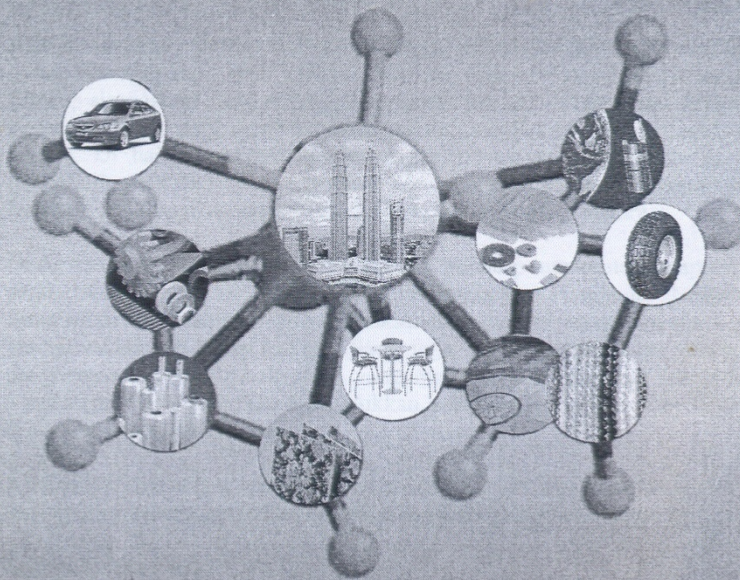


SIMPOSIUM POLIMER KEBANGSAAN 2005

Hotel Residence, UNITEN
23-24 Ogos 2005

PROSIDING



Penyunting:

Dr. Ishak Ahmad

Dr. Rozaidi Rasid

En. Ramli Ismail @ Mamat



Anjuran:

Fakulti Sains & Teknologi,
Universiti Kebangsaan Malaysia



"Penyelidikan Polimer Teras Pembangunan Industri Negara"



*KATA-KATA ALUAN
PENGKERUSI PPSKTM*



Assalamualaikum wrth dan salam sejahtera,

Saya bersyukur ke hadrat Allah s.w.t kerana dengan izinNya Simposium Polimer Kebangsaan ke-5 (NSPM 2005) dapat diadakan seperti dirancang. Bagi pihak Pusat Pengajian Sains Kimia dan Teknologi Makanan (PPSKTM) saya mengucapkan syabas dan tahniah kepada Jawatankuasa Simposium yang telah berusaha memberikan komitmen yang begitu tinggi bagi menjayakan seminar ini walaupun sibuk dengan tugas dan kewajipan lain.

Saya mengambil kesempatan ini untuk mengucapkan setinggi-tinggi penghargaan kepada YBhg. Prof Dato' Dr. Mohd Salleh Mohd Yasin di atas kesudian beliau untuk merasmikan simposium ini. Saya juga mengucapkan ribuan terima kasih kepada Fakulti Sains dan Teknologi (UKM), para penyelidik dan wakil-wakil syarikat di atas segala sokongan dan bantuan yang diberikan kepada Jawatan kuasa penganjur untuk menjayakan NSPM 2005 ini.

NSPM 2005 merupakan perhimpunan bagi menemukan sebilangan besar para ilmuan dalam bidang polimer dari pelbagai institusi dan industri di Malaysia. Penglibatan ramai penyelidik daripada beberapa universiti dan institusi penyelidikan dalam simposium ini merupakan suatu platform yang begitu baik bagi memperkembangkan penyelidikan polimer dan bidang-bidang yang berkaitan. Di samping itu, simposium ini juga diharapkan dapat menggalakkan lebih banyak penyelidikan bersama dapat dilakukan dalam bidang polimer.

Saya juga berharap semoga simposium ini akan diteruskan pada masa depan.

Akhir sekali saya mengucapkan selamat berseminar kepada semua peserta.

Sekian, terima kasih.

