

END FUNCTIONALIZED POLY(3-ALKYLTHIOPHENES) AS BUILDING BLOCKS FOR THE SYNTHESIS OF DIBLOCK COPOLYMERS

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Introduction

In recent years poly(3-alkylthiophene)s have been widely studied due to their potential applications in nanophotonics and nanoelectronics. Within this time period a variety of protocols have been developed that allow for the synthesis of regioregular head-to-tail poly(3-alkylthiophene)s (HT-PAT)s,¹⁻³ creating material with improved electronic and photonic properties over regiorandom analogs.³ While, a large amount of work has been done to control the properties of HT-PATs via modification and variation of the side chain,⁴ less attention has been given to the nature and control of the end groups of such polymers.⁵⁻⁸ End group functionalization of HT-PATs would enable the polymer to be grafted onto surfaces or used as building blocks for the synthesis of block copolymers.

Previously, our group reported a multistep synthesis of HT-PAT-styrene diblock copolymers.⁹ These copolymers self-assemble into nanowires through phase separation, resulting in unexpectedly high conductivities with low percentages of HT-PAT within the polymer. While these novel materials have very interesting properties, the seven step synthesis limits their usefulness. Herein we describe a facile approach to HT-PAT di- and tri-block copolymers using end-functionalized HT-PAT's as building blocks.

Experimental

The monomer 2,5-dibromo-3-hexylthiophene **1** was synthesized according to the literature procedure.² All reactions were performed under prepurified nitrogen or argon, using oven-dried glassware. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. Ni(dppp)Cl₂, allylmagnesium bromide, vinylmagnesium bromide and *tert*-butylmagnesium chloride were purchased from Aldrich Chemical Co. and used without further purification. Size exclusion chromatography (SEC) measurements were conducted using chloroform as the eluent (flow rate 1 mL/min, 30 °C), and a Waters 2487 dual λ absorbance UV detector. Polystyrene standards were employed for the SEC calibration. End-group composition was evaluated with MALDI-TOF MS (Voyager-DE STR BioSpectrometry workstation by Biosystems, terthiophene matrix and confirmed with ¹H NMR (Bruker 300 Mhz instrument).

Typical Synthesis of end-capped regioregular Poly(3-alkylthiophene) 2,5-dibromo-3-hexylthiophene **1** (1.63g, 5.0 mmol) was dissolved in THF (50 mL). *tert*-Butylmagnesium chloride (2.0M, 2.5 mL, 5.0 mmol) was added via syringe and the mixture was refluxed for 1.5 hours. The reaction mixture was then allowed to cool to room temperature and Ni(dppp)Cl₂ (45 mg, 0.08 mmol) was added in one portion. The mixture was stirred for 10 minutes at room temperature, then a large excess of a Grignard reagent (10-30 mole % of monomer) was added via syringe to the reaction mixture. The mixture was stirred for 2 minutes and then poured into methanol to precipitate the polymer. The polymer was filtered into an extraction thimble and then washed by Soxhlet extraction with methanol, hexane and chloroform. The polymer was isolated from the chloroform extraction. Vinyl terminated polymer: ¹H NMR (500 MHz, CDCl₃): Hexyl peaks are the same as above with δ 5.11 (d, *J*=11 Hz, 1H), 5.49(d, *J*=11 Hz, 1H), 6.20 (m, 1H), 7.14 (s, 55H); GPC: *M_n*: 11,218, PDI: 1.1; MALDI-MS: *m/z*: 4927.2 [*M*⁺] (calcd: 4927.7, DP of 29, Br/Vinyl end groups). Allyl terminated polymer: ¹H NMR (500 MHz, CDCl₃): Hexyl peaks same as above with δ 3.49 (d, *J*=6.5 Hz, 2H), 5.12 (d, *J*=6.5 Hz, 2H), 5.98 (m, 1H), 7.14 (s, 44H); GPC: *M_n*: 6,068, PDI: 1.1; MALDI-MS: *m/z*: 4110.3 [*M*⁺] (calcd: 4111.6, DP of 24, Br/Allyl end groups).

