Regioregular Polythiophene Nanowires and Sensors

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ABSTRACT

We have developed and synthesized highly conductive regioregular poly(3-alkylthiophene) (rr-PAT) derivatives for use in sensor arrays on a chip. Poly(3-alkylthiophene)s are ideally suited for this application because of their excellent electrical properties, solution processability and our ability to modify their chemical structure. Here, we synthesized rr-PATs that have different side chains and different end groups. The polymers were ink-jetted onto ChemFET devices on a chip and their chemical sensing properties were tested to a variety of volatile organic compounds (VOCs). The sensors demonstrated ppm level sensitivity and selectivity to all VOCs tested, including both polar and non-polar compounds.

Keywords: polythiophene, conducting polymer, electronic nose, chip, sensor

1. INTRODUCTION

One of the most promising and versatile approaches to chemical sensing developed in recent years involves the use of arrays of sensors based on intrinsically conducting polymers and conducting polymer composites.[1] Their major advantages include low cost, possibility of tailoring for different analytes, and ease of processing into thin films. More recently, sensors based on thin film field effect transistors (FETs) made of semiconducting polymers, in particular regioregular polythiophenes, were demonstrated.[2, 3] The high conductivities of regioregular polythiophene are a consequence of their ability to self-assemble into π-stacked, planar aggregates. Small changes in conformational order and solid state organization should transduce into large changes in conductivities, thus providing for excellent sensitivity. In addition, rr-PATs have the capability to have tremendous diversity of response by changing the structure of the polymer. The structure of polythiophene can be altered by changing the side chain substituents or the end groups. Previous work in our lab has shown that both conformational order and solid state organization in regioregular polythiophene (rr-PT) derivatives are remarkably sensitive to the placement and nature of the side chain substituents,.[4, 5] as well as to the presence of certain analytes.[6] At this time, much less is known about the effect of end-groups on the polymer's electrical properties. However, some work done with oligomers with different end groups showed that the degree of odor response increased as the length of the hydrocarbon end group increased.[2]

Recently, we have gained tremendous understanding into the polymerization mechanism of rr-P3AT.[7] The polymerization mechanism was shown to proceed via a chain growth mechanism rather than the generally accepted step growth mechanism.[7] The polymerization exhibited an increase in molecular weight in direct proportion to the molar ratio of the monomer to the initiator concentration. As a result, rr-PAT with predetermined molecular weights and relatively low polydispersities can be synthesized. A better understanding of the polymerization mechanism also allowed us to develop a new facile one-pot method to end-functionalize rr-PATs.[8] This is done by simply adding a 'capping' Grignard reagent at the end of the polymerization. By combining this new method with post-polymerization modifications, we can incorporate a wide variety of functional groups at the end of the polymer. In addition, we also have the ability to make rr-PTs with a wide variety of side chain substituents,[9] including different alkyl groups,[4 10] etheric groups,[11] acid groups,[6] alcohol groups,[12] bromine groups, amine groups and thiol groups.[13] All these changes add specificity to the sensing ability of the polymer and affect the electronic change experienced by the devices.

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In this work, we have synthesized a variety of rr-PT derivatives with different side chains and different end groups. These polymers were tested in ChemFET chip.

2. EXPERIMENTAL

2.1 Polymers

Polymer **1**, **2** and **3** were synthesized using the Grignard metathesis method.[14]. Polymer **4** was obtained from Plextronics (Pittsburgh, PA, USA) and used as received. Polymer **5** was obtained by post-polymerization reactions on a vinyl-terminated P3HT.[15] Polymer **6** was synthesized using the in-situ end capping method.[8] Gel Permeation Chromatography (GPC) 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, 30°C, λ=450nm) with a series of three Styragel columns (10^4, 500, 100 Å; Polymer Standard Services) and was calibrated with polystyrene standards.

2.2 Tapping Mode Atomic Force Microscopy

TMAFM studies were carried out with the aid of a Nanoscope III-M system (Digital Instruments, Santa Barbara, CA), equipped with a J-type vertical engage scanner. The AFM observations were performed at room temperature in air using silicon cantilevers with nominal spring constant of 50 N/m and nominal resonance frequency of 300 kHz (standard silicon TESP probes). Typical value AFM detector signal corresponding to r.m.s. cantilever oscillation amplitude was equal to ~ 1000 mV and the images were acquired at 2 Hz scan frequency in 2 × 2 μm^2 scan areas.

