

# Controlling the end-groups of Poly (3-Hexylthiophene) via Vilsmeier-Haack reaction

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## ABSTRACT

*$\pi$ -Conjugated oligomeric and polymeric semiconductors have been the focus of intense research over the past few decades as alternatives to inorganic semiconductors for low-cost electronic applications such as organic thin-film transistors (OTFTs), light-emitting diodes (OLEDs), and photovoltaics (OPVs). These materials enable vapor- or solution-phase fabrication of large-area, lightweight electronic devices and are compatible with plastic substrates for mechanically flexible,*

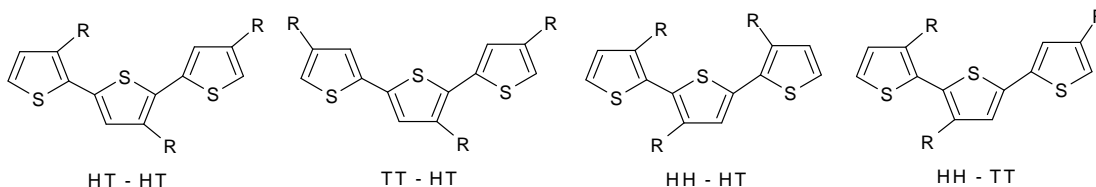
*conformable, and wearable electronics. In this research, we aim at modification of the H/Br end groups of poly (3-hexylthiophene) to CHO/Br end groups via Vilsmeier-Haack reaction using POCl<sub>3</sub> and DMF as the catalytic system in toluene medium. The end groups of the obtained polymer were determined via FT-IR spectroscopy and were further confirmed by Maldi-ToF. The result showed that completion of the Vilsmeier-Haack reaction was obtained after 24 h at 75 °C.*

**Keywords:** Poly (3-hexylthiophene), GRIM, Conjugated Polymers, Maldi-ToF spectroscopy.

## 1. INTRODUCTION

Polythiophenes have become the subject of extensive study. These materials are viewed as

potentially useful components in field-effect transistors, optical and electronic sensors, light-emitting devices, non-linear optical materials, etc [1,4].



However, these polymers exhibit an intrinsic insolubility which makes purification, as well as chemical modification and processability, difficult. To overcome this major inconvenience, the introduction of long alkyl chains in the  $\beta$ -position of the thiophene ring has been envisaged. In fact, the poly(3-alkylthiophenes) P3AT shows a very good solubility in common organic solvents. However, the alkyl substituent in a thiophene ring can be incorporated into a polymer with different regioregularities head-to-tail (HT), tail-to-tail (TT) and head-to-head (HH) [5-7].

Recent research on P3AT has focused on the HT regioregularity. Indeed, these HT regiospecific polymers have improved electroconductivity, optical nonlinearity and magnetic properties over regiorandom polymers in which more sterically hindered HH linkages can cause defects in the conjugated polymer chains and reduce the desired physical properties of the materials.

Therefore, in this study, we aim to modify the end groups of P3HT via Vilsmeier-Haack reaction using  $\text{POCl}_3$  and DMF as the catalytic system. The end-groups of P3HT were characterized via FTIR and Maldi-ToF spectroscopies.

## 2. EXPERIMENT

### 2.1 Materials

3-Hexyl thiophene, N-bromosuccinimide, iodine, iodobenzene diacetate were purchased from Acros and used as received. Ni (dppp) $\text{Cl}_2$ , i-PrMgCl in tetrahydrofuran (THF) (2 mol/l) were

also purchased from Acros and stored in glove box at room temperature. 2-Bromoisobutyryl bromide (Br-iBuBr), triethylamine ( $\text{NEt}_3$ , 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), N,N-dimethylformamide anhydrous (DMF, 99.8%), sodium borohydride ( $\text{NaBH}_4$ , 99%) and phosphorus(V)oxychloride ( $\text{POCl}_3$ , 99%) were purchased from Aldrich. Copper(I) bromide ( $\text{CuBr}$ , 98%) was purchased from Fluka and used without further purification. Chloroform ( $\text{CHCl}_3$ , Labscan, 99%), toluene (Labscan, 99%), tetrahydrofuran (THF, Labscan 99%) were dried using an MBraun solvent purification system under  $\text{N}_2$ . Dichloromethane (Chem-Laboratory, 99.8%), n-heptane (Labscan, 99%), n-hexane (Labscan, 99%) and methanol (Chem-Laboratory, 99.8%) were used as received. All reactions were performed in oven-dried glassware under purified nitrogen.

