

Supporting Information for:

**Synthesis and Crystallization Behavior of Regioregular-*block*-
Regiorandom Poly(3-hexylthiophene) Copolymers**

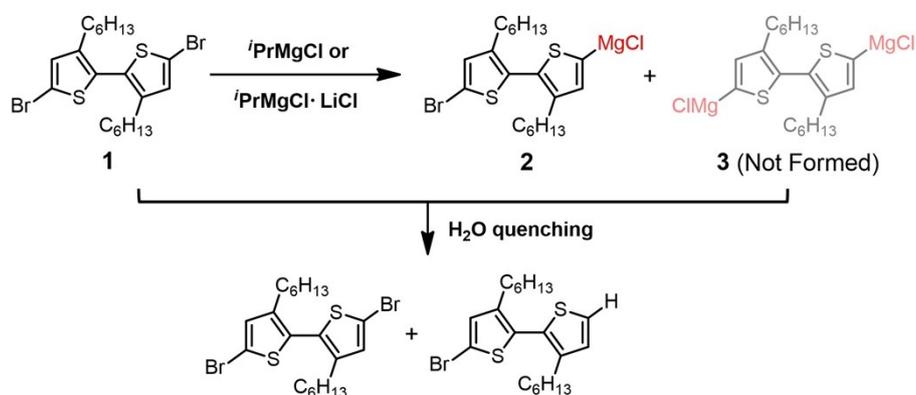
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Grignard metathesis reaction



Scheme S1. Grignard metathesis reaction of the H–H coupled bithiophene (BT) monomer and possible products after quenching the reaction.

In order to optimize the reaction conditions, the formation of Grignard monomers from the H–H coupled BT monomer as a function of time and temperature was investigated. The H–H coupled BT monomer **1** was synthesized by the Kumada coupling of 3,3'-dibromo-2,2'-bithiophene and hexylmagnesium bromide solution followed by dibromination with recrystallized *N*-bromosuccinimide.¹ Since the RR is determined by the ratio between (5-bromo-4-hexylthiophene-2-yl)magnesium chloride (converted from 3HT monomer) and **2**, quantitative conversion of **1** to **2** is important to obtain P3HT with the targeted RR. To determine the conversion of the BT monomer in different reaction conditions, several Grignard metathesis reactions were performed. The reaction mixture was quenched and washed three times with H₂O to replace -MgCl with H atoms and examined by ¹H NMR (**Scheme S1 and Fig. S1**). ¹H NMR results revealed that the reaction mixture contained only **1** and **2**, which is evidence for no formation of the bis-Grignard monomer **3** during the magnesium–halogen exchange reaction (**Fig. S1**). However, the reaction over 1 hr at room temperature yielded only about 70% BT monomer conversion. It is well-known that the conversion of 3HT monomer to (5-bromo-4-hexylthiophene-2-yl)magnesium chloride, which participates in the polymerization, is about 85% under identical reaction conditions.² Thus, further optimization of the reaction conditions was carried out to achieve higher conversions. As shown in **Table S1**, reaction temperature and the presence of LiCl did not significantly increase the conversion within a 1 hr reaction time. In contrast, lengthening the reaction time from 1 to 2 hrs appeared to be effective as the conversion increased from *ca.* 70% to 90%, which is comparable to that of the 3HT monomer. Further increase of the reaction time resulted in a similar level of the conversion. Therefore, it is clear that the reaction time is a crucial factor for the determination of conversion in the magnesium–halogen exchange reaction of BT monomers and the optimized reaction conditions of test 5 were used in all polymerization experiments in this paper.

Table S1. Percentage of components present at different reaction conditions in Grignard metathesis reaction of H–H coupled BT monomer^a

Test	Reaction conditions			Composition		
	Reagent	Temperature	Time	%1	%2	%3
1	<i>i</i> PrMgCl w/o LiCl	0 °C	1 hr	33	67	0
2		RT		26	74	0
3	<i>i</i> PrMgCl with LiCl	0 °C	1 hr	29	71	0
4		RT	1 hr	35	65	0
5			2 hr	11	89	0
6			5 hr	10	90	0

