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Material Issues for Construction of Organic and Polymeric Driving Circuits for Display and Electronic Applications

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SUMMARY: Organic and polymeric driving circuits may be a possible alternative to realize low cost flexible and large area flat panel displays. Recent efforts have been directed to the discovery of solution processable polymeric semiconductors for the ease of fabrication and low cost. In this paper, we report the investigation of various 3-substituted regioregular polythiophenes as active semiconductors for field-effect transistors. The best transistor performance has been found with regioregular poly(3-heaxylthiophene). The difference in their device performance was correlated to the structure and morphological behavior of these regioregular polythiophenes.

Introduction

There has been tremendous effort in recent years to develop low cost flexible and large area flat panel displays. It remains challenging to manufacture the commonly used silicon-based thin film transistor driving circuits on flexible plastic substrates at low cost. Organic and polymeric materials are attractive as active materials for such transistor driving circuits because of their natural compatibility with plastic substrates and solution processability.[1-3] In addition, high transistor performance (field-effect mobility and on/off ratio), comparable to amorphous Si, has been demonstrated with organic semiconductors.[4] Simple organic-based circuits have been reported.[5-6] Challenges remain in realizing high performance solution processable semiconductors since they are most desired to avoid high temperature and high vacuum processes. They also allow the possibility to utilize casting, spraying, and printing technologies for fabrication and patterning. In this paper, we have investigated various 3-substituted regioregular polythiophenes as the semiconducting materials for thin film transistors. High field-effect mobility has been achieved with regioregular poly(3-hexylthiophene). Structure, morphology, and device performance relationship is discussed.

Experimental

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The synthesis of monomers and polymers were reported elsewhere.[7-10] The molecular weights of polymers prepared for this study are listed below as determined by Gel permeation chromatography (GPC) using chloroform (at 45 °C) and N-methylpyrrolidinone (NMP) (at 85 °C) as solvents and calibrated with polystyrene standards.

Polymer 1, n=6, prepared from Rieke method, GPC (chloroform, 45 °C), M_n = 12,100, M_w = 40, 000 , polydispersity = 3.29.

Polymer 1, n=6, prepared from Stille method, GPC (chloroform, 45 °C), M_n = 8,100 , M_w = 17,200, polydispersity = 2.12.

Polymer 1, n=6, prepared from McCullough method 1, GPC (chloroform, 45 °C), M_n = 10,220, M_w = 25,250 , polydispersity = 2.47.

Polymer 1, n=6, prepared from McCullough method 2, GPC (chloroform, 45 °C), M_n = 40, 000 , M_w = 70,800 , polydispersity = 1.77.

Polymer 1, n=8, prepared from Rieke method, GPC (chloroform, 45 °C), M_n = 20,100 , M_w = 41,000 , polydispersity = 2.04.

Polymer 1, n=12, prepared from Rieke method, GPC (chloroform, 45 °C), M_n = 23,000 M_w = 51,000 , polydispersity = 2.22.

Polymer 2, GPC (chloroform, 45 °C), M_n, 7,200, M_w, 15,800, polydispersity, 2.20.

Polymer 3, GPC (NMP, 85 °C), M_n, 6,200, M_w, 8,000, polydispersity, 1.31.

Results and discussions

Four types of regioregular polythiophenes as shown in Figure 1 and 2 were investigated. Polymer 1 is substituted with simple linear alkyl chains with various chain lengths from hexyl to dodecyl. Polymer 2 is substituted with optically active and slightly branched sidechains. Polymer 3 is the precursor polymer for polymer 4, and its bulky protecting group can be used to investigate the effect of sidechain bulkiness on device performance. Polymer 4 is substituted with carboxylic acid sidechains, which can form H-bonds and may help promote self-assembly of the polymer on polar substrates. In all four polymers, the sidechains are connected to the polymer backbone through methylene ($-CH_2-$) linkages so that the electronic properties of the polymer backbones are not chemically changed; thus, morphological effects should be the major factor affecting electronic properties.

The above polymers were synthesized according to literature procedures.[7-11] The synthetic schemes are outlined in Figure 1 and 2. Polymer 1 was synthesized using three methods, i.e.

