

# LIVING RADICAL POLYMERIZATION TECHNIQUES APPLIED TO THE SYNTHESIS OF WELL-DEFINED COPOLYMERS CONTAINING REGIOREGULAR POLY(3-ALKYLTHIOPHENE)

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## Introduction

Polythiophenes constitute a particularly important class of conjugated polymers, which has been extensively studied. Alkyl substituted polythiophenes are chemically and thermally stable, which makes them very attractive materials for opto-electronics.<sup>1-3</sup>

The synthesis of regioregular poly(3-alkylthiophenes) (PATs), first discovered by McCullough *et al.*,<sup>4,5</sup> resulted in the formation of defect-free, head-to-tail coupled PATs with greatly improved electronic and photonic properties over their regiorandom analogues.<sup>6-8</sup> Grignard Metathesis Method (GRIM) has been reported later as an alternative methodology for the synthesis of regioregular PATs, as well.<sup>9,10</sup>

Integration of PATs in block copolymer structures with other polymers is expected to generate new materials with tunable properties as a function of the composition of the copolymers.

In 2002, our group reported a method for the synthesis of PATs di- and tri-block copolymers,<sup>11</sup> followed recently by an alternative, simpler method for generating di-block copolymers.<sup>12</sup> Chain end-functionalization of PATs allows the synthesis of vinyl- and allyl-terminated polymer in high yield (> 90%).<sup>13</sup>

We are reporting here the synthesis of poly(3-alkylthiophene) block-copolymers using ATRP and RAFT techniques.<sup>14-16</sup> Furthermore, polystyrene-*g*-poly(3-alkylthiophene) was synthesized via NMP or ATRP using grafting through technique.

## Experimental

**Synthesis of vinyl- or allyl-terminated PHT.** 4.9 g (15 mmol) 2,5-dibromo-3-hexylthiophene was dissolved in 150 mL of dry THF. 7.5 mL (15 mmol) solution of alkylmagnesium chloride (2 M) in diethyl ether was added via syringe under nitrogen and the reaction mixture was stirred at reflux for 90 minutes. The reaction mixture was cooled to room temperature and 0.15 g (0.27 mmol) of Ni(dppp)Cl<sub>2</sub> catalyst was added. The mixture was stirred for additional 10 minutes at room temperature followed by the addition of 3 mL (3 mmol) solution of allyl- or vinylmagnesium bromide (1 M). After 5 minutes, the reaction mixture was poured into methanol and the polymer precipitated.

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

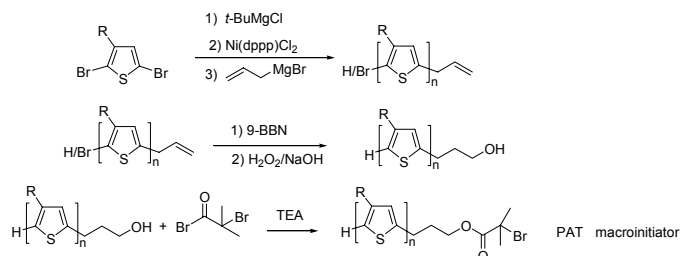
**ATRP macroinitiator** was synthesized as described previously.<sup>12</sup>

**Poly(3-hexylthiophene) RAFT agent** was synthesized from hydroxyethyl-terminated polymer according to Scheme 3.<sup>16</sup>

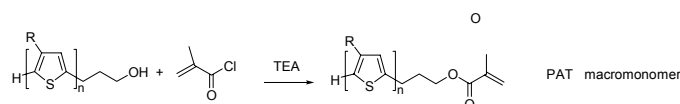
## Results and discussion

The synthesis of ATRP macroinitiator is shown in Scheme 1. The bromoester-terminated poly(3-hexylthiophene) was used as a macroinitiator for ATRP of styrene, methyl acrylate and methyl methacrylate.

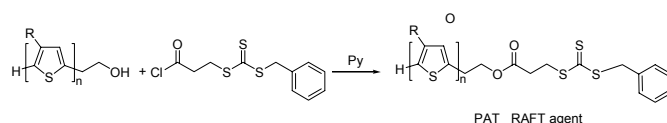
Hydroxy-terminated poly(3-hexylthiophene) was also converted to a macromonomer, as shown in Scheme 2. Polystyrene-*g*-poly(3-hexylthiophene) was synthesized using ATRP and NMP.



**Scheme 1.** Synthesis of bromoester-terminated poly(3-alkylthiophene).

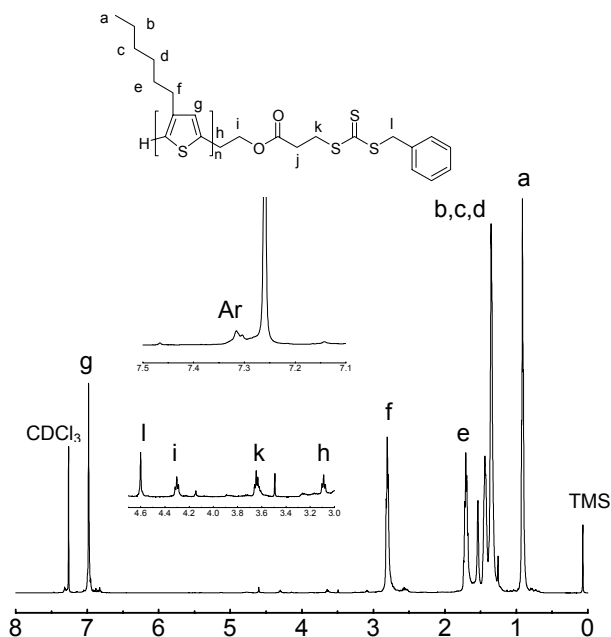


**Scheme 2.** Synthesis of poly(3-alkylthiophene) methacrylate macromonomer.



**Scheme 3.** Synthesis of poly(3-alkylthiophene) RAFT agent.

Hydroxyethyl-terminated poly(3-hexylthiophene) was reacted with 3-benzylsulfanylthiocarbonylsulfanylpropionic acid chloride generating a RAFT agent<sup>16</sup> as shown in Scheme 3. <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) RAFT agent is shown in Figure 1.



**Figure 1.** <sup>1</sup>H NMR spectrum of poly(3-hexylthiophene) RAFT agent.

## Conclusion

New copolymers based on regioregular poly(3-alkylthiophene) for electronic applications were synthesized via living radical polymerization techniques, such as ATRP, RAFT, and NMP. These block- and graft-copolymer structures, which conserve good electronic properties of alkyl functionalized polythiophenes, create a new generation of materials with improved mechanical and processing properties.

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