SYNTHESIS, CHARACTERIZATION, AND PHOTOLUMINESCENCE PROPERTIES OF ESTER OLIGOMERS CONTAINING FLUORENE, FLUORESCEIN AND CURCUMIN RESPECTIVELY FOR POTENTIAL CHEMOSENSOR APPLICATION

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SYNTHESIS, CHARACTERIZATION, AND PHOTOLUMINESCENCE PROPERTIES OF ESTER OLIGOMERS CONTAINING FLUORENE, FLUORESCEIN AND CURCUMIN RESPECTIVELY FOR POTENTIAL CHEMOSENSOR APPLICATION

by

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TABLE OF CONTENTS

ACKNOWLEDGEMENT ..... **ii**

TABLE OF CONTENTS ..... **iii**

LIST OF TABLES ..... **vi**

LIST OF FIGURES ..... **viii**

LIST OF SYMBOLS ..... **xi**

LIST OF ABBREVIATIONS ..... **xii**

LIST OF APPENDICES ..... **xiv**

ABSTRAK ..... **xv**

ABSTRACT ..... **xvi**

CHAPTER 1 INTRODUCTION **1**

1.1 Polymers 1

1.1.1 Polymer topology 2

1.1.2 Oligomers 5

1.1.3 Polymerization process 6

1.1.4 Polyesters 11

1.1.5 Photoluminescent polymers 12

1.1.6 Chemosensors 16

1.1.7 Heavy metal ions 19

1.2 Problem statements 22

1.3 Research objectives 22

1.4 Scope of studies 23

CHAPTER 2 EXPERIMENTAL **24**

2.1 Chemicals 24

2.2 Synthesis of oligo[9,9-bis(4-hydroxyphenyl)fluorene-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **PF10-PF16** (m = 10, 12, 14, 16) 25

2.2.1 Synthesis of diethyl 5-hydroxyisophthalate, **S1** 27

2.2.2 Synthesis of 1-azidoalkane, **S2** (m = 10, 12, 14, 16) 27

2.2.3 Synthesis of diethyl 5-(prop-2-ynyloxy)isophthalate, **S3** 27

2.2.4 Syntesis of diethyl 5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalate, **S4** (m = 10, 12, 14, 16) 28

2.2.5 Synthesis of 5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids, **MS10-MS16** (m = 10, 12, 14, 16) 29

2.2.6 Synthesis of 5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalyl chloride, **MT10-MT16** (m = 10, 12, 14, 16) 29

2.2.7 Synthesis of oligo[9,9-bis(4-hydroxyphenyl)fluorene-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **PF10-PF16** (m = 10, 12, 14, 16) 29

2.3 Synthesis of oligo[fluorescein-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **FL10-FL16** (m = 10, 12, 14, 16) 30

2.4 Synthesis of oligo[curcumin-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **CM10-CM16** (m = 10, 12, 14, 16) 31

2.5 Characterization of the synthesized monomers and ester oligomers 31

2.5.1 Melting points 32

2.5.2 CHN elemental microanalyses 32

2.5.3 ATR-Fourier transform infrared (FT-IR) spectroscopy 32

2.5.4 One dimensional (1D) and two dimensional (2D) Fourier Transform Nuclear Magnetic Resonance (NMR) 32

2.5.5 Gel permeation chromatography (GPC) 33

2.5.6 Thermogravimetric analyses (TGA) 33

2.5.7 UV-Vis spectroscopy 33

2.5.8 Photoluminescence analyses 34

2.5.9 Chemosensor studies 34

CHAPTER 3 RESULTS AND DISCUSSION 35

3.1 Oligo[9,9-bis(4-hydroxyphenyl)fluorene-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **PF10-PF16** (m = 10, 12, 14, 16) 35

3.1.1 Physical characterization 35

3.1.2 ATR-Fourier transform infrared (FT-IR) spectroscopy 36

3.1.3 Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopy 41

3.1.4 Molecular weights, **PF10-PF16** 58

3.2 Oligo[fluorescein-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **FL10-FL16** (m = 10, 12, 14, 16) 58

3.2.1 Physical characterization 58

3.2.2 ATR-Fourier transform infrared (FT-IR) spectroscopy 59

3.2.3 Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopy 62

3.2.4 Molecular weights, **FL10-FL16** 73

3.3 Synthesis of oligo[curcumin-*alt*-5-(1-m-alkyl-1H-[1,2,3]-triazol-4-yl)isophthalic acids], **CM10-CM16** (m = 10, 12, 14, 16) 73

3.3.1 Physical characterization 73

3.3.2 ATR-Fourier transform infrared (FT-IR) spectroscopy 74

3.3.3 Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopy 77

3.3.4 Molecular weights, **CM10-CM16** 89

3.4 Solubility and thermal analysis of ester oligomer 89

3.5 Photophysical studies 99

3.6 Chemosensor studies 102

CHAPTER 4 CONCLUSION AND FUTURE RECOMMENDATIONS ... 113

4.1 Conclusion 113

4.2 Recommendations for future research 114

REFERENCES 115

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

Page

Table 2.1 Chemicals used in the synthesis of monomers and oligomers.....24

Table 3.1 Melting points, CHN microanalytical data, molecular formulas and molecular weights of **MS10-MS16** (m = 10, 12, 14, 16).....35

