

# Regioregular poly(3-alkylthiophene) conducting block copolymers

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## Abstract

Regioregular poly(3-alkylthiophenes) (PATs) represent an important class of polymers that are environmentally stable and display high electrical conductivity. Despite their excellent electrical properties, PATs do not exhibit very good mechanical and processing properties. This issue is addressed here by integrating poly(3-alkylthiophene) in copolymer structures with various polymer blocks that display better mechanical properties, leading to a variety of polymeric materials with desired properties. We describe a new method for the synthesis of poly(3-alkylthiophene) block copolymers using vinyl terminated regioregular poly(3-alkylthiophene) as precursors via atom transfer radical polymerization (ATRP).

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## 1. Introduction

Poly(3-alkylthiophenes) represent a class of conducting polymers that have good solubility and environmental stability [1,2]. The synthesis of regioregular poly(3-alkylthiophenes) (PATs), first discovered by McCullough et al., resulted in the formation of defect-free, structurally homogeneous, head-to-tail coupled poly(3-alkylthiophenes) (HT-PATs) that have greatly improved electronic and photonic properties over regiorandom analogues [3–8].

The Grignard metathesis method (GRIM) has been reported by our group as another method to synthesize regioregular poly(3-alkylthiophenes) [9]. A recent discovery revealed that the nickel-initiated cross-coupling polymerizations (e.g. McCullough and GRIM methods) proceed via a chain growth mechanism and the molecular weight of poly(3-alkylthiophenes) can be predicted by the molar ratio of monomer to Ni(dppp)Cl<sub>2</sub> [10]. Furthermore, addition of various Grignard reagents (R'MgX) at the end of polymerization results in end-capping of regioregular poly(3-alkylthiophenes) with R' end group, which leads to the synthesis of a variety of end-functionalized PATs [11].

Despite their high conductivity and good solubility, regioregular poly(3-alkylthiophenes) do not possess optimal mechanical and processing properties. This issue could be addressed by integrating poly(3-alkylthiophene) in copolymer structures with various polymer blocks that display desirable mechanical properties, leading to a variety of polymeric materials with improved properties (e.g. flexible plastics, rigid plastics, elastomers). Our group had previously reported a multi-step method for the synthesis of poly(3-hexylthiophene) di- and tri-block copolymers [12].

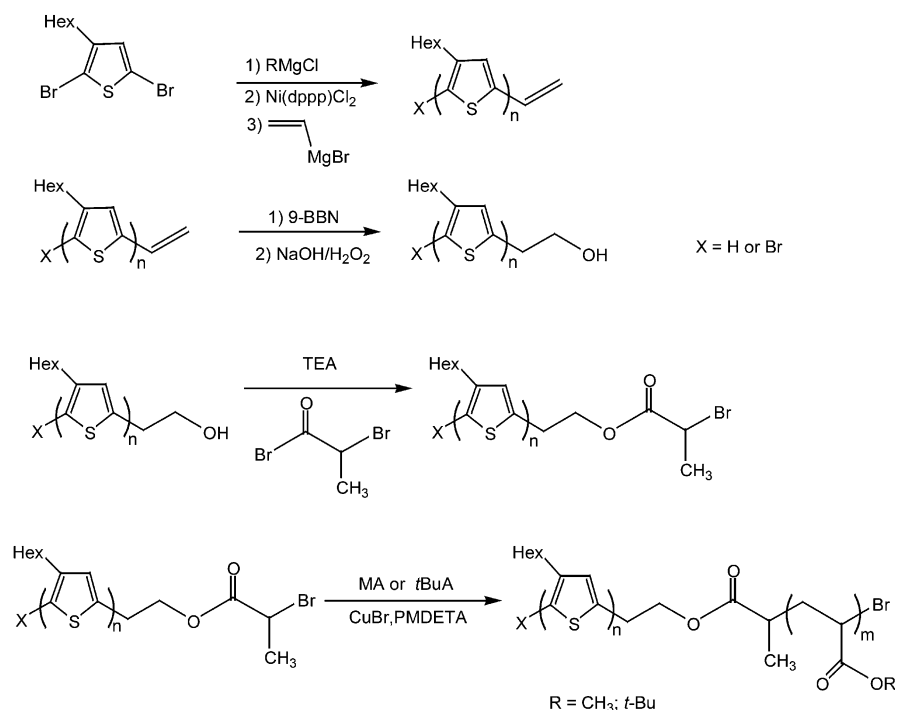
Here we describe an alternative method that involves fewer steps for the synthesis of poly(3-hexylthiophene)-*b*-polyacrylates (Scheme 1) employing atom transfer radical polymerization (ATRP) [13]. The block-copolymers generated by this method showed great film forming properties leading to higher conductivities (e.g.  $\sigma \sim 3\text{--}30$  S/cm) than previously reported [12].