^areaction concentration = 0.05 mol L⁻¹

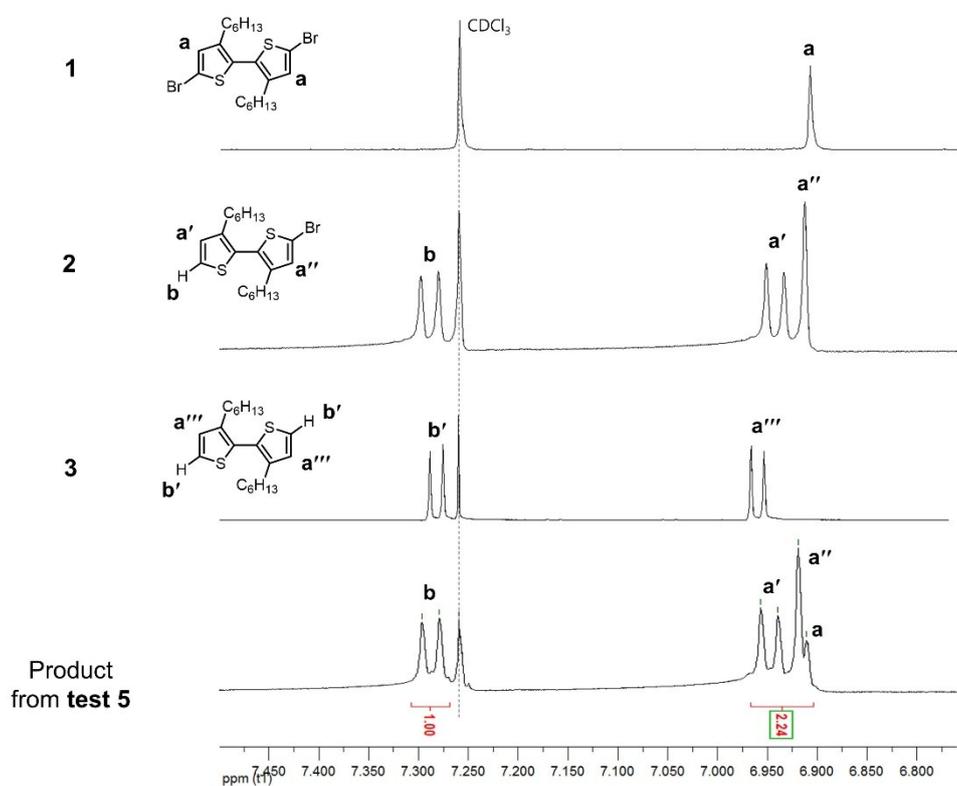


Figure S1. Aromatic region of ¹H NMR spectra of the possible BT monomer derivatives after quenching the Grignard reaction and the products from test reaction 5.

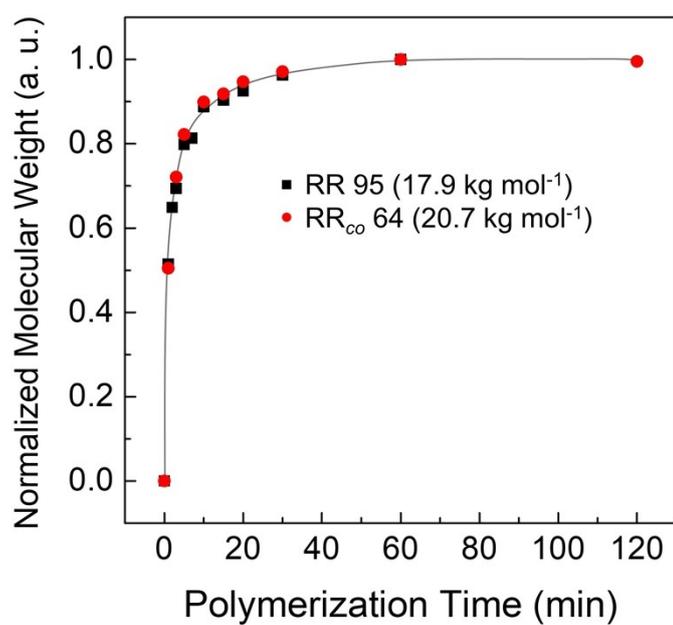


Figure S2. Plot of normalized peak molecular weights (M_p) versus polymerization time for RR 95 and RR_{co} 64 P3HT.

