Inexpensive FeCl3 Oxidative Polymerizations

By: Robert B. Login   rloginconsulting.com

One of the major problems confronting organic solar cell commercialization is cost. Not only the steps required to synthesize the monomers, which can be complicated, have low yields and struggle with removal of toxic by-products, and their polymerization can also require toxic metal catalysis that are also hard to remove with commercially expensive chromatogry. What is needed is a simpler approach. I would like to suggest such a conceivably simpler approach based on FeCl3 and an organic oxidant to replace H2O2.

There are problems with FeCl3 polymerizations. Typically the literature indicates the a 6:1 mole ratio of FeCl3 to monomer is required and that the polymerization is usually run in CCl4,CHCl3, or CH3NO2. The work-up is usually to precipitate the polymer with excess methanol, collect the precipitate and extract it with methanol or water(containing sequesterants or NH3 etc.) until tests for Fe are negative. Then to extract the soluble polymer from the residual powder with a suitable solvent which is then removed. When I read these work-up procedures, I was sure that the FeCl3 approach was only good for academic pursuits. Then I found several references to a very clever improvement:

> $FeCl_3/H_2O_2$ (catalyst/oxidant) combination system [9], which can make roughly 30 nm PTh nanoparticles with only a trace of $FeCl_3$. A simple procedure for PTh nanoparticle synthesis with controllable particle size was also reported, in which sodium dodecyl sulfate (SDS) was used in an aqueous medium [10,11]. However, the addition of a surfactant can deteriorate the film properties of the PTh nanoparticles; thus, a purification step to remove the surfactant is needed [12]. Conjugated polymer nanoparticles prepared by surfactant free oxidative polymerization can be directly utilized for the film application without any further purification process compared with surfactant system. In addition, enhanced photoluminescence property of polythiophene nanoparticles can be revealed because of high molecular weight of polythiophene nanoparticles via surfactant free oxidative polymerization than emulsion oxidative polymerization in our previous study [9].

H.W. Ryu et al. / Polymer 55 (2014) 806–812

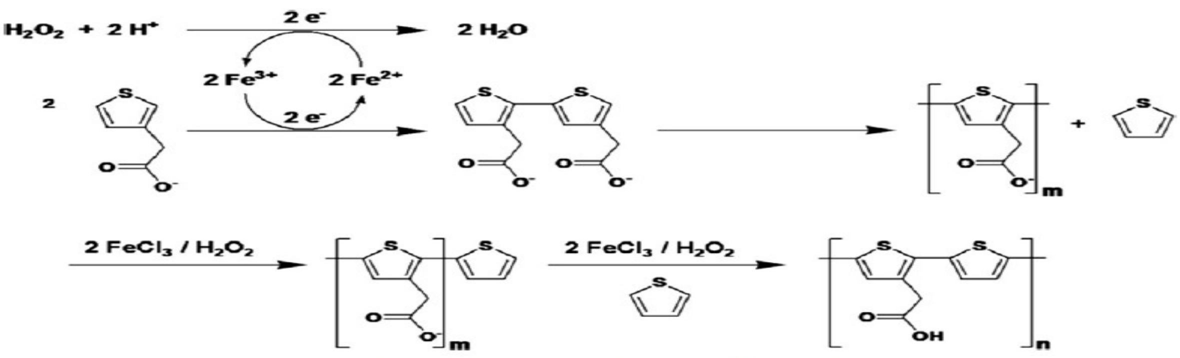


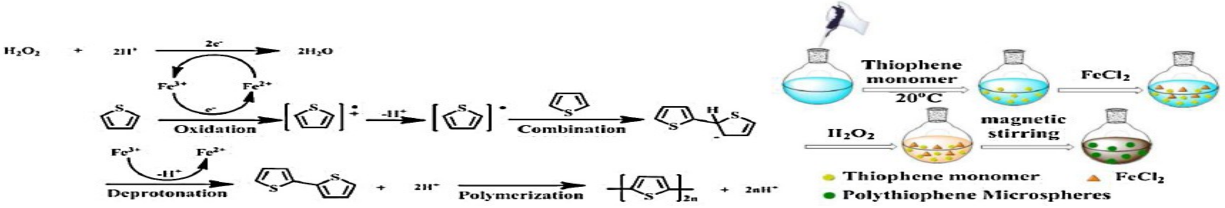
Fig. 7. A schematic diagram of the copolymerization of Th and TA salt by $FeCl_3/H_2O_2$ in the water phase.

Ryu, H. W., Kim, Y. S., Kim, J. H., & Cheong, I. W. (2014). Direct synthetic route for water-dispersible polythiophene nanoparticles via surfactant-free oxidative polymerization. *Polymer*, *55*(3), 806-812.

Also:

Lee, S. H., Kim, Y. S., & Kim, J. H. (2014). Synthesis of polythiophene/poly (3, 4-ethylenedioxythiophene) nanocomposites and their application in thermoelectric devices. *Journal of electronic materials*, *43*(9), 3276-3282.

L. Ai et al. / Synthetic Metals 191 (2014) 41–46



Scheme 1. Mechanism of chemical oxidative polymerization of polythiophene (left) and its experiment procedure (right).

Ai, L., Liu, Y., Zhang, X. Y., Ouyang, X. H., & Ge, Z. Y. (2014). A facile and template-free method for preparation of polythiophene microspheres and their dispersion for waterborne corrosion protection coatings. *Synthetic Metals*, *191*, 41-46.