Table 3.2 Selective infrared absorption bands of **MS10-MS16** (m = 10, 12, 14 and 16).....37

Table 3.3 Selective infrared absorption bands of **PF10-PF16** (m =10, 12, 14 and 16).....38

Table 3.4 ^{1}H NMR chemical shift values, δ (ppm) of **MS10-MS16** 43

Table 3.5 ^{13}C NMR chemical shift values, δ (ppm) of **MS10-MS16** 44

Table 3.6 ^{1}H NMR chemical shift values, δ (ppm) of **PF10-PF16**.....49

Table 3.7 ^{13}C NMR chemical shift values, δ (ppm) of **PF10-PF16** 50

Table 3.8 ^{1}H-^{1}H correlations as inferred from the COSY spectrum of **PF10**.....56

Table 3.9 ^{1}H-^{13}C correlations as inferred from the HMQC and HMBC spectra of **PF10** 57

Table 3.10 The GPC data and degree of polymerization for **PF10-PF16** 58

Table 3.11 Selective infrared absorption bands of **FL10-FL16** (m =10, 12, 14 and 16).....60

Table 3.12 ^{1}H NMR chemical shift values, δ (ppm) of **FL10-FL16** 64

Table 3.13 ^{13}C NMR chemical shift values, δ (ppm) of **FL10-FL16**.....65

Table 3.14 ^{1}H-^{1}H correlations as inferred from the COSY spectrum of **FL10**.....69

Table 3.15 ^{1}H-^{13}C correlations as inferred from the HMQC and HMBC spectra of **FL10**.....69

Table 3.16 The GPC data and degree of polymerization for **FL10-FL16**.....73

Table 3.17 Selective infrared absorption bands of **CM10-CM16** (m =10, 12, 14 and 16).....75

Table 3.18 ^{1}H NMR chemical shift values, δ (ppm) of **CM10-CM16**.....79

Table 3.19 ^{13}C NMR chemical shift values, δ (ppm) of **CM10-CM16**.....80

Table 3.20 ^{1}H-^{1}H correlations as inferred from the COSY spectrum of **CM10**.....83

Table 3.21 ^{1}H-^{13}C correlations as inferred from the HMQC and HMBC spectra of **CM10**.....84

Table 3.22 The GPC data and degree of polymerization for **CM10-CM16**.....89

Table 3.23 Solubility results of **PF10-PF16**.....93

Table 3.24 Solubility results of **FL10-FL16**.....94

Table 3.25 Solubility results of **CM10-CM16**.....95

Table 3.26 Thermal decomposition data of **PF10-PF16**.....96

Table 3.27 Thermal decomposition data of **FL10-FL16**.....97

Table 3.28 Thermal decomposition data of **CM10-CM16**.....98

Table 3.29 Photophysical data of **PF10**, **FL10** and **CM10**.....101

Table 3.30 Data obtained from the plots of fluorescence intensity against concentration of Fe^{3+} and Pb^{2+} ions.....112

LIST OF FIGURES

Page

Figure 1.1 Variations in thermoplastic and thermoset polymers.....2

Figure 1.2 Stereoisomers of polypropylene. (A) isotactic; (B) syndiotactic; (C) atactic.....3

Figure 1.3 Geometrical isomers of isoprene.....3

Figure 1.4 Types of copolymers: (A) random; (B) alternating; (C) block; (D) graft.....4

Figure 1.5 Reaction of vinyl chloride and vinylidene chloride.....4

Figure 1.6 Mechanism of free radical polymerization of styrene.....7

Figure 1.7 Mechanism of cationic polymerization of CH_2=CHZ 8

Figure 1.8 Mechanism of anionic polymerization of CH_2=CHA.....9

Figure 1.9 Formation of polyamide, polyester, polyurethane and polycarbonate 10

Figure 1.10 Synthesis of the conjugated photoluminescent poly[2-methoxy-5-(2- ethylhexyloxy)-1,4-phenylenevinylene] 13

Figure 1.11 Functional units of typical light-emitting polymers.....13

Figure 1.12 The non-conjugated photoluminescent polymer, polyethyleneimine 14

Figure 1.13 Structures of chemosensors for heterochromatic protein detection 17

Figure 1.14 Top: Structures of expanded porphyrins; bottom: the formation of photoluminescent supramolecular polymer using porphyrins and diacid as the building blocks 18

