The Tuning of Conjugation by Recipe: the Synthesis and Properties of Random Head-to-tail Poly(3-alkylthiophene) Copolymers

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Regioregular head-to-tail coupled poly(3-alkylthiophene) random copolymers have been synthesized and show that the conjugation can be tuned by variation of the length and relative ratios of alkyl side chains.

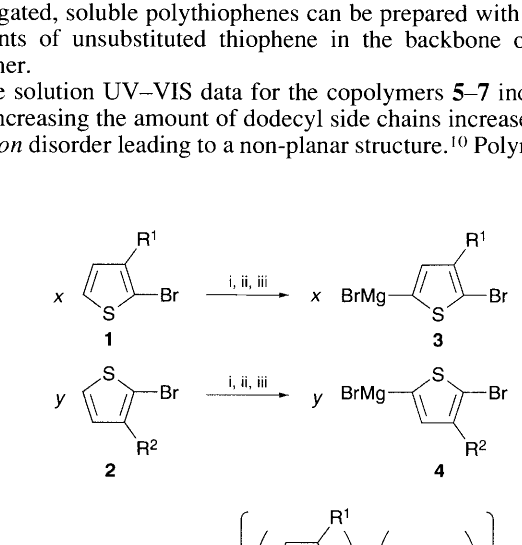
Polythiophenes continue to be very important in the development of new materials and are useful tools for understanding the chemistry and physics of conducting polymers.[1] We are interested in developing synthetic methods that lead to structurally well-defined conjugated polymer structures and in controlling the physical properties of conducting polymers by rational design. Progress toward these goals has led to the first synthesis of regioregular, head-to-tail (HT) coupled polythiophenes.[2–4] Studies on HT polythiophenes have provided new insights into structure–property relationships in conducting polymers.[3–5] We now have extended our method to the synthesis of head-to-tail coupled random copolymers of 3-alkylthiophenes with the aim of tuning the polymer backbone conformation and controlling polymer assembly. (HT refers to 2,5 couplings; random means that R^1 substituted thiophene is equally likely to have two R^2 substituted neighbours or two R^1 substituted neighbours or one of each.)

Recent work has shown that copolymers of dialkylterthiophenes[6] and regiorandom copolymers of 3-alkylthiophenes[7] exhibit unique properties. Kanatzidis and coworkers have found that the solution structure of poly(3′,4′-dibutyl-2,2′:5′2″-terthiophene) appears to exist in a planar, extended conformation due to the presence of unsubstituted thiophenes in the polymer.[6] The presence of unsubstituted thiophenes reduces the steric interaction between the alkyl chains on adjacent thiophene rings, thereby allowing the polymer backbone to assume a planar conformation. Another approach to highly conjugated conducting polymers is to use the side chains to self-assemble a planar polythiophene structure.[5] We have found that in HT-poly(3-alkylthiophenes) that the regular placement of the alkyl groups allows for the formation of a self-assembled, planar solid-state structure with high electrical conductivities.[5] The backbone planarity is attributed to the lack of coupling defects in HT poly(3-alkylthiophenes). These defects found in regiorandom PATs force the polymer into a non-planar conformation leading to lower conjugation lengths, larger band gaps, and lower electrical conductivities.[3,8,9] The larger the twist, the smaller the bandwidth will be and the electrical conductivity will be reduced. We have tested these two approaches to planar, highly conjugated polymers using the copolymers of 3-alkylthiophene synthesized here.

Head-to-tail coupled polythiophene random copolymers are synthesized by the route shown in Scheme 1. The Grignard compounds **3** and **4** were generated using a previously reported[2,3] procedure or were prepared as is shown in Scheme 1. We prepared random copolymers **5**–**9** using both procedures without any effect on the properties of the resulting polymers. In the case of the random HT copolymers **5**–**7**, we have found it convenient to prepare Grignards **3** ($R^1 = C_{12}H_{25}$) and **4** (R^2 = Me) in large batches (*e.g.* 30 mmol of each) and simply mix aliquots of **3** and **4** in direct proportion to the amount of incorporation desired. For example for the synthesis of **5**, we mix 2 mmol of **3** ($R^1 = C_{12}H_{25}$) and 1 mmol of **4** (R^2 = Me) and then polymerize by adding [Ni(dppp)Cl_2]. The polymers are isolated as reported previously.[3] The polymers were precipitated by the addition of MeOH, filtered, and the solid was washed with MeOH, H_2O, and then again with MeOH. The polymer is then subjected to Soxhlet extractions with MeOH, hexanes and finally with $CHCl_3$. All the studies reported here were carried out on the polymers isolated from $CHCl_3$ soluble polymer fraction. The copolymers are very soluble in typical organic solvents and possess excellent film forming abilities. Polymers **5**–**7** and **9** all form violet films, while polymer **8** forms red films.

The polymers have been characterized[8,9] by ^1H and ^{13}C NMR spectroscopy and we find that the polymers have ≈ 100% HT couplings. In addition, the ratio of each alkylthiophene component can be also determined by NMR. It is found that the ratio of 3-alkylthiophene incorporation is proportional to the feed ratio. In Table 1, the physical properties of these random, HT poly(3-alkylthiophene) copolymers are reported. Copolymer **9** exhibits a solution λ_{max} of 510 nm, which corresponds to one of the *longest* conjugation lengths known for a polythiophene in solution. It can also be seen that there is little difference in the absorption maximum between solution and the solid state (25 nm). It is clear that **9** has an extended planar conformation even in solution, due to the lack of steric hindrance caused by alkyl side chains. The properties and structural behaviour for polymer **9** are quite similar to those found by Kanatzidis and coworkers for poly(3′,4′-dibutyl-2,2′:5′,2″-terthiophene).[6] These results show that very highly conjugated, soluble polythiophenes can be prepared with large amounts of unsubstituted thiophene in the backbone of the polymer.