### 2.2 Characterization

Attenuated total reflection Fourier transform infrared (ATR FT-IR) spectra were recorded using BIO-RAD Excalibur spectrometer equipped with an ATR Harrick Split PeaTM. Size exclusion chromatography (SEC) of P3HT was performed in THF (sample concentration: 1 wt %) at 35 °C using a polymer laboratories (PL) liquid chromatograph equipped with a PL-DG802 degazer, an isocratic HPLC pump LC1120 (flow rate: 1 ml/min), a Basic-Marathon Autosampler, a PL-RI refractive index detector and three columns: a guard column PL gel 10  $\mu\text{m}$  and two columns PL gel mixed-B 10  $\mu\text{m}$ . Molecular

weight and molecular weight distribution were calculated with reference to polystyrene standards. Data were acquired in continuum mode until acceptable averaged data were obtained. MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 mW delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analyses were performed in the reflectron mode at a resolution of about 10,000. All the samples were analyzed using trans-2-[3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]-malononitrile (DCTB), that matrix was prepared as 20 mg/mL solution in CH<sub>2</sub>Cl<sub>2</sub>. The matrix solution (1  $\mu$ L) was applied to a stainless steel target and air dried. Polymer samples were dissolved in CH<sub>2</sub>Cl<sub>2</sub> to obtain 1 mg/mL solutions. 1  $\mu$ L aliquots of those solutions were applied onto the target area already bearing the matrix crystals, and air-dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 750 to 3000 Th, and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass analyzed with 1 s integration time

### 2.3 Preparation of P3HT with controlled end-groups

Into the flask under nitrogen atmosphere containing 2-bromo-3-hexyl-5-iodothiophene (2,36 g, 6,31 mmol) was added dry THF (30.0 mL) via a syringe, and the mixture was stirred at 0°C. *i*-PrMgCl (2.0 M solution in THF, 3,16 mL, 6,31 mmol) was added via a syringe, and the mixture

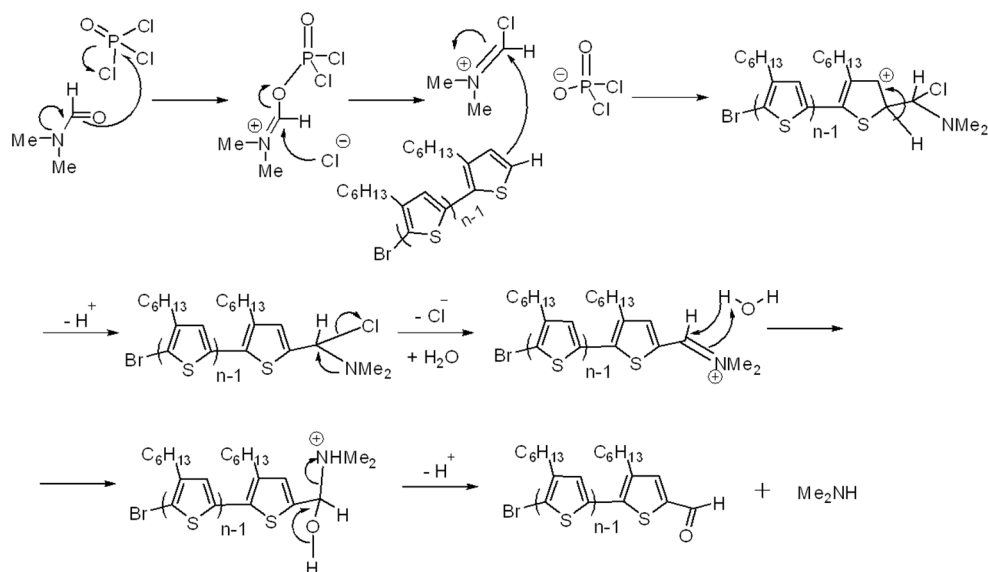
was stirred at 0°C for 0.5h. A suspension of Ni(dppp)Cl<sub>2</sub> (72 mg, 0.13 mmol) in THF (10.0 mL) was added to the mixture via a syringe at 0°C, and then the mixture was stirred at room temperature. After the reaction mixture was stirred for 1 day, the HCl aqueous solution 5N was added drop by drop. The mixture was stirred for another 0.5h and then precipitated in cold MeOH. The product was washed well with MeOH to afford a purple solid, > 98.5% rr-HT-P3HT (1,2 g, 72%,  $M_n$  = 7606, PDI = 1.12).