So, the above references show that a very small amount of FeCl3 can be oxidized back to the active catalyst in water with H2O2. FeCl3 is soluble in several solvents, so can an organic oxidant which is also soluble in said solvents replace H2O2? This would result in reduced Fe removal problems and since Fe is a rather innocuous metal ion, at low enough levels, it may not need to be removed at all reducing the cost of this step? If this crossed my mind possibly this is already known? I looked at every reference I could find concerning FeCl3 oxidative polymerization and none were found! It seems to me that it should be possible to find an acceptable organic oxidant to work with FeCl3 like H2O2!

Organic Semiconductor Polymers

Many if not most monomers (thiophenes, furans, pyrroles, anilines etc.) employed in the preparation of conductive polymers can be polymerized by an oxidative mechanism. Oxidative polymerization with ferric chloride is very inexpensive and can be optimized to afford high mw polymers but usually with broad polydispersities. Color and solubility are other potential problems; however, it can also be used to synthesize random or block copolymers. So this is the idea I have for the lowest cost pi conjugated donor and acceptor polymers or oligomers. I think you can work out how to use ferric chloride or other oxidants to synthesize usable AD and ADA copolymers. This would be an inexpensive approach avoiding toxic byproducts and dangerous heavy metal contamination.

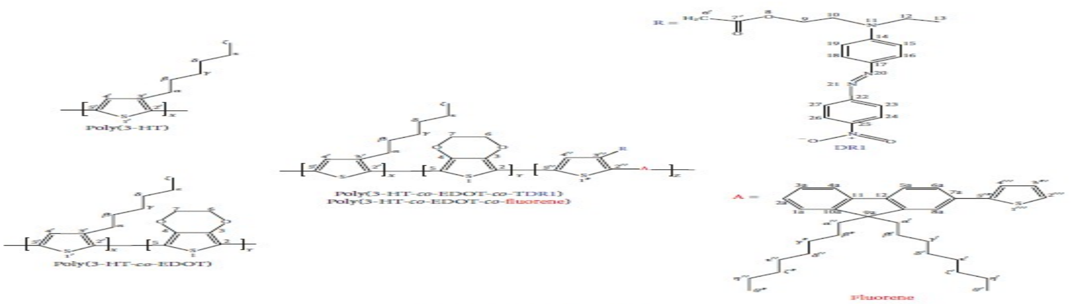
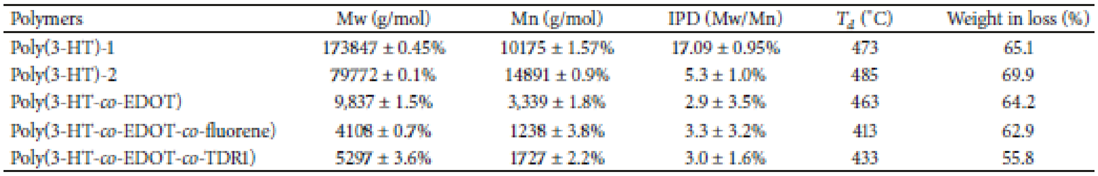


FIGURE 1: Structures of the polymers.

Table 3: Molecular weight distributions and thermal properties of the polymers.



Polymers	Mw (g/mol)	Mn (g/mol)	IPD (Mw/Mn)	T_d (°C)	Weight in loss (%)
Poly(3-HT)-1	173847 ± 0.45%	10175 ± 1.57%	17.09 ± 0.95%	473	65.1
Poly(3-HT)-2	79772 ± 0.1%	14891 ± 0.9%	5.3 ± 1.0%	485	69.9
Poly(3-HT-*co*-EDOT)	9,837 ± 1.5%	3,339 ± 1.8%	2.9 ± 3.5%	463	64.2
Poly(3-HT-*co*-EDOT-*co*-fluorene)	4108 ± 0.7%	1238 ± 3.8%	3.3 ± 3.2%	413	62.9
Poly(3-HT-*co*-EDOT-*co*-TDR1)	5297 ± 3.6%	1727 ± 2.2%	3.0 ± 1.6%	433	55.8

All of these copolymers were synthesized with FeCl3.

Ramírez-Gómez, M. A., Guzmán-Rabadán, K. K., Gonzalez-Juarez, E., Güizado-Rodríguez, M., Ramos-Ortiz, G., Alba-Rosales, J. E., ... & Basurto-Pensado, M. Á. (2017). Physicochemical and Luminescent Properties of Copolymers Composed of Three Monomers: Polythiophenes Based on 3-Hexylthiophene and 3, 4-Ethylenedioxythiophene. *International Journal of Polymer Science*, *2017*.

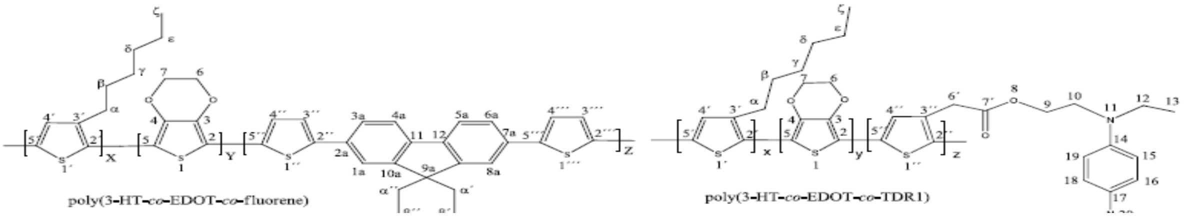
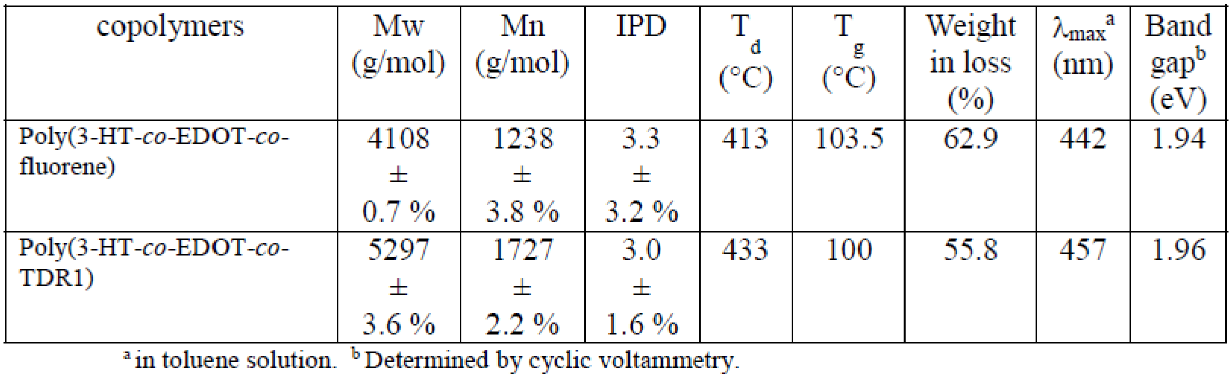


