THE STUDY OF POLY((M-PHENYLENEVINYLENE)-CO-(2,5-DIOCTOXY-P-PHENYLENE)VINYLENE) (PMPV) AS SENSING MATERIALS TO DETECT OXYGEN GAS.

TEO CHIN TECK

FAKULTI SAINS DAN TEKNOLOGI
KOLEJ UNIVERSITI SAINS DAN TEKNOLOGI MALAYSIA

2005

THE STUDY OF POLY(1,3-PHENYLENE-1,2-DI(*p*-METHOXYPHENYL)VINYLENE) (*m*-PPV-MP) AS SENSING MATERIALS TO DETECT OXYGEN GAS.

By

TEO CHIN TECK

Research Report submitted in partial fulfillment of
the requirements for the degree of
Bachelor of Science (Chemical Science)

Department of Chemical Science
Faculty of Science and Technology

JABATAN SAINS KIMIA
FAKULTI SAINS DAN TEKNOLOGI
KOLEJ UNIVERSITI SAINS DAN TEKNOLOGI MALAYSIA

PENGAKUAN DAN PEGESAHAN LAPORAN PROJEK PENYELIDIKAN I DAN II

Adalah ini diakui dan disahkan bahawa laporan penyelidikan bertajuk: The Study of Poly(1,3-phenylene-1,2-di (*p*-methoxyphenyl)vinylene) (*m*-PPV-MP) As Sensing Materials To Detect Oxygen Gas oleh Teo Chin Teck, No. Matrik UK 6803 telah diperiksa dan semua pembetulan yang disarankan telah dilakukan. Laporan ini dikemukakan kepada Jabatan Sains Kimia sebagai memenuhi sebahagian daripada keperluan memperolehi Ijazah Sarjana Muda Sains Kimia. Fakulti Sains dan Teknologi, Kolej Universiti Sains dan Teknologi Malaysia.

Disahkan oleh:

Penyelia Utama

Nama: Puan Faizatul Shimal Binti Mehamod

Cop Rasmi: FAIZATUL SHIMAL MEHAMOD
Pensyarah
Jabatan Sains Kimia
Fakulti Sains dan Teknologi
(KUSTEM)
Mengabang Telipot
21030 Kuala Terengganu.

Tarikh: 6/4/05

Ketua Jabatan Sains Kimia

Nama: Prof. Madya Dr. Ku Halim Ku Bulat

Cop Rasmi: PROF. MADYA DR. KU HALIM KU BULAT
Ketua
Jabatan Sains Kimia
Fakulti Sains dan Teknologi
Kolej Universiti Sains dan Teknologi Malaysia
21030 Kuala Terengganu.
Tel: 09-6683257

Tarikh: 6 April 2005

ACKNOWLEDGEMENT

I would like to express my deepest gratitude and appreciation to my supervisor, Madam Faizatul Shimal binti Mehamod for her great support, valuable advice, encouragement, guidance and patience in ensuring that I have successfully completed my final year project. I would also like to take this opportunity to thank Mr. Ruzeman bin Abdul Manaf from the analytical laboratory, Mr. Mohd Jamaluddin Jusoh and Mohd Tarmizi Manaf from Organic Laboratory for their guidance and assistance in helping me to operate the analytical instruments. My most sincere thanks are dedicated to my project colleagues Lee Ting Ting, Poon Che Wei, Masturina and Hajar for their support, co-operation and understanding. Finally, I would like to thank my family for all of their encouragement, care and financial support given to me during my three years study at Universiti College of Sience and Technology Malaysia (KUSTEM), Terengganu.

