

Polymerization of 3-hexylthiophene with FeCl₃ in aromatic solvents

| | |
|------------------------------|---|
| 著者 | Liu Yi, Nishiwaki Nagatoshi, Saigo Kazuhiko, Sugimoto Ryuichi |
| journal or publication title | Polymer Bulletin |
| volume | 72 |
| number | 7 |
| page range | 1817-1826 |
| year | 2015-07 |
| URL | http://hdl.handle.net/10173/1466 |

doi: 10.1007/s00289-015-1373-9

Polymerization of 3-hexylthiophene with FeCl₃ in aromatic solvents

Yi Liu¹, Nagatoshi Nishiwaki¹, Kazuhiko Saigo², Ryuichi Sugimoto¹

-
- (1) Yi Liu, Nagatoshi Nishiwaki, Ryuichi Sugimoto
School of Environmental Science and Engineering, Kochi University of Technology,
Miyakouchi, Tosayamada, Kami, Kochi 782-8502, Japan
- (2) Kazuhiko Saigo
Kochi University, Kohasu, Oko, Nankoku, Kochi 783-8505, Japan
E-mail: Sugimoto.Ryuichi@kochi-tech.ac.jp
-

(Abstract)

The polymerization of 3-hexylthiophene with FeCl₃ was carried out in aromatic solvents. The incorporation of aromatic solvent molecules such as benzene, toluene, xylene, and mesitylene into the resultant polymer main chain was clarified by ¹H NMR and matrix-assisted laser desorption/ionization mass spectrometry for the first time. More amount of benzene (12 mol%) was incorporated into the resultant polymer, compared with toluene, xylene, and mesitylene. The polymeric product prepared in benzene at 23 °C afforded an electrical conductivity (0.3 Scm⁻¹) much better than that of the polymer prepared in toluene (0.05 Scm⁻¹).

Keywords: Conducting polymer; 3-hexylthiophene; aromatic solvents; FeCl₃

Introduction

Poly(3-alkylthiophene)s (P3ATs), which are distinguished in the high electrical conductivity, optimum solubility in common organic solvents such as CHCl₃, THF, benzene, and toluene, and superior film-forming properties, have been the subject of

extensive research endeavor for their applications in organic light-emitting diodes (OLEDs) , dye-sensitized solar cells (DSSCs), organic field effect transistors (OFETs), and electrochromic devices etc. [1-4]. For the large scale application of P3ATs in OLEDs and other research fields, it is essential that the polymerization of 3-alkylthiophenes proceeds through a simple route and in high yield. To date, three type methodologies (metal-catalyzed coupling reactions, electropolymerizations, and chemical oxidative polymerizations) have been developed to afford P3ATs [5-7]. FeCl₃ oxidative polymerization is more prevalent in industrial applications, compared with the other two synthetic methodologies, owing to its relative simplicity of experimental set-up and to higher monomer-to-polymer conversion. Although tremendous efforts have been devoted to the investigations on the synthesis and application of P3ATs, detail knowledge about the effect of reaction conditions, especially the reaction solvent against the resulting P3AT structure, is insufficient yet. On the other hand, various polymerization methods for benzene derivatives have been also reported [8,9]. For example, Polyphenylene obtained by Kovacic method (oxidative polymerization of benzene with CuCl₂) has been known to have branched structure, and polyphenylene obtained by Yamamoto method (Ni catalyzed dehalogenative polycondensation of p-C₆H₄X₂) has been reported not to have branched structure in the polymer chain. Polymerization mechanisms of chemically polymerized thiophene derivatives or benzene derivatives using catalyst (e.g. FeCl₃) are not clear yet. Although the exact reaction mechanism is unclear, the most plausible mechanism is radical, cation or radical cation path according to prior literature [10].

In this study, we carried out the polymerization of 3-hexylthiophene in aromatic solvents in order to obtain further insights into the relationship between poly(3-hexylthiophene) structures and reaction conditions.

Experimental section

Materials : 3-Hexylthiophene and FeCl₃ were purchased from Wako Pure Chemical Industrials Ltd and used without any further purification. Aromatic solvents used in this study were also purchased from Wako Pure Chemical Industrials Ltd, dried by standing over 4A molecular sieves one night, and purged with argon for 10 min prior to use. α -Cyano-4-hydroxycinnamic acid (CCA) was purchased from Tokyo Chemical Industry Co., Ltd and used as the matrix in the MALDI-TOF MS measurement of oligo(3-hexylthiophene)s.

