



Synthesis and molecular characterization of polythiophene and polystyrene copolymers: Simultaneous preparation of diblock and miktoarm copolymers



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ABSTRACT

During the synthesis of polystyrene-*b*-polythiophene diblock copolymers (PS-*b*-PT) via combination of anionic polymerization (PS block) and polymerization of thiophene with iron trichloride (PT block), the simultaneous preparation of another product is observed and verified as a miktoarm star copolymer of the (PS)₂PT type. This parallel synthesis is initially detected through size exclusion chromatography studies and then, after the complete separation of the two different products, it is certified by ¹³C NMR spectroscopy. IR and UV–Vis spectra of the two different products also display characteristic peaks for the PT chains, leading to proof of its presence in both cases. Furthermore, the products are studied thermally by thermogravimetric analysis and their morphology is preliminarily investigated by scanning electron microscopy.

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1. Introduction

More than three decades have passed since the initial discovery that conjugated polymers are electrically conductive [1] and the scientific interest on this type of materials as well as on their potential applications continues to grow [2–6]. Polythiophene (PT) is a conjugated polymer which exhibits significant and remarkable properties such as conductivity, thermal stability and thermochromism [7], but on the other hand the limited and reduced solubility and processability of this particular polymer is a drawback that needs to be resolved [8]. In order to overcome this major disadvantage well-established techniques most commonly used are: (a) incorporation of several alkyl groups

on the stiff PT backbone [9–15], usually at the 3rd ring position [ex. poly(3-hexyl thiophene), P3HT], (b) synthesis of PT copolymers with several common polymers [16–19], such as polystyrene (PS) and (c) combination of both aforementioned strategies [19–22], as for example the case of P3HT-*b*-PS. More specifically, the formation of such rod-coil copolymers is attractive since it has been found that they self-assemble, leading to different chain conformations and adopted structures by varying the PT content [22–26].

We have previously reported the successful copolymerization of PT with PS (PS-*b*-PT), polyisoprene (PI, PI-*b*-PT) and furthermore the synthesis of a PS-*b*-PI-*b*-PT terpolymer [18]. In this manuscript we report a slightly different synthetic procedure and additional results which prove the simultaneous preparation of two different copolymers: a linear diblock of the PS-*b*-PT sequence and a miktoarm star of the (PS)₂PT type. The molecular characterization was performed via size exclusion chromatography (SEC) and carbon nuclear magnetic resonance (¹³C NMR).

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Table 1

Quantities used for the synthesis of the PS-PT final products.

Sample PS-PT	Styrene (g)	s-BuLi (mmol)	2-BrT (mmol)	Thiophene (ml)	FeCl ₃ (g)
A1	8.34	0.42	0.83	1	6
A2	8.34	0.42	0.83	2	12
A3	10.8	0.27	0.54	2	12
A4	10.8	0.27	0.54	4	24

Moreover, infrared (FT-IR) and ultraviolet (UV-Vis) spectroscopies verified the existence of polythiophene chains in the final materials, whereas scanning electron microscopy (SEM) was used to determine the morphology.

2. Experimental

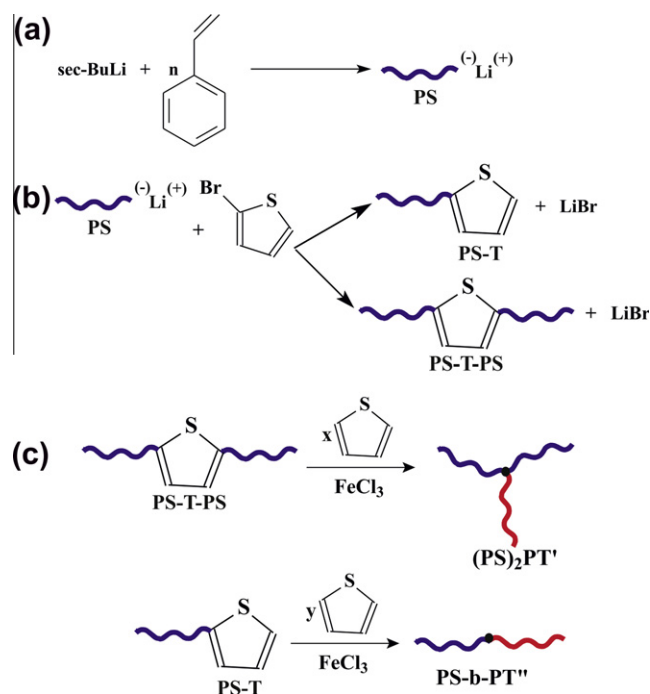
2.1. Materials and synthetic procedure

The materials and the main synthetic procedure are described elsewhere [18]. The only differences are that in the synthetic route adopted in the present research work the use of methanol is not necessary since the PS⁻Li⁺ living ends proved to be fully terminated by 2-bromothiophene (2BrT) and moreover the quantity of 2VT used is larger ($\text{mol}_{2\text{BrT}} = 2 \times \text{mol}_{\text{initiator}}$). The exact quantities used for each experiment are included in Table 1.

For a typical experiment the polymerization of St occurs under high vacuum conditions in benzene (~120 ml in all cases), as the solvent, with *sec*-butyllithium (*s*-BuLi) as the initiator. The mixture is left to react for 20 h and after-

wards 2-BrT. Benzene is then removed via distillation under high vacuum, the PS is redissolved in chloroform (100 ml) and polymerization of thiophene using iron trichloride (FeCl₃) takes place under ambient conditions in chloroform for approximately 12 h. The product is filtrated twice; the first filtration is for removing the PT homopolymer and the second is performed after the precipitation of the product in methanol in order to isolate the copolymer mixture. Controlled fractionation through precipitation was adopted in a solvent/non-solvent mixture (toluene/methanol in our case) to completely isolate the diblock from the miktoarm star copolymer (not for all samples). The successful copolymerization was determined by ¹³C NMR and IR spectroscopies.

¹³C NMR (250 MHz, CDCl₃, (al.: aliphatic and ar.: aromatic) δ : (ppm) 145.01 (C1), 125–128 (C9), 40–45 (C2); FT-IR (KBr, ν): (cm⁻¹) 550–570 (C–S, PT), 670–720 (C=C, ar.PT and PS), 700–760 (CH₂, al.PS), 650–900 (–CH, ar.PT, al.PS), 960–1135 (–CH₃, PS ends), 1190–1300 (C–CH, ar.PT and PS), 1350–1470 (–CH, al.PS), 1410–1535 (C–C, ar.PT and PS), 1620–1670 (C=C, ar.PT and PS), 2800–2990 (–CH, al.PS, ar.PT and PS), 3000–3100 (=CH, ar. PT and PS).



Scheme 1. Synthesis reactions for the preparation of PS-PT copolymers: (a) anionic polymerization of 'living' polystyrene, (b) 'two-way' termination reactions of 'living' PS⁻Li⁺ and (c) polymerization of thiophene and simultaneous preparation of diblock PS-b-PT and miktoarm (PS)₂PT copolymers respectively.

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