SYNTHESIS AND CHARACTERIZATION OF TRI-BLOCK COPOLYMERS CONTAINING REGIOREGULAR POLY(3-ALKYLTHIOPHENE)

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Introduction

In the field of conducting polymers, progress is driven towards the application of these unique materials. In order to employ conducting polymers efficiently, there is a need to engineer properties through the control of chemical structure, and thus there is an emphasis on synthetic methods[1,2,3]. One synthetic strategy is to introduce particular properties into a material by creating block copolymers. By covalently bonding two different polymers together, one can produce an extremely unique and specific material.

Due to its chemical structure, regioregular poly(3-alkylthiophene) (PAT) possesses an array of desired electrical properties[4,5]. However, its chemical structure also causes PAT to form brittle and highly inflexible rod like microstructures. The objective is to produce a material that has the electrical properties of polythiophene and the flexiblility of soft polymers such as poly(methyl acrylate)[7].

This work is focused on the synthesis and characterization of a ABA triblock copolymer, poly(methyl acrylate)-*b*-poly(3-hexylthiophene)-*b*-poly (methyl acrylate). Regioregular poly(3-hexylthiophene) (PHT) was synthesized by using Grignard Metathesis reaction[6]. End group modification of regioregular polythiophene leads to the production of a macroinitator[8]. Atom Transfer Radical Polymerization (ATRP)[9,10,11] then is utilized to produce triblock copolymers using the PHT macrointiator as the precursor.

Experimental

Materials. All reactions were performed under pre-purified nitrogen, using either flame-dried or oven-dried glassware. All solvents were distilled prior to use. $LiAlH_4$ and Grignard reagents were purchased from Aldrich Chemical Co. and used without further purification. N-methylformanilide, $POCl_3$, triethylamine, and 2-bromopropionyl bromide were distilled prior to use.

Instrumentation. ^{1}H spectra were recorded on an IBM Bruker FT500 MHz spectrometer. All NMR spectra were recorded in $CDCl_3$ containing 0.003% TMS as an internal standard. MALDI-TOF MS was performed using a Voyager-DE STR BioSpectrometry Workstation by PerSeptive Biosystems. All GPC spectra were recorded using a Waters 6000A apparatus and a Waters R410 differential refractometer. The eluent was THF, which was kept at 25ºC. Flow rate was 1.0 mL/min. The system was calibrated using polystyrene standards obtained from Polymer Standards Service. GC/MS was performed on a Hewlett-Packard Agilient 6890-5973 GC-MS workstation.

Synthesis of poly(3-hexylthiophene) with H/H end groups. Regioregular poly(3-hexylthiophene) (1.0 g, 0.1 mmol) was dissolved in THF (150 mL). One equivalent of Grignard reagent (2M, 10 mL) was added and the mixture was refluxed for 2 hours. The solution was then precipitated in methanol.

Synthesis of poly(3-hexylthiophene) with CHO/CHO end groups. Poly(3-hexylthiophene) with H/H end groups (0.9g, 0.09 mmol) was dissolved in toluene (200 mL). N-methylformanilide (2 mL, 16 mmol) and $POCl_3$ (1.3 mL, 14 mmol) were added, and the mixture was stirred at 75ºC for 24 hours. The solution was cooled to room temperature and then stirred with saturated sodium acetate. The solution was precipitated in methanol.

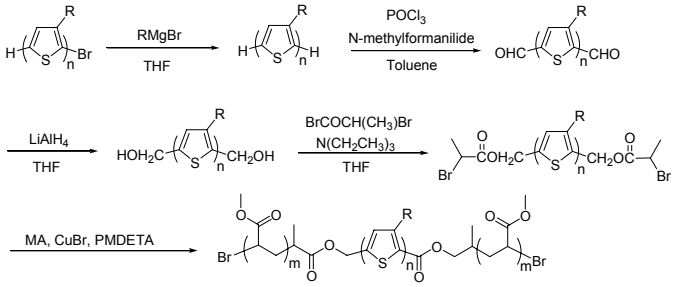
Synthesis of poly(3-hexylthiophene) with CH_2OH/CH_2OH end groups. Poly(3-hexylthiophene) with CHO/CHO end groups (0.8 g, 0.08 mmol) was dissolved in THF (200 mL). $LiAlH_4$ (1M, 1 mL) was added to the solution. The mixture was allowed to stir at room temperature for 1 hour and then precipitated in methanol.