Figure 3.1 ATR-FTIR spectrum of **MS10**.....39

Figure 3.2 ATR-FTIR spectrum of **PF10**.....40

Figure 3.3 The resonance structures of 1,4-disubstituted triazole moiety……...43

Figure 3.4 ^{1}H NMR spectrum of **MS10 (**in DMSO-d_6) 45

Figure 3.5 ^{13}C NMR spectrum of **MS10 (**in DMSO-d_6) 46

Figure 3.6 ^{1}H NMR spectrum of **PF10 (**in $CDCl_3$) 51

Figure 3.7 ^{13}C NMR spectrum of **PF10 (**in $CDCl_3$) 52

Figure 3.8 ^{1}H-^{1}H COSY spectrum of **PF10 (**in $CDCl_3$) 53

Figure 3.9 ^{1}H-^{13}C HMQC spectrum of **PF10 (**in $CDCl_3$) 54

Figure 3.10 ^{1}H-^{13}C HMBC spectrum of **PF10 (**in $CDCl_3$) 55

Figure 3.11 ATR-FTIR spectrum of **FL10** 61

Figure 3.12 ^{1}H NMR spectrum of **FL10 (**in $CDCl_3$) 67

Figure 3.13 ^{13}C NMR spectrum of **FL10 (**in $CDCl_3$) 68

Figure 3.14 ^{1}H-^{1}H COSY spectrum of **FL10 (**in $CDCl_3$) 70

Figure 3.15 ^{1}H-^{13}C HMQC spectrum of **FL10 (**in $CDCl_3$) 71

Figure 3.16 ^{1}H-^{13}C HMBC spectrum of **FL10 (**in $CDCl_3$) 72

Figure 3.17 ATR-FTIR spectrum of **CM10** 76

Figure 3.18 ^{1}H NMR spectrum of **CM10 (**in $CDCl_3$) 81

Figure 3.19 ^{13}C NMR spectrum of **CM10 (**in $CDCl_3$) 82

Figure 3.20 ^{1}H-^{1}H COSY spectrum of **CM10 (**in $CDCl_3$) 85

Figure 3.21 ^{1}H-^{1}H COSY (expanded) spectrum of **CM10 (**in $CDCl_3$) 86

Figure 3.22 ^{1}H-^{13}C HMQC spectrum of **CM10** (in $CDCl_3$) 87

Figure 3.23 ^{1}H-^{13}C HMBC spectrum of **CM10** (in $CDCl_3$) 88

Figure 3.24 TGA thermograms of **PF10-PF16** 96

Figure 3.25 TGA thermograms of **FL10-FL16** 97

Figure 3.26 TGA thermograms of **CM10-CM16** 98

Figure 3.27 UV-Vis spectra of **PF10**, **FL10** and **CM10** after the addition of various metal ions 100

Figure 3.28 Photoluminescence spectrum of (A) **PF10**; (B) **FL10**; and (C) **CM10** in tetrahydrofuran 101

Figure 3.29 UV-Vis spectra of (A) **PF10**; (B) **FL10**; and (C) **CM10** with various metal ions in tetrahydrofuran at ambient temperature.....103

Figure 3.30 Photoluminescence spectra of (A) **PF10**; (B) **FL10**; and (C) **CM10** with various metal ions in tetrahydrofuran.....104

Figure 3.31 Fluorescence images of (A) **PF10**; (B) **FL10**; and (C) **CM10** in tetrahydrofuran.....105

Figure 3.32 Selectivity of (A) **PF10** for Fe^{3+} and Pb^{2+} ions; (B) **FL10** for Fe^{3+} and Pb^{2+} ions; and (C) **CM10** for Fe^{3+} ions in the presence of other metal ions.....107

Figure 3.33 UV-Vis absorbance of (A1-2) **PF10**; (B1-2) **FL10**; and (C) **CM10** with various concentration of Fe^{3+} and Pb^{2+} ions, respectively 108

Figure 3.34 Photoluminescence response of (A1-2) **PF10**; (B1-2) **FL10**; and (C) **CM10** at various concentrations of Fe^{3+} and Pb^{2+} ions, respectively 109

Figure 3.35 Plots of fluorescence intensity of ester oligomers in tetrahydrofuran against concentration of Fe^{3+} and Pb^{2+} ions; Insets: plots of linear range of fluorescence intensity against concentration of Fe^{3+}/Pb^{2+} ions (A1) **PF10** with Fe^{3+}; (A2) **PF10** with Pb^{2+}; (B1) **FL10** with Fe^{3+}; (B2) **FL10** with Pb^{2+}; and (C) **CM10** with Fe^{3+} 110

LIST OF SYMBOLS

%	Percent
µL	Microliter
µM	Micromolar
Hz	Hertz
J	Coupling constant
M	Molar
mg	Milligram
mL	Milliliter
mM	Millimolar
Mol dm^{-3}	Mole per cubic decimeter
nm	Nanometer
^{o} C	Degree Celcius
$^{o}C\ min^{-1}$	Degree Celcius per minute
R	Regression coefficient
s	Standard deviation
$T_{d,\ 50\%}$	Decomposition temperature at a weight loss of 50 percent
δ/ppm	Chemical shift in part per million unit
λ	Wavelength
λ_{ex}	Excitation wavelength
λ_{max}	Maximum wavelength
ν (cm^{-1})	Wavenumber in centimeter unit