*Prof. Madya Dr. Musa Ahmad
Pengerusi PPSKTM*

JADUAL PEMBENTANGAN SIMPOSIUM POLIMER KEBANGSAAN KE-5

SELASA - 23 OGOS 2005

DEWAN MUSYTARI

SESI IA

| MASA | TAJUK |
|---------------|---|
| 11.00 – 11.15 | Preliminary Study Of Fly Ash Filled NR/LLDPE Blends, Dr. Azizan Ahmad |
| 11.15 – 11.30 | Thermal Expansion and Flexural Properties of Particulate Fillers Filled Epoxy Composite, Teh Pei Leng |
| 11.30 – 11.45 | Kenaf-Low Density Polyethylene (LDPE) Composite, Mohd. Saffaridha Mohamad Soib |
| 11.45 – 12.00 | The effect of oil palm empty fruit bunch as filler on the mechanical properties of polyurethane composites, Ilyati Mohamad Razali |

SESI IIA

| | |
|-------------|---|
| 2.40 – 2.55 | Modification Of The Preparation Bisilylated Tetrathiophene By The Coupling Method With Chloromethoxysilane, Shahrul Ismail |
| 2.55 – 3.10 | Sifat kehidrofilikan ko-polimer metakrilik-akrilik dan kesannya ke atas pemegunan enzim tirosinase untuk biopenderia fenol, Sharina Abu Hanifah |
| 3.10 – 3.25 | Synthesis And Characterisation Of Acrylonitrile-Acrylic Acid-Itaconic Acid Terpolymer For Production Of Carbon Fiber, Syara Kassim |
| 3.25 – 3.40 | Kopolimer Metilmetakrilat terfluorin sebagai bahan penyalut rintang ai, Nik Rohaida Wan Daud |
| 3.40 – 3.55 | Preparation of carboxylated Poly(NIPAM) by using AIBN as initiator and conjugation of ligand to the polymer with N-hydroxy Secinimide, Syaubari |
| 3.55 – 4.10 | Synthesis of polyurethane/clay intercalated nanocomposites based on palm oil polyol, Teuku Rihayat |

MODIFICATION OF THE PREPARATION BISILYLATED TETRATHIOPHENE BY THE COUPLING METHOD WITH CHLOROMETHOXYSILANE

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ABSTRACT

Tetrathiophene compound in this decade currently are explored especially as the precursor in the new material production that had the competitive characteristics matter, example in case of: coating, optic, art and ceramic modelling, both as nanocomposite or nanostructure. The preparation of tetrathiophene was done in the laboratory by conventional of Grinard method from its monomer, afterwards was continued with the method coupling used CuCl_2 anhydrate, with results rendements of 8.6 %. Conventionally, the preparation of silylated tetrathiophene was done directly with bromination from N-bromosuccinimide (NBS) and substituted of brom that was linked with chloromethoxysilane in hexane. Whereas the modification of the silylated terthiophene preparations did the addition reaction mechanism of the double bond in tetrathiophenes with lithium (LiAlH_4) in hexane. Afterwards the intermediate results of lithiation are substituted with methoxysilane radical of chloromethoxysilane $(\text{CH}_3\text{O})_3\text{-SiCl}$ in the pressure of 0.1 mmBar or 75 mmHg. The silylated tetrathiophene could be received with farctional distillation until temperature of 273 °C. Results characterization of the tetrathiophene silylated or the bis(trimethoxysilyl)tetrathiophene by this modification was carried out with NMR spectroscopy's of ^1H , ^{13}C , and ^{29}Si , that showed with confidentially of high purity, and so from three times preparation it was produced of average rendement significantly more higher than the conventional method.

Keyword: tetrathiophene, bis(trimethoxysilyl)tetrathiophene, modification method with lithiation.

I. INTRODUCTION

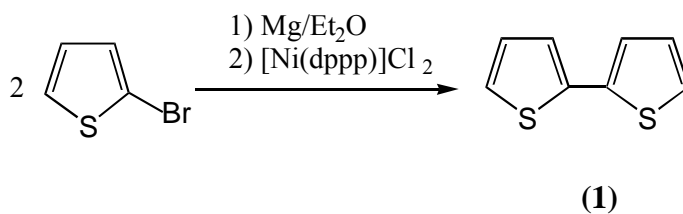
Oligothiophenes is molecules rich in electrons which very interesting properties in the chemistry of materials. These properties are: 1) a high thermal stability¹, 2)