Instruments: A UNICO UN 650 F mode glove box was utilized to weigh FeCl₃. ¹H NMR spectra (400 MHz) were recorded on a Bruker Ascend 400 spectrometer. All chemical shifts are reported in δ units with reference to the proton signal of internal tetramethylsilane (TMS). Gel permeation chromatography (GPC) was conducted on a system equipped with a Shimadzu LC-6A pump, Shodex GPC LF-804 columns, and a Jasco RI-2031 plus intelligent RI detector. A ChromNAV software was applied to determine the molecular weight and molecular weight distribution of the polymers relative to polystyrene standards. The system was equilibrated at 40 °C in THF (THF served as the polymer solvent and eluent). GPC was carried out with an injection volume of 100 μ L at a flow rate of 1 mL min⁻¹. The MALDI-TOF MS spectra were acquired on a Bruker autoflex speed-KE in a reflector mode. Uv-vis absorption spectra were measured

at room temperature on a Jasco V-550 Uv/vis spectrophotometer between 300 nm to 600 nm.

Typical polymerization of 3-hexylthiophene (3HT) with FeCl₃ in an aromatic solvent:

All reactions in this study were performed in an oven-dried schlenk flask with stopcock under an atmosphere of argon, unless specified otherwise. The polymerizations of 3-hexylthiophene with FeCl₃ in aromatic solvents were performed according to the procedure described in a literature except for the solvent; an aromatic solvent was used in place of CHCl₃[7].

FeCl₃ (0.65 g, 4 mmol) and dry benzene (6.5ml, 73mmol) were put into a schlenk flask and flask was cooled to 0°C in ice bath or 23 °C. 3-Hexylthiophene (0.17 g, 1 mmol) was added dropwise to a magnetically stirred suspension of FeCl₃ (0.65 g, 4 mmol) in dry benzene (6.5ml, 73mmol) and the reaction mixture was stirred for 2 hours under an atmosphere of argon. Then, methanol (100mL) was added to the mixture to quench the polymerization reaction. The black residue was collected, obtained by removal of the solvents on a rotary evaporator, transferred into a thimble filter, and then successively extracted with methanol (100 mL), acetone (100 mL), and CHCl₃ (100 mL) by using a Soxhlet extractor; methanol was used to remove remaining FeCl₃ in the obtained polymer. The acetone extract was condensed to dryness to afford oligo(3-hexylthiophene)s. Poly(3-hexylthiophene) was recovered from the CHCl₃ extract.

The polymerizations of 3-hexylthiophene with FeCl₃ in toluene, xylene, and mesitylene were conducted by a similar protocol.

Results and discussions

(1) Incorporation of aromatic solvent molecule(s) into the resultant polymer skeleton

As presented in Figure 1, the appearance of poly(3-hexylthiophene) prepared in benzene at 23 °C for 2 h (P3HT/benzene) was purple black and lusterless, quite different from that of an analogue synthesized in CHCl_3 (P3HT/ CHCl_3).



Fig. 1. The appearance of P3HT/ CHCl_3 and P3HT/benzene

To clearly quantify the difference in appearance between P3HT/ CHCl_3 and P3HT/benzene, Uv-vis spectroscopy was adopted (Figure 2).

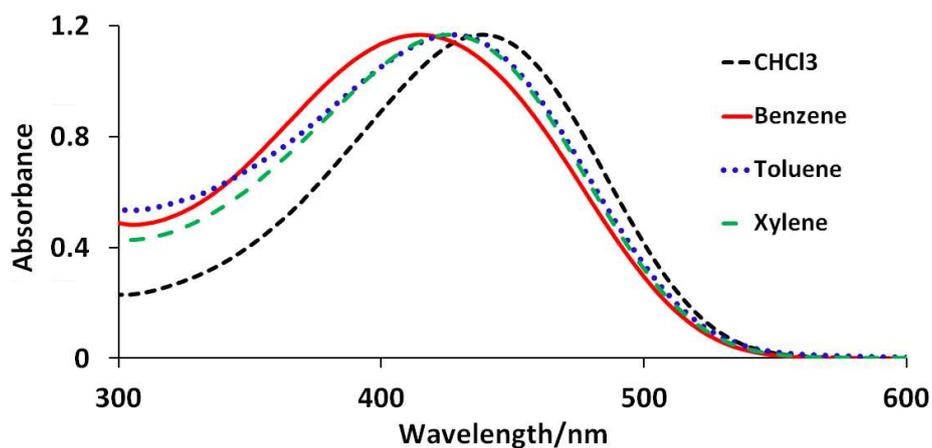


Fig. 2. Uv-vis spectra of P3HT/ CHCl_3 , P3HT/benzene, P3HT/toluene and P3HT/xylene in THF at room temperature

Figure 2 indicates that the absorption maximum ($\lambda_{\max}^{\text{abs}}$) of P3HT/benzene (415 nm), P3HT/toluene (427 nm) and P3HT/xylene (428 nm) blue-shifted about 23 nm, 11 nm and 10 nm respectively, compared with that of P3HT/ CHCl_3 (438 nm), which may be responsible for the appearance difference of P3HTs. Further insight into the effect of aromatic solvents on the structure of resulting P3HTs was acquired by the ^1H NMR analysis of the polymer prepared in benzene (Figure 3).