## 2. Experimental

### 2.1. Synthesis of vinyl terminated PHT

A dry 100 mL three-neck flask was flushed with N<sub>2</sub> and was charged with 2,5-dibromo-3-hexylthiophene (4.9 g, 15 mmol) and anhydrous THF (150 mL). A 2 M solution of butyl magnesium chloride (7.5 mL, 15 mmol) in diethyl

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Scheme 1. Synthesis of poly(3-hexylthiophene)-*b*-polyacrylates.

ether (Et<sub>2</sub>O) was added via a syringe, and the reaction mixture was gently refluxed for 90 min. The reaction mixture was allowed to cool down to room temperature, at which time Ni(dppp)Cl<sub>2</sub> (0.15 g, 0.27 mmol) was added to the reaction mixture. The polymerization was allowed to proceed for 15 min at room temperature followed by the addition of a 1 M solution of vinyl magnesium bromide (3 mL, 3 mmol). The reaction mixture was stirred for 5 min followed by quenching in methanol. The polymer was purified by sequential Soxhlet extractions with methanol, hexanes, and chloroform. The polymer was isolated from the chloroform solution.

## 2.2. Hydroboration/oxidation of vinyl terminated PHT

Vinyl terminated PHT (2 g, 0.2 mmol,  $M_n(\text{NMR}) = 10,000$ ) was dissolved in anhydrous THF (100 mL) under N<sub>2</sub>. To this reaction mixture, a 0.5 M solution of 9-BBN (4 mL, 2 mmol) in anhydrous THF was added via a syringe. The reaction mixture was stirred for 24 h at 40 °C, at which point a 6 M solution of NaOH (2 mL) was added to the reaction flask. The reaction mixture was stirred for another 15 min (at which point the oil bath was removed). The reaction mixture was allowed to cool down to RT followed by addition of a 33% aqueous solution of hydrogen peroxide (2 mL), and the reaction was allowed to proceed for additional 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 a Soxhlet extraction with methanol.

## 2.3. Synthesis of PHT macroinitiator

Hydroxy terminated PHT (1 g, 0.1 mmol) was dissolved in anhydrous THF (100 mL) under N<sub>2</sub>. The reaction mixture was stirred for 15 min at 40 °C followed by addition of triethylamine (9 mL, 66 mmol) and a drop-wise addition of 2-bromopropionyl bromide (7.5 mL, 60 mmol). The reaction mixture was stirred for 24 h at 40 °C. The resulting PHT macroinitiator was precipitated in methanol and purified by a Soxhlet extraction with methanol.

## 2.4. ATRP of acrylates using PHT macroinitiator

ATRP of methyl acrylate and *t*-butyl acrylate was performed using CuBr–PMDETA, in toluene (50 vol%) at 80 °C. The molar ratio was [M]<sub>0</sub>: [PHT-MI]<sub>0</sub>: [CuBr]<sub>0</sub>: [PMDETA]<sub>0</sub> = 300:1:1:2. A dry Schlenk flask was charged with PHT macroinitiator (1 g, 0.1 mmol), methyl acrylate (2.7 mL, 30 mmol), 0.1 g *p*-dimethoxy benzene (GC internal standard) and CuBr (0.014 g, 0.1 mmol). After three freeze–pump–thaw cycles the reaction mixture was immersed in a thermostated oil bath at 80 °C. Then, PMDETA (0.04 mL, 0.2 mmol) was added to the reaction mixture via a deoxygenated syringe and an initial sample was removed. Samples were periodically withdrawn from the reaction mixture to follow conversion and the molecular weight.