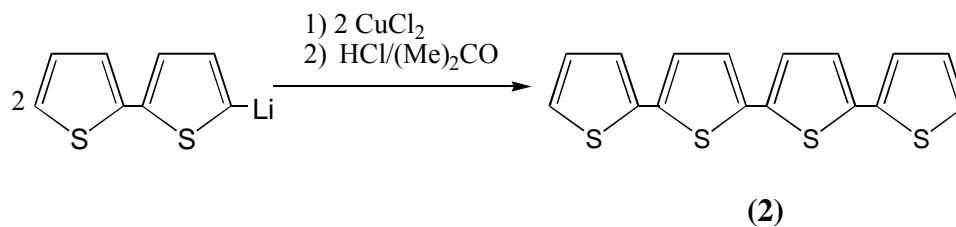
semiconductive properties¹, of the non-linear optics, electrochromic and non-linear optics and electrochimic, 3) the formation of charge transfert complexes with the TCNQ.^{2,3}

The colour of oligothiophenes varies according to the length of the chain, being colorless for the bithiophene^{1,4-6} orange for the terthiophene^{2,4,6} and yellow for the tetrathiophene.^{3,7,8} The terthiophene was synthesized for the first time in 1941^{9,10} and in 1945. Zechmeister observed that this compound exists naturally in the marigolds.^{11,12}

Oligothiophenes^{1, 11 2, 4, 11, 12} and^{36, 8} was synthesized by coupling of the thiophene and catalysed by complexes of metals transitions. The tetrathiophene compound³ was synthesized by Kagan¹³ in 1988 by the reaction of coupling of Kumada. Oligothiophenes with longer chains were prepared by oxidatif coupling by-products of 2,2'-bithiophene⁷ and the polymerisation by electrochemistry⁸ to obtain of tetrathiophene. The bisilylation in position of (2,5') of these compounds was made by coupling of their lithiation products with the chlorotrimethoxysilane.

The synthesis of 2,2'-bithiophene was realized by coupling of the magnesium with the 2-bromothiophène in the presence of the nickels chloride catalyst; 1,3-bis(diphenylphosphino)propanenickel(II), [(Ni(dppp)Cl₂)] according to condition of the reaction of the Kumada. The bithiophene compound is obtained in the form of crystals transparent green. Then synthesis of tetrathiophene by the conventional methode are coupling of thiophene by catalyst of the CuCl₂.





The dilithiation of three compounds thiopheniques 1, 2, 3 was realized in room temperature by treatment with n-BuLi. The silylation of these dilithiens is made in -10°C by reaction with equivalents 2 of chlorotrimethoxysilane. Compounds: 2,5-bis(trimethoxysilyl)thiophene⁴, 2,5'-bis(trimethoxysilyl)bithiophene⁵, 2,5''-bis(trimethoxysilyl)-terthiophene⁶, and 2,5'''-bis(trimethoxysilyl) tétrathiophène⁷ can be produced by the modified of coupling methode in addition of lithium.

The preparation of tetrathiophene was done in the laboratory by conventional of Grinard method from its monomer, afterwards was continued with the method coupling used CuCl_2 anhydrate, with results rendements of 8.6 %. Conventionally, the preparation of silylated tetrathiophene was done directly with bromination from N-bromosuccinimide (NBS) and substituted of brom that was linked with chloromethoxysilane in hexane. Whereas the modification of the silylated terthiophene preparations did the addition reaction mechanism of the double bond in tetrathiophenes with lithium (LiAlH_4) in hexane. Afterwards the intermediate results of lithiation are substituted with methoxysilane radical of chlorome-thoxysilane $(\text{CH}_3\text{O})_3\text{-SiCl}$ in the pressure of 0.1 mmBar or 75 mmHg. The silylated tetrathiophene could be received with farctional distillation until temperature of 273°C .

II. MATERIALS AND METHODE

General conditions:

All the manipulations were realized under 1 atmosphere in inert condition (argon) in tubes of Schlenk or balloons, by using the vacuum technique. The solvents are dried and distilled under atmosphere of argon just before use (Table-1).