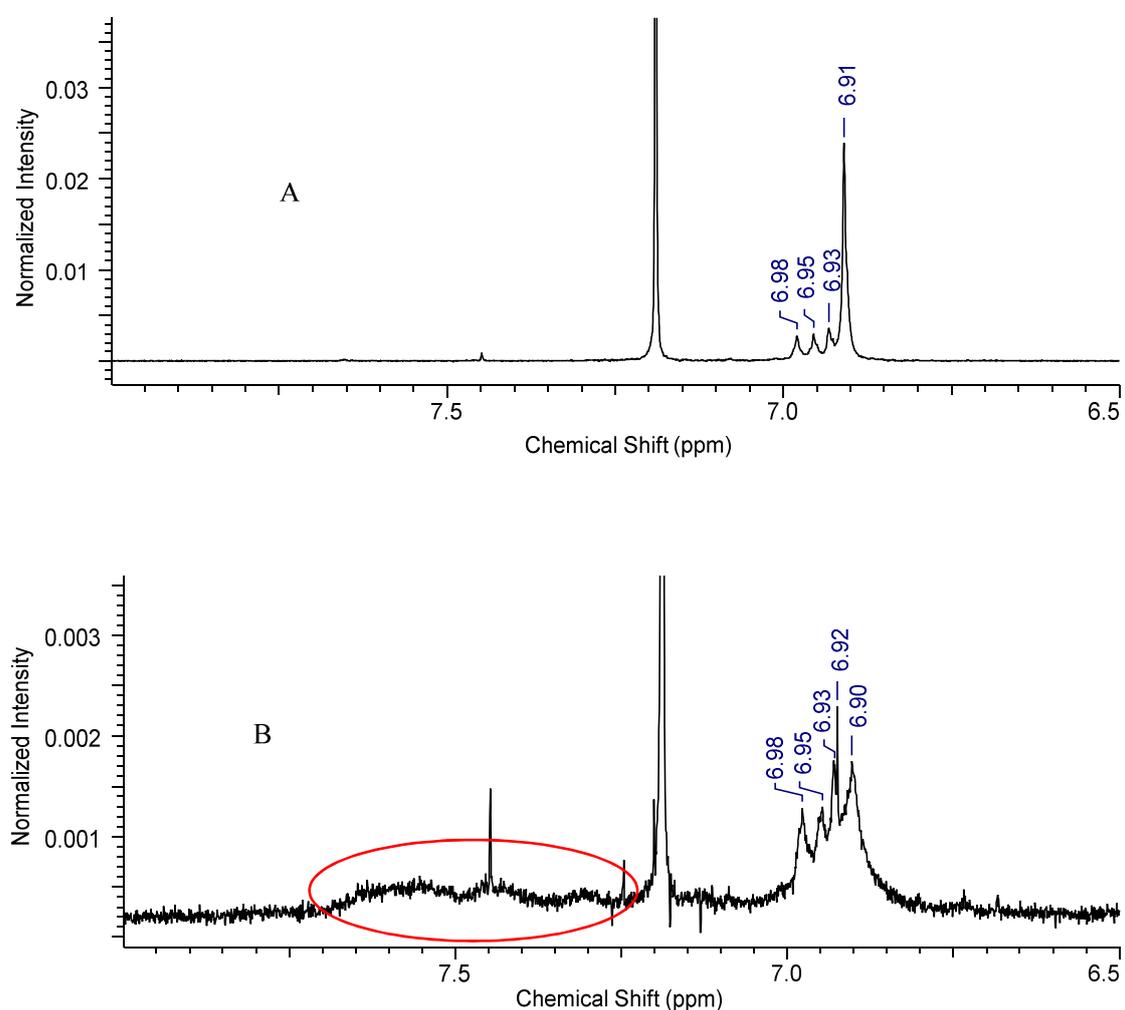


Fig. 3. ^1H NMR spectra of P3HT/ CHCl_3 (A) and P3HT/benzene (B) in CDCl_3 at room temperature

As shown in Figure 3, a comparison of the ^1H NMR spectra of P3HT/ CHCl_3 and P3HT/benzene revealed that new broad peaks in a range from 7.25 ppm to 7.75 ppm appeared in the ^1H NMR spectrum of P3HT/benzene. These new proton signals may be assigned to those protons on benzene rings, most likely due to the incorporation of benzene molecules into the P3HT skeleton because these chemical shifts are almost same as proton signals of terphenyl or phenylene unit of nitrated polyphenylene [11]. The incorporation of benzene content (12mol%) were determined by ^1H NMR via comparison of the integrated intensity of thienylene unit of 3HT (6.9 ppm) and phenylene unit (in a range from 7.25 ppm to 7.75 ppm) in Figure 2. Similar new broad peaks in a range from 7.25 ppm to 7.75 ppm also appeared in the ^1H NMR spectra of P3HT/toluene and P3HT/xylene.