2.3 Device

To investigate the chemical sensing properties of these nanostructured polymers, ChemFET devices were fabricated by standard photolithography processes on thermally oxidized N^+ silicon substrates. A 200 nm silicon dioxide was employed as gate insulator. The conducting substrate was used as common gate electrode. 50 nm gold was sputtered and patterned as source and drain electrode with a channel length of 3 μm. The ChemFETs were 200 μm in diameter and had a spiral geometry. The polymers were dissolved in trichlorobenzene (5mg/mL) and deposited accurately on the chemiresistor electrodes using an automated Ink-jet system. Polymer spots of 100-200 μm in diameter were obtained by using 5 to 10 drops (drop size: 43 μm). A photography of a typical sensor covered with polythiophene is shown in Figure 1(a). Figure 1(b) shows the cross-section of the device. The ChemFETs were tested for their chemical sensing properties to various VOC vapors. The VOC vapors were blended with 1 liter/min nitrogen carrier gas at different ppm concentrations Typically, a DC voltage of 0.5 Volts was applied between the source and drain electrodes, and a DC voltage of -0.5 Volts was applied between the gate and source , so that the ChemFET was turned on during operation. The source-drain current was monitored as a reponse signal during analyte exposure. The VOC vapors were turned on and off every 10 minutes.

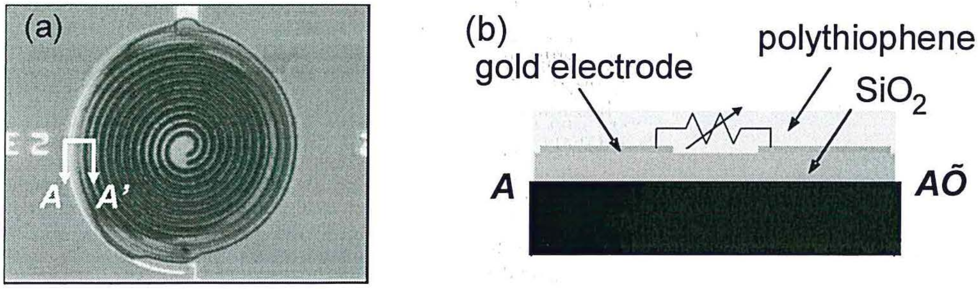
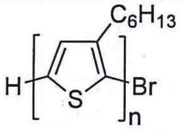
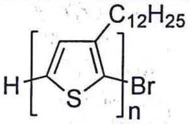
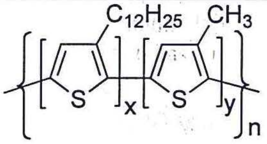
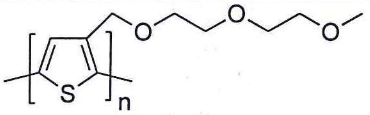
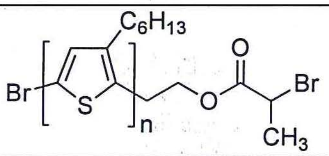
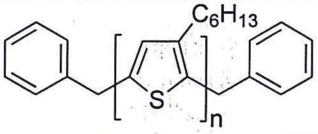


Figure 1. Photography of chemiresistor covered with polythiophene; (b) cross-section of device.

3. RESULTS AND DISCUSSION

Table 1 lists the polymers that were tested. All polymers are regioregular and are well-defined with low polydispersities (PDIs). In this work, we use P3HT (Polymer **1**) as the point of reference. Polymer **2**, **3**, and **4** differ from polymer **1** by their side chains. Polymer **2** has a longer side chain (dodecyl) and polymer **3** is a random copolymer with methyl and dodecyl side chains. Polymer **4** has a polar etheric side chain. Polymer **5** and **6** differ from polymer **1** by their end groups. Polymer **5** has a more polar end group and polymer **6** has a non-polar, benzene-like end group.

Table 1: Regioregular poly(3-alkylthiophene) derivatives tested

	Polymer	Chemical Structure	M_n (GPC)	PDI (GPC)
1	Poly(3-hexylthiophene)		11 570	1.17
2	Poly(3-dodecylthiophene)		34 040	1.39
3	Poly(3-dodecylthiophene-*ran*-3-methylthiophene)	 x:y = 1:1	10 550	1.13
4	Poly(3-methoxyethoxy-ethoxymethylthiophene)		-	-
5	Bromoester terminated rr P3HT		11 200	1.21
6	Benzyl terminated rr P3HT		13 670	1.21

Regioregular P3HTs are found to self-assemble into highly crystalline nanowire structures, where the width of the nanowire corresponds to the length of rr-P3HT (see Figure 2). This morphology is obtained by drop-casting a solution of rr-P3HT from a slow evaporating solvent, such as toluene. As compared to an amorphous morphology, these nanowire structures may enable our chemical sensors to have a higher sensitivity and faster response times.