LIST OF ABBREVIATIONS

^{13}C NMR	Carbon nuclear magnetic resonance
1D	One dimensional
^{1}H NMR	Proton nuclear magnetic resonance
2D	Two dimensional
ATR	Attenuated total reflectance
$CDCl_3$	Deuterated chloroform
CHN	Carbon, hydrogen, nitrogen
COSY	Correlation spectroscopy
$CuSO_4.5H_2O$	Copper(II) sulfate pentahydrate
DMF	N,N'-dimethylformamide
DMSO-d_6	Deuterated dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DP	Degree of polymerization
Equiv.	Equivalent
FT-IR	Fourier transform infrared
FT-NMR	Fourier transform nuclear magnetic resonance
GPC	Gel permeation chromatography
H_2SO_{4conc}	Concentrated sulfuric acid
HMBC	Heteronuclear multiple bond correlation
HMQC	Heteronuclear multiple quantum correlation
K_2CO_3	Potassium carbonate
KOH	Potassium hydroxide
KOtBu	Potassium tert-butoxide
LED	Light emitting diode

m	Multiplet
Mn	Number average
Mw	Weight average
p	Pentet
PDI	Polydispersity index
PL	Photoluminescence
PLED	Polymer light emitting diode
q	Quartet
r. t.	Room temperature
s	Singlet
$SOCl_2$	Thionyl chloride
t	Triplet
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMS	Tetramethylsilane
USM	Universiti Sains Malaysia
VOCs	Volatile organic compounds
w/w	Weight by weight

LIST OF APPENDICES

APPENDIX A FT-NMR SPECTRUM

SINTESIS, PENCIRIAN DAN SIFAT KEFOTOPENDARCAHAYAAN OLIGOMER ESTER YANG MASING-MASING MENGANDUNGI FLUORENA, FLUORESCEIN DAN KURKUMIN SERTA POTENSI APLIKASI SEBAGAI KEMOSENSOR

ABSTRAK

Tiga siri homolog oligomer ester baharu yang masing-masing mengandungi fluorena, fluorescein dan kurkumin telah disintesis dan dicirikan. Struktur molekul bagi monomer dan oligomer ester tersebut telah disahkan oleh analisis CHN, spektroskopi ATR-FTIR, 1D dan 2D-NMR. Oligomer ester yang disintesis mempunyai keterlarutan dalam pelbagai jenis pelarut organik umum seperti kloroform, tetrahidrofuran dan aseton. Kestabilan haba untuk oligomer ester tersebut telah dikaji dengan menggunakan TGA dalam nitrogen. Oligomer ester yang mengandungi fluorescein menunjukkan kestabilan haba yang tertinggi diikuti oleh oligomer ester yang mengandungi kurkumin dan fluorena. Tambahan pula, oligomer ester yang mengandungi rantai sisi alkil pendek menunjukkan kestabilan haba yang lebih tinggi. Oligomer ester untuk **PF**, **FL** dan **CM** dalam tetrahidrofuran menunjukkan keamatan pendarcahayaan masing-masing pada λ= 320, 322 and 505 nm. **PF** dan **FL** menunjukkan tindak balas pemadaman pendarcahaya terhadap ion Fe^{3+} dan Pb^{2+} dengan had pengesanan dalam lingkungan 2.92×10^{-4} M - 4.15×10^{-4} M. Manakala, pendarcahaya bagi **CM** dipadamkan dengan ketara oleh ion Fe^{3+} sahaja dengan had pengesanan sebanyak 7.90×10^{-6} M. Tetapi, hanya **FL** dan **CM** menunjukkan kepekaan terhadap ion Fe^{3+} dalam kehadiran ion lain.

SYNTHESIS, CHARACTERIZATION, AND PHOTOLUMINESCENCE PROPERTIES OF ESTER OLIGOMERS CONTAINING FLUORENE, FLUORESCEIN AND CURCUMIN RESPECTIVELY FOR POTENTIAL CHEMOSENSOR APPLICATION

ABSTRACT

Three new homologous series of new ester oligomers containing fluorene (**PF**), fluorescein (**FL**) and curcumin (**CM**) on the backbone, respectively had been successfully synthesized and characterized. The molecular structures of the synthesized monomers and ester oligomers were elucidated by CHN, ATR-FTIR and FT-NMR (1D and 2D NMR). The synthesized ester oligomers showed high solubility in most of the common organic solvents, such as chloroform, tetrahydrofuran and acetone. Their thermal stabilities were investigated using TGA under nitrogen atmosphere. Ester oligomers with fluorescein units exhibited the highest thermal stability, followed by the curcumin- and fluorene- containing analogues, respectively. The synthesized ester oligomers with shorter alkyl side chain showed higher thermal stability. Ester oligomers of **PF**, **FL** and **CM** in tetrahydrofuran showed a maximum photoluminescence intensity at λ= 320, 322 and 505 nm, respectively. **PF** and **FL** also showed turn-off response towards Fe^{3+} and Pb^{2+} ions with the respective detection limit in the range of 2.92×10^{-4} M - 4.15×10^{-4} M. Whereas, fluorescence of **CM** was quenched significantly by Fe^{3+} ions only with the detection limit of 7.90×10^{-6} M. However, only **FL** and **CM** showed selectivity toward Fe^{3+} among other coexisting metal ion