To verify this hypothesis, MALDI-TOF MS (matrix-assisted laser desorption/ionization mass) was adopted for acetone-soluble oligo(3-hexylthiophene)s (O3HTs) in the product synthesized by FeCl_3 in CHCl_3 (O3HTs/ CHCl_3 (A)) and benzene (O3HTs/benzene (B)) for 2 h at 23 °C (Figure 4).

Conventionally, when the polymerization of 3-alkylthiophenes was conducted by FeCl_3 in CHCl_3 for 2 h at 23 °C, the chlorination reaction has occurred [12]. MALDI-TOF MS spectra of (O3HTs/ CHCl_3) shows three or more ion series: $[166n+2\text{H}]^+$, $[166n+\text{H}+\text{Cl}]^+$ and $[166n + 2\text{Cl}]^+$ (Figure 4 (A)). This means that the substitution of terminal proton(s) or some proton(s) at the 4-position of the thiophene ring in the oligomer was substituted with chlorine(s) generated from FeCl_3 .

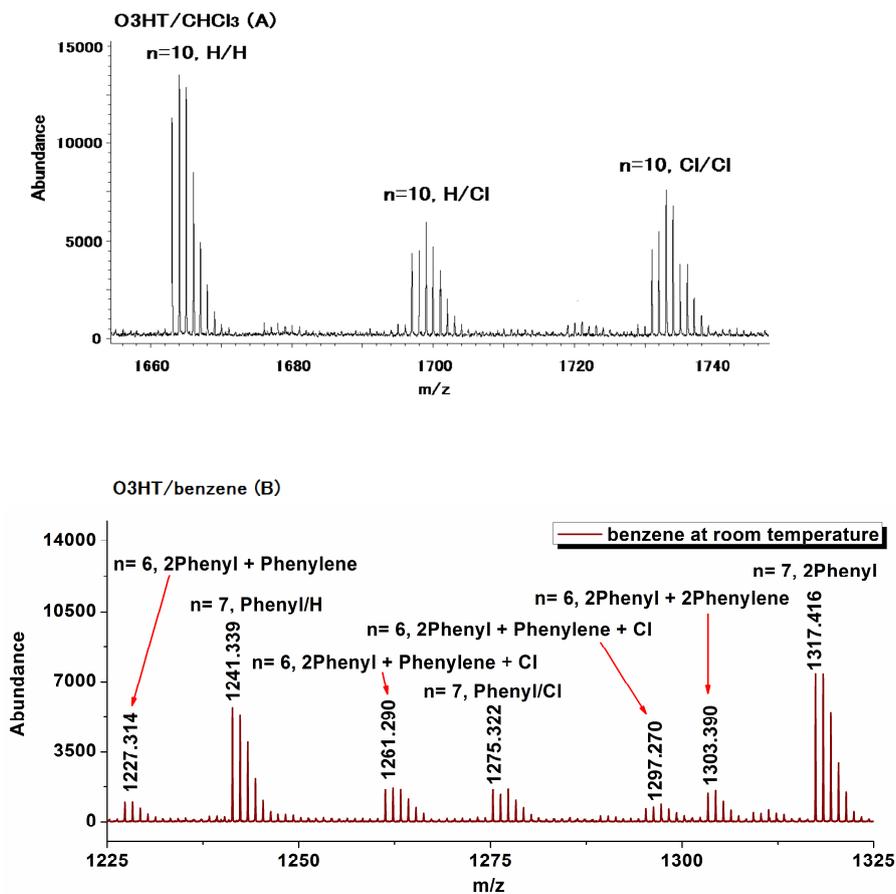


Fig. 4. MALDI-TOF MS spectrum of O3HT/CHCl₃ (A) and O3HTs/benzene (B)
(CCA as the matrix)

To our surprise, common peak series like $[166n+2Cl]^+$, $[166n+H+Cl]^+$ and $[166n+2H]^+$ were not found in the spectrum of O3HTs/benzene (Figure 4 (B)). In contrast, the presence of six novel peak series, $([166n+phenyl+Cl]^+$, $[166n+phenyl+H]^+$, $[166n+2phenyl]^+$, $[166n+2phenyl+phenylene]^+$, $[166n+2phenyl+phenylene+Cl]^+$ and $[166n+2phenyl+2phenylene]^+$ were undoubtedly observed. The appearance of $[166n+phenyl+H]^+$ and $[166n+2phenyl]^+$ peak series strongly indicate that the end groups at the termini of the oligomers are most likely to be phenyl/H or phenyl/phenyl. Moreover, the existence of $[166n+2phenyl+phenylene]^+$ and

$[166n+2\text{phenyl}+2\text{phenylene}]^+$ peak series shows that benzene molecule(s) are also incorporated in the backbone of the oligomers. These oligomers would easily react with each other or with the 3-hexylthiophene or benzene in the presence of FeCl_3 to give a copolymer of 3-hexylthiophene and benzene.