TABLE OF CONTENTS

		Pages
APPROVAL FORM		ii
ACKNOWLEDGEMENT		iii
TABLE OF CONTENTS		iv
LIST OF TABLES		viii
LIST OF FIGURES		ix
LIST OF ABBREVIATIONS AND SYMBOLS		xi
LIST OF APPENDIXES		xiii
ABSTRAK		xiv
ABSTRACT		xv
CHAPTER 1	**INTRODUCTION**	
1.1	Introduction	1
1.2	Poly(arylene vinylene), PAV As Sensing Materials	3
1.3	Poly(1,3-phenylene-1,2-di(*p*-methoxyphenyl)vinylene) (*m*-PPV-MP)	4
1.4	Sensor	5
1.5	Objectives	7

CHAPTER 2 LITERATURE REVIEW

2.1	Introduction of Basic Polymerization Process	8
	2.1.1 Condensation Polymerization	8
	2.1.2 Addition Polymerization	9
2.2	Conjugated Polymer	10
2.3	Poly(arylene vinylene), PAV	11
	2.3.1 Friedel-Crafts Reaction	14
	2.3.2 Mechanism For The Friedel-Crafts Reaction	16
	2.3.3 McMurry Coupling Reaction	19
	2.3.4 Mechanism For McMurry Coupling Reaction	21
2.4	Oxygen Gas	23
2.5	Discovery And Development of Oxygen Gas Sensors	24
2.6	Luminescence	26
2.7	The Principles of Fluorescence Quenching	29

CHAPTER 3 METHODOLOGY AND MATERIALS

3.1	Materials	33
3.2	Apparatus And Analytical Instrument	34
3.3	Preparation of Poly(1,3-phenylene-1,2-di (*p*-methoxyphenyl)vinylene) (*m*-PPV-MP) Solution	35
3.4	Characterization of *m*-PPV-MP polymer	36
	3.4.1 Fourier Transform Infrared Spectrometer (FTIR)	36
	3.4.2 UV-Visible Absorption Spectroscopy	36
	3.4.3 Thermogravimetric Analysis (TGA)	37

	3.4.4	Differential Scanning Calorimetry (DSC)	37
	.4.5	Fluorescence Spectrophotometer	37
3.5		Characterization of *m*-PPV-MP Solution As Sensing Material	38
	3.5.1	Fluorescence Spectrum	38
	3.5.2	Regenerative Testing	39
	3.5.3	Photostability Study	39
	3.5.4	The Reproducibility And Repeatability of Sensing Reagent Towards O_2 Gas	40
	3.5.5	The Study of Steady-state Response Towards O_2 Gas	41
	3.5.6	The Effect of The O_2 Gas Concentration	41

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1		Characterization of *m*-PPV-MP polymer	42
	4.1.1	Infrared Spectroscopy (FTIR)	43
	4.1.2	Ultraviolet-Visible Absorption Spectroscopy	43
	4.1.3	The Thermogravimetric Analysis (TGA)	47
	4.1.4	Differential Scanning Calorimetry (DSC)	47
4.2		The Study Of *m*-PPV-MP Solution As Sensing Material	50
	4.2.1	Introduction	50
	4.2.2	*m*-PPV-MP Solution As Sensing Material for O_2 Gas	51
		4.2.2a Fluorescence Spectra	54
		4.2.2b Regeneration	54
		4.2.2c Photostability	57
		4.2.2d The Reproducibility And Repeatability Of The Sensing Material Towards O_2 Gas.	69

4.2.2e The Steady State Response Towards O_2 Gas 61

4.2.2f The Effect Of The O_2 Gas Volume 62

CHAPTER 5 CONCLUSION AND SUGGESTIONS

5.1 Conclusion 65

5.2 Suggestions to enhance the performance and result of this research. 67

REFERENCES 69

APPENDIXES 73

CURRICULUM VITAE 83

LIST OF TABLES

Tables		Pages
3.1	Chemical substances require in this experiment	34
3.2	Apparatus required in this research	34
3.3	The analytical instrument required	35