Table-1: Drying agents used in the drying of solvents

| Solvants | Agent desséchant |
|-------------------|--|
| THF | CaH ₂ puis Na/ Benzophénone |
| Et ₂ O | Na/Benzophénone |
| Hexane | CaH ₂ |
| Pentane | CaH ₂ |

The acetone, ethanol, and DMF are commercial quality products analytic and are conserved under argon. The chloride of the copper (CuCl₂) is shaken during six hours, then dried in the dimethylchlorosilane under vacuum and conserved under argon. The bis(trimethosilyl)tetrathiophene is stored in Schlencks excicators under the inert condition of argon.

Melting points were determined by apparatus of Gallenkamp, and are not corrected. Mass-spectres were recorded on spectrometers Jeol JMS-D100 and Jeol JMS-SX102. Spectres of infrared were used a Perkin Elmer-1600 in Transformed by Fourier. The spectres of RMN in solution were recorded on the NMR Bruker DPX200 Model for analysis of ¹H, ¹³C and Bruker AC200 Model for analysis of ²⁹Si.

The values of the chemical displacement (δ) are expressed in ppm, those of the constants of couplings in Hertz. The signals are indicated by letters as: **s** (singlet), **d** (doublet), **t** (triplet), **m** (multiplet) and **Ar** (Aromatic).

Syntheses of the : 2,2'-Bithiophene, (2)

In a tricol provided with a cooler, with a mechanical agitator and with a light bulb with bromine, we introduce under argon 12.5 g of magnesium (0.5 mole) into 70 mL of diethylether. The magnesium is covered by a small quantity of ether. After activation by addition of 2-bromothiophene, a solution of 81.52 g (0.5 mole) of 2-bromothiophene in 250 mL of diethylether is added. Be cool the balloon with some water. In the end addition, the environs reaction is dark colors. After 2 hours of excitement with room temperature, a solution of 81.52 g (0.5 mole) of 2,5-dibromothiophène and 2.72 g (1 % mole) of the catalyst [Nor (dppp) Cl₂] in 150 mL of diethyl ether is added in 0°C on the magnesium. The environs of the reaction take at a black color. After 2 hours of excitement in the ether, the solvent is evaporated and the black residue is covered by excess of ether. The etherize phase is washed in the distilled water (3 x 150 mL), dried on MgSO₄, filtered then evaporated, finally the filtrate are distilled on 273 °C.

Syntheses of the 2, 2': 5', 2'': 5'', 2''': 5''', 2''''-Tetrathiophene, (2)

In Schlenk provided with a cooler, with a magnetic stirrer, and introduce under argon 3.32 g of bithiophene (2×10^{-3} mole) into 250 mL of THF, then add in 11.0 mL (22×10^{-3} mole) of n BuLi (2.0 M) and shake 1 hour in temperature of 70°C. Add 5.38 g of anhydrate CuCl₂ (40×10^{-3} mole) and shake during 18 hours in room temperature. Add

then a solution of HCl to have an environment of pH = 4 - 5. The yellow products is isolated by filtration and washed with HCl 4N in the acetone.

Synthese of the 2,5'''-bis(trimethoxysilyl)tetrathiophene, (3)

In the Schlenk of 100 mL provided with a cooler, with a mechanical agitator, we introduce 50 mL of Et₂O and 1.5 g of tetrathiophene in room temperature 3 (4.55×10^{-3} mole), and shake to obtain one clear yellow solution. We add to 4.55 mL of BuLi (n-buthyllithium 2.0 M in the hexane, 9.09×10^{-3} mole), the solution becomes yellow. When the addition is ended, and shaken during one hour. Then add in -78°C, 1.66 mL of chloromethoxysilane (9.09×10^{-2} mole). And shake during 15 hours under argon. Finally washed with hexane, and obtain a clear yellow solution which is evaporated under vacuum to give a dark yellow liquid. The liquid is washed in the pentane (3 x 150 mL), and evaporate in the pentane under vacuum, dried the residue and extracted in 100°C.