## 2.5. Analyses

Conversions were determined on a Shimadzu GC-14A

gas chromatograph using a capillary column (CEC-Wax, 30 m × 0.53 mm × 1.0 μm, Chrom Expert Co.). Size exclusion chromatography (SEC) measurements were performed on a Waters 2690 separations module apparatus and a Waters 2487 dual λ absorbance detector with chloroform as the eluent (flow rate 1 mL/min, 35 °C, λ = 350 nm) with a series of three Styragel columns (10<sup>4</sup>, 500, 100 Å; Polymer Standard Services). Calibration based on polystyrene standards was applied for determination of molecular weights. NMR spectra of the polymer solutions in CDCl<sub>3</sub> were recorded on a Bruker Avance 500 MHz spectrometer. MALDI-TOF MS (Voyager-DE STR BioSpectrometry workstation by Biosystems) was used for estimation of end groups (terthiophene matrix, linear mode). Polymer films were prepared by drop casting from toluene solutions. The casting solutions were prepared by dissolving 5 mg of polymer in 1 mL of dry toluene, sonicating for 5 min, followed by the filtration of clear solutions through PTFE 0.45 μm filters. Films were drop cast onto 22 mm<sup>2</sup> cover glass that were washed with chromic acid solution, rinsed several times with acetone and hexanes and dried before drop casting. Conductivities were measured for films of the block copolymers oxidized with I<sub>2</sub> by the 4-point probe method. The film thickness was measured by scanning electron microscopy (SEM) and the conductivity calculated according to the following equation:

$$\sigma = \frac{1}{4.53Rl}$$

where  $R$  is the resistance ( $R = V/I$ ) and  $l$  is the film thickness.

### 3. Results and discussion

#### Incorporation of poly(acrylate) blocks into copolymer

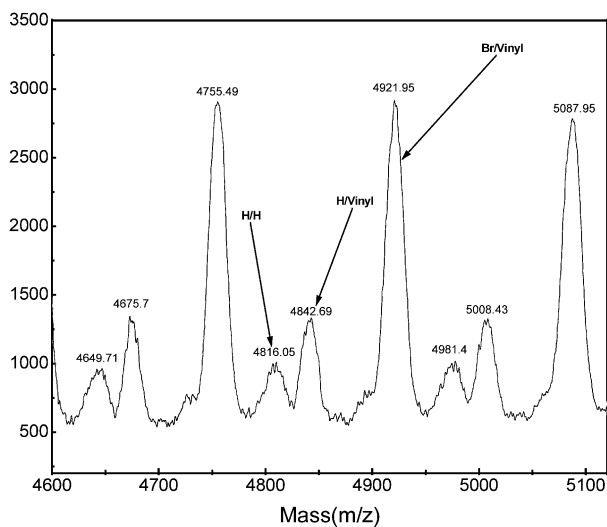


Fig. 1. MALDI-TOF-MS spectrum of vinyl terminated poly(3-hexylthiophene).

structures with poly(3-hexylthiophene) should result in improved solubility and film forming abilities.

The new method developed for the synthesis of poly(3-hexylthiophene) di-block copolymers with acrylates uses vinyl terminated PHT as precursor as shown in Scheme 1. The vinyl end group was easily converted to hydroxyethyl end group, that reacts with 2-bromopropionyl bromide to give bromoester terminated PHT. The latter was used as macroinitiator for ATRP of acrylates [14–16].