Hydroboration/oxidation of vinyl terminated HT-PAT. Vinyl terminated HT-PAT (2.0g, 0.2 mmol; *M_n*(NMR) = 10000) was dissolved in 100 mL dry THF. Then a 4 mL of a 0.5M solution of 9-BBN in THF was added via syringe, under nitrogen. The reaction mixture was stirred for 24 h at

40°C. Next 2 mL of a 6M NaOH solution was added to the reaction flask and the reaction mixture was stirred for an additional 15 min. and cooled to room temperature. Then 2 mL of hydrogen peroxide (33%) was added to the reaction mixture and the reaction stirred for 24 h at 40°C. The hydroxy terminated PAT was isolated by precipitation in a methanol-water mixture. The polymer was filtered and purified by Soxhlet extraction with methanol.

Synthesis of HT-PAT macroinitiator. The hydroxy terminated HT-PHT (1 g, 0.1 mmol) was dissolved in 100 mL of dry THF and the mixture warmed to 40°C until the polymer was completely dissolved. Then triethylamine (9 mL, 0.066 mol) was added to the polymer solution followed by dropwise addition of (2-bromopropionyl bromide (7.5 mL, 0.06 mole) added dropwise under nitrogen. The reaction mixture was stirred at room temperature for 24 h and the resulting HT-PAT macroinitiator was precipitated in methanol and purified.

Results and Discussion

Allyl and Vinyl terminated HT-PAT. The synthesis of the allyl- and vinyl- terminated HT-PAT's depicted in **Figure 1**, uses the *in-situ* end group functionalization of the Grignard Metathesis reaction previously described in our group (**Figure 1**).¹⁰⁻¹² While this method can be used to synthesize a plethora of end capped polymers, the allyl and vinyl capped polymers are the most promising for use in the synthesis of block copolymers. The vinyl terminated polymer can be transformed to the corresponding hydroxy-terminated HT-PAT via hydroboration/oxidation reaction. The resultant polymer can then be reacted with bromoesters to yield HT-PAT ATRP macroinitiators (**Figure 3**).¹³ These initiators can be used to grow a variety of blocks (eg acrylates, methacrylates and styrene) from the HT-PAT. The hydroxyl terminated polymer can be coupled with carboxylic acid terminated polymers to yield triblock copolymers. In the example shown below hydroxy terminated HT-PHT is coupled with carboxylic acid terminated PEG to yield PEG-b-PT-PEG triblock copolymers.

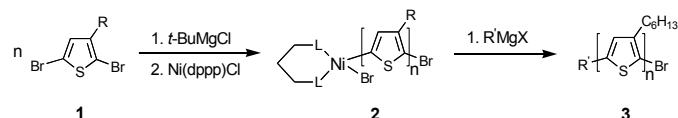


Figure 1. Synthesis of End Functionalized Poly(3-alkylthiophenes) via Grignard Metathesis reaction.

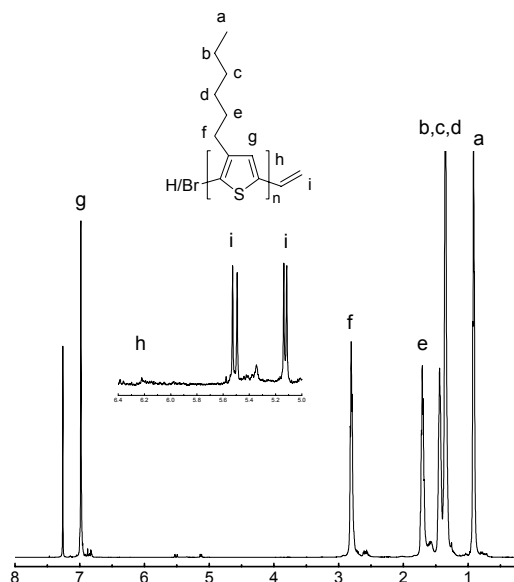


Figure 2. ¹H NMR spectra of vinyl terminated HT-PHT.

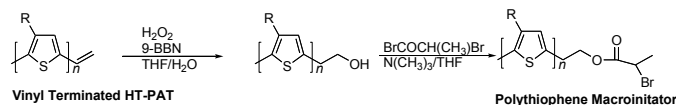


Figure 3. Synthesis of ATRP macroinitiator from vinyl terminated HT-PAT.