Synthesis of poly(3-hexylthiophene) with bromoester end groups. Poly(3-hexylthiophene) with CH_2OH/CH_2OH end groups (0.7 g, 0.07 mmol) was dissolved in THF (200mL). The solution was heated to 50ºC followed by the addition of triethylamine (3 mL, 20 mmol) and drop-wise addition of 2-bromopropionyl bromide (2.5 mL, 20 mmol). The solution was allowed to stir at room temperature for 12 hours and then precipitated in methanol.

ATRP of methyl acrylate (MA) using PHT macroinitiator (PHT-MI). ATRP of methyl acrylate was performed at molar ratio: [MA] : [PHT-MI] : [CuBr] : [PMDETA] = 1000 : 1 : 10 : 10, at 90ºC.

Results and Discussion

Regioregular poly(3-hexylthiophene) (PHT) was used as the starting material for subsequent chemical conversions completed on end groups. Scheme 1 illustrates the sequence of reactions used to convert the PHT homopolymer to a triblock copolymer. The first reaction involves magnesium-halogen exchange converting H/Br polymer to H/H terminated polymer. Through utilization of Vielsmier reaction, the polymer end groups are converted to aldehydes, which are then subsequently reduced to hydroxy groups. The hydroxy end groups were easily converted to bromoester end groups generating ATRP macroinitiator. ^{1}H NMR spectroscopy and MALDI TOF were utilized to analyze the product of each chemical reaction. Methyl acrylate was polymerized using PHT macroinitiator as the precursor, yielding poly(methyl acrylate)-*b*-poly(3-hexylthiophene)-*b*-poly(methyl acrylate) copolymer. Figure 1 shows the ^{1}H NMR spectra of the final triblock copolymer



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

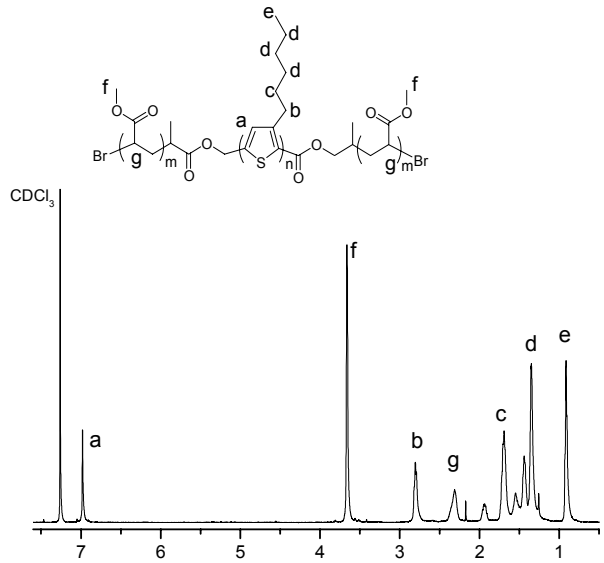


Figure 1. ^{1}H NMR of poly(methyl acrylate)-*b*-poly(3-hexylthiophene)-*b*-poly(methyl acrylate).

GPC was used to monitor the molecular weight of the copolymers. Table 1 demonstrates the progressive incorporation of poly(methyl acrylate) in the copolymer function of the reaction time.

Table 1. Composition and Molecular Weight of Synthesized Triblock Copolymers.

Sample	Rxn Time (min)	% mol MA	% mol HT	Mn (GPC)
1	0	0	100	22 K
2	30	30	70	24 K
3	60	40	60	25 K
4	90	50	50	32 K
5	180	60	40	33 K
6	480	70	30	36 K

Conclusion

Poly(methyl acrylate)-*b*-poly(3-hexylthiophene)-*b*-poly (methyl acrylate) was successfully synthesized using end group modification of poly(3-hexylthiophene) followed by atom transfer radical polymerization (ATRP) of methyl acrylate.

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