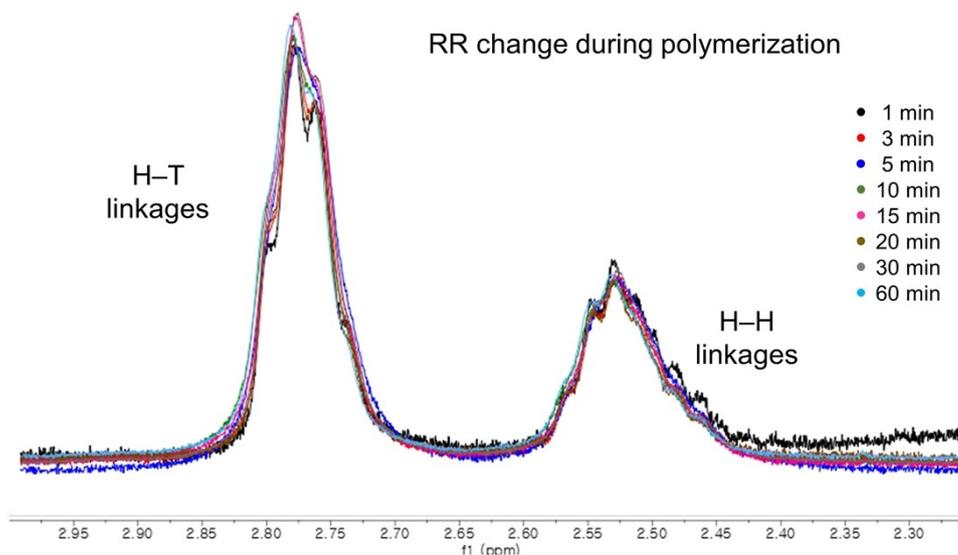


Figure S3. Normalized ¹H NMR spectra from δ 2.30 to 3.00 for the RR_{co} 64 during polymerization. The polymer batch shows almost constant RR of 64% from 1 to 60 min.

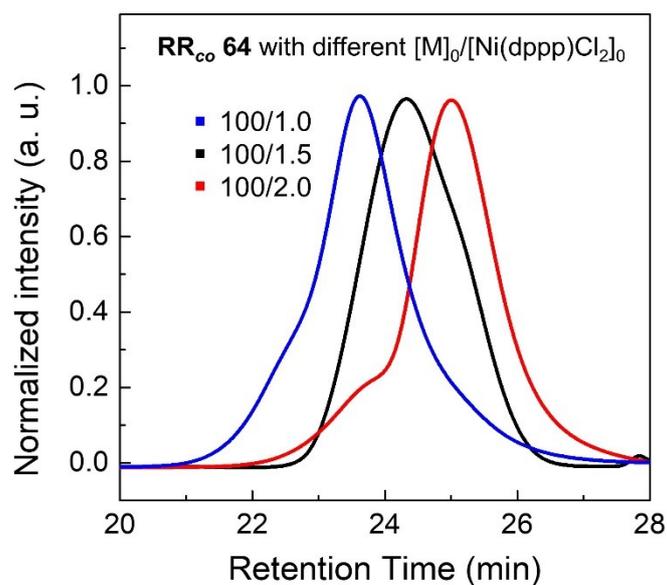


Figure S4. SEC traces of a series of RR_{co} 64 with different monomer/catalyst ratios from 100/1 to 100/2.

Reaction I , RR_{block} 71

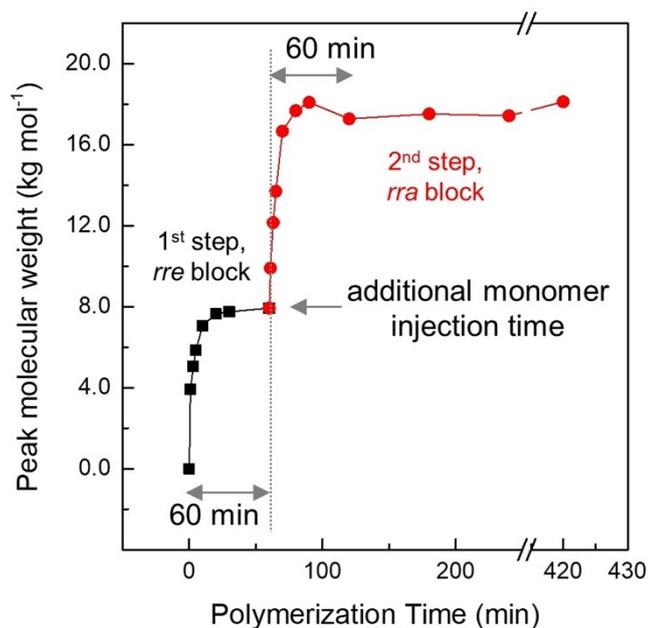


Figure S5. Plot of peak molecular weights (M_p) versus polymerization time for RR_{block} 71 P3HT, prepared by identical synthetic procedures with reaction I. The M_p of the BCP began to increase drastically when the second monomer batch was injected. The molecular weight of *rre* and *rra* blocks gradually increased and almost completed within 60 min for each step.

