pressure and analysed by GPC equipped with refractive index and photodiode-array detectors. The molecular weights of the polymers obtained are shown in Table S1-Table S3.

Table S1. Styrene polymerizations in the presence of thiophene model compounds.^a

	[St] : [Dye] : [I]	Conversion (NMR)	M_n	\bar{D}
St	500 : - : 1	88.0%	80,800	1.76
St + 9	500 : 4.2 : 1	56.1%	83,100	1.92
St + 10	500 : 4.2 : 1	66.9%	73,500	1.59
St + 11	500 : 4.2 : 1	71.1%	58,700	1.59

^a Solution polymerization (500 mg St with 500 mg CBz) at 90°C with Vazo-88 for 12h.

Table S2. Methyl acrylate polymerizations in the presence of thiophene model compounds.^a

	[MA] : [Dye] : [I]	Conversion (NMR)	M_n	\bar{D}
MA	500 : - : 1	68.8%	n.d. ^b	
MA + 9	500 : 4.2 : 1	45.1%	378,000	2.15
MA + 10	500 : 4.2 : 1	0.9%	116,900 ^c	1.34
MA + 11	500 : 4.2 : 1	0.9%	105,300 ^c	1.39

^a Solution polymerization (410 mg MA with 500 mg CBz) at 60°C with AIBN for 2h.

^b Molecular weight was too high for GPC analysis. ^c Very small peak in GPC chromatogram.

Table S3. Methyl acrylate polymerizations in the presence of thiophene model compounds^a

	[MA] : [Dye] : [I]	Conversion (NMR)	M_n	\bar{D}
MA	9 : - : 1	99.1%	5,890	4.62
MA + 11	9 : 1 : 1	79.0%	1,350	2.01
MA + 12	9 : 1 : 1	96.7%	1,610	3.73

^a Solution polymerization (76 mg MA with 1 mL Bz-*d*₆) at 70°C with AIBN for 22h.

Table S4. Methyl methacrylate polymerizations in the presence of thiophene model compounds^a

	[MMA] : [Dye] : [I]	Conversion (NMR)	M_n	\bar{D}
MMA	10 : - : 1	97.9%	2,720	2.61
MMA + 11	10 : 1 : 1	96.0%	1,850	2.01
MMA + 12	10 : 1 : 1	98.9%	2,440	2.20

^a Solution polymerization (100 mg MA with 1 mL Bz-*d*₆) at 70°C with AIBN for 22h.

Synthesis of TBT monomer - 4-(Thiophen-2-yl)-7-(5-((4-vinylbenzyloxy)methyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (Error! Reference source not found.)

4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (11)

A solution of 4,7-dibromobenzo[c][1,2,5]thiadiazole (3.0 g, 10.2 mmol) and thiophen-2-ylboronic acid (2.87 g, 22.4 mmol) in 150 mL of 1,2-dimethoxyethane and 50 mL anhydrous ethanol was carefully degassed by bubbling nitrogen through the solution. Next, 7.16 g (67.2 mmol) of sodium carbonate dissolved in 30 mL water was added. The resulting emulsion was degassed, and the catalyst Pd(PPh₃)₄ (200 mg, 0.17 mmol) was added. Afterwards, the mixture was refluxed under nitrogen overnight. After removal of the organic solvent by reduced pressure, the mixture was poured into water (300 mL) and was extracted with chloroform (3×40 mL). The organic phase was washed with water (30 mL), dried over magnesium sulphate, and the solvent was removed *in vacuo*. Purification by flash silica gel column chromatography [hexane:chloroform = 1:1 (v/v)] followed by recrystallization from hexane/dichloromethane yielded orange crystals of **11** (2.6 g, 84.9%). ¹H NMR (CDCl₃): δ 8.12 (d, 2H, J = 3.8 Hz, 3,3' Tp-H), 7.88 (s, 2H, 5,6 B-H), 7.46 (d, 2H, J = 5.1 Hz, 5,5' Tp-H), 7.21 (dd, 2H, J = 5.1, 3.8 Hz, 4,4' Tp-H).