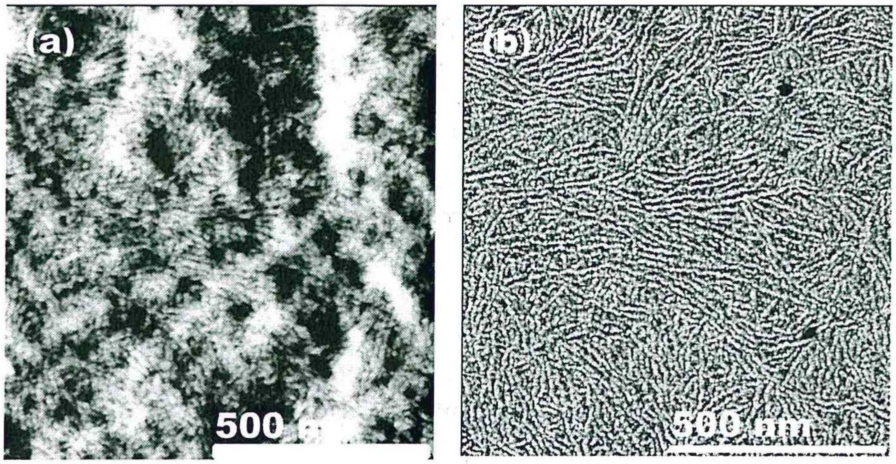


Figure 2. Atomic Force Microscopy image of drop-casted poly(3-hexylthiophene) on SiO_2/Si substrate, (a) height image, (b) phase image.

The sensor responses of the six polymers to methylene chloride and benzene are shown in Figure 3(a) and (b), respectively. The relevant responses, reported in Figure 3, have been evaluated as described in the following:

$$\Delta = \frac{I_{DS}(response) - I_{DS}(baseline)}{I_{DS}(baseline)}$$

The typical response time t_{90} was around 20 seconds. We note that the sensor responses changed reversibly upon analyte exposure, and that the amplitude of these changes increased with analyte concentrations. The sensors were sensitive to the analytes in the ppm range.

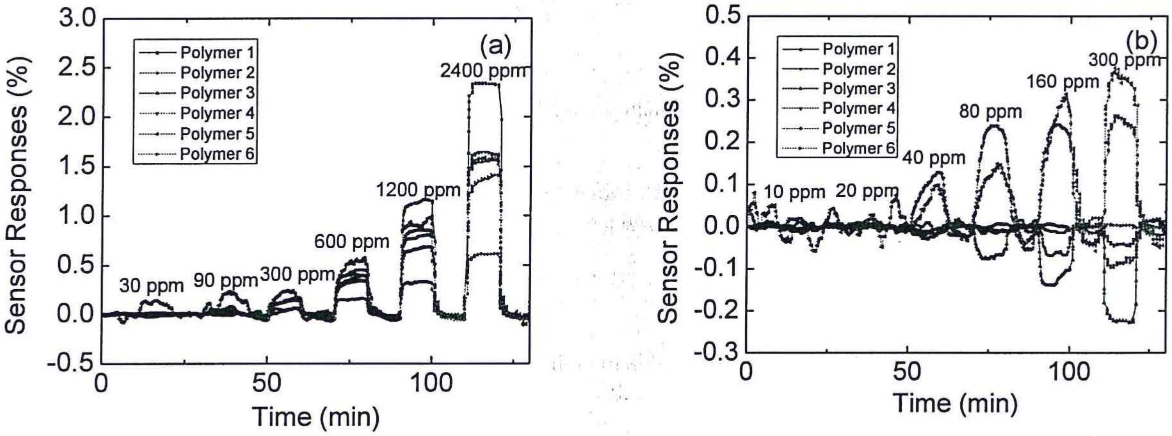


Figure 3. Normalized sensor responses as a function of time to (a) methylene chloride, (b) benzene. Analytes were introduced at 10 min. intervals.