### 2.4 Optimization of Vilsmeier-Haack reaction

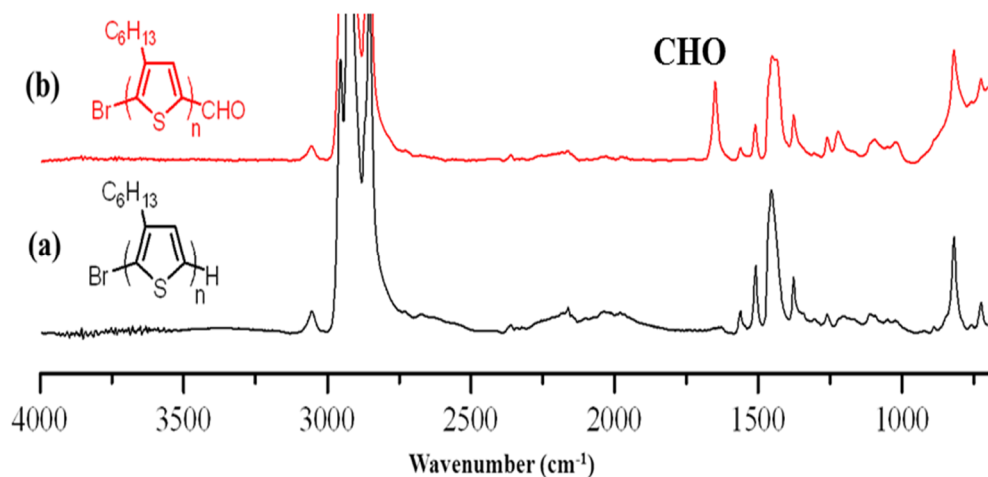
H-P3HT-Br ( $M_n$ =4061, PDI=1.24) (300 mg, 0.074 mmol) was dissolved in anhydrous toluene (80 mL) under N<sub>2</sub>. *N,N*-Dimethylformamide (1 mL, 13 mmol) and POCl<sub>3</sub> (0.7 mL, 7.6 mmol) were added. The reaction was carried out first at 75 °C for 3h. The solution was cooled to room temperature, followed by the addition of saturated aqueous solution of sodium acetate. The solution was stirred for another 2h. The polymer was precipitated in cold methanol and washed well with water, then methanol.

## 3. RESULTS AND DISCUSSION

A formyl-de-hydrogenation of the as-obtained  $\alpha$ -bromo P3HT (Br-P3HT-H) protic end-group was successfully performed by Vilsmeier reaction (second step). The evolution of the reaction was followed by MALDI-ToF analysis until complete transformation of the  $\alpha$ -bromo P3HT (Scheme 1) to  $\alpha$ -bromo,  $\omega$ -formyl P3HT (Scheme 1). The mechanism of the Vilsmeier-Haack reaction can be described as in Scheme 1.