The incorporation of solvent molecule(s) into a polymer main chain was also observed for O3HTs prepared in toluene, xylene, and mesitylene (O3HT/toluene, O3HT/xylene and O3HT/mesitylene, respectively). Different from O3HT/benzene, in O3HT/toluene, just $[166n+2\text{tolyl}]^+$, $[166n+2\text{tolyl}+\text{tolylene}]^+$ and $[166n+2\text{tolyl}+2\text{tolylene}]$ peak series could be clearly assigned. Xylene and mesitylene molecules were also found to exist as the end groups of O3HT/xylene and O3HT/mesitylene, respectively (Figure 5).

The incorporation of benzene molecules into poly(3-hexylthiophene) was found to be heavily affected by the reaction temperature. The rise of the reaction temperature from 0 °C to 23 °C resulted in the evident increase of introduced benzene molecules.

Based on these results, we would explain the large blue shift of the Uv/vis absorption maximum of P3HT/benzene, compared with that of P3HT/ CHCl_3 as follows (scheme 1): Oligothiophene units would be introduced into the three positions (ortho, meta, and para) of a benzene molecule. The incorporation of oligothiophene units into the ortho and meta positions of benzene may deteriorate the effective conjugation length of the resulting copolymer, compared with the oligothiophene units at the para position of benzene, because of the steric repulsion between the incorporated oligothiophene units making the coplanarity of the three units difficult. Similar explanation would be applicable to the blue shift of the absorption maximum of P3HT/toluene and P3HT/xylene.

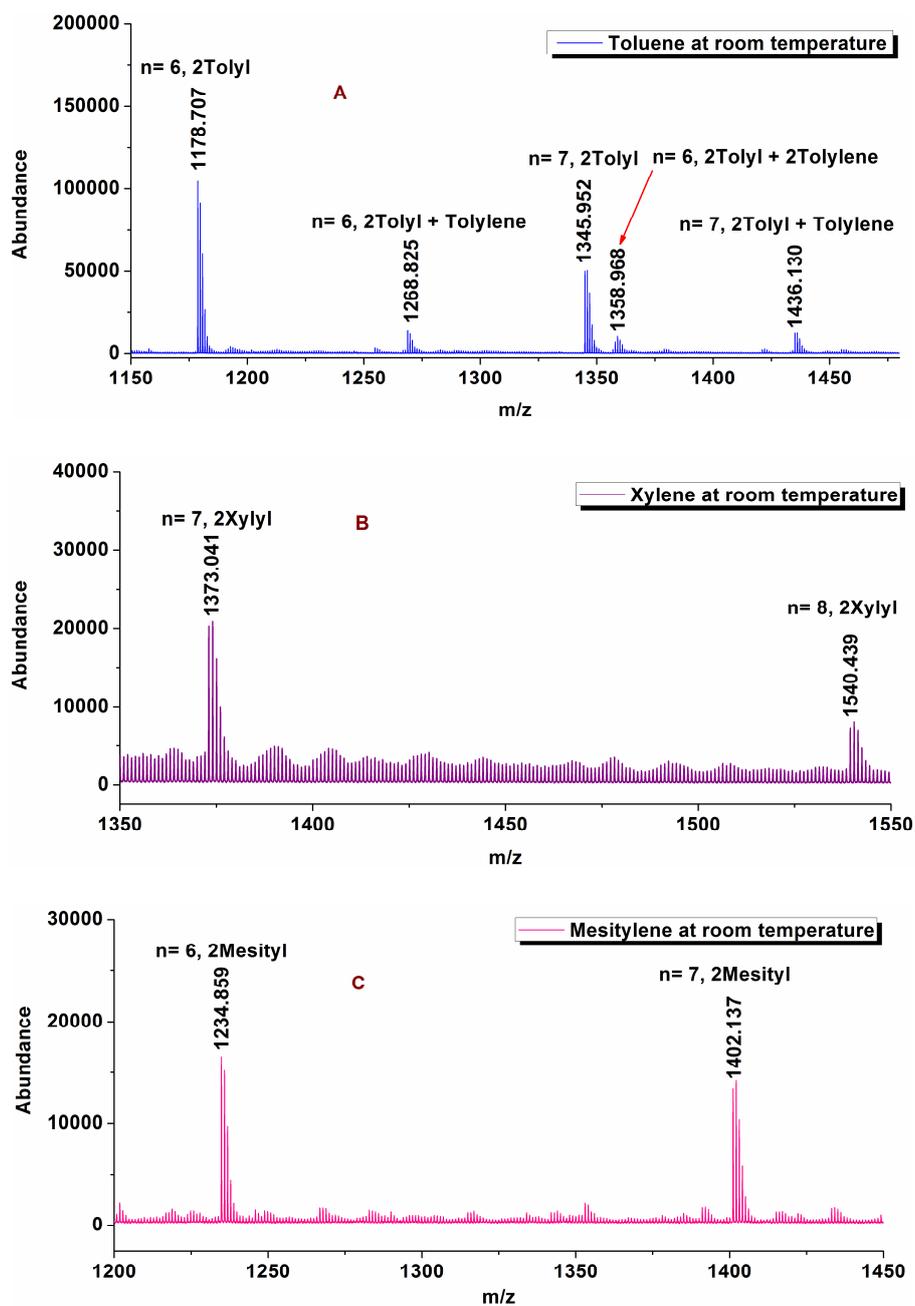
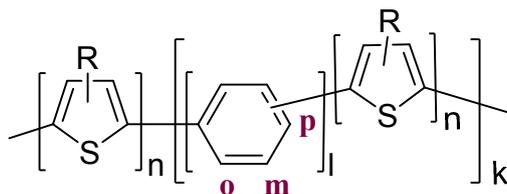


