

SYNTHESIS OF POLY(3-HEXYLTHIOPHENE) DI-BLOCK COPOLYMERS USING ATOM TRANSFER RADICAL POLYMERIZATION

Mihaela C. Iovu, Elena E. Sheina, Geneviève Sauv , Malika Jeffries-EL, Jessica Cooper and Richard D. McCullough

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Introduction

Poly(3-alkylthiophenes) (PAT) constitute an important group of conjugated polymers due to their conductivity and good solubility. Regioregular poly(3-alkylthiophenes) (head-to-tail) show improved electrical conductivity as compared to regiorregular PAT.¹ The first synthesis of regioregular poly(3-alkylthiophenes) was described in 1992 by McCullough and Lowe.² Regioregular poly(3-alkylthiophene) can also be synthesized using the Grignard metathesis (GRIM) method, as reported by McCullough *et al.*³

Despite their good conductivity and solubility, regioregular poly(3-alkylthiophenes) do not have good mechanical properties. The synthesis of poly(3-alkylthiophene) block-copolymers is a strategy for improving the mechanical and processing properties. Our group developed a protocol for the synthesis of poly(3-hexylthiophene) di- and tri-block copolymers.⁴

A method for *in situ* end functionalization of poly(3-hexylthiophene) (PHT) was recently reported in our group. This new technique allows the synthesis of vinyl terminated PHT in high yield (more than 95 % vinyl end group).

We report here a new and facile method for the synthesis of poly(3-hexylthiophene)-*b*-poly(acrylates) di-block copolymers using atom transfer radical polymerization (ATRP) employing vinyl terminated PHT as precursor.

Experimental

Synthesis of vinyl terminated PHT. 4.9 g (15 mmole) 2,5-dibromo-3-hexylthiophene was dissolved in 150 mL dry THF. 7.5 mL (15 mmole) solution *t*-butyl magnesium chloride 2M in diethyl ether was added via syringe under nitrogen and the reaction mixture was refluxed for 90 min. The reaction mixture was cooled to room temperature and 0.15 g (0.27 mmole) Ni(dppp)Cl₂ catalyst was added. The mixture was stirred for additional 10 min at room temperature followed by the addition of 3 mL (3 mmole) solution of vinyl magnesium bromide 1M. After 5 min. the reaction mixture was poured into methanol and the polymer precipitated.

Hydroboration/oxidation of vinyl terminated PHT. 2g (0.2 mmole; M_n(NMR) = 10000) vinyl terminated PHT was dissolved in 100 mL dry THF. 4 mL (2 mmole) 9-BBN solution 0.5 M in THF was added with using a deoxygenated syringe, under nitrogen. The reaction mixture was stirred for 24 h at 40°C. 2 mL 6M NaOH solution was then added to the reaction flask under nitrogen. The reaction mixture was stirred for an additional 15 min. and cooled to room temperature. 2 mL hydrogen peroxide (33%) was added to the reaction mixture and the reaction stirred for 24 h at 40°C. The hydroxy terminated PHT was isolated by precipitation in a methanol-water mixture. The polymer was filtered and purified by Soxhlet extraction with methanol.

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

ATRP of methyl acrylate using PHT macroinitiator. The polymerization was performed using CuBr –PMDETA as catalyst, in toluene (50 vol.%), at 80°C. The molar ratio for the polymerization of methyl acrylate was [MA] : [PHT-MI] : [CuBr] : [PMDETA] = 100 : 1 : 1 : 2.

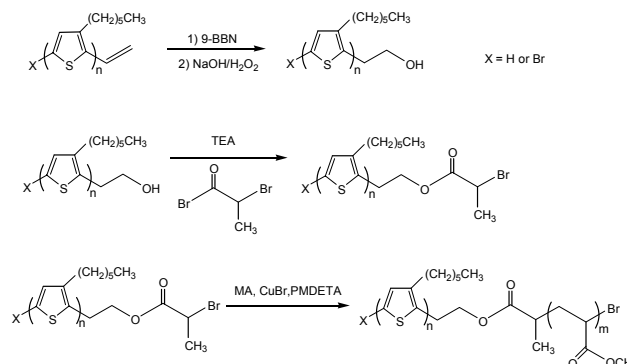
ATRP of *t*-butyl acrylate using PHT macroinitiator. The reaction procedure is similar to the one used for methyl acrylate polymerization.

Analyses. Conversions were determined on a Shimadzu GC-14A gas chromatograph using a capillary column (CEC-Wax, 30 m x 0.53 mm x 1.0 µm, Chrom Expert Co.). 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. NMR spectra of the polymers solutions in CDCl₃ were collected on a Bruker Avance 500 MHz

spectrometer. MALDI-TOF MS analysis was performed using a Voyager-DE STR BioSpectrometry workstation by Biosystems.

Results and Discussion

The ability to mono-cap poly(3-hexylthiophene) with vinyl group it is extremely important since it opens a way for the synthesis of di-block copolymers. The new method developed for the synthesis of poly(3-hexylthiophene) di-block copolymers with acrylates uses the vinyl terminated PHT as the precursor (Scheme 1). The vinyl end group is easily converted to CH₂CH₂OH end group which is then reacted with 2-bromopropionyl bromide to give a bromoester terminated PHT. The latter was used as macroinitiator for the atom transfer radical polymerization (ATRP)⁵⁻⁷ of acrylates.



Scheme 1. Synthetic protocol for the synthesis of poly(3-hexylthiophene)-*b*-poly(methyl acrylate)

End-capping of PHT results in 90 – 100 % vinyl end groups as indicated by MALDI-TOF MS (Figure 1). MALDI-TOF MS spectra of vinyl mono-capped PHT show to major peaks corresponding to Br/vinyl and H/vinyl.

