Synthesis of Poly(3-hexylthiophene) by Using the $VO(acac)_2$-$FeCl_3$-O_2 Catalytic System

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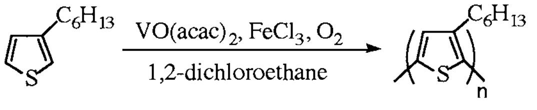
Poly(3-hexylthiophene) (P3HT) was prepared by the oxidation coupling polymerization of 3-hexylthiophene (3HT) with molecular oxygen as an oxidant in the presence of vanadyl acetylacetonate (IV) ($VO(acac)_2$) and ferric chloride ($FeCl_3$). The polymerization at a molar ratio of $VO(acac)_2$ / $FeCl_3$ / 3HT =1 / 2 / 5 in 1,2-dichloroethane at 0 °C for 164 h under oxygen gave P3HT in 61% yield. The resulting polymer gave a number average molecular weight (Mn) of 2.1 x 10^4 (Mw / Mn = 3.0; Mw: weight average molecular weight) and a head-to-tail content of 65%. The $VO(acac)_2$ - $FeCl_3$ complex is supposed to work as a catalyst.

Conducting polymers have received great attention over the last 20 years. Poly(3-alkylthiophene)s (P3AT) are one of the most attractive materials because of their excellent solubility and processability besides a promising electrical conductivity.[1,2] Many methods, including electrochemical polymerization[3,4] and chemical polymerization,[1,5-9] have been developed for polymer syntheses. Chemical oxidative polymerization by oxidants notably $FeCl_3$ gave an excellent regioselective product of head-to-tail P3AT.[6,10] However, such oxidative coupling requires at least twice molar amount of $FeCl_3$ toward to monomers, which is not an economic way and makes the purification of the polymer very troublesome.

We are interested in preparing P3AT by oxidative coupling polymerization using a catalytic system. We already succeeded in synthesizing regioregular poly(3-(4-dodecylphenyl)thiophene) through oxidative coupling polymerization using vanadyl acetylacetonate ($VO(acac)_2$) as an oxidation catalyst in the presence of trifluoromethanesulfonic acid, and trifluoroacetic anhydride under oxygen atmosphere.[9] But unfortunately, we found that this catalytic system is not suitable for preparing P3AT due to the acylation reaction of thiophene ring by trifluoroacetic anhydride during the polymerization procedure.

The oxidation potential of $VO(acac)_2$ -alcohol-O_2 system ,which is a good catalyst for epoxidation of olefins, is around 1.0 V(vs. Ag/Ag^+), and is difficult to oxidize 3-alkylthiophene (3AT)(1.6V vs. Ag/Ag^+). However, oligomers of 3AT have an lower oxidation potential than 1.0V. Thus, we expected that the combination of $FeCl_3$ and $VO(acac)_2$-O_2 system works for the oxidative coupling polymerization of 3AT. Because, a small amount of $FeCl_3$ initiates oligomerization of 3AT and then the formed oligomers are oxidized with the $VO(acac)_2$-O_2 system to produce the active species, which again react with another active species and 3AT. The process repeats to yield P3AT.

In this letter, we report the polymerization behaviors of 3-hexylthiophene (3HT) by using the $VO(acac)_2$ - $FeCl_3$ - O_2 catalytic system (Scheme 1).



Scheme 1.

A typical polymerization was carried out as follows. Vanadyl acetylacetonate ($VO(acac)_2$, 53.0 mg, 0.2 mmol) and ferric chloride ($FeCl_3$, 64.8 mg, 0.4 mmol) were placed in a two-necked flask under nitrogen. Dry 1,2-dichloroethane (DCE, 0.7 cm^3) was added dropwise into the stirred mixture. After the mixture was stirred for 1 h, a solution of monomer 3-hexylthiophene (3HT, 0.168 g, 1.0 mmol) in DCE (0.3 cm^3) was added through a syringe, and the atmosphere was changed into oxygen. The reaction mixture was stirred for 24 h at room temperature and then poured into methanol containing 10% aqueous hydrogen chloride solution. The precipitate was collected by filtration and washed with methanol in a Soxhlet apparatus for 24 h. The resulting dark red solid was extracted with chloroform in the same apparatus and the solvent was evaporated to give the product. Molecular weights of the polymers were estimated by a size exclusion chromatography (SEC) using polystyrene as a standard on a JASCO TRIROTAR-III HPLC equipped with Shodex KF-80M column at 40 °C in THF. The head-to-tail content of the resulting polymers were determined from the area ratio of peaks of α-methylene group appeared around 2.56 (head-to-head) and 2.80 (head-to-tail) ppm in their ^1H NMR spectra.

Table 1 shows the polymerization results of 3HT using $VO(acac)_2$ - $FeCl_3$ - O_2 catalytic system. A dispersed solution of vanadyl acetylacetonate ($VO(acac)_2$) and 3HT in 1,2-dichloroethane (DCE) could not form poly(3-hexylthiophene) (P3HT) by contact with oxygen at room temperature (Run 1). However, the addition of $FeCl_3$ to the dispersed solution could form a homogeneous solution and produce P3HT precipitates in considerably good yield (60%) by contact with oxygen (Run 3).