Table III. Data of thermogravimetric analysis, molecular weights distribution and band gap of the copolymers.



copolymers	Mw (g/mol)	Mn (g/mol)	IPD	T d (°C)	T g (°C)	Weight in loss (%)	λ_{max}[a] (nm)	Band gap[b] (eV)
Poly(3-HT-*co*-EDOT-*co*-fluorene)	4108 ± 0.7 %	1238 ± 3.8 %	3.3 ± 3.2 %	413	103.5	62.9	442	1.94
Poly(3-HT-*co*-EDOT-*co*-TDR1)	5297 ± 3.6 %	1727 ± 2.2 %	3.0 ± 1.6 %	433	100	55.8	457	1.96

[a] in toluene solution. [b] Determined by cyclic voltammetry.

Guzmán-Rabadán, K. K., Ramírez-Gómez, M. A., Güizado-Rodríguez, M., Guerrero-Álvarez, J. A., Barba, V., Basurto-Pensado, M. A., ... & Maldonado, J. L. (2015). Synthesis and physiochemical characterization of new polythiophenes based on three different monomers. *MRS Online Proceedings Library Archive*, *1767*, 57-62.

Both of the above copolymerizations were oxidative, employing FeCl3; however, I fault these preparations because what they did was to simply mix the monomers and polymerize. I suggest that monomers that can be oxidatively polymerized have reactivity ratios like the free radical vinyl and acrylic copolymer monomers. You would not just mix these monomers together and expect uniform polymerization! The fast monomers are usually added at some rate, to the slow monomers according to their reactivity ratios; however, I don't believe this has been done with monomers used in oxidative polymerization. I suggest reviewing free radical monomer reactivity. The best book here are Odian's and more recently Moad and Solomon(2006, Elsevier).

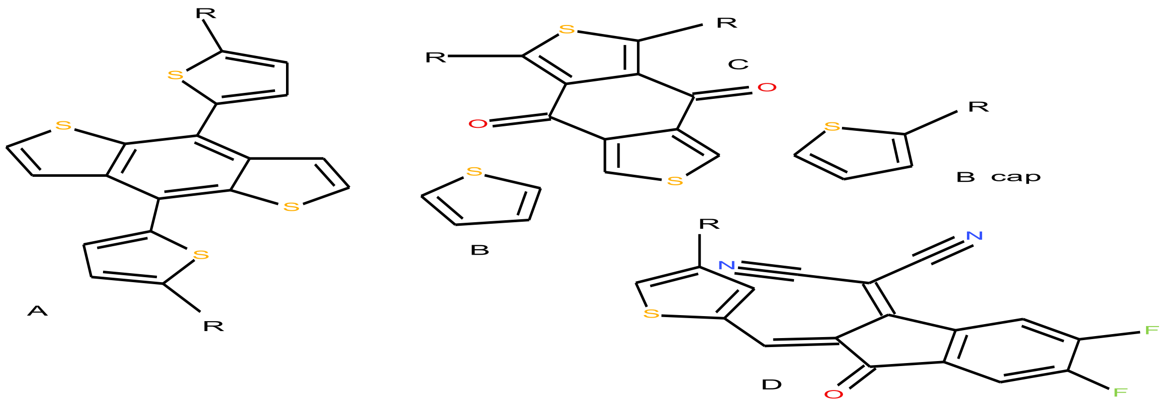
7.3.3 Estimation of Reactivity Ratios (Moad & Solomon)

Methods for evaluation of reactivity ratios comprise a significant proportion of the literature on copolymerization. There are two basic types of information that can be analyzed to yield reactivity ratios. These are (a) copolymer composition/conversion data (Section 7.3.3.1) and (b) the monomer sequence distribution (Section 7.3.3.2). The methods used to analyze these data are summarized in the following sections

Not only the above techniques but a careful consideration of the monomers structure at the reactive site as to its effect on the formation of the reactive specie. Since this FeCl3 generated polymerization is a one electron oxidation, the first thing to know is the oxidation potential (IP) of each monomers alpha protons. I would think that if they are close together for example two similar thiophenes, then I would expect a random polymer no matter the ratio of the monomers employed. Lets say that the next example is two monomers with enough separation of oxidation potentials to cause homogeneity problems. In this case, I would experiment adding the fast(low IP) monomer to the slow one. FeCl3 polymerizations are fast, so to gain more control, the temperature can be lowered to slow the copolymerization. If slow enough then adding the faster to the slow monomers or mixtures might give control?