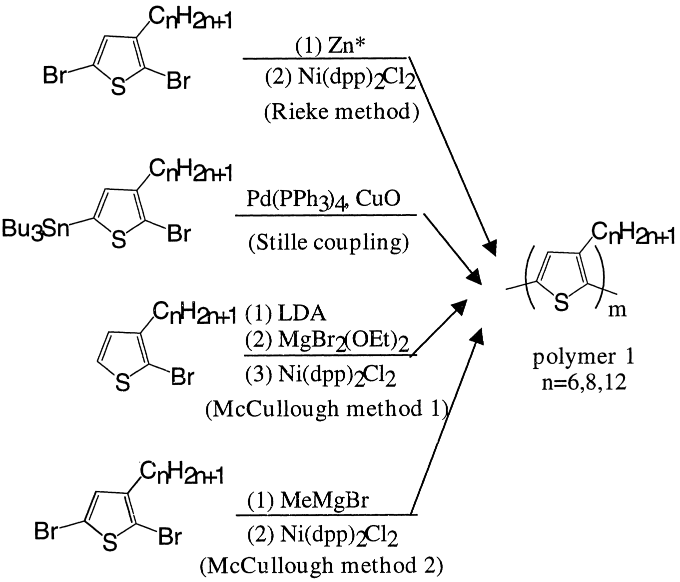
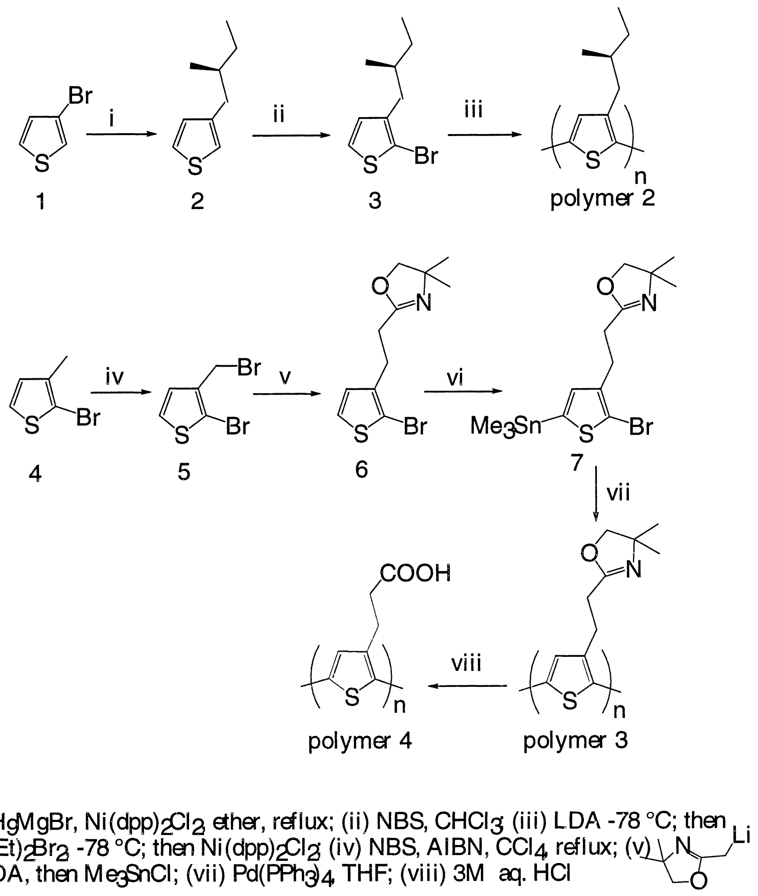


Figure 1. Synthesis of regioregular poly(3-alkylthiophene)s using various polymerization methods.

the Rieke method using activated Zn*,[10] the McCullough method using Grignards,[7-8] and the Stille coupling from tributyltin and bromo monomers.[11] Polymer 2 was synthesized using the McCullough method and polymer 3 was prepared using the Stille coupling reaction. The elemental analysis results for polymers synthesized using the Stille reaction had a relatively large deviation from the calculated values possibly due to its relatively low molecular weight and the high molecular weight of trimethylstannyl end groups. However, the molecular weight obtained here is similar to that reported in the literature using the same polymerization method. Polymer 4 was obtained by refluxing polymer 3 in 3M aqueous solution of HCl and is soluble in polar solvents such as N,N-dimethylforamide (DMF), NMP, and aqueous base solutions. The de-protection reaction of polymer 3 appears to be almost quantitative since no trace of nitrogen has been found in the elemental analysis.



(i) C_4H_9MgBr, $Ni(dpp)_2Cl_2$ ether, reflux; (ii) NBS, $CHCl_3$ (iii) LDA -78 °C; then $Mg(OEt)_2Br_2$ -78 °C; then $Ni(dpp)_2Cl_2$ (iv) NBS, AIBN, CCl_4 reflux; (v) (vi) LDA, then Me_3SnCl; (vii) $Pd(PPh_3)_4$ THF; (viii) 3M aq. HCl

Figure 2. Synthesis of regioregular polythiophene derivatives.

Polymers 1-3 are soluble in common organic solvents such as chloroform, tetrahydrofuran (THF) and DMF. The regioregularity of the polymers has been examined by ^{1}H NMR and ^{13}C NMR. For all polymers, only one kind of aromatic proton and four kinds of thiophene carbons were detected indicating that the regioregularity is greater than 95%.