Fig. 5. MALDI-TOF MS spectra of O3HT/toluene (A), O3HT/xylene (B), and O3HTs/mesitylene (C)



Scheme 1. A possible copolymerization mode between 3-hexylthiophene and benzene

To the best of our knowledge, this is the first report about the direct incorporation of aromatic compounds into P3HT backbones. Although the mechanism is still ambiguous, the most plausible mechanism is the radical cation path which means that FeCl_3 pull an electron out of the π electrons of thiophene derivative or benzene derivative, which propagates the polymerization.

(2) Effect of the reaction temperature on the polymerization of 3-hexylthiophene with FeCl_3 in aromatic solvents

The influence of the reaction temperature on the polymerization of 3-hexylthiophene in aromatic solvents was well studied. The results are summarized in Table 1.

The monomer conversion obviously rose up from 45% to 88%, when the reaction temperature for the polymerization of 3-hexylthiophene by FeCl_3 in benzene was elevated from 6 °C to 23 °C; the polymerization was accompanied by the formation of a large amount of cross-linked gel (from 0 % at 6 °C to 33 % at room temperature).

Similar upward tendency in the monomer conversion was also observed, when the polymerizations were conducted in toluene and xylene. However, the significant increase in the yield of acetone-soluble oligomers was found when polymerizations were carried out at 23 °C in toluene or xylene. These results may indicate the less reactivity of these

tolyl- and xylyl-terminated oligomers. Only yellow oily oligomers were obtained by the polymerization of 3-hexylthiophene in mesitylene.

Table 1. Influence of reaction temperatures on the polymerization of 3-hexylthiophene with FeCl₃ in aromatic solvents

| Run | Temp (°C) | Solvent | Yield of acetone-soluble oligomer (wt/wt%) | Yield of polymer (wt/wt%) | Yield of gel (wt/wt%) | Molecular weight of polymer | | |
|-----|--------------|------------|---|---------------------------------|-----------------------------|--------------------------------|--------|-----|
| | | | | | | Mn | Mw | PDI |
| 1 | 6 | Benzene | 6 | 39 | 0 | 53400 | 236000 | 4.4 |
| 2 | 23 | Benzene | 8 | 47 | 33 | 48000 | 254000 | 5.3 |
| 3 | 0 | Toluene | 3 | 34 | 0 | 44200 | 164000 | 3.7 |
| 4 | 23 | Toluene | 24 | 39 | 0 | 15300 | 68500 | 4.5 |
| 5 | 0 | Xylene | 22 | 16 | 0 | 12800 | 22300 | 1.7 |
| 6 | 23 | Xylene | 60 | 11 | 0 | 4100 | 8600 | 2.1 |
| 7 | 0 | Mesitylene | 19 | 0 | 0 | --- | --- | 0 |
| 10 | 23 | Mesitylene | 7 | 0 | 0 | --- | --- | 0 |
| 11 | 0 | Chloroform | 4 | 67 | 0 | 48400 | 161000 | 3.3 |
| 12 | 23 | Chloroform | 3 | 53 | 41 | 117000 | 411000 | 3.5 |

Furthermore the molecular weight of resultant P3THs synthesized in aromatic solvents was also affected by the reaction temperature. The polymerization of 3HT in CHCl₃ has been found to be larger as the molecular weight the polymerization temperature becomes higher. However, elevating the reaction temperature at the polymerizations of 3-hexylthiophene in aromatic solvents produced the formation of polymers with lower

molecular weight and wide molecular weight distributions (PDI) (Table 1, run 1 vs run 2, run 3 vs run 4 and run 5 vs run 6).