III. RESULT AND DISCUSSION

Product of the 2,2'-Bithiophene (1):

After distillation, obtained of 50.60 g (0.304 mole, 60.9 %) of blue product (1). The melting point (F) = 32.2 °-33°C (Litt.: 33-34°C)^{6,15}. Characterization of RMN ¹H (δ ppm 200 MHz, CDCl₃): 7.09 - 7.31 (3 H, m). RMN ¹³C (δ ppm CDCl₃): 124.23; 124.82; 128.24; 137.87.

An then the 2,2; 5',2"; 5",2'''-tétrathiophene compound is obtained by coupling in -70°C from the lithiathion of 2,2'-bithiophene-bithiophene in the presence of 2

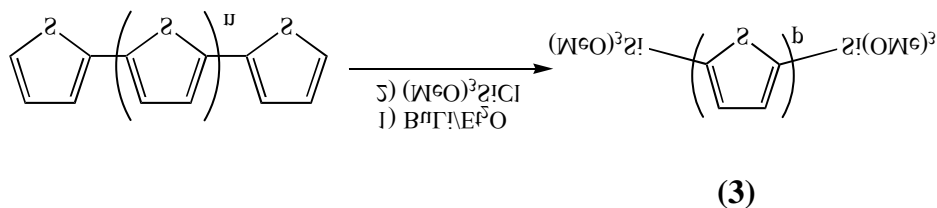
equivalents of cuprum chloride anhydrate is obtained in the form of yellow powder with rendement of 55 %.

Product of the 2, 2': 5', 2'': 5'', 2'''-Tétrathiophene (2):

The product is dried under vacuum on P₂O₅ for obtain yellow powder product 2.23 g (5.3 x 10⁻³mole, 55 %) . Characterization : melting point have 212 ° - 212.2°C (litt. 212 °-213°C).⁸ RMN ¹H (δ ppm 200 MHz, CDCl₃): 7.07 (2 H, dd); 7.12 (2 H, d); 7.24 (2 H, m); 7.29 (2 H, dd). RMN ¹³C (δ ppm 200 MHz, CDCl₃): 124.179; 124.809; 128.330; 136.743; 137.

Preparation of compounds thiophene bisilylated⁴⁻⁷

The preparation of the 2, 5-bis(trimethoxysilyl)thiophene was realized by silylation of the magnesium of the 2,5-dibromothiophene with the chloromethoxysilane. The product compound (3) is obtained 0.3 g (11.6 %) in the form of a yellow viscous.



Characterization by RMN

The spectres of RMN of ¹H, ¹³C and ²⁹Si terthiophène bisilylated^{6,3,11} indicated in figures I-1, I-2 and I-3.

The spectre of RMN of ¹H shows a singlet in 3.70 ppm for methoxy grouping. The aromatic protons apparait as a singlet in 7.18 ppm, and a doublet-doublet in 7.36 ppm. RMN ¹H (δ, 200 MHz, CDCl₃): 3.65 (18H,s); 7.24; 7.27; 7.30; 7.33 (8H, m).

RMN ^{13}C (δ , 200 MHz, CDCl_3): 51.43; 124.18 ; 124.80 ; 128.35; 136.78; 139.50.

RMN ^{29}Si (δ , CDCl_3) : -58.26.