**Scheme 1.** Vilsmeier-Haack mechanism for formyl-de-hydrogenation of P3HT.

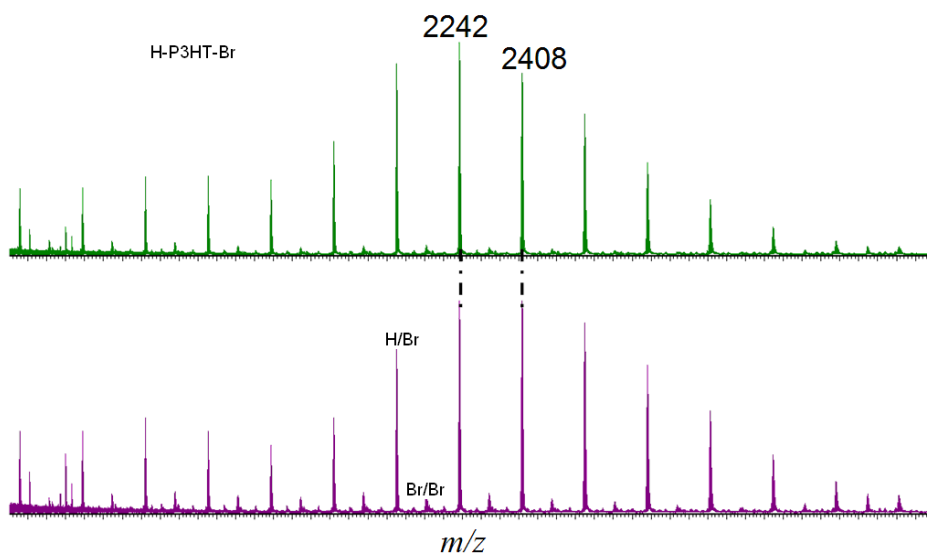


**Figure 1.** FT-IR spectra of (a) Br-P3HT-H, (b) Br-P3HT-CHO

The FT-IR spectroscopy in Figure 1 shows the characteristic peak at  $1650\text{ cm}^{-1}$  attributed to the CHO groups of P3HT.

The MALDI-ToF result of  $\alpha$ -bromo,  $\omega$ -formyl is presented in Figure 2. The results showed that the end-groups may be controlled with the HCl

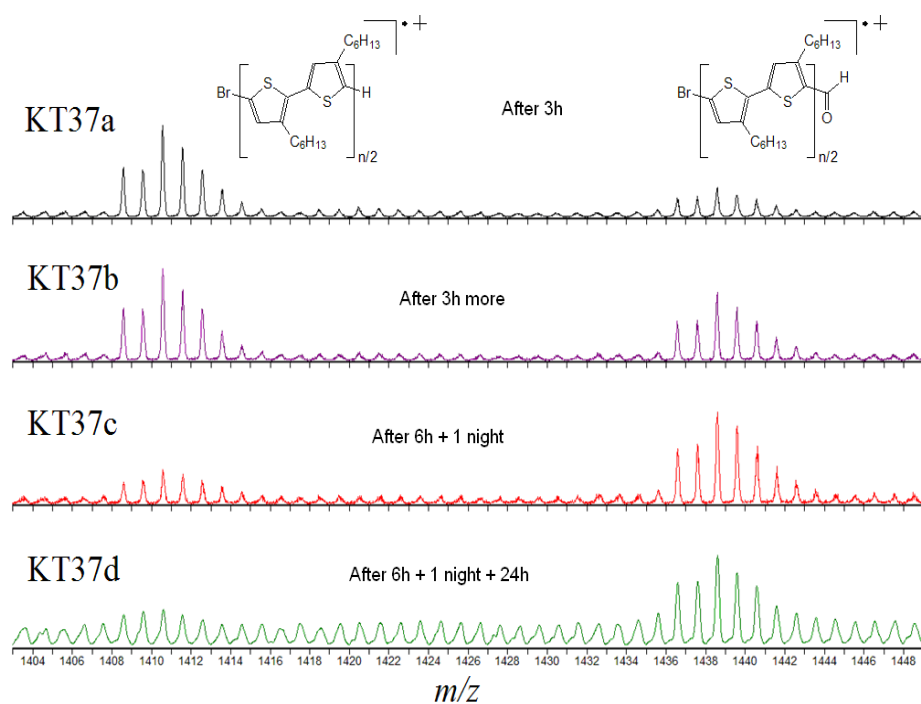
addition rate. To confirm this observation, two P3HT samples, with the same  $M_n$  ( $D_p=30$ ), were synthesized with different quenching rates. With a fast quenching, only H/Br end-groups were obtained (Figure 2, above), whereas with a slow quenching, a mixture of H/Br and Br/Br end-groups was obtained (Figure 2, below).