(3) Electrical conductivity of P3HT/benzene and P3HT/toluene

Table 2. Conductivity of poly(3-hexylthiophene) synthesized for 2h in the aromatic solvents (doped with iodine)

| Solvent | Benzene | Toluene | Chloroform |
|--------------------|----------------------|----------------------|------------|
| Conductivity(S/cm) | 3.0×10^{-1} | 5.0×10^{-2} | 1.0 |

P3HT/benzene outputted about 0.3 S cm^{-1} , comparable with that of analogue prepared in CHCl_3 (about 1 S cm^{-1}), implying the trivial influence of the incorporation of benzene molecules in a considerably large amount into the resulting polymer main chain on the electrical conductivity of the resulting polymer[13]. Whereas, the introduction of toluene molecules even in a relatively small amount evidently decreased the electrical conductivity of the resulting polymer to about 0.05 S cm^{-1} , lowering about one order of magnitude.

Conclusion

The polymerization of 3-hexylthiophene with FeCl_3 was performed in aromatic solvents. By MALDI-TOF MS and ^1H NMR analyses, the incorporation of the aromatic solvent molecules such as benzene, toluene, xylene and mesitylene into the resultant poly(3-hexylthiophene)s was confirmed for the first time. More amount of benzene (12mol%)

was incorporated into the polymer main chain, compared with toluene, xylene and mesitylene molecules, possibly forming a copolymer of 3-hexylthiophene and benzene. When the polymerization was conducted in mesitylene, only a small amount of oligomer was produced. It seems that the reactivity of mesitylene with FeCl₃ might be higher than that of 3-hexylthiophene with FeCl₃. On the other hand, the obvious increase in the yield of acetone-soluble oligomers with elevating the reaction temperature for the polymerizations of 3-hexylthiophene with FeCl₃ in toluene and xylene indicated the low polymerization activity of the generated tolyl- and xylyl-terminated oligomers. Compared with P3HT prepared in toluene, P3HT obtained by the reaction in benzene outputted better electrical conductivity (about 0.3 S cm⁻¹), which is comparable to that of P3HTs prepared in CHCl₃.

Reference

- [1] Cheng, C. C., Chu, Y. L., Huang, P. H., Yen, Y. C., Chu, C. W., Yang, A. C. M., Ko, F. H., Chen, J. K., Chang, F. C. (2012) Bioinspired hole-conducting polymers for application in organic light-emitting diodes. *J. Mater. Chem.*, 22 (35): 18127-18131. DOI: 10.1039/C2JM32665E
- [2] Lechmann, M., Koll, D., Kessler, D., Theato, P., Tremel, W., Gutmann, J. (2010) Comparison of Hybrid Blends for Solar Cell Application. *Energies*, 3 (3): 301-312. doi:10.3390/en3030301
- [3] Urien, M., Wantz, G., Cloutet, E., Hirsch, L., Tardy, P., Vignau, L., Cramail, H., Parneix, J. P. (2007) Field-effect transistors based on poly(3-hexylthiophene): Effect of impurities. *Org. Electron.*, 8 (6): 727-734. DOI: 10.1016/j.orgel.2007.06.003

- [4] Izuhara, D., Swager, T. M. (2011) Poly(3-hexylthiophene)-block-poly(pyridinium phenylene)s: Block Polymers of p- and n-Type Semiconductors. *Macromolecules.*, 44 (8): 2678-2684. DOI: 10.1021/ma102566u
- [5] (a) Loewe, R. S., Ewbank, P. C., Liu, J., Zhai, L., McCullough, R. D. (2001) Regioregular, Head-to-Tail Coupled Poly(3-alkylthiophenes) Made Easy by the GRIM Method: Investigation of the Reaction and the Origin of Regioselectivity. *Macromolecules.*, 34 (13): 4324-4333. DOI: 10.1021/ma001677+ (b) Chen, T. A., Rieke, R. D. (1992) The first regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) and a regiorandom isopolymer: nickel versus palladium catalysis of 2(5)-bromo-5(2)-(bromozincio)-3-hexylthiophene polymerization. *J. Am. Chem. Soc.*, 114 (25): 10087-10088. DOI: 10.1021/ja00051a066 (c) Yamamoto, T., Sanechika, K., Yamamoto, A. (1980) Preparation of thermostable and electric - conducting poly (2, 5 - thienylene). *J. Polym. Sci. B Polym. Lett. Ed.*, 18(1): 9-12.
- [6] Pang, Y., Li, X., Ding, H., Shi, G., Jin, L. (2007) Electropolymerization of high quality electrochromic poly(3-alkyl-thiophene)s via a room temperature ionic liquid. *Electrochim. Acta.*, 52(20): 6172-6177. DOI: 10.1016/j.electacta.2007.04.015
- [7] Sugimoto, R., Takeda, S., Gu, H. B., Yoshino, K. (1986) Preparation of soluble polythiophene derivatives utilizing transition metal halides as catalysts and their property. *Chem. Express.*, 1(11): 635-638.
- [8] Kovacic, P., Kyriakis, A., (1963) Polymerization of aromatic nuclei. II. Polymerization of benzene to p-polyphenyl by aluminum chloride-cupric chloride. *J. Am. Chem. Soc.*, 85: 454-458. DOI:10.1021/ja00887a019