The solution UV–VIS data for the copolymers **5**–**7** indicate that increasing the amount of dodecyl side chains increases the *solution* disorder leading to a non-planar structure.[10] Polymer **5**



5 $R^1 = C_{12}H_{25}$, R^2 = Me
$x = 2$ $y = 1$
6 $R^1 = C_{12}H_{25}$, R^2 = Me
$x = 1$ $y = 1$
7 $R^1 = C_{12}H_{25}$, R^2 = Me
$x = 1$ $y = 2$
8 $R^1 = C_{12}H_{25}$, $R^2 = C_6H_{13}$
$x = 1$ $y = 1$
9 $R^1 = C_{12}H_{25}$, R^2 = H
$x = 1$ $y = 1$

Scheme 1 *Reagents and conditions*: i, LDA, THF, −60 °C, 1.5 h; ii, $MgBr_2 \cdot OEt_2$, −60 °C, 0.33 h; iii, −60 → 25 °C, 1.5 h; iv, 0.5 mol% [Ni(dppp)Cl_2], 25 °C, 14 h; v, 0.5 mol% [Ni(dppp)Cl_2], 12 h (dppp = 1,3-bis(diphenylphosphino)propane)

(2 : 1, $C_{12}H_{25}$: Me) has the shortest conjugation length, and polymer **6** (1 : 1, $C_{12}H_{25}$: Me) and polymer **7** (1 : 2, $C_{12}H_{25}$: Me) have essentially the same conjugation length in *solution.* However, in the solid state, the polymers with more dodecyl side chains self-assemble in order to form planar structures with long conjugation lengths. The conjugation in the solid state was greatest in polymer **5** (2 : 1, $C_{12}C_{25}$: Me) (λ_{max} = 565 nm), and decreased in polymer **6** (1 : 1, $C_{12}H_{25}$: Me) (λ_{max} = 550 nm), and polymer **7** (1 : 2, $C_{12}H_{25}$: Me) (λ_{max} = 545 nm). In addition, cyclic voltammetry of thin films of **5**–**7** also indicates that there are longer conjugation lengths in the solid state for **5** and that the oxidation potential decreases as the amount of dodecyl side chains decreases. The first oxidation potential decreases from **7** (1 : 2, $C_{12}H_{25}$: Me) (0.65 V) to **6** (1 : 1, $C_{12}H_{25}$: Me) (0.5 V) to **5** (2 : 1, $C_{12}H_{25}$: Me) (0.45 V), indicating that in cases where there are more dodecyl groups, there is a more planar the conformation. This results in more stable charge carriers. This data supports the notion that the dodecyl side chains are playing the role of inducing a planar structure along the backbone of the conducting polymer chain.[11]

Preliminary conductivity results indicate that I_2 doped thin films (0.5–4 μm) of polymers **5** and **6** exhibit electrical conductivities in the range of 50–200 S cm^{-1}. It appears that polymer **5** has a slightly higher conductivity than that of polymer **6**. The conductivity results are consistent with both the solid-state UV–VIS and the electrochemical data for **5** *v*. **6**. In addition, the physical properties of these polymers are unchanged over molecular masses of number average molecular masses (M_n) ranging from 9–28 K (PDI = 1.6). Therefore, these properties are not a function of the molecular mass of the polymer.

Table 1 Properties of random, HT copolymers of 3-alkylthiophenes

Polymer	Solution (xylene) absorbance maxima/nm	Solid state absorbance maxima/nm	Cyclic voltammetry[a] E_{ox}/V	Electrical conductivity[b] of I_2 doped films/S cm^{-1} (0.5–4 μm)
5	458	565[c]	0.45	90 av.
		526	0.85	(27 samples)
				190 max.
6	470	550[c]	0.5	70 av.
		520	0.85	(11 samples)
	600[d]	600		70 max.
7	466	545[c]	0.65	
		510	0.85	—
	600[d]	600		
8	450	556[c]	0.66	
		525	0.99	—
		604		
9	510	535[c]	0.71	
	575[d]	580	0.97	—
HT-Poly		561[c]	0.65	150–500 av.
(3-dodecyl	450	526	0.99	1000 max.
thiophene)		609		

[a] Electrochemistry on thin films in 0.2 mol dm^{-3} NBu_4PF_6 *vs.* SCE. [b] Measured by four-probe method on films cast from xylene. Films exposed to I_2 for 4 h. Exact film thickness measured by stylus profilometer. [c] λ_{max}. [d] Well resolved peak.

It can be seen from the physical properties of these HT random copolymers of 3-alkylthiophenes that we have been able to tune the physical properties by recipe—*that is*, an increase of one ingredient leads to increases or decreases in conjugation, *etc.* Since the principle of tuning conjugation carries over to tuning the conductivity in conducting polymers and the performance of polymer LEDs,[11–14] then design of conjugated polymers with controlled properties can be realized.

We are grateful to the NSF (CHE-9201198) and to the AT&T Special Foundation for financial support.

Received, 22nd August 1994; Com. 4/05130K

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