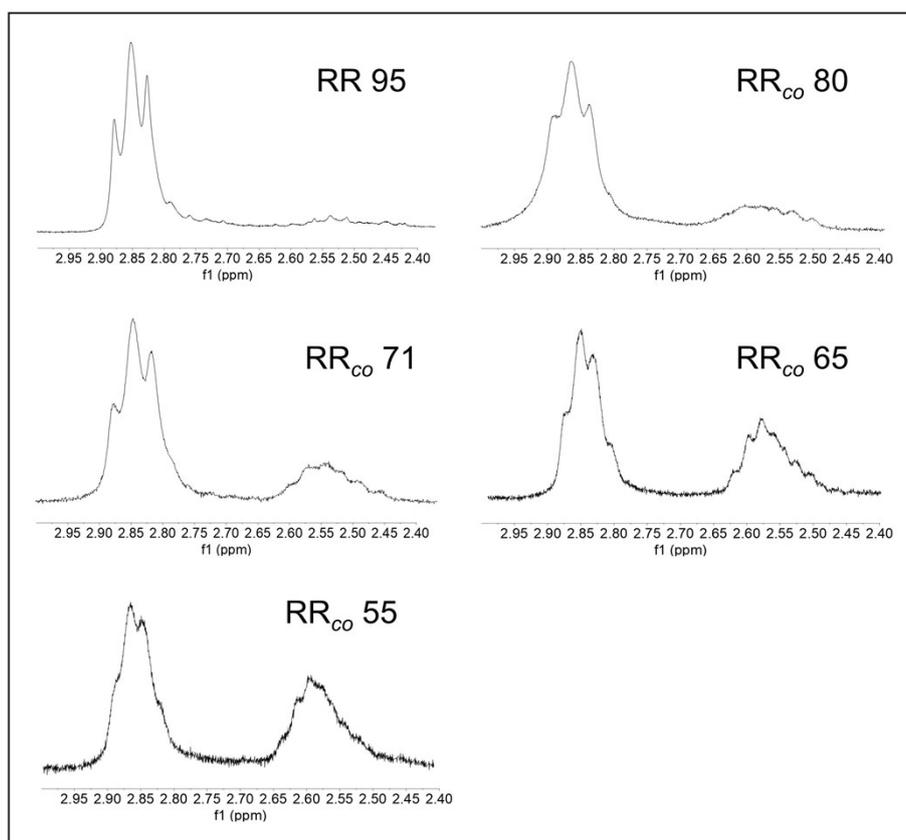


Figure S6. ^1H NMR spectra for RR 95 and *co*-P3HTs from δ 2.40 to 3.00.

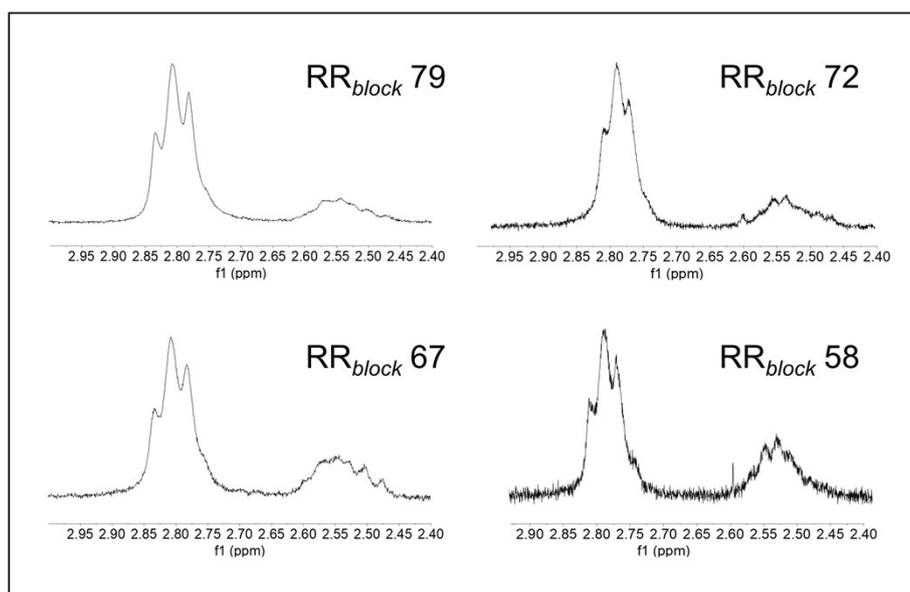


Figure S7. ^1H NMR spectra for *block*-P3HTs from δ 2.40 to 3.00.