The UV-vis spectra of thin films prepared from all polymers are shown in Figure 3. Polymer 1 and 2 showed the three-peak structure at 514, 540, and 600 nm, which is typical for highly regioregular poly(3-alkylthiophene)s. In polymer 3, there is an indication of a vibronic structure even though the position of maximal absorption is shifted to a lower wavelength. Polymer 4 does not show any vibronic structure, but has a similar peak absorption position as polymer 3, and they are both blue-shifted compared to those of polymer 1 and 2. Many factors could contribute to this blue shift, such as lower degrees of polymerization, steric hindrance in polymer 3, and random H-bonding formation causing chain twisting in polymer 4. Despite their blue-shifts, polymers 2 and 3 are significantly red-shifted compared to regiorandom PHT with about 70% head-to-tail ratio (λ_{max} = 460 nm). Films of polymers 2 and 3 still appear blue-purple (similarly color to regioregular PHT films), while films of regiorenadom PHT appear yellow-orange.

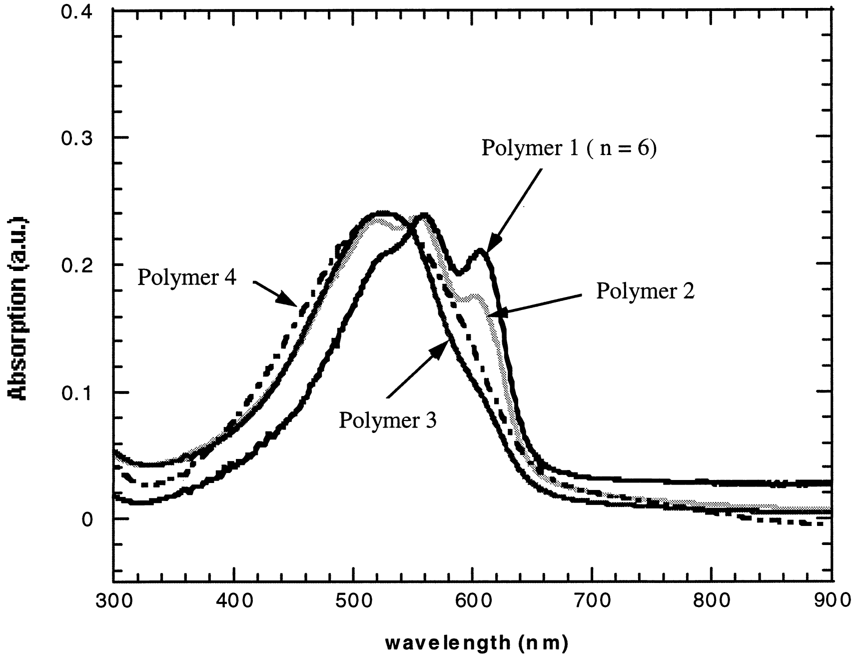


Figure 3. UV-vis spectra of regioregular poly(3-hexylthiophene) and its derivatives.

Thin-film FETs have been fabricated with the four types of regioregular polythiophenes. The transistor device structure is shown in Figure 4. The *n*-doped Si substrate with gold contact functions as the gate, while an oxide layer of 3000 Å is the gate dielectric having a capacitance per unit area of 10 nF/cm^2. The drain and source electrodes define channel widths W = 250 μm and channel lengths L = 1.5, 4, 12, and 25 μm. Table 1 summarizes the field-effect mobility and on/off ratio for FETs prepared under various conditions based on polymers

1-4. All polymers functioned as *p*-channel FET devices operating in the accumulation mode in which the drain-source currents (I_{DS}) of negative signs scale up with negative gate voltages (V_G).

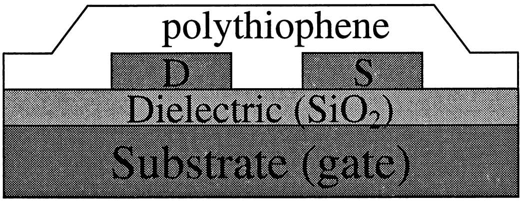


Figure 4. Schematic structure of a thin film filed-effect transistor.

Table 1. Transistor performance of regioregular polythiophene derivatives.

Polymer	Solvent	Mobility (cm^2/Vs)
Polymer 1 n = 6	$CHCl_3$, room temperature (prepared from Rieke method)	0.05
Polymer 1 n = 6	$CHCl_3$, room temperature (prepared from McCollough method 1)	0.03
Polymer 1 n = 6	$CHCl_3$, room temperature (prepared from McCollough method 2)	0.03
Polymer 1 n = 6	$CHCl_3$, room temperature (prepared from Stille method)	0.003
Polymer 1 n = 8	$CHCl_3$, room temperature (prepared from Rieke method)	0.04
Polymer 1 n = 12	$CHCl_3$, room temperature (prepared from Rieke method)	2.1×10^{-6}
Polymer 2	$CHCl_3$, room temperature	1.0×10^{-3}
	chlorobenzene, vacuum (25 Torr), 80 °C	3.7×10^{-4}
	$CHCl_3$, substrate HMDS treated	6.3×10^{-4}
Polymer 3	$CHCl_3$, room temperature	2.8×10^{-5}
	NMP, vacuum (25 Torr), 80 °C	(-)*
Polymer 4	DMF, vacuum (25 Torr), 80 °C	2.9×10^{-4}
	NMP, vacuum (25 Torr), 80 °C	(-)*
	DMSO, vacuum (25 Torr), 80 °C	(-)*
	DMSO, solution covered with a petri dish, 50 °C	8.0×10^{-5}