MALDI-TOF MS spectrum (Fig. 1) shows the presence of Br/vinyl and H/vinyl end groups [11]. <sup>1</sup>H NMR spectrum of vinyl terminated PHT (Fig. 2) indicated the presence of vinyl protons at 5.1 ppm (dd), 5.5 ppm (dd) and 6.8 ppm (m). Degree of polymerization (DP<sub>n</sub>) of vinyl terminated PHT was estimated from <sup>1</sup>H NMR spectrum (DP<sub>n</sub> = 60). The conversion of vinyl to hydroxyethyl terminated PHT was indicated by the complete disappearance of vinyl protons and the appearance of new signals at 3 ppm (*t*), 3.9 ppm (*t*) due to the methylene protons [13]. Formation of the bromoester terminated PHT was also confirmed by <sup>1</sup>H NMR (Fig. 3).

#### 3.1. ATRP of methyl acrylate

ATRP of methyl acrylate was performed using CuBr as a catalyst, PMDETA as a ligand and bromoester terminated poly(3-hexylthiophene) as macroinitiator (PHT-MI). Polymerization of methyl acrylate was performed at molar ratio [MA]<sub>0</sub>: [PHT-MI]<sub>0</sub>: [CuBr]<sub>0</sub>: [PMDETA]<sub>0</sub> = 300:1:1:2 in toluene ([MA]<sub>0</sub>/[toluene]<sub>0</sub> = 1/1 (v/v)) at 80 °C.

<sup>1</sup>H NMR spectrum of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) is shown in Fig. 4.

Composition of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) copolymers was estimated from the <sup>1</sup>H NMR spectra, by integrating *i* protons vs *f* protons. The obtained results are shown in Table 1.

The resulting copolymers were very soluble in many organic solvents and possessed excellent film forming properties. Solid state morphology of these materials was investigated via SEM. In contrast to the solution processed conducting films of PATs, where the film quality ranges from brittle to cracked [1], the films of block-copolymers showed a very dense, uniform morphology, which correlated well with the observed high conductivities (Table 2).

Table 1  
Composition of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) di-block copolymers

Time (min)	PHT (mol%)	PMA (mol%)	M <sub>n</sub> (GPC)	PDI (GPC)
0	100	0	12,200	1.17
5	97.0	3.00	12,290	1.24
105	67.0	33.00	14,350	1.27
190	52.4	47.6	15,180	1.33
380	42.5	57.5	15,340	1.49
480	41.2	58.8	15,400	1.60

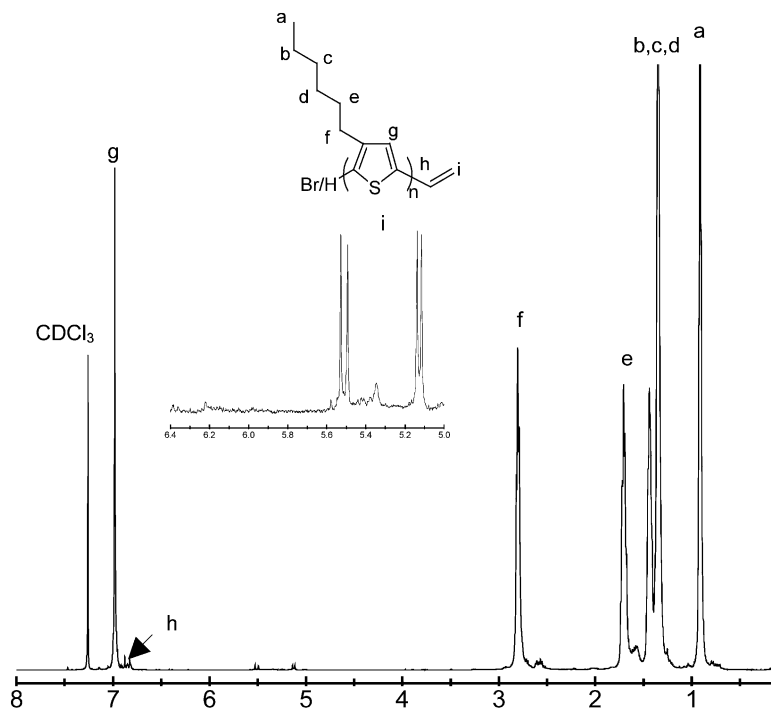
Fig. 2.  $^1\text{H}$  NMR spectrum of vinyl terminated poly(3-hexylthiophene).