Once the copolymer starts to grow, its IP drops because with more unsaturation, the terminal IP drops. This adds another layer of complications as the growing oligomer can have either slow or fast terminals or both. I would add enough slow monomer in order to cap the growing polymer, then aliquots of fast followed by slow might facilitate some randomness if that's what you want. I would think that block copolymers might be easier to synthesize.

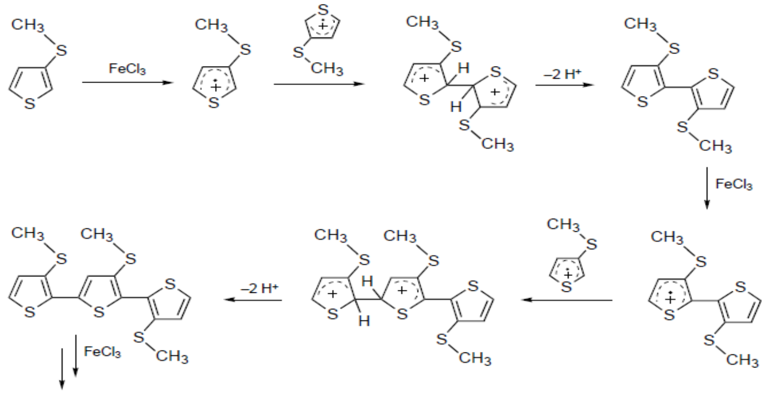
Obviously, I can not apriori design suitable monomers to generate organic solar cells (OSC's). The donor polymers can be complicated as are the acceptor compounds but let me speculate:



Scheme 1: An example of a FeCl3 monomer tool kit.

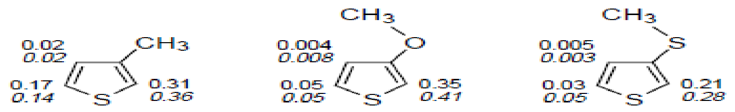
Looking at these monomers, I would guess that A would be the easiest to polymerize because as you increase the conjugation, the lower the ionization potentials of the alpha protons. FeCl3's mechanism is to generate a cationic radical.

Scheme 6. Possible Mechanism for the Reaction of 3-(Methylsulfanyl)thiophene with Ferric Chloride



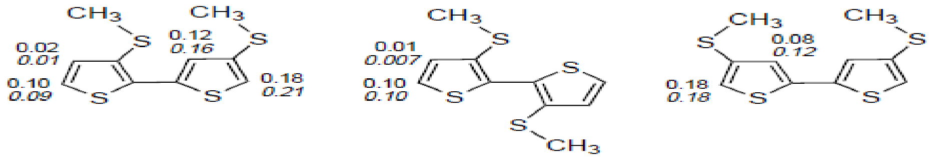
And:

Scheme 4. Square Values of the Calculated Coefficients of the HOMO of 3-Methyl-, 3-Methoxy- and 3-(Methylsulfanyl)thiophene[a]



[a] Values in italics are those for the SOMO of the corresponding radical cations.

Scheme 5. Square Values of the Calculated Coefficients of the HOMO of 3,3′-, 3,4′- and 4,4′-Bis(methylsulfanyl)-2,2′-bithiophenes[a]



6 **7** **8**

Barbarella, G., Zambianchi, M., Di Toro, R., Colonna Jr, M., Iarossi, D., Goldoni, F., & Bongini, A. (1996).

Regioselective oligomerization of 3-(alkylsulfanyl) thiophenes with ferric chloride. *The Journal of organic chemistry*, *61*(23), 8285-8292.

This paper illustrates that the reaction of FeCl3 occurs at the most easily oxidized IP proton because the 3 substituent electron donating group is conjugated with this alpha thiophene proton. For this reason, monomer 7 is the least active while 8 forms high polymers.

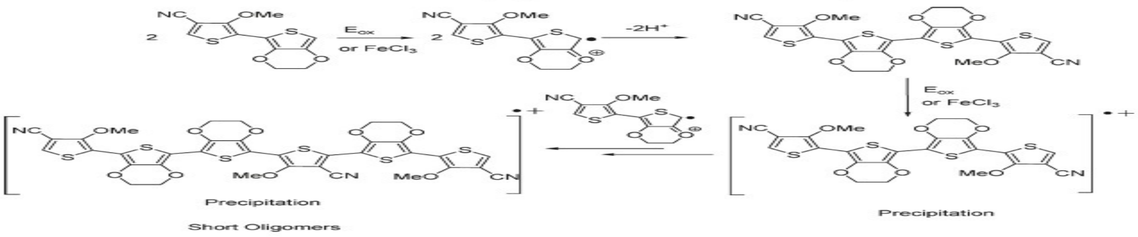
Rasmussen, S. C., Pickens, J. C., & Hutchison, J. E. (1998). A new, general approach to tuning the properties of functionalized polythiophenes: The oxidative polymerization of monosubstituted bithiophenes. *Chemistry of materials*, *10*(7), 1990-1999.

Beta protons are not very active and usually not a problem unless they are the only ones available.

Engelmann, G., Jugelt, W., Kossmehl, G., Welzel, H. P., Tschuncky, P., & Heinze, J. (1996). Doped Polymers by Oxidative Polymerization. 4. Oxidative Coupling of Methylated Oligothiophenes by FeCl3⊙6H2O as a Model Reaction for the Oxidative Polymerization of Thiophene Derivatives. *Macromolecules*, *29*(10), 3370-3375.

Here is another example of the effect of IP.

Scheme 3. Oxidative Coupling Reaction Postulated for Compound 2



Hergue, N., Mallet, C., Frere, P., Allain, M., & Roncali, J. (2009). Electrogenerated low band gap polymers based on the 3-cyano-4-methoxythiophene building block. *Macromolecules*, *42*(15), 5593-5599.