The normalized sensor responses of polymer **1** (P3HT) to 11 VOC vapors is shown in Figure 4. The sensor responses to different analytes varied both in amplitude and sign. The response was positive for the polar compounds (methanol, ethanol, IPA, acetone, MIBK, acetonitrile and methylene chloride), indicating that the polymer conductivity increases upon interaction with these analytes. On the other hand, the response was negative for the non-polar compounds (n-hexane, cyclohexane, toluene and benzene), indicating that the conductivity of the polymer decreased upon interaction with these analytes. We believe that the interaction of the analytes with rr-PATs alters the polymer film morphology and/or the polymer backbone conformation. Alcohols, for example, are expected to interact with rr-P3HT in a way that is similar to oil with water. This immiscibility between the analyte and the polymer forces the polymer chains closer together and conductivity increases. Other analytes, such as methylene chloride, may be "annealing" the polymer to a more ordered structure, resulting in a conductivity increase. Finally, the analyte may interact with rr-PATs polymer and break up the structure or cause twisting in the polymer backbone. This would result in a conductivity decrease, and is observed with hexane, cyclohexane, toluene and benzene.

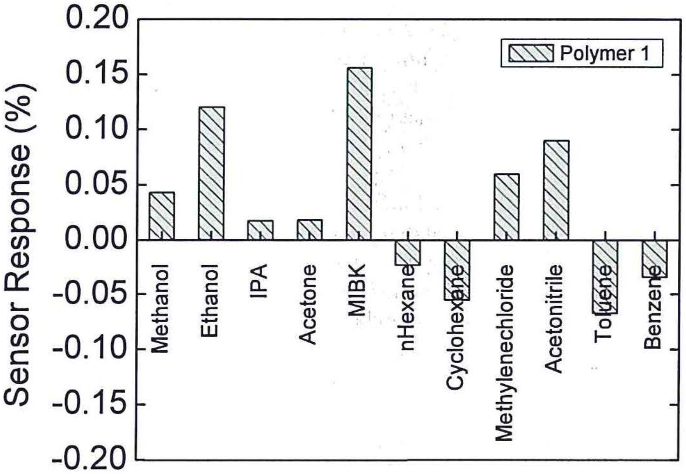


Figure 4. Normalized Sensor responses for Polymer **1** to 11 VOC vapors at 200 ppm concentration.

Changing the side chains and end groups of polythiophene resulted in completely different responses. For example, polymer **3** showed negative responses for all the analytes except for methylene chloride. Polymer **4**, on the other hand, showed positive responses for all the analytes, especially MIBK. Changing the end groups of the polymer also had dramatic effects on the sensory responses. Polymer **5** showed a large positive response to toluene and benzene. Also, it showed no response to ethanol, IPA, acetone, and cyclohexane. Polymer **6**, on the other hand, differed from Polymer **1** for acetone (opposite sign), acetonitrile (oppoisite sign) and benzene (no response). Changing the side chains and end groups therefore add other dimensionalities to the sensing properties of the rr-PATs.

Figure 5(a) summarizes the sensor responses of the six polymers to the eleven different VOC vapors. It is clear that each VOC vapor tested resulted in a unique sensor response pattern (or fingerprint). We used principal component analysis to reduce the complexity of the data set while maximizing variances. The results are shown in Figure 5(b). It is clear from this graph that our sensor array can easily distinguish between all of the 11 analytes.