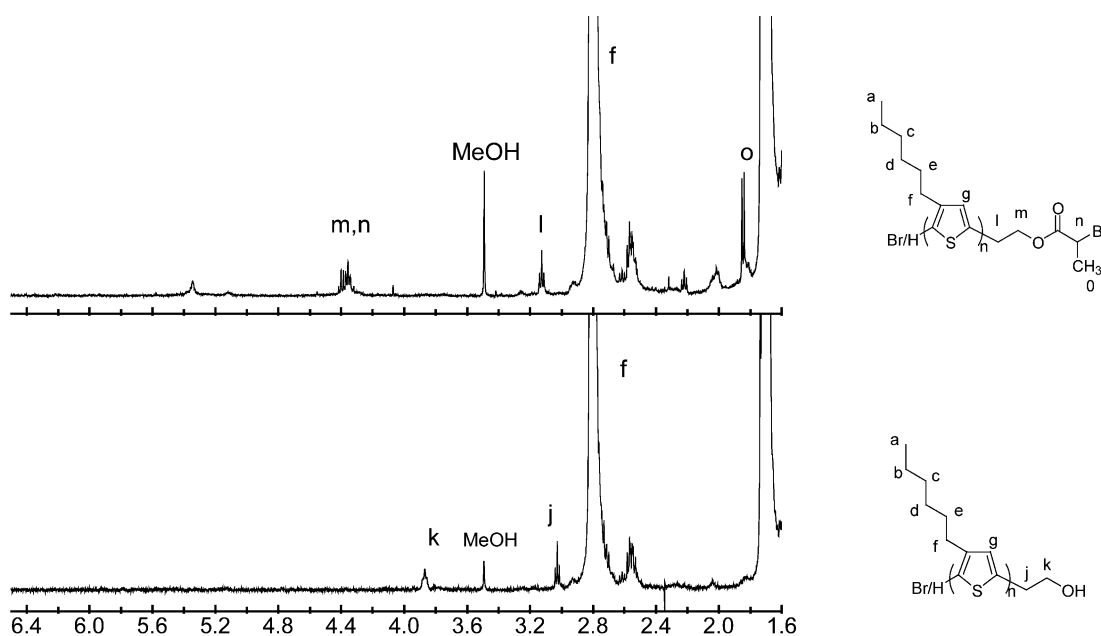
Table 2  
Conductivities of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) function of the copolymer composition

PHT (mol%)	PMA (mol%)	Conductivity ( $\sigma$ , S/cm)	Film thickness ( $\mu\text{m}$ )
100	0	32	1.14
67	33	14	1.35
52.4	47.6	28	0.55
41.2	58.8	4	1.66

Conductivity of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) is a function of copolymer composition and film thickness.

### 3.2. ATRP of *t*-butyl acrylate

The incorporation of poly(*t*-butyl acrylate) block serves as the same function as poly(methyl acrylate). In addition, hydrolysis of poly(*t*-butyl acrylate) block will generate

Fig. 3.  $^1\text{H}$  NMR spectrum of hydroxyethyl and bromoester terminated poly(3-hexylthiophene).