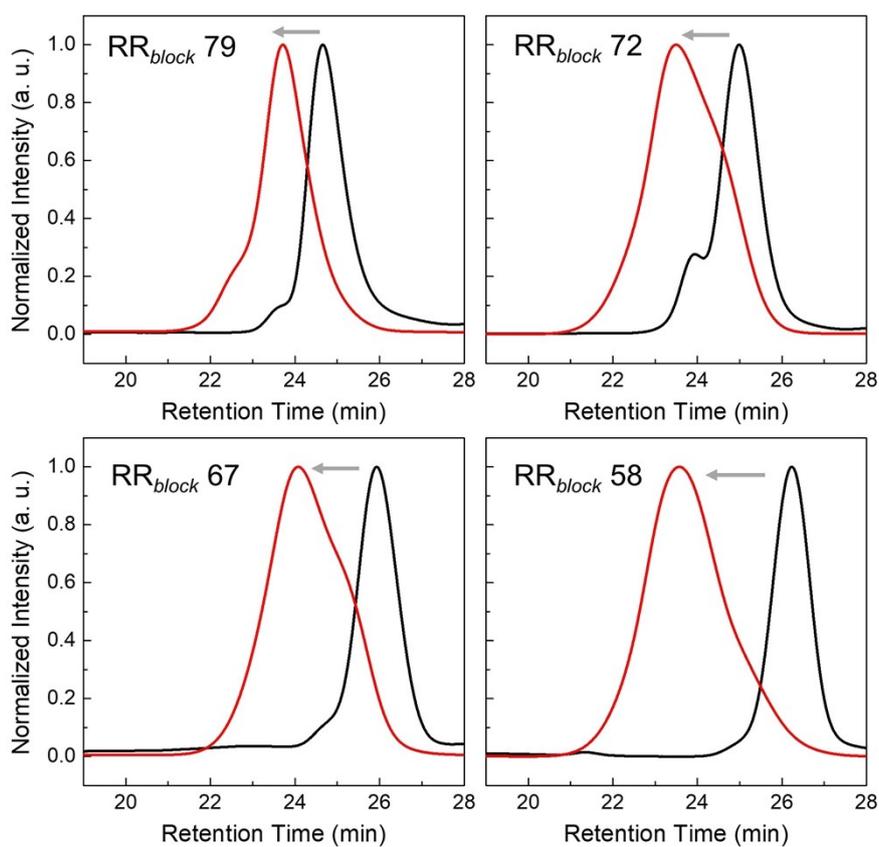


Figure S8. Peak shift toward higher molecular weight in SEC traces of *block*-P3HTs. The black lines indicate *rre* first block and red lines indicate *rre*-*rra* regiblock copolymers.

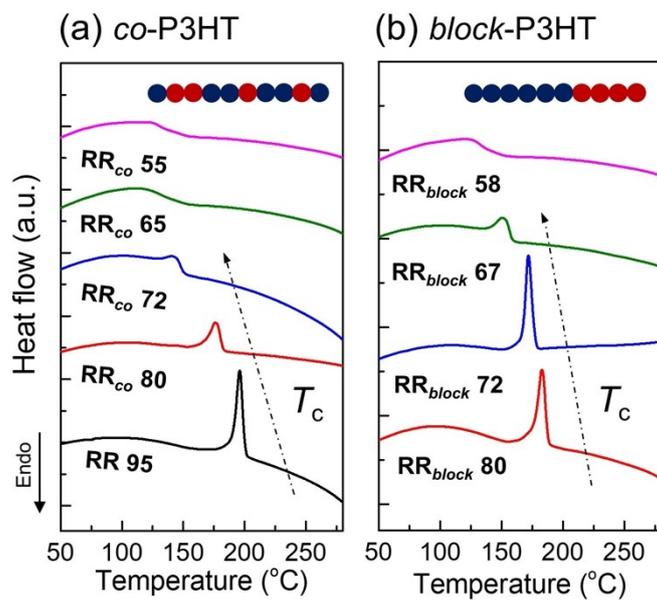


Figure S9. DSC thermograms (2nd cooling cycle) of a series of (a) *co*-P3HTs and (b) *block*-P3HTs.