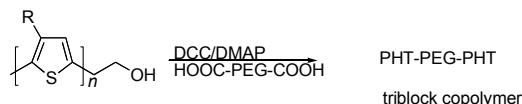


Figure 4. Synthesis of PHT-PEG-PHT triblock copolymer.

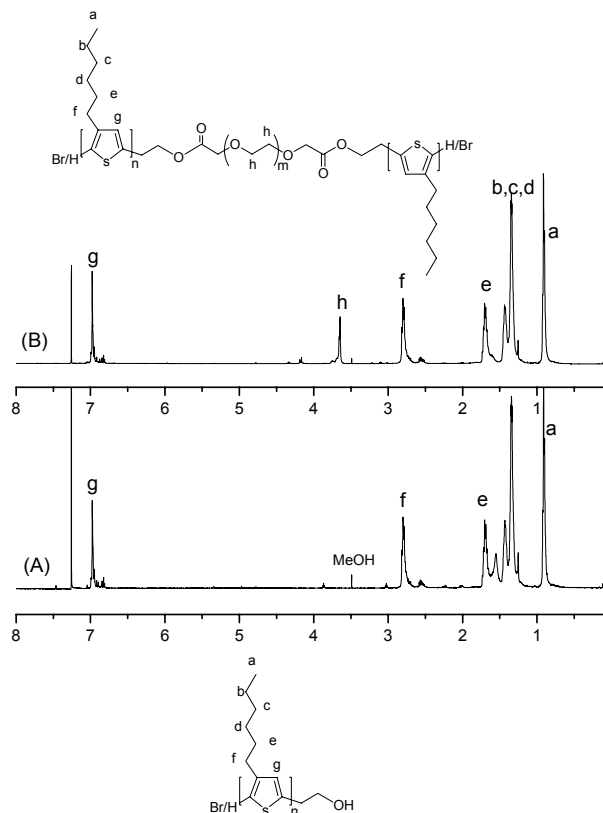


Figure 5. ^1H NMR of hydroxyl-terminated HT-PHT (A) and PHT-PEG-PHT triblock copolymer (B).

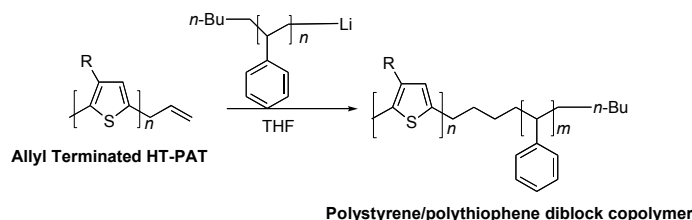


Figure 6. Synthesis of HT-PAT-PS diblock copolymer from allyl terminated polymer.

We have also found that the allyl terminated polymer can be easily coupled with living polystyryl lithium to give rise to HT-PAT-b-PS di-block copolymers. This general approach can be used to couple any living chain with the HT-PAT to yield diblock copolymers. This method is particularly

attractive as it allows for greater control over the polydispersity of the second block.

Conclusions

We have demonstrated that end functionalized HT-PAT's can be used as building blocks for di- and triblock copolymers using a several different approaches. These methods open the door for the creation of a variety of novel materials. Thus allowing for better control of the properties and morphology of the polymer.

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References

- (1) Chen, T. A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
- (2) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250-258.
- (3) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904-912.
- (4) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93-116.
- (5) Liu, J.; McCullough, R. D. *Macromolecules* **2002**, *35*, 8.
- (6) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Spiering, A. J. H.; van Dongen, J. L. J.; Vonk, E. C.; Claessens, H. A. *J. Chem. Soc. Chem. Comm.* **2000**, *2000*, 81.
- (7) Jayakannan, M.; Dongen, J. L. J. v.; Janssen, R. A. J. *Macromolecules* **2001**, *34*, 8.
- (8) Iraqi, A.; Barker, G. W. *J. Mater. Chem.* **1998**, *8*, 25.
- (9) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 4.
- (10) Jeffries-El, M.; Sauve, G.; Iovu, M.; McCullough, R. D. *Polym. Prepr.*, *45*(1) 183.
- (11) Sauve, G.; Jeffries-El, M.; McCullough, R. *Pollm. Prepr.*, *44*(2), 432.
- (12) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Advanced Materials in press*.
- (13) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.