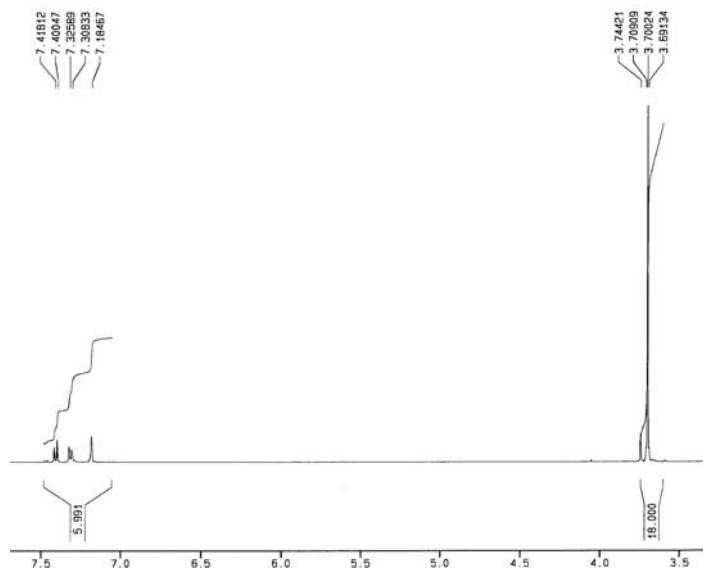


Figure I-1: spectre RMN of ^1H of 2,5"-bis(triméthoxysilyl)tetrahiophene

The spectre of RMN of the ^{13}C of (**3**) shows a singlet in 50.7 ppm for C of the methoxy groups, C aromatic apparait in 124.8, 1245.0 and 125.0 ppm.

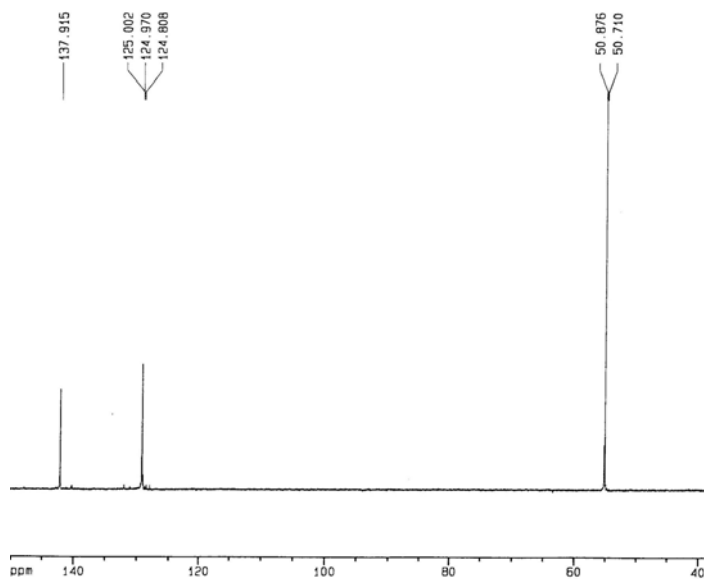


Figure I-2: Spectre RMN ^{13}C of 2,5"-bis(triméthoxysilyl)tetrahiophene

The spectre RMN of ^{29}Si of 2,5"-bis(trimethoxysilyl)tetrathiophene (3), show corespondant peak of (-OMe)₃ in - 58.3 ppm (**Figure I-3**).

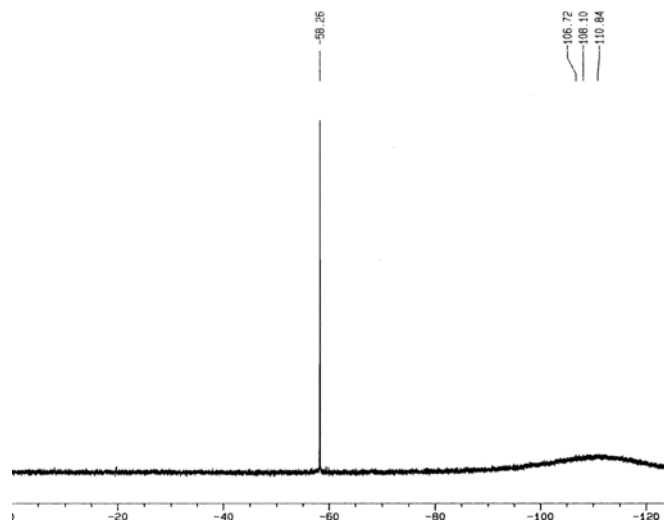


Figure I-3: spectre RMN of ^{29}Si of 2,5"-bis(trimethoxysilyl)terthiophène (3)

IV. CONCLUSION

Results characterization of the tetrathiophene silylated or the bis(trimethoxysilyl)tetrathiophene by this modification was concluded that characterization carried out with NMR spectroscopy's of ^1H , ^{13}C , and ^{29}Si , showed that with confidentiality of high purity, and so from three times preparation it was produced of average rendement significantly more higher than the conventional method.

V. ACKNOWLEDGMENT

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