LIST OF FIGURES

Figures		Pages
1.1	Shematic representation of 1,3-dianisolybenzene monomer synthesized via Friedel-Crafts reaction	4
1.2	Shematic representation of *m*-PPV-MP synthesized via McMurry coupling reaction.	5
2.1	(a) Poly(1,3-phenylene diphenylvinylene) (b) poly(4,4'-diphenylene-1,2-bis(pentafluorophenyl) (c) poly(3,3'-diphenylene diphenylvinylene)	12
2.2	The synthesis of poly(4,4'-diphenylene diphenylvinylene) via Yamamoto polycondensation with control of cis/trans ratio.	13
2.3	The synthesis of poly(tetra-*p*-phenylene diphenylvinylene) via Suzuki polycondensation with control of cis/trans ratio.	13
2.4	The synthesis of ketone via Friedel-Crafts reaction.	15
2.5	The reaction to produce acyl chlorides.	15
2.6	A general McMurry coupling reaction equation.	20
2.7	General steps involve in McMurry reaction mechanism.	21
2.8	Mechanism for McMurry coupling reaction by Dams *et al.* (1982).	22
2.9	Jablonsky diagram	28
2.10	The main components in a luminescence spectrophotometer.	29
4.1	*m*-PPV-MP polymer structure.	43
4.2	FTIR spectrum for *m*-PPV-MP polymer.	45
4.3	Ultraviolet-Visible absorption spectrum for *m*-PPV-MP polymer.	46
4.4	Thermogravimetric Analysis (TGA) for *m*-PPV-MP polymer.	48
4.5	Differential Scanning Calorimetry (DSC) for *m*-PPV-MP polymer.	49

4.6	The excitation (a) and emission (b) spectra of *m*-PPV-MP in DMF solution (λ_{ex} : 392 nm and λ_{em}: 499 nm).	53
4.7	The fluorescence spectra of *m*-PPV-MP before (a) and after (b) quenching with O_2 gas.	53
4.8	The mechanism of fluorescence quenching process of *m*-PPV-MP solution with O_2 gas.	54
4.9	The response time of *m*-PPV-MP solution towards the same concentration of O_2 gas. The N_2 gas is used to regenerate the polymer after quenching with O_2 gas.	56
4.10	The photostability of *m*-PPV-MP solution for 16 hours.	58
4.11	Repeatability (■ RSD: 1.68%) and reproducibility (□ RSD: 2.34%) of the *m*-PPV-MP as sensing material towards O_2.	60
4.12	The flow-rate effects at 0.67 ml/s (Δ) , 1.00 ml/s (O) and 2.50 ml/s (♦) on the response time of *m*-PPV-MP sensing reagent towards O_2 gas.	62
4.13	The plot of O_2 gas volume against fluorescence intensity of *m*-PPV-MP sensing reagent.	64
4.14	The plot of Log (O_2 gas volume) against I_0/I of *m*-PPV-MP sensing reagent.	64

LIST OF ABBREVIATIONS AND SYMBOLS

$AlCl_3$	Aluminum (III) chloride
ArR	alkylbenzenes
ArCOR	acylbenzenes
BF_3	boron (III) fluorida
Cu	Copper
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
FRET	Resonance Energy Transfer
FTIR	Fourier Transform Infrared Spectrometer
HCl	Hydrochloric Acid
H_2O	Water
HOMO	highest occupied molecular orbital
K_{sv}	Stern-Volmer constant
LEDs	light-emitting diodes
$LiAlH_4$	Lithium Aluminum hydroxide
LUMO	lowest unoccupied molecular orbital
Mg	Magnesium
m-PPV-MP	poly(1,3-phenylene-1,2-di(*p*-methoxyphenyl)vinylene)
Ni	Nickel
O_2	Oxygen
Pd	Palladium
PAV	Poly(arylene vinylene)
PCl_5	phosphorus penthachloride

PDPV	Poly(4,4'-diphenylene diphenylvinylene)
PLEDs	Polymer Light Emitting Devices
p-PDV	poly(1,4–phenylene diphenylvinylene)
ppm	parts per million
PPV	poly(*para*-phenylene vinylene)
RSD	relative standard deviation
$SOCl_2$	thionyl chloride
$SrTiO_3$	Strontinum Titanate
T_g	glass transition temperature
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
$TiCl_4$	Titanium tetrachloride
Zn	Zinc
Å	Armstrong
τ	The fluorescence lifetime
λ	wavelength
^0C	Degree Celsius

LIST OF APPENDIXES

APPENDIXES		Pages
A1	Fourier Transform Infrared Spectrometer (FTIR)	73
A2	UV-Visible Absorption Spectrometer	74
A3	Thermogravimetric Analysis (TGA)	75
A4	Differential Scanning Calorimetry (DSC)	76
A5	Fluorescence Spectrophotometer	77
A6	Data for Figure 4.11	78
A7	Data for Figure 4.12	79
A8	Data for Figure 4.13 and 4.14	82