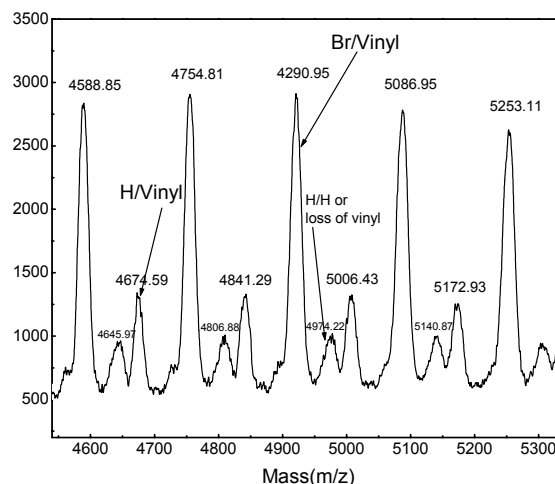


Figure 1. Expansion of MALDI-TOF MS spectra of vinyl terminated PHT

¹H NMR spectrum of vinyl terminated PHT shows the presence of vinyl protons at 5.1 ppm (*dd*), 5.5 ppm (*dd*) and 6.2 ppm (*m*) (Figure 2). Molecular weight of vinyl terminated PHT was estimated by integrating (c) protons vs. (b) protons.

The conversion of vinyl to CH₂CH₂OH terminated PHT was indicated by the complete disappearance of the (a) and (b) vinyl protons and the appearance of new signals at 3 ppm (*t*), 3.9 ppm (*t*) due to the methylene protons and a broad singlet at 4.9 ppm due to the OH proton.

Formation of the bromoester terminated PHT was also confirmed by ¹H NMR.

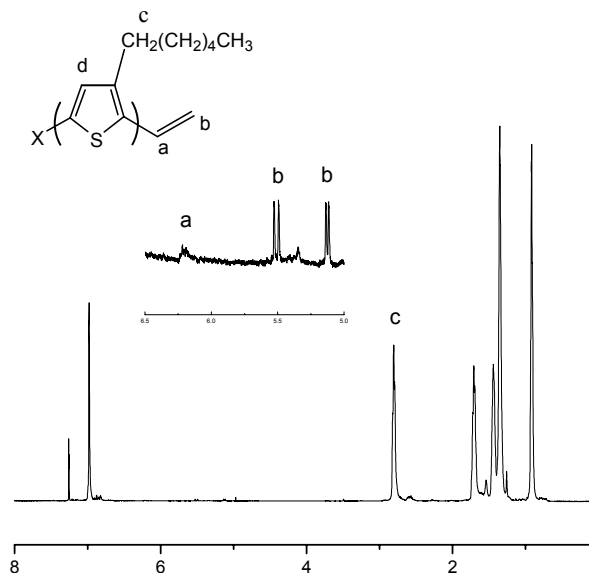


Figure 2. ^1H NMR spectrum of vinyl terminated PHT

ATRP of methyl acrylate and *t*-butyl acrylate using CuBr-PMDETA and bromoester terminated PHT as macroinitiator resulted in the formation of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) and poly(3-hexylthiophene)-*b*-poly(*t*-butyl acrylate).

The ^1H NMR spectrum of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) is shown in Figure 3.

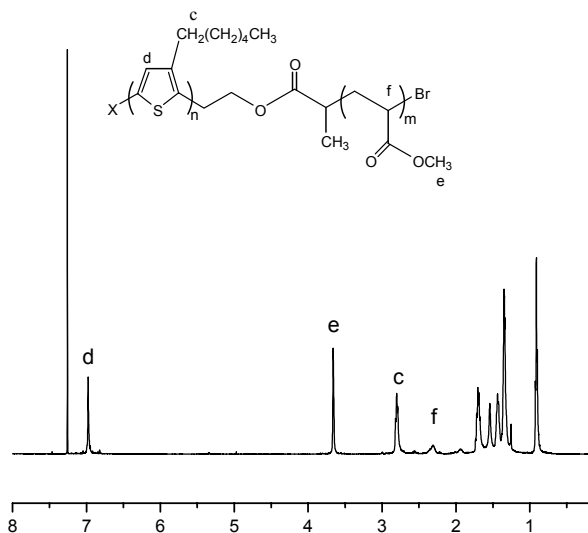


Figure 3. ^1H NMR spectrum of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) ($\text{DP}_n(\text{PHT}) = 50$; $\text{DP}_n(\text{PMA}) = 25$)

The methine protons of methyl acrylate block absorb 2.4 ppm, while the methoxy protons absorb at 3.6 ppm (Figure 3).

Conductivities of the di-block copolymers synthesized by ATRP were measured and they show a dependence on the composition of the di-block copolymers.

Conclusions

A new simple method for the synthesis of poly(3-hexylthiophene) di-block copolymers was developed using vinyl terminated PHT as precursor.

Acknowledgments. The authors are thankful to Professor Krzysztof Matyjaszewski for the useful discussions. Special thanks to Dr. Roberto R. Gil for the NMR analysis. The financial support from NSF is gratefully acknowledged.

References

- (1) McCullough, R. D. *Adv. Mat.* **1998**, *10*, 93.
- (2) McCullough, R. D.; Lowe, R. S. *J. Chem. Soc., Chem. Commun.* **1992**, 70.
- (3) McCullough, R. D.; Lowe, R. S.; Khersonsky, S. M. *Adv. Mat.* **1999**, *11*, 250.
- (4) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem. Int. Ed.* **2002**, *41*, 329.
- (5) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614-5615.
- (6) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921-2990.
- (7) Matyjaszewski, K.; Davis, T. P. Eds. *Handbook of radical polymerization*; Wiley-Interscience: Hoboken, 2002.