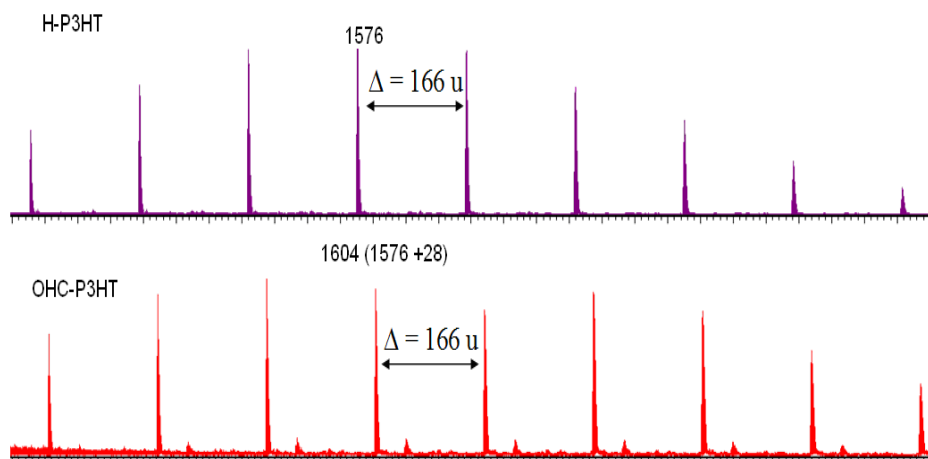
**Figure 2.** P3HT with HCl fast addition (above), HCl slow addition (below)

MALDI-ToF analysis showed that the H-P3HT-Br was partially transformed into CHO-P3HT-Br. This product was re-used to carry out

the Vilsmeier reaction until finding the optimal reaction time (that ensures the completion of the end group modification).



**Figure 3.** Evolution of Vilsmeier reaction.



**Figure 4.** Before (above) and after (below) Vilsmeier-Haack reaction.

As seen in Figure 3, the  $\omega$ -H end group was totally transformed into  $\omega$ -CHO end group after almost 48h. Therefore, the Vilsmeier reaction was carried out in 24h and the DMF/ $\text{POCl}_3$  quantity was doubled. In fact, with this condition, another H-P3HT-Br ( $M_n=3481$ ,  $\text{PDI}=1.24$ ) was totally transformed into CHO-P3HT-Br ( $M_n=3504$ ,  $\text{PDI}=1.23$ ) with 94% yield (Figure 4).

#### 4. Conclusion

The end-groups of P3HT were successfully transferred from H/Br to CHO/Br via Vilsmeier-Haack reaction. The end groups of P3HT were

determined via FT-IR and MALDI-ToF spectroscopies. The comparison of the MALDI-ToF traces manifested the end-group change of the starting Br-P3HT-H to Br-P3HT-CHO after completion of the Vilsmeier-Haack reaction (24 h, 75 °C).

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# Điều khiển nhóm cuối mạch của Poly (3-Hexylthiophene) bằng phản ứng Vilsmeier-haack

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## TÓM TẮT

Các oligomer và polymer cấu trúc mạch liên hợp đã được nhắm đến cho những nghiên cứu mạnh mẽ qua những thập kỷ vừa qua như là sự lựa chọn thay thế cho các bán dẫn vô cơ vì mang lại lợi ích về giá thành rẻ trong những ứng dụng linh kiện điện tử như là bán dẫn hữu cơ, phát quang OLED và pin năng lượng mặt trời hữu cơ. Những loại vật liệu này có thể gia công bằng phương pháp bay hơi hoặc phương pháp tráng phủ dung môi. Những phương pháp này sẽ cho phép quy trình gia công trên một diện tích lớn. Bên cạnh đó, các sản phẩm điện tử nền hữu cơ sẽ có trọng lượng nhẹ, mềm dẻo thuận tiện cho việc di chuyển của người sử dụng. Trong nghiên cứu

này, chúng tôi nhắm đến việc biến tính nhóm chức cuối mạch H/Br của polymer poly(3-hexylthiophene) thành nhóm CHO/Br bằng phản ứng Vilsmeier-haack sử dụng hệ xúc tác POCl<sub>3</sub> và DMF trong dung môi toluene. Nhóm chức cuối mạch của polymer thu được được phân tích qua phổ hồng ngoại FT-IR và được xác định lại bằng phương pháp phổ khối Maldi-ToF. Kết quả biến tính nhóm chức cuối mạch bằng phản ứng Vilsmeier-haack cho thấy rằng để đạt được hiệu quả chuyển hóa hoàn toàn, phản ứng Vilsmeier-haack cần phải thực hiện trong 24 giờ tại nhiệt độ 75 °C.

**Keywords:** Poly(3-hexylthiophene), GRIM, Conjugated Polymers, Maldi-Tof spectroscopy.

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