* (-), no field-effect transistor activity.

For linear alkyl substituted regioregular poly(3-alkylthiophene)s, polymers with hexyl and octyl sidechains showed the highest field-effect mobilities, in the range of 0.01 cm^2/Vs to 0.1 cm^2/Vs. When dodecyl sidechains were used, the mobility is much lower. This could be that the film matrix is dominated by the insulating alkyl substituents and result in low mobilities when the alkyl chain is too long. It is noted that poly(3-hexylthiophene)s (PHTs) synthesized from Rieke and McCullough methods showed higher field-effect mobilities than the one synthesized using the Stille coupling polymerization. X-ray diffraction measurements showed that all of the films, cast from polymers synthesized with different methods, have similar diffraction patterns. The difference in their mobilities may be due to the poorer film forming property of the low molecular weight PHT made from the Stille coupling reaction. Those films appeared grainy compared to the higher molecular weight PHTs. The field-effect mobilities for the regioregular polythiophene derivatives polymer 2-4 are smaller than for the regioregular PHT synthesized using similar polymerization and purification methods. However, the mobility for polymer 2, which has chiral sidechains, is still relatively high for solution processable polymeric semiconductors.

X-ray diffraction and electron-diffraction measurements have been performed with powders (X-ray only) of polymers 1-4 and their thin films prepared under the same conditions as their transistors. The X-ray diffraction patterns for as-precipitated powders are similar to those for thin films, indicating that the features obtained in these thin films are not the result of preferred orientation. Since solvent and film preparation conditions can significantly affect morphology and device performance, we have used several different solvents to prepare films and transistors under various temperature and annealing conditions as shown in Table 1. Indeed, the transistor performance of these films varied significantly depending on solvent and film forming conditions. The X–ray diffraction patterns were also dependent on the above factors. Polymer 1 and 2 showed relatively high crystallinity indicated by their sharp diffraction peaks. Both of them showed spacings corresponding to the distance between two polythiophene backbones separated by interdigitated sidechains. On the other hand, polymer 3 is characterized by a very broad and diffuse diffraction shoulder (indicating very limited ordering and crystallinity) at a spacing of about 20 Å. The bulky sidechains in polymer 3 may make it more difficult for good chain packing. Under most conditions, films cast from polymer 4 did not show any diffraction peak by either X-ray or electron diffraction measurements, indicating that those films are essentially amorphous. Low crystallinity was found with polymer 4 film cast from DMSO solution under very slow evaporation rate in an almost closed environment by covering the solution and substrate with a petri dish at elevated temperature (50 °C). Its X-ray diffraction pattern shows a weak peak at 11.5 Å, which corresponds well to the separation of the backbone macromolecules by the side chains. However, film cast under the same condition from DMF only showed a very broad shoulder in X-ray diffraction pattern, indicating much lower crystallinity.

Both polymer 1 and 2 showed sharp diffraction rings corresponding to the π–π stacking distances. Interestingly, this spacing for polymer 1 is about 4.3 Å, which is much larger than that of PHT (3.8 Å). This larger spacing may be caused by the methyl branches on the sidechains separating the polymer backbones further apart. The substantially reduced π-overlap in polymer 2 may be an important factor for the significant lowering of its field-effect mobility in comparision to PHT, despite its substantial crystallinity. The electron diffraction patterns of polymers 3 and 4 show only diffuse scattering indicating essentially no crystallinity, which is probably at the root of their very low mobilities.

Conclusion

Various regioregular poly(3-alkylthiophene)s and their derivatives have been synthesized and their semiconducting properties in field-effect transistors have been investigated. Regioregular polythiophenes with non-bulky linear sidechains showed the best field-effect mobilities. The introduction of slightly branched sidechains lowered the field-effect mobility by ten times, most likely because of the increased π–π stacking distance. In addition, regioregular polythiophenes with bulky sidechains or H-bonding carboxylic acid sidechains are difficult to form highly crystalline films and therefore yield very low field-effect mobilities. The above results indicate that the nature of the sidechains has a critical impact on the self-assembly, crystallization, and semiconducting properties of regioregular poly(3-alkylthiophene) derivatives.

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