In this case the EDOT side is more easily oxidized. The cyano group is a electron deficient substituent that raises the IP of the associated alpha proton.

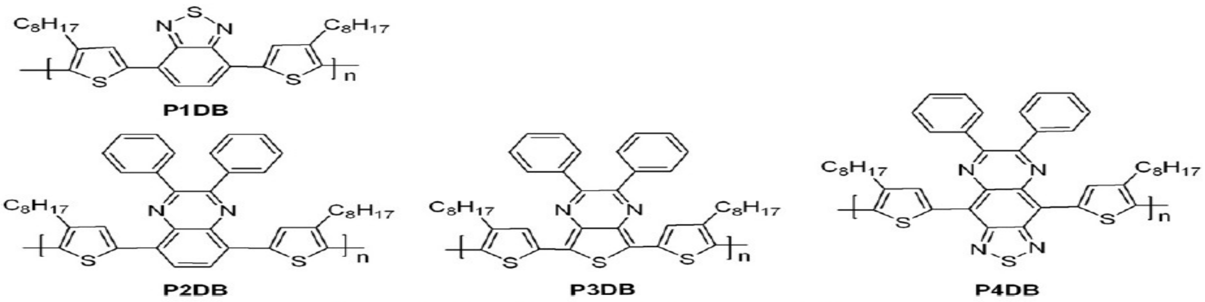
In scheme 1, A would have the lowest IP, B would be next followed by D and then C. I pick C as the least reactive because both alpha protons are next to electron withdrawing groups. So with these ideas and the cationic/radical mechanism in mind, how would I prepare say a donor polymer? I would mix C and B and an organic oxidant, initiate at some temperature with a small amount of FeCl3. I would add A dropwise and expect a variety of copolymer structures with C-B, A-B-C, A-A-B-C-A, C-A-A-B-A-B-C and so forth as the polymerization continues. The temperature might have to be raised to increase the reactivity of C terminals and at some point Bcap would be added to stop the polymerization. Obviously, you could play around with these monomer structures besides the ones shown in scheme 1, the point is that this would be cheap and environmentally safe once you got the right combinations of monomer structures, temperature, monomer sequence and rate of addition.

Now once you have after experimentation arrived at your donor polymer, you could prepare the acceptor compound in the same reactor on top of the donor because the donor is capped and blocked from further reaction. Some combination of A and B capped by D might work as an acceptor. I would add the D drop wise to the actively polymerizing A and B so that some combination can be capped with D. Now the solvent can be removed to form the BHJ mixture.

There would be a great deal of experimentation to come up with the best monomers and polymerization strategy but several expensive steps would be eliminated. Besides monomer synthesis(and several logical monomers are commercially available), the rest of the BHJ components could be prepared in the same reactor. The key of course is the idea of replacing H2O2 with an organic solvent soluble replacement, allowing a small amount of FeCl3 to work effectively.

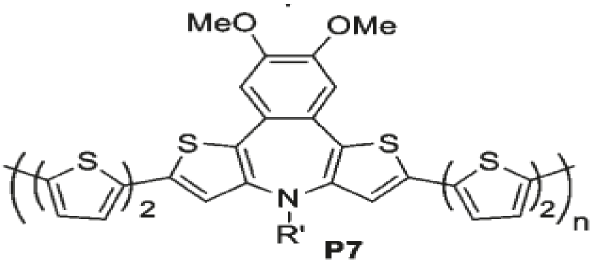
<u>Other Monomers that were polymerized with FeCl3:</u>

T. Cai et al. / Solar Energy Materials & Solar Cells 94 (2010) 1275–1281

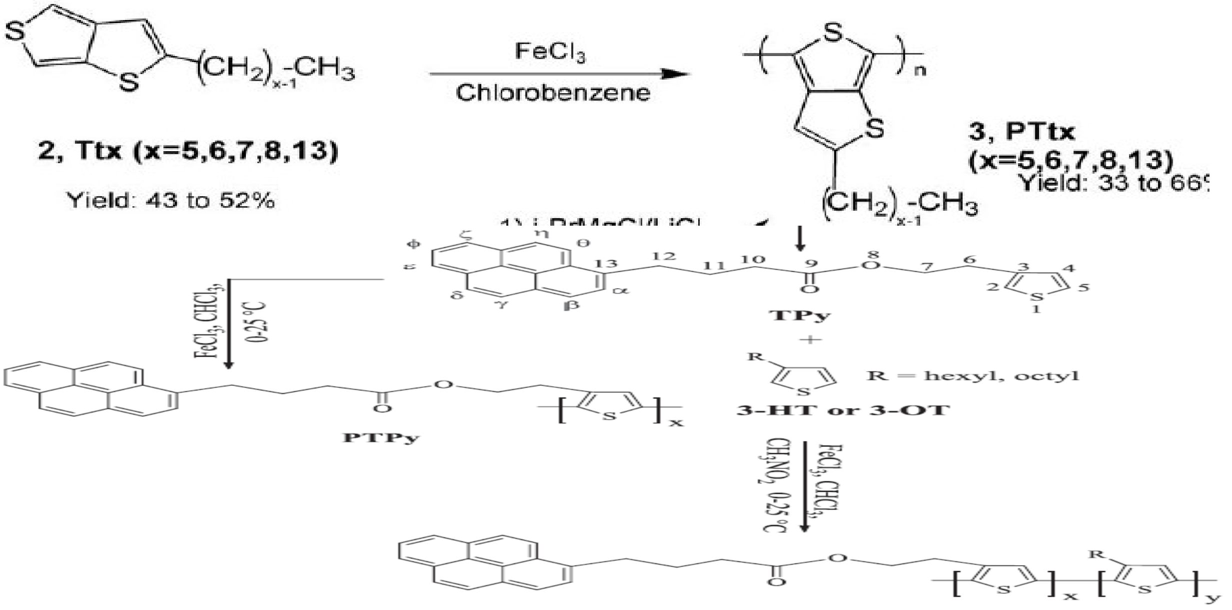


Scheme 1. The chemical structures of the synthesized polymers.