[9] Yamamoto, T., Yamamoto, A. (1977) A novel type of polycondensation of polyhalogenated organic aromatic compounds producing thermostable polyphenylene-type polymers promoted by nickel complexes. *Chem. Lett.*, (4): 353-356. DOI:10.1246/cl.1977.353

[10] (a) Kovacic, P., Koch, W., (1963) Polymerization of benzene to p-polyphenyl by ferric chloride. *J. Org. Chem.*, 28 (7): 1864-1867. DOI:10.1021/jo01042a031 (b) Niemi, V. M., Knuutila, P., Osterholm, J. E., Korvola, J., (1992) Polymerization of 3-alkylthiophenes with ferric chloride. *Polymer*, 33 (7): 1559-1562. DOI:10.1016/0032-3861(92)90138-M (c) Andersson, M. R., Selse, D., Berggren, M., Jarvinen, H., Hjertberg, T., Inganas, O., Wennerstrom, O., Osterholm, J. E., (1994) Regioselective polymerization of 3-(4-octylphenyl)thiophene with FeCl₃. *Macromolecules* 27(22):6503-6506. DOI:10.1021/ma00100a039 (d) Barbarella, G., Zambianchi, M., DiToro, R., Colonna, M., Larrosi, D., Goldoni, F., Bongini, A., (1996) Regioselective Oligomerization of 3-(Alkylsulfanyl)Thiophenes with Ferric Chloride. *J. Org. Chem.*, 61: 8285-8292. DOI:10.1021/JO960982J

[11] Yamamoto, T., Abe, M., Wu, B., Choi, B-K., Harada, Y., Takahashi, Y., Kawata, K., Sasaki, S., Kubota, K. (2007) Basic Information on Nonsubstituted Polyphenylene and Polythiophene Obtained via Solubilization of Polymers. *Macromolecules* 40 (15) 5504-5512. DOI:10.1021/ma0626517

[12] Liu, Y., Nishiwaki, N., Saigo, K., Sugimoto, R. (2013) Kinetics Study on 3-Hexylthiophene Polymerization with Iron(III) Chloride. *Bull. Chem. Soc. Jpn.*, 86 (9): 1076-1078. DOI :10.1246/bcsj.20130128

[13] Zhu, H, F., Liu, C, C., Song, H, J., Xu, J, K., Kong, F, F., Wang, J, M. (2014)
Thermoelectric Performance of Poly(3-hexylthiophene) Films Doped by Iodine Vapor
with Promising High Seebeck Coefficient. *Electron. Mater. Lett.*, 10(2): 427-431.
DOI :10.1007/s13391-013-3150-y

Figure and Table legends

Figure 1. The appearance of P3HT/CHCl₃ and P3HT/benzene

Figure 2. Uv-vis spectra of P3HT/CHCl₃, P3HT/benzene, P3HT/toluene and P3HT/xylene in THF at room temperature

Figure 3. ¹H NMR spectra of P3HT/CHCl₃ (A) and P3HT/benzene (B) in CDCl₃ at room temperature

Figure 4. MALDI-TOF MS spectrum of O3HT/CHCl₃ (A) and O3HTs/benzene (B)) (CCA as the matrix)

Figure 5. MALDI-TOF MS spectra of O3HT/toluene (A), O3HT/xylene (B), and O3HTs/mesitylene (C)

Scheme 1. A possible copolymerization mode between 3-hexylthiophene and benzene

Table 1. Influence of reaction temperatures on the polymerization of 3-hexylthiophene with FeCl₃ in aromatic solvents

Table 2. Conductivity of poly(3-hexylthiophene) synthesized for 2h in the aromatic solvents (doped with iodine)