POLI (1,3-FENILENA-1,2-DI(*p*-METOKSIFENIL)VINILENA) (*m*-PPV-MP) SEBAGAI BAHAN PENDERIA UNTUK MENGESAN GAS OXYGEN

ABSTRAK

Poli(1,3-fenilena-1,2-di(metoksifenil)vinilena) (*m*-PPV-MP) ialah sejenis polimer konjugat yang berpendarflour dan berasal dari kumpulan poli(arilena vinilena), PAV. *m*-PPV-MP disintesis melalui tindak balas gandingan McMurry dengan menggunakan 1,3-dianisoilbenzena dalam pelarut tetrahidrofuran (THF), titanium tetraklorida ($TiCl_4$) sebagai mangkin dan serbuk zink sebagai agen penurunan. Penyelidikan ini dijalankan untuk mengkaji potensi *m*-PPV-MP sebagai bahan penderia untuk mengesan gas oksigen berdasarkan konsep perlindapan pendarflour. Pencirian ke atas *m*-PPV-MP dijalankan dengan menggunakan kalorimeter imbasan pembeza (DSC), analisis gravimetri terma (TGA), spektroskopi infra merah (FTIR), dan spektroskopi serapan ultralembayung-nampak. Larutan *m*-PPV-MP disediakan untuk mengkaji ciri-ciri penderiaan dalam polimer tersebut dengan menggunakan spektrometer pendarflour. Tempoh masa yang diambil untuk sekali pengesanan gas O_2 ialah 6 minit 25 saat. Kestabilanfoto dijalankan selama 16 jam dibawah pendedahan radiasi lampu xenon dan dilaporkan stabil serta tidak mengalami kelunturanfoto. Nilai sisihan piawai relatif (RSD) bagi kebolehulangan adalah 1.68 % manakala bagi kebolehasilan adalah 2.34 %. Rangsangan keadaan mantap dicapai dalam masa 185 s, 90 s and 70 s untuk kadar alir 0.67 ml/s, 100 ms/l dan 2.50 ms/l masing-masing. Suatu graph linear diperolehi apabila nilai I_0/I diplotkan melawan log (isipadu gas O_2) dengan nilai kecerunan 8.1 x 10^{-3} ml^{-1}. Kesimpulannya, *m*-PPV-MP mempunyai potensi untuk dijadikan sebagai bahan penderia untuk mengesan gas oksigen.

ABSTRACT

Poly(1,3-phenylene-1,2-di(*p*-methoxyphenyl)vinylene) (*m*-PPV-MP) is a type of luminescent conjugated polymer and is a derivative of poly(arylene vinylene), PAV. *m*-PPV-MP has been synthesized via McMurry coupling reaction by using 1,3-dianisolybenzene, titanium tetrachloride and zinc dust as the monomer, catalyst and reducing agent respectively in tetrahydrofuran (THF). This research was carried out to investigate the potential of *m*-PPV-MP as sensing material to detect oxygen gas (O_2) based on fluorescence quenching. *m*-PPV-MP was characterized by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared spectrometer (FTIR) and UV-Visible absorption spectrometer. *m*-PPV-MP solution was prepared to investigate the sensing characteristics of this polymer by using fluorescence spectrophotometer. The response time for a complete detection of O_2 gas by the sensing materials was 6 minutes and 25 seconds. Photostability testing was conducted for 16 hours under continuous exposure to radiation of xenon lamp. The sensing reagent was reported to be stable and did not undergo photodegradation. The relative standard deviation (RSD) for repeatability was found to be 1.68 % whereas for reproducibility was 2.34 %. The steady state response of *m*-PPV-MP sensing reagent was established at the time of 185 s, 90 s and 70 s for flow rate of 0.67 ml/s, 100 ms/l and 2.50 ms/l respectively. A linear relationship between the log (O_2 gas volume) and fluorescence intensity, I_0/I was established when the graph was plotted with a slope of 8.1×10^{-3} ml^{-1}. The overall results proved that *m*-PPV-MP has the potential to be developed as sensing material to detect O_2 gas.