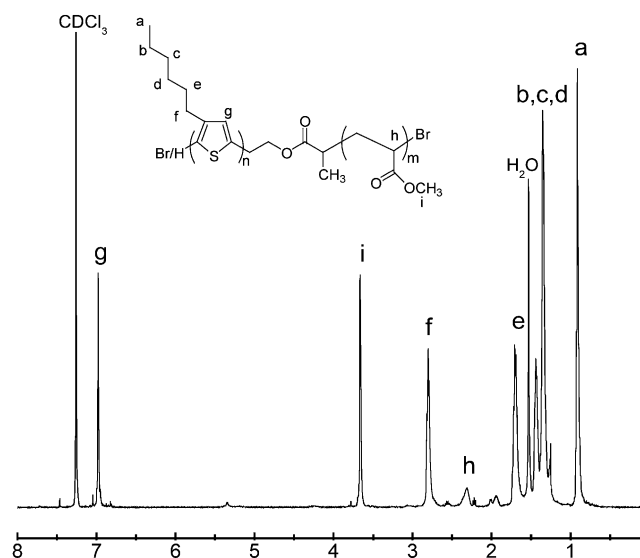


Fig. 4.  $^1\text{H}$  NMR spectrum of poly(3-hexylthiophene)-*b*-poly(methyl acrylate) (sample collected after 105 min; entry 3 in Table 1).

poly(3-hexylthiophene)-*b*-poly(acrylic acid) copolymer which can introduce novel properties.

ATRP of *t*-butyl acrylate was performed at molar ratio  $[\text{t-BuA}]_0:[\text{PHT-MI}]_0:[\text{CuBr}]_0:[\text{PMDETA}]_0 = 300:1:1:2$  in toluene ( $[\text{t-BuA}]/[\text{toluene}] = 1/1$  (v/v)) at  $90^\circ\text{C}$ .  $^1\text{H}$  NMR spectrum of poly(3-hexylthiophene)-*b*-poly(*t*-butyl acrylate) is shown in Fig. 5.

Composition of poly(3-hexylthiophene)-*b*-poly(*t*-butyl acrylate) copolymer was estimated from  $^1\text{H}$  NMR and is shown in Table 3. Poly(3-hexylthiophene)-*b*-poly(*t*-butyl acrylate) showed similar electrical properties with poly(3-hexylthiophene)-*b*-poly(methyl acrylate) copolymer.

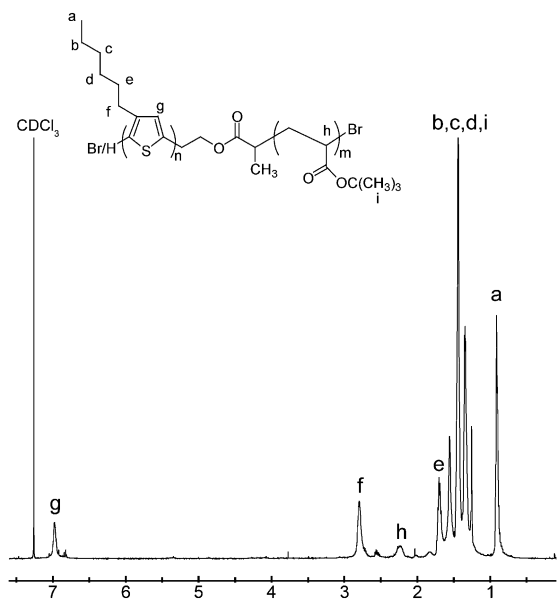


Fig. 5.  $^1\text{H}$  NMR spectrum of poly(3-hexylthiophene)-*b*-poly(*t*-butyl acrylate).

Table 3

Composition of poly(3-hexylthiophene)-*b*-poly(*t*-butyl acrylate) di-block copolymers

Time (min)	PHT (mol%)	PrBuA (mol%)	$M_n$ (GPC)	PDI (GPC)
0	100	0	5600	1.40
300	53.2	46.8	6800	1.55

#### 4. Conclusion

The described method affords poly(3-hexylthiophene)-*b*-poly(acrylates) copolymers in a new and simpler way than previously described. This method elegantly demonstrates the ability to utilize ATRP in order to produce novel materials. The resulting block copolymers demonstrated excellent electrical and processing properties. These block copolymer can lead to the new generation of materials with new applications and properties.

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