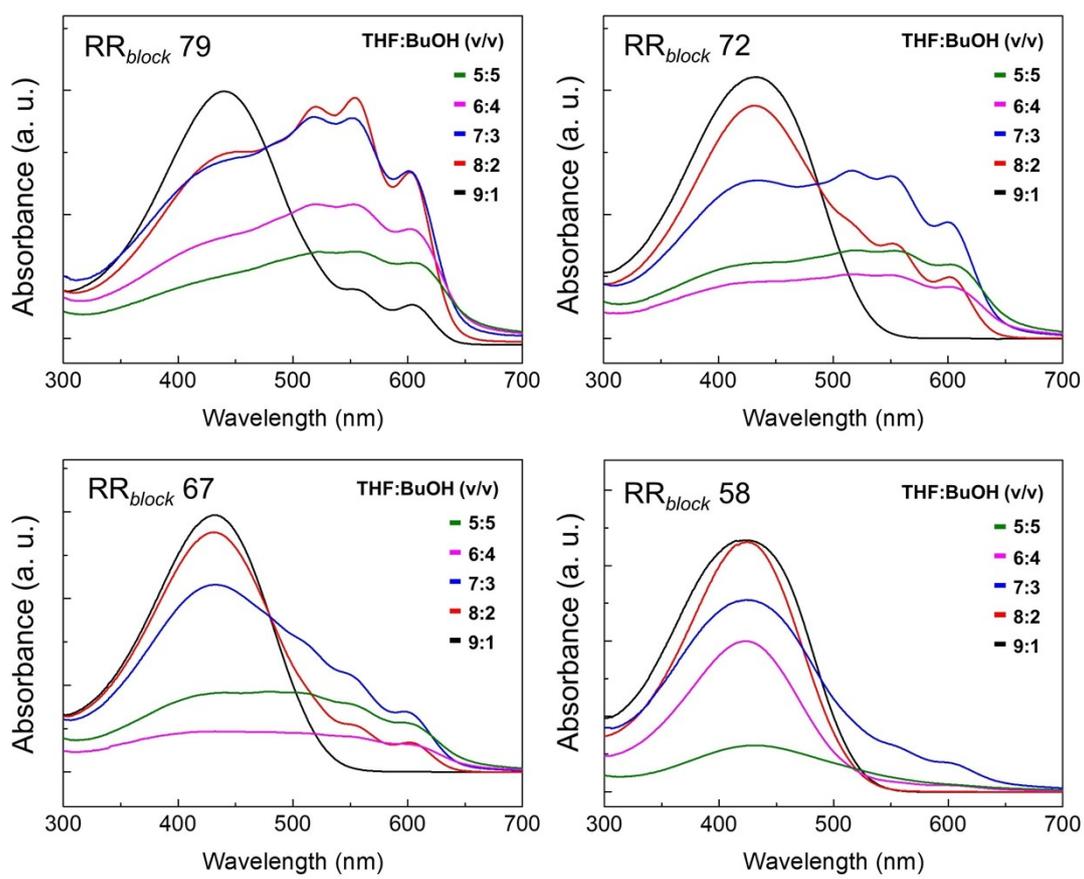


Figure S10. UV-vis absorption spectra of the *block*-P3HTs at different volume ratios of solvent mixtures (THF/BuOH (v/v), 0.5 mg mL⁻¹).

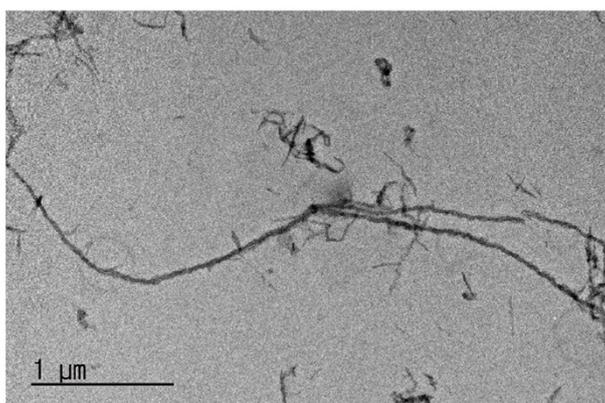


Figure S11. TEM images of solution assembled RR 95 nanowires in THF/BuOH co-solvent.

References

- 1 B. C. Schroeder, S. Rossbauer, R. J. Kline, L. Biniek, S. E. Watkins, T. D. Anthopoulos, I. McCulloch and C. B. Nielsen, *Macromolecules* 2014, **47**, 2883.
- 2 R. S. Loewe, P. C. Ewbank, J. S. Liu, L. Zhai and R. D. McCullough, *Macromolecules* 2001, **34**, 4324.