CHAPTER 1

INTRODUCTION

1.1 Polymers

A Swedish chemist, Jőns Jakob Berzelius coined the word “polymer” which composed of two Greek terms, *polys* meaning “many” and meros meaning “unit” in 1833 [William B. J., 2008]. In other words, a polymer is a complex macromolecule that is built up by a number of repeating units called monomers. Monomers are combined together by a chemical reaction called polymerization. Polymers can be found around us and affect our everyday life. DNA, starch, cellulose, rubber are natural polymers occurring since the very existence of life. A man-made polymers or synthetic polymer is commonly used in building trades, pharmaceutical, and biomedical application [Shradha T. *et al*, 2016]. Resins and fibers are types of commonly used polymers, such as polyethylene, polypropylene, polystyrene, polyvinylchloride, polyethylene terephthalate, polyester, polyamide and acrylic fibers. The demand for resins and fibers had increased 190-fold since 1950 to 2015. 380 Million metric tons of the global resins and fibers production were recorded in 2015 [Roland G., Jenna R. J. & Kara L. L., 2017]. The increase in demand for polymers is attributed to its interesting mechanical and electrical properties. In many applications, the types of materials used depends on the stiffness, toughness, elasticity and conductivity. For instance, polymer lenses are widely used in optical application instead of normal silica lens which the latter are heavier and less resistant to scratching [Catherine B. L. & Brinson H. F., 2008]. Conducting polymers especially the poly(3,4-ethylenedioxythiophene) (PEDT) and its derivatives are used in transparent electrodes for inorganic electroluminescent devices, cathode ray tube and rechargeable batteries [Hummel R. E., 2001].

1.1.1 Polymer topology

In general, polymers are classified into thermoset or thermoplastic polymers. Thermoset polymers are cross-linked and their interchain interaction forces are from secondary (hydrogen, London dispersion, dipole, etc.) and covalent bonding. Eventually, these cause thermoset polymers to remain solid once hardened. Thermoplastic or linear polymers consist of secondary interchain bonds only and they can be melted. There are variations in thermoplastic and thermoset polymers as shown in Figure 1.1 [Catherine B. L. & Brinson H. F., 2008].

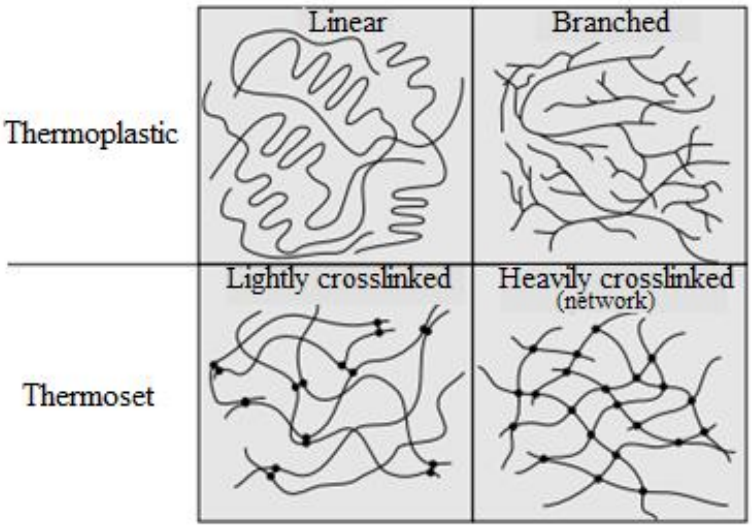


Figure 1.1 Variations in thermoplastic and thermoset polymers [Catherine B. L. & Brinson H. F., 2008]

However, there is a more precise classification of polymers based on molecular structure characteristics. On the basis of structures, there are linear, branched, cross-linked and network polymers. Linear and branched polymers have different molecular configurations due to rotation of groups of atoms about a single bond. Polymers that consist of same chemical composition, but different atom arrangements are called isomers. They are further divided into stereoisomers and geometrical isomers. Stereoisomers can be distinguished as isotactic, syndiotactic

and atactic. Examples of stereoisomers of polypropylene are shown in Figure 1.2 [Catherine B. L. & Brinson H. F., 2008].