5-(7-(Thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (S1)

Phosphorus oxychloride (0.16 ml, 1.8 mmol) was slowly added into a solution of **11** (0.5 g, 1.65 mmol) and *n*-methyl formanilide (0.22 mL, 1.8 mmol) dissolved in 15 mL dichloromethane. The mixture was stirred for 15 min at room temperature and then heated at 70 °C overnight. After cooling to room temperature 50ml saturated sodium acetate solution was added to the dark red solution and stirrer for 15 min. The resulting mixture was poured into ice water and neutralized (pH = 7) through the addition of potassium hydroxide. The organic layer was separated and the water phase three times extracted with dichloromethane (30 mL). The combined organic phases were consecutively washed with sodium bicarbonate and brine solution and dried over MgSO₄. Purification by silica gel column chromatography with hexane:chloroform (1:1 v/v) gave red crystals of **S1** (0.5 g, 91.1%). ¹H NMR (CDCl₃): δ 9.98 (s, 1H, -CHO), 8.21 (d, 1H, J = 4.1 Hz, 4 T-H), 8.18 (d, 1H, J = 3.8 Hz, 3' T-H), 8.0 (d, 1H, J = 7.7 Hz, 5 B-H), 7.92 (d, 1H, J = 7.7 Hz, 6 B-H), 7.85 (d, 1H, J = 4.1 Hz, 3 T-H), 7.51 (d, 1H, J = 5.1 Hz, 5' T-H), 7.23 (dd, 1H, J = 5.1 and 3.8 Hz, 4' T-H).

(5-(7-(Thiophen-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)methanol (S2)

To a solution of **1** (1.4g, 4.27 mmol) in 80 mL THF and 5 mL dry ethanol was

added 163.4 mg (4.3 mmol) sodium borohydride in small portions. The reaction mixture quickly changed colour from red to orange and the stirring was continued for 20 min. Removal of the solvent under reduced pressure followed by purification with flash silica gel column chromatography with chloroform as eluent yielded orange crystals of **S2** (1.4 g, 99.4%) m.p. 77-78 °C. ¹H NMR (CDCl₃): δ 8.12 (d, 1H, J= 3.8 Hz, 4 Tp-H), 7.98 (d, 1H, J=3.8 Hz, 3' Tp-H), 7.88 (d, 1H, J=7.6 Hz, 5 B-H), 7.84 (d, 1H, J=7.6 Hz, 6 B-H), 7.46 (d, 1H, J=5.2 Hz, 5' Tp-H), 7.21 (dd, 1H, J=5.1, 3.8 Hz, 4' Tp-H), 7.11 (d, 1H, J=3.8 Hz, 3 Tp-H), 4.91 (s, 2H, -OCH₂) (B=benzothiadazole).

4-(Thiophen-2-yl)-7-(5-((4-vinylbenzyloxy)methyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**31**)

To a solution of 1.37g (4.15 mmol) of **2** and 0.71 mL (5 mmol) of vinylbenzyl chloride in 60 mL DMF was added 200 mg (8.3 mmol) sodium hydride. The mixture was stirred at room temperature overnight, poured into 300 mL water and extracted with dichloromethane for three times (3x30 mL). The combined organic phases were consecutively washed with water and brine solution and dried over MgSO₄. Purification by silica gel column chromatography with hexane:chloroform in a ratio 3:1 (v/v) gave orange powder of **31** (1.2 g, 64.8%). TLC (CHCl₃) R_f = 0.67. ¹H NMR (CDCl₃): δ 8.12 (d, 1H, J=3.5 Hz, 4 T-H), 7.98 (d, 1H, J=3.8 Hz, 3' T-H), 7.88 (d, 1H, J=7.6 Hz, 5 B-H), 7.84 (d, 1H, J=7.6 Hz, 6 B-H), 7.46 (d, 1H, J=5.2 Hz, 5' T-H), 7.42 (d, 2H, J=8.1, 3 Ph-H), 7.42 (d, 2H, J=8.1 Hz, 2 Ph-H), 7.22 (dd, 1H, J=5.2, 3.8 Hz, 4' T-H), 7.10 (d, 1H, J=3.5 Hz, 3 T-H), 6.73 (dd, 1H, J=17.6 and 10.9 Hz, =CHH), 5.76 (d, 1H, J=17.6 Hz, =CHH), 5.25 (d, 1H, J=10.9 Hz, CH=CH₂), 4.77 (s, 2H, -OCH₂T), 4.62 (s, 2H, -OCH₂Ph). UV (dichloromethane): λ_{max} 448, 310 nm. HRMS (EI) Found 446.0553 Calculated for C₂₄H₁₈N₂O³²S₃ 446.0576.

References

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