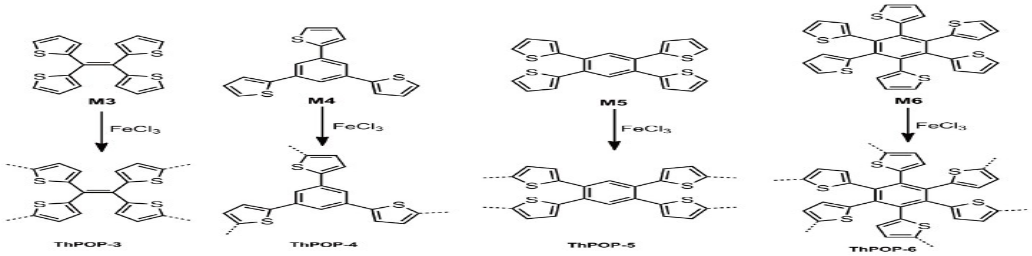
5234 *Macromolecules, Vol. 43, No. 12, 2010*



Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 3260–3271 (2011) © 2011 Wiley Periodicals, Inc.

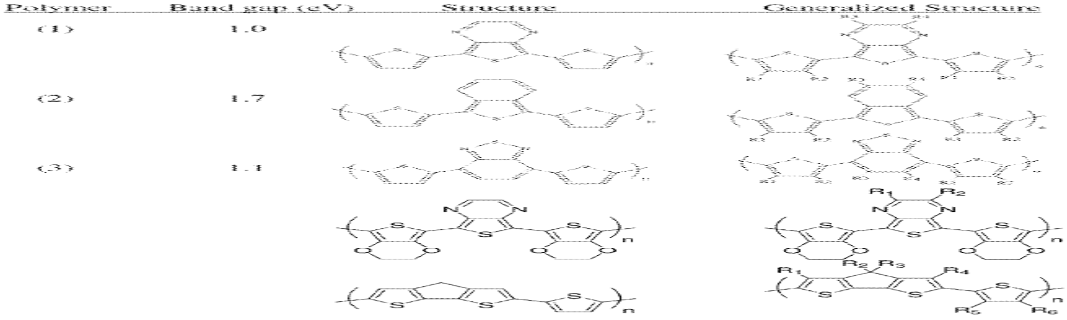


E. González-Juárez et al. / Journal of Molecular Structure 1103 (2016) 25–34



Scheme 2 Synthesis routes to ThPOPs.

SCIENCE CHINA Chemistry **60**, 1067 (2017); doi: 10.1007/s11426-017-9069-6



Polymer	Band gap (eV)	Structure	Generalized Structure
(1)	1.0		
(2)	1.7		
(3)	1.1		

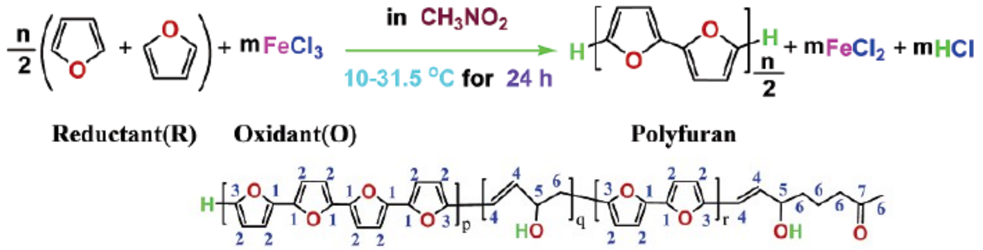
FIG. 11B

(10) **Patent No.: US 9,793,479 B2**
(45) **Date of Patent: Oct. 17, 2017**

Furan Copolymer Possibilities:
Can other monomer components of conjugated conductive polymers besides thiophene be polymerized with FeCl3? Every example to this point depended on thiophene which can be modified if necessary to be active FeCl3 polymerizable monomers. What about Furan? It has a significant thiophene copolymer semiconductor literature.

Furan/Aniline Polymerization Condition Optimization *Journal of Combinatorial Chemistry, 2006, Vol. 8, No. 5* **671**

Scheme 1. An Ideal Chemical Oxidative Polymerization of Furan and Possible Structure of the Polyfuran Formed



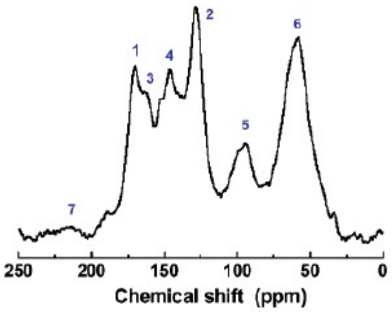


Figure 7. Solid-state high-resolution ^{13}C NMR spectrum of polyfuran obtained at the furan concentration of 0.2 M in CH_3NO_2 at a polymerization temperature of 31.5 °C and $FeCl_3$/furan molar ratio of 1/1 for 24 h.

However, copolymerization of furan with aniline prove to be retarded for some unexplained reason.

Li, X. G., Kang, Y., & Huang, M. R. (2006). Optimization of polymerization conditions of furan with aniline for variable conducting polymers. *Journal of combinatorial chemistry*, *8*(5), 670-678.