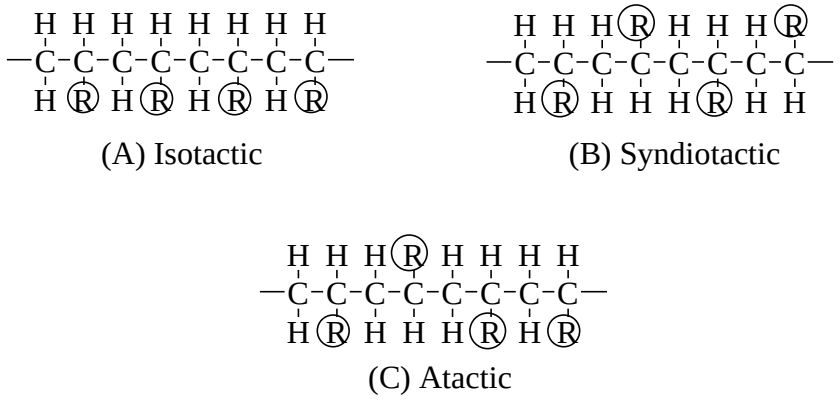


Figure 1.2 Stereoisomers of polypropylene. (A) isotactic; (B) syndiotactic; (C) atactic [Catherine B. L. & Brinson H. F., 2008]

On the other hand, there are two types of geometrical isomers, namely the *cis* isomer and *trans* isomer such as the isoprene subunit. In the *cis*- isoprene, both CH_2 groups are on the same side of the C=C bond, whereas the CH_2 groups are on opposite sides in the *trans*-isoprene. The double bond is rigid as the molecular rotation is forbidden due to the presence of π bond, therefore the spontaneous conversion between two configurations is impossible. The geometrical isomers of isoprene are given in Figure 1.3 [Catherine B. L. & Brinson H. F., 2008].

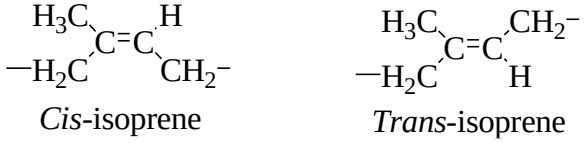


Figure 1.3 Geometrical isomers of isoprene [Catherine B. L. & Brinson H. F., 2008]

The examples of polymers described above are homopolymers which are made up of a single type of monomer. There are many polymers derived from more than one

types of monomer, they are known as copolymers. Random, alternating, block and graft are the variations of copolymer, as illustrated in Figure 1.4 [Catherine B. L. & Brinson H. F., 2008].

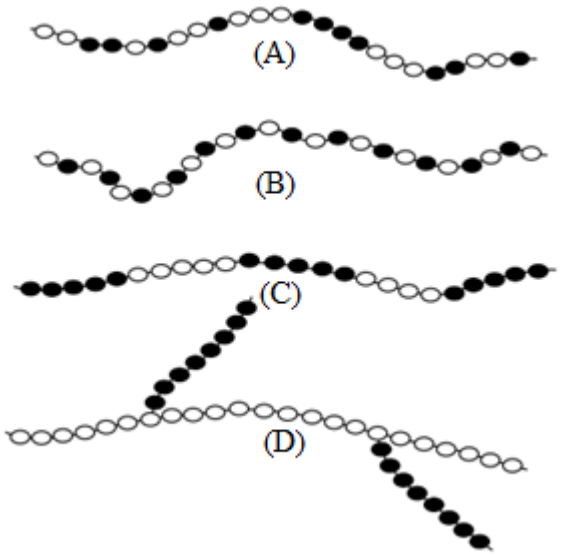


Figure 1.4 Types of copolymers: (A) random; (B) alternating; (C) block; (D) graft [Catherine B. L. & Brinson H. F., 2008]

Most of the sequence copolymer chains depended on the types of monomers. For example, it is preferentially not to add the monomer at the end of the chain in the polymerization between vinyl chloride and vinylidene chloride (1,1-dichloroethylene). This selective reaction forms the alternating copolymer, Saran®, which is commonly used as a film for wrapping food as shown in Figure 1.5 [Wade L. G., Jr, 2006].

Overall reaction

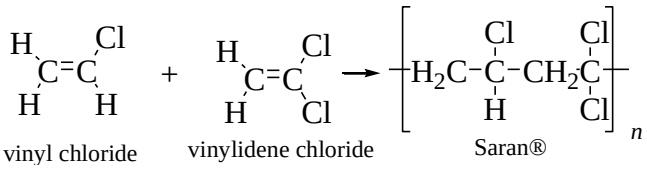


Figure 1.5 Reaction of vinyl chloride and vinylidene chloride [Wade L. G., Jr, 2006]

1.1.2 Oligomers

Oligomers are low molecular weight polymers that consists two to twenty repeating units. Oligomers are often referred as prepolymers because they are intermediates capable to undergo further polymerization by reactive groups to a fully polymerized high molecular weight material. Oligomers are, in general, high viscosity liquids and they have all the physical characteristics of those of small molecules [Hagen A. P., 2009]. Oligomers of polyester are a drawback to the textile manufacturing industry. This is due to the migration of oligomers to the surfaces of fibers during dyeing process at high temperature and this in turn will affect the quality of dyeing and the processing of dyed polyester fiber negatively. Several techniques such as the use of different surfactants to disperse dye and oligomers, and alkaline solution treatment to remove the oligomers have been utilized to eliminate the negative effect brought by oligomers [Vavilova S. Y. *et al*, 2003].