Table 1. Oxidative polymerization of 3-hexylthiophene (3HT) using $VO(aac)_2$-$FeCl_3$-O_2 system[a]

Run	$VO(acac)_2$ mmol	$FeCl_3$ mmol	Temp. °C	Time h	Yield %	HT[c] %	Mn[b] x 10^4	Mw/Mn
1	0.2	-	20	24	0	-	-	-
2	-	0.4	20	24	18	54	0.48	3.7
3	0.2	0.4	20	24	60	61	1.7	5.9
4	0.1	0.2	20	24	25	63	1.8	6.5
5	0.3	0.6	20	24	75	63	1.9	6.0
6	0.2	0.4	0	48	43	65	2.0	2.9
7	0.2	0.4	0	164	61	65	2.1	3.0
8	0.2	0.4	-20	164	18	81	1.6	2.3

[a]Reaction condition: 1.0 mmol of monomer, solvent: 1 cm^3 of 1,2-dichloroethane (DCE), O_2 atmosphere; [b]Measured by GPC based on standard PSt; [c]Head-to-tail content, determined by ^1H NMR.

The structure of the resulting polymer was confirmed by a comparison of the IR spectrum with that of the authentic P3HT, prepared from 3HT by oxidation with an excess amount of $FeCl_3$.[6,10] When the molar ratio of 3HT to the $VO(acac)_2$ / $FeCl_3$ (1 / 2) catalyst was changed from 3 to 10, the yields of P3HTs increased from 25% to 75% upon decreasing the ratio (Runs 3 - 5). The Mn of the polymers obtained also changed slightly from 1.7 x 10^4 to 1.9 x 10^4 and the head-to-tail contents remained almost the same from 61% to 63%.

In contrast with the above results, the reaction practically proceeded by the addition of only $FeCl_3$ without $VO(acac)_2$. In this case, however, only oligomer (Mn = 4.8 x 10^3) was obtained at low yield (18%) (Run 2). On the other hand, polymerization of oligomers (Mn = 4.8 x 10^3) using $VO(acac)_2$-O_2 system gave P3HT with lower molecular weights than that of P3HT obtained in Run 3. This means, $VO(acac)_2$ and $FeCl_3$ activated each other and the combination of $VO(acac)_2$ and $FeCl_3$ enable them to work as an effective catalyst. In fact, the strong UV absorption of $VO(acac)_2$ at 301 nm disappeared upon the addition of $FeCl_3$. On the other hand, the absorbance of $FeCl_3$ at 244, 315.5 and 362 nm increased upon the addition of $VO(acac)_2$. These results suggest the formation of a new complex of $VO(acac)_2$ due to the coordination of $FeCl_3$. The complex formation of $VO(acac)_2$ with $FeCl_3$ improved the catalytic activity, resulting in an increase in the yield and molecular weight of P3HT.

It has been reported that lowering the reaction temperature is very effective to increase the head-to-tail content of the product.[10] Furthermore, it may also lower the high dispersity of the polymers prepared at room temperature. Therefore, the polymerization at a molar ratio of $VO(acac)_2$ / $FeCl_3$ / 3HT = 1 / 2 / 5 was carried out at 0 and -20 ℃, respectively (Runs 6 - 8). The polymer prepared at -20 ℃ gave an increased head-to-tail content up to 81%, determined by ^{1}H NMR as shown in Figure 1, but correspondingly, the yield decreased to 18%. When the polymerization was carried out at 0 ℃ for 164 h, it gave a relatively high yield (61%), head-to-tail content (65%), high molecular weight (Mn = 2.1 x 10^4), and low dispersity (3.0).

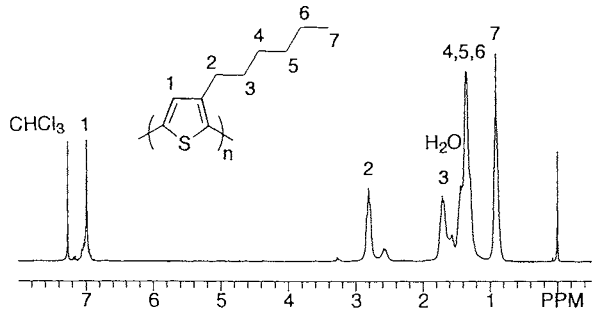


Figure 1. ^{1}H-NMR spectrum of P3HT (Run 8).

In summary, we succeeded in preparing poly(3-hexylthiophene) through oxidative polymerization using molecular oxygen as an oxidant and $VO(acac)_2$ - $FeCl_3$ as a catalyst. 20 mol% of $VO(acac)_2$ and 40 mol% of $FeCl_3$ resulted in a polymer yield of 61% at 0 ℃ for 164 h. The mechanism of this polymerization is now under investigation.

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