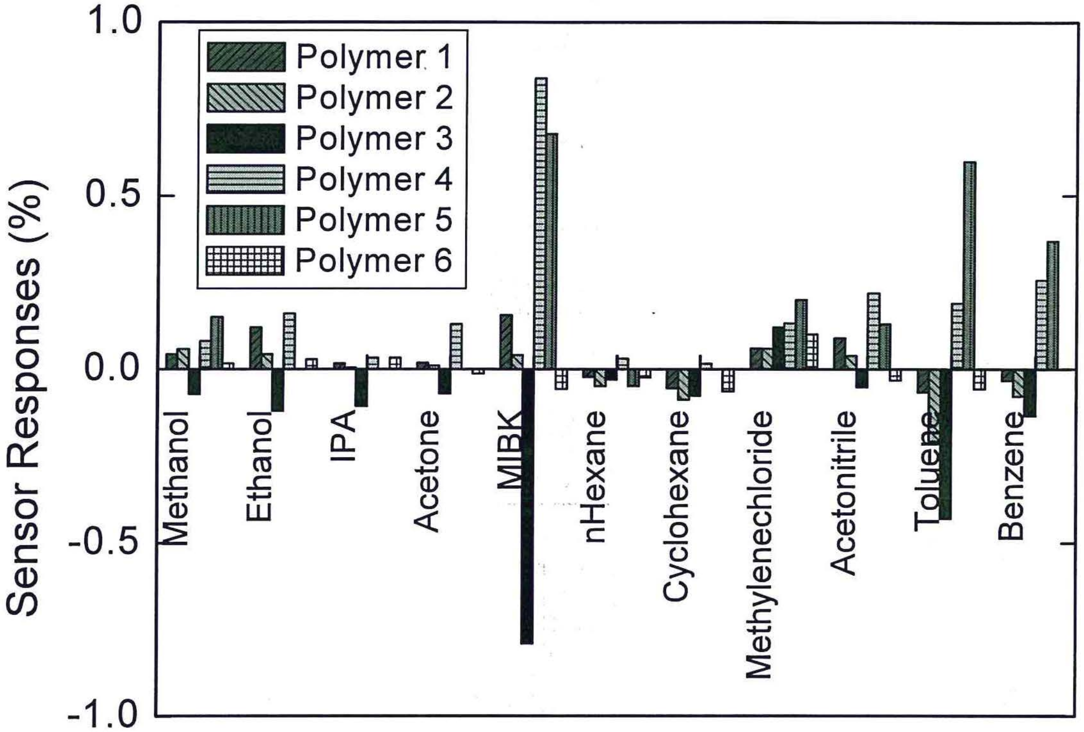


Figure 5. Normalized Sensor responses to 11 VOC vapors at 200 ppm concentration

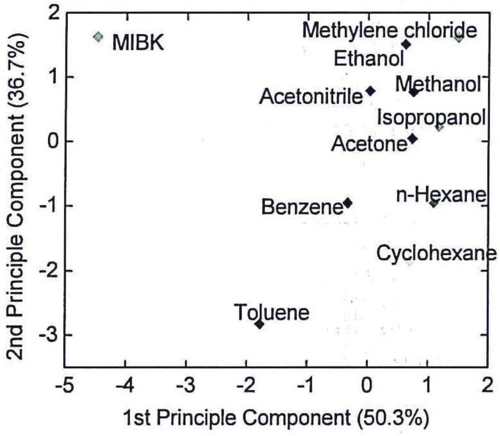


Figure 6. Principle component analysis result from data plotted in Figure 5.

4. CONCLUSIONS

We have shown that Regioregular poly(3-alkylthiophene) derivatives are ideally suited for use in chemical sensor arrays on chips. They showed adequate sensitivity. Furthermore, by using rr-P3AT with different side chains and end groups, we gain the selectivity required for the next generation of electronic nose.

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REFERENCES

1. K. Cammann, B. Ross, A. Katerkamp, J. Reinbold, R. Renneberg, Chemical and biochemical sensors. In *Handb. Anal. Tech.*, 2001; Vol. 2, pp 951-1059.
2. B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H. E. Katz, A. J. Lovinger, *Appl. Phys. Let.* **2001,** 78, (15), 2229-2231.
3. L. Torsi, A. Tafuri, N. Cioffi, M. C. Gallazi, A. Sassella, L. Sabbatini, P. G. Zambonin, *Sensors and Actuators B* **2003,** 93, 257-262.
4. R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *J. Org. Chem.* **1993,** 58, (4), 904-912.
5. R. D. McCullough, S. P. Williams, *J. Am. Chem. Soc.* **1993,** 115, (24), 11608-11609.
6. P. C. Ewbank, R. S. Loewe, L. Zhai, J. Reddinger, G. Sauve, R. D. McCullough, *Tetrahedron* **2004,** 60, 11269-11275.
7. E. Sheina, J. Liu, M. C. Iovu, D. W. Laird, R. D. McCullough, *Macromolecules* **2004,** 37, 3526-3528.
8. M. Jeffries-EL, G. Sauve, R. D. McCullough, *Adv. Mater.* **2004,** 16, (12), 1017-1019.
9. R. D. McCullough, *Adv. Mater.* **1998,** 10, (2), 93-116.
10. R. D. McCullough, M. Jayaraman, *J. Chem. Soc., Chem. Commun.* **1995,** (2), 135-136.
11. R. D. McCullough, S. P. Williams, *J. Am. Chem. Soc.* **1993,** 115, (24), 11608-11609.
12. K. A. Murray, A. B. Holmes, S. C. Moratti, G. Rumbles, *J. Mater. Chem.* **1999,** 9, (9), 2109-2115.
13. L. Zhai, R. L. Pilston, K. L. Zaiger, K. K. Stokes, R. D. McCullough, *Macromolecules* **2003,** 36, (1), 61-64.
14. R. S. Loewe, S. M. Khersonsky, R. D. McCullough, *Adv. Mater.* **1999,** 11, (3), 250-.
15. M. C. Iovu, M. Jeffries-EL, E. Sheina, J. R. Cooper, R. D. McCullough, *Polymer* **2005**, in press.