## **Supporting Information**

## RAFT Polymerization of Vinylthiophene Derivatives and Synthesis of Block Copolymers Having Cross-Linkable Segments

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**Figure S1.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>) of (a) 2,5-dibromo-3-thiophenecarboxaldehyde and (b) 2,5-dibromo-3-vinylthiophene (DB3VT).



**Figure S2.** (a) <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of 2,5-dibromo-3-vinylthiophene (DB3VT), and (b) DEPT135-<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>) of DB3VT.



**Figure S3.** <sup>1</sup>H and <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>) of 2-vinylthiophene (2VT).



**Figure S4.** <sup>1</sup>H and <sup>13</sup>C NMR spectra (CDCl<sub>3</sub>) of 3-vinylthiophene (3VT).



Scheme S1. Structures of vinylthiophene derivatives

run	monomer	solvent	temp. (°C)	time (h)	conv. <sup>b)</sup> (%)	$M_n^{c)}$	$M_{\rm w}/M_{\rm n}^{\rm c)}$
1		bulk	100	48	88	2,700	2.37
2	2 V 1	bulk	80	48	75	5,200	1.83
3		bulk	100	24	39	7,500	2.23
4	2VT	bulk	100	48	53	5,800	2.00
5	311	bulk	100 <sup>d)</sup>	24	28	6,900	2.57
6		bulk	100 <sup>d)</sup>	48	48	7,500	2.23
7		bulk	80	24	97	64,500	3.06
8	DB3VT	bulk	60	24	97	153,100	2.73
9		dioxane <sup>e)</sup>	60	24	94	34,300	2.40

Table S1. Free radical polymerization of vinylthiophene derivatives <sup>a)</sup>

a) 3VT 2-vinylthiophene, 2VT = 3-vinylthiophene, DB3VT = = 2,5-dibromo-3-vinylthiophene,  $[monomer]_0/[AIBN]_0 = 100$ .<sup>b)</sup> Determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>. In the case of the polymerization of 2VT, the monomer conversion was determined by the integration of one proton of the monomer resonance at 5.5-5.7 ppm compared with the methine proton of the polymer main chain at 2.2-3.0 ppm. For 3VT, c) similarly the peaks at 5.5-5.7 ppm were compared with the peaks at 2.0-2.8 ppm. Calculated by size exclusion chromatography using polystyrene standards in THF.<sup>d)</sup>  $[Monomer]_0/[AIBN]_0 = 200.$  <sup>e)</sup> Polymerization in 1,4-dioxane ([M] = 2.0 mol/L).



**Figure S5.** SEC curves of poly(DB3VT)s obtained by free radical polymerization of DB3VT in (a) bulk, and (b) 1,4-dioxane (2.0 M). See Table S1 for detailed polymerization conditions.

run	CTA <sup>b)</sup>	[CTA]/	temp.	time	conv. <sup>c)</sup>	M <sub>n</sub>		M /M <sup>e)</sup>
		[AIBN]	(°C)	(h)	(%)	theory <sup>d)</sup>	SEC <sup>e)</sup>	<i>w</i> <sub>w</sub> / <i>w</i> <sub>n</sub>
1	CTA 1	2	80	72	71	7,900	2,700	2.70
2		5	100	48	93	10,500	2,300	1.95
3		2	120	48	96	10,800	3,200	2.17
4		2	100	48	91	10,300	4,000	2.11
5	CTA 4	2	80	72	70	8,000	4,000	1.67
6		5	100	48	83	9,600	2,300	2.56
7		10	100	48	80	9,100	2,200	1.97
8	CTA 5	2	100	48	95	10,700	1,900	2.79

**Table S2.** Reversible addition-fragmentation chain transfer (RAFT) polymerization of 2-vinylthiophene (2VT) in 1,4-dioxane  $a^{a}$ 

<sup>a)</sup>[2VT]/[CTA] = 100. <sup>b)</sup> See Scheme 2. <sup>c)</sup> Determined by <sup>1</sup>H MNR in CDCl<sub>3</sub>. <sup>d)</sup> The theoretical molecular weight  $(M_{n, \text{theory}}) = [2VT]_0/[CTA]_0 \times (Mw \text{ of } 2VT) \times \text{conv.} + (Mw \text{ of } CTA)$ . <sup>e)</sup> Calculated by size exclusion chromatography using polystyrene standards in THF (RI detector).



**Figure S6.** SEC traces of poly(DB3VT)s obtained by polymerization using different chain transfer agents (CTAs). See Table 1 for detailed polymerization conditions.



**Figure S7.** SEC traces of poly(DB3VT)s obtained by RAFT polymerization of DB3VT with CTA 3 at different [CTA]/[AIBN] ratios; (a) [CTA]/[I] = 2 and (b) [CTA]/[I] = 5. See Table 2 for detailed polymerization conditions.



**Figure S8.** <sup>1</sup>H NMR spectra of polymer end groups of poly(DB3VT)s prepared with CTA 1 (a, [M]/[CTA]/[AIBN] = 200/2/1, conv. = 89%), CTA 2 (b, [M]/[CTA]/[AIBN] = 1000/10/1, conv. = 73%), CTA 3 (c, [M]/[CTA]/[AIBN] = 200/2/1, conv. = 91%), and without CTA (d, [M]/[AIBN] = 200/1, conv. = 94%).

run	time	conv. <sup>b)</sup>		M /M <sup>d)</sup>			
	(h)	(%)	theory <sup>c)</sup>	NMR <sup>b)</sup>	SEC <sub>RI</sub> <sup>d)</sup>	SEC <sub>RALLS</sub> <sup>e)</sup>	<i>W</i> <sub>W</sub> / <i>W</i> <sub>n</sub>
1	3	0	300	-	600	-	1.30
2	8	18	5000	6900	2400	-	1.15
3	12	34	9400	11200	4400	10,400	1.07
4	15	42	11600	12900	5200	13,100	1.07
5	24	63	17200	19100	6200	15,200	1.05
6	36	79	21400	22700	8300	-	1.10
7	45	83	22400	25900	8800	22,700	1.09

**Table S3.** Reversible addition-fragmentation chain transfer (RAFT) polymerization of DB3VT in 1,4-dioxane at 60  $^{\circ}C^{a)}$ 

<sup>a)</sup> [DB3VT]<sub>0</sub>/[CTA 2]<sub>0</sub>/[AIBN]<sub>0</sub>= 1000/10/1, [DB3VT]<sub>0</sub> = 2.0 mol/L. <sup>b)</sup> Calculated by <sup>1</sup>H NMR in CDCl<sub>3</sub>. <sup>c)</sup> The theoretical molecular weight ( $M_n$ , theory) = [DB3VT]<sub>0</sub>/[CTA]<sub>0</sub> × (MW of monomer) × conv. + (MW of CTA). <sup>d)</sup> Determined by SEC using polystyrene standards in THF (RI detector). <sup>e)</sup> Determined by SEC in THF with RALLS detector.



**Figure 9.** SEC traces (THF) of poly(DB3VT) and poly(vinyl terthiophene)s obtained by Suzuki coupling reaction with 2-thiopheneboronic acid in the presence of KOH and NaHCO<sub>3</sub>.



**Figure S10.** Appearance of poly(DB3VT) (left) and cross-linked product (right) obtained by Suzuki coupling reaction with 2,5-thiophenediboronic acid.



**Figure S11.** Appearance of the cross-linked block copolymer illuminated by visible (left) and UV ( $\lambda$  ex = 365 nm, right) light measured in THF.