Tibaoui, T., Zaidi, B., Bouachrine, M., Paris, M., & Alimi, K. (2011). A study of polymers obtained by oxidative coupling of furan monomers. *Synthetic Metals*, *161*(21-22), 2220-2225.

The problem with furan copolymers is that the IP of the alpha furan protons is higher than those in thiophene. One way around this problem is to use a furan dimer or trimer where the additional unsaturation reduces said IP.

“The difference in the twisting potential can be explained by the less aromatic and more quinoid character of oligofurans relative to oligothiophenes and is supported by the difference in the calculated average inter-ring C-C bond lengths. For example, the average calculated inter-ring C-C bond lengths in **6F** and **6T** are 1.432 and 1.443 Å, respectively, which correlates nicely with the experimental values mentioned above. The smaller size of the oxygen atom compared with sulfur atom, which leads to less steric demand in oligofurans than in oligothiophenes, may also contribute to the significant difference in the rigidity.

CV of **3F**-**8F** shows an irreversible oxidation peak that ranges from 0.91 V (vs SCE) for **3F** and 0.71 V for **5F** to 0.67 V for **8F** (Figure 4a and Table 1, calibrated using Fc/Fc$^+$) 0.34 V vs SCE).[25] This is in agreement with the calculated difference of only

0.14 eV in the HOMO energies of **5F**-**8F** (Table 1).[22] Long oligofurans are significantly more electron-rich than oligothiophenes, as evident from their relatively low oxidation potentials. For comparison, the oxidation potentials of **3T** and **4T** are 1.16 and 1.14 V, respectively, under similar conditions. In the cases of **4F**-**7F**"

Gidron, O., Diskin-Posner, Y., & Bendikov, M. (2010). α-Oligofurans. *Journal of the American Chemical Society*, *132*(7), 2148-2150.

(Prof. Bendikov was a great proponent of the Oligofurans and has authored many articles concerning their utility.)

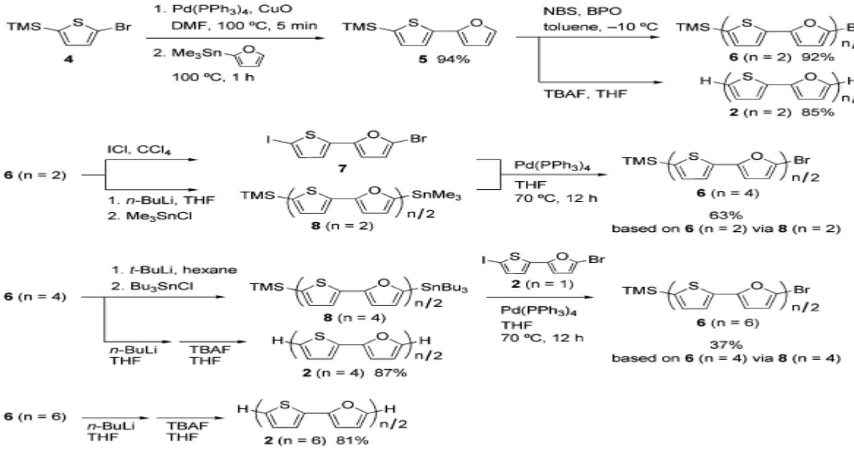
"The calculation results show that nFs possess high intrinsic hole-transfer mobilities and suitable IP values for use as p-type materials. Significantly, the maximum hole-transfer mobility of 6F is nearly 17 times larger than that of 6T and the IP value of 6F is 0.14 eV smaller than the IP value of 6T. On the basis of these detailed calculations, we draw the conclusion that oligofurans or oligofuran-based materials have wide application prospects as promising novel p-type organic semiconductor materials."

Huang, J. D., Wen, S. H., Deng, W. Q., & Han, K. L. (2011). Simulation of hole mobility in α-oligofuran crystals. *The Journal of Physical Chemistry B*, *115*(10), 2140-2147.

I believe this shows that because of the lower aromatic character of furan that its oligomers are coplanar because the quinoid form is favored while with thiophene oligomers, because of the greater bond lenth between their more aromatic structure, they can twist and therefore they exhibit less quinoidal characteristics. Formation of a cationic radical would therefore be easier with oligofurans. Hence, placing furan in say OSC donor and NFAccetors would favor the desired planarity extending quinoidal conjugation. In addition furan containing semiconductors are more solvent soluble.

The easiest way to make said oligofurans compatible with the thiophene base compounds that are now of significant interest in the literature is to cap them with thiophenes. This would make them compatible with the many thiophenes used in OSC's.

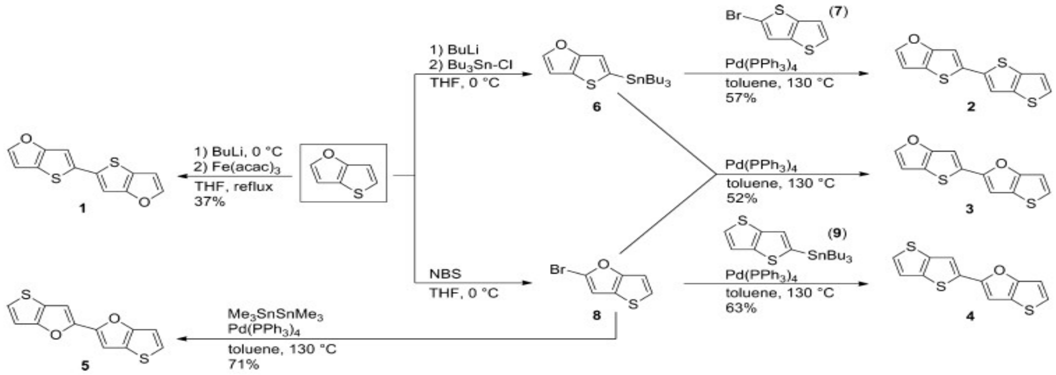
SCHEME 1



Miyata, Y., Nishinaga, T., & Komatsu, K. (2005). Synthesis and structural, electronic, and optical properties of oligo (thienylfuran) s in comparison with oligothiophenes and oligofurans. *The Journal of organic chemistry*, *70*(4), 1147-1153.