However, hydrocarbon oligomers that are made up of ethylene and propylene with limited degree of polymerization are commonly used in lubricants and biodegradable detergents. They were synthesized through cationic polymerization by using transition metals or organoaluminium compounds that acted as catalysts. The degree of oligomerization was manipulated by varying the concentrations of catalysts, polarity of solvent, pressure and temperature of the reaction [Constantin V. U., 1998]. On the other hand, sulphur-containing oligomers are in great demand in the sealing of interpanel seams and glass packets. Different types of vulcanization and modification of polysulfide oligomers-based sealants were expanded due to their high durability and high resistivity to ultraviolet radiation, ozone, water in a broad temperature range of -6 to 100^{o}C. Polysulfide oligomers were produced by

decomposition of high molecular weight polysulfides to shorter chains in industry [Yuri N. K., Vladimir S. M. & Timur R. D., 2015].

Apart from that, coating technology has drawn great a deal of interest over the past decade, especially the ultraviolet curable coatings. Blends of curable oligomers and monomers as well as photoinitiators that formed reactive species when exposed to ultraviolet radiation to initiate polymerization are the main components in ultraviolet curable coating. This coating technique is known as ultraviolet curing or photo polymerization [Mittal K. L. & Ravi J., 2015]. Despite the interesting physical properties such as abrasion, chemical and weather resistance, ultraviolet curable coating has the advantages of instant drying, fast curing time, and ambient temperature curing. It is environmentally friendly with low or no volatile organic compounds (VOCs) emission and lower cost compared to water-based coatings or solvent-based coating. Hence, the ultraviolet curing technology plays a major role in paint, automotive and printing industries [Keizo M. & Song C., 2012]. In order to improve the performance of ultraviolet curable oligomers, research of ultraviolet curable oligomers as pressure sensitive adhesives (PSAs) has been developed mainly for the semiconductor industry as a peelable material needed for dicing or back grinding processing [Ozawa T., 2000]. Recent studies showed that the peel adhesion decreased upon the photo induced decrosslinking in PSAs composed of *O*-acyloxime based oligomers [Suyama K. & Tachi H., 2015].

1.1.3 Polymerization process

Polymers have been prepared either by chain-growth or by step-growth polymerization. Chain-growth polymerization happens when unsaturated monomer is added one by one onto the radical or ionic active site of growing polymer chain, with

regeneration of reactive sites at the end of each growth step. The mechanism of chain-growth polymerization is categorized into three stages: initiation, propagation and termination [Smith J. G., 2011].

Free-radical polymerization occurs when a radical initiator is heat-activated and further react with a suitable alkene. Benzoyl peroxide is commonly used to form peroxy radical due to weak O-O bond that cleaves when heated. Figure 1.6 shows the mechanism of a free-radical polymerization with styrene as the monomer [Smith J. G., 2011].

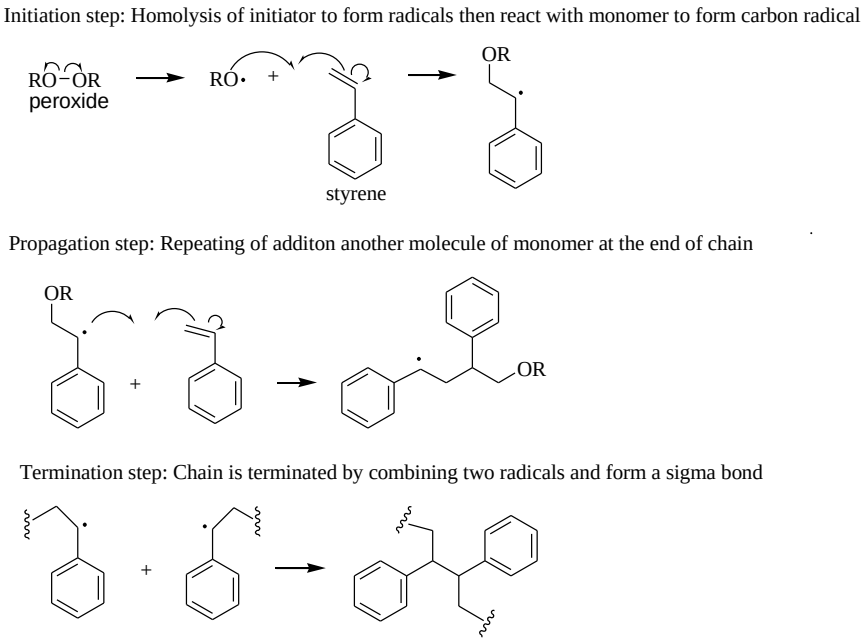


Figure 1.6 Mechanism of free radical polymerization of styrene [Smith J. G., 2011]

On the other hand, the reactive site of a polymer chain is ion or ion pairs in ionic polymerization. Strong acid catalysts like boron trifluoride, BF_3 is used for cationic polymerization and the rate of reaction is speed up by using water or methanol.

