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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).

Keywords: Transfer radical polymerization; Soxhlet extraction; Macroinitiator

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_2 [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 posses 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. $\sigma \sim 3$–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_2 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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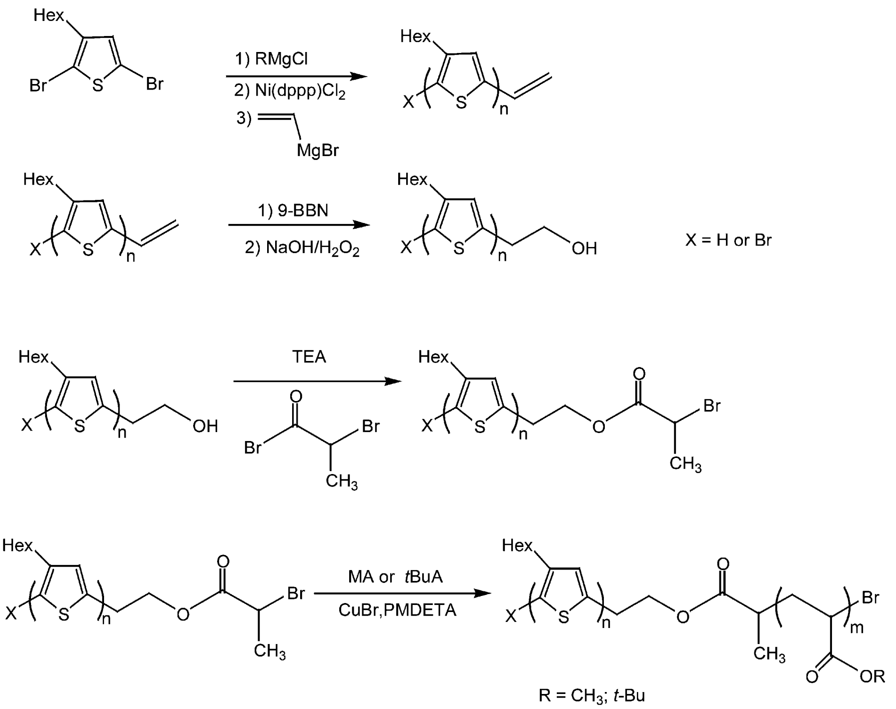

Scheme 1. Synthesis of poly(3-hexylthiophene)-*b*-polyacrylates.

ether (Et_2O) 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_2 (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(NMR) = 10,000) was dissolved in anhydrous THF (100 mL) under N_2. 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_2. 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 $[M]_0:[PHT\text{-}MI]_0:[CuBr]_0:[PMDETA]_0 = 300:1:1:2$. 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