Although these copolymers were not prepared with FeCl3 oxidative polymerization, their properties are instructive because they are much more coplanar versus the polyT homopolymers.

Scheme 1. Synthetic Route to Oligomers 1−5[a]



[a] Yields represent the material isolated by column chromatography in >96% purity (<4% regioisomers).

“Substitution of furan rings at the terminal positions yields oligomers with a narrower HOMO−LUMO gap relative to the all-thiophene analogue 2,2′-bithieno[3,2-b]thiophene, and incorporation of furan rings at the interior positions results in oligomers with an increase in rigidity and a higher fluorescence quantum yield. Packing motifs of the oligomers were determined using single crystal X-ray diffraction. In contrast to the herringbone crystal packing observed for nonfused oligothiophenes, oligofurans, thiophene−furan hybrid oligomers, and the all-thiophene analogue 2,2′-bithieno[3,2-b]thiophene, all three regioisomers derived from the dimerization of thieno[3,2-b]furan arrange in a π-stacked packing motif in the solid state.”

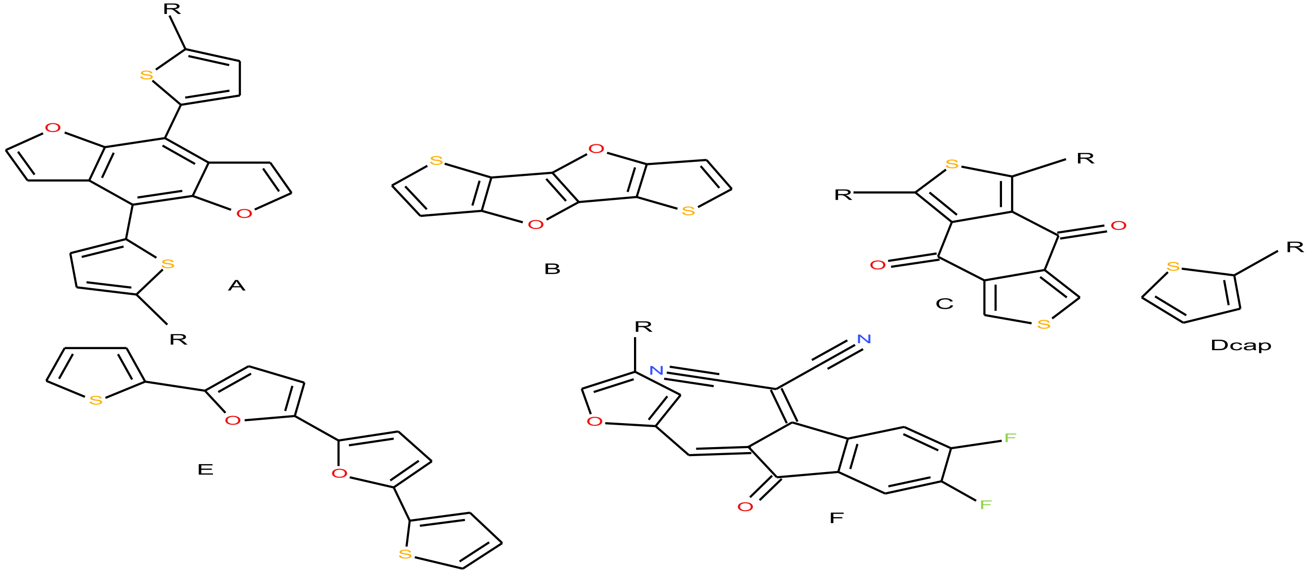
Henssler, J. T., & Matzger, A. J. (2012). Regiochemical Effects of Furan Substitution on the Electronic Properties and Solid-State Structure of Partial Fused-Ring Oligothiophenes. *The Journal of organic chemistry*, *77*(20), 9298-9303.

The following reference affords a complete overview as of 2014 of the oligofurans;

Gidron, O., & Bendikov, M. (2014). α-oligofurans: an emerging class of conjugated oligomers for organic electronics. *Angewandte Chemie International Edition*, *53*(10), 2546-2555.

Note: The quinoidal structure is of current interest. For example:
Yamamoto, K., Ie, Y., Nitani, M., Tohnai, N., Kakiuchi, F., Zhang, K., ... & Aso, Y. (2018). Oligothiophene quinoids containing a benzo [c] thiophene unit for the stabilization of the quinoidal electronic structure. *Journal of Materials Chemistry C*.

Rather than venture into areas I don't fully understand such as quantum physics, I would rather illustrate the use of said furans with FeCl3 to prepare OSC type compounds.



Scheme 2: Potential F-T tool box.

Donor polymer: [(A-B)n-C]n-D or E replaces B
Acceptor compound: (A-B)n or (A-C)n capped with F

The above ideas are just illustrative and many other structures can be conceived of; however, the inexpensive environmentally friendly use of FeCl3/organic soluble oxidant's (if this idea would work) ability to generate useful compounds, I would hope would be investigated.

As an Organic/Polymer Chemist, I'm a fan of the BHJ approach to OSC but I have not found a cost comparison with the other approaches to solar cell compositions. Possibly a cost per PCE unit would be interesting? Sooner or later the economics and environmental impact will determine the best commercial approach.

Thank you for reading these proposals!
Dr. Robert B. Login   rloginconsulting.com