On the contrary, organolithium or aryl-magnesium halides are employed as a source of carbanion in anionic polymerization. Monomers having electron withdrawing groups like nitro, cyano, carboxyl, vinyl and phenyl moieties are most susceptible to anionic polymerization. The mechanism of cationic and ionic polymerization is shown in Figures 1.7 and 1.8 respectively [Smith J. G., 2011].

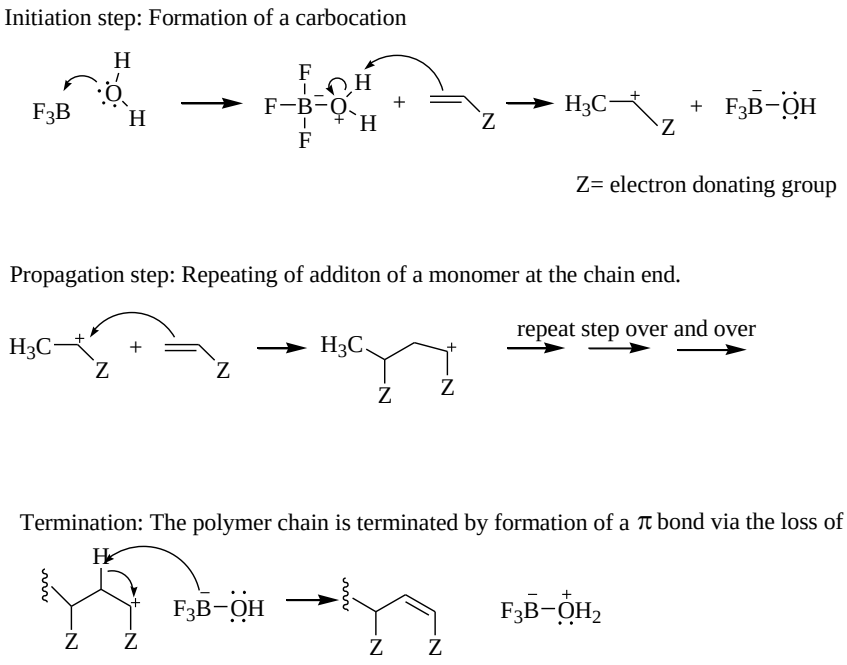


Figure 1.7 Mechanism of cationic polymerization of CH_2=CHZ [Smith J. G., 2011]

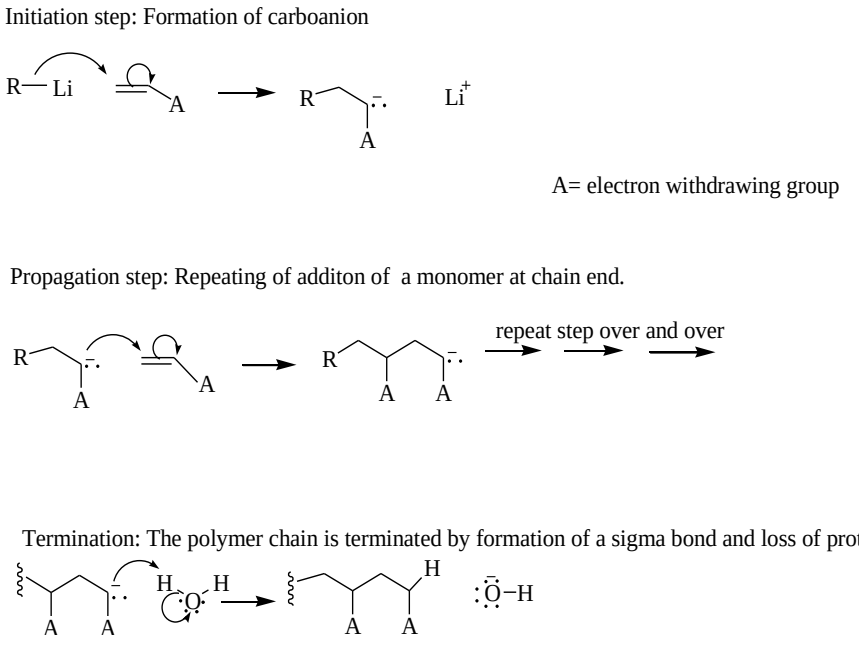


Figure 1.8 Mechanism of anionic polymerization of CH_2=CHA [Smith J. G., 2011]

Step-growth polymerization, on the other hand, occurs via a stepwise condensation of bifunctional monomers which results in the formation of ester or amide linkages between the bifunctional molecules. The most common types of step-growth polymers are polyamides, polyesters, polycarbonates, and polyurethanes as shown in Figure 1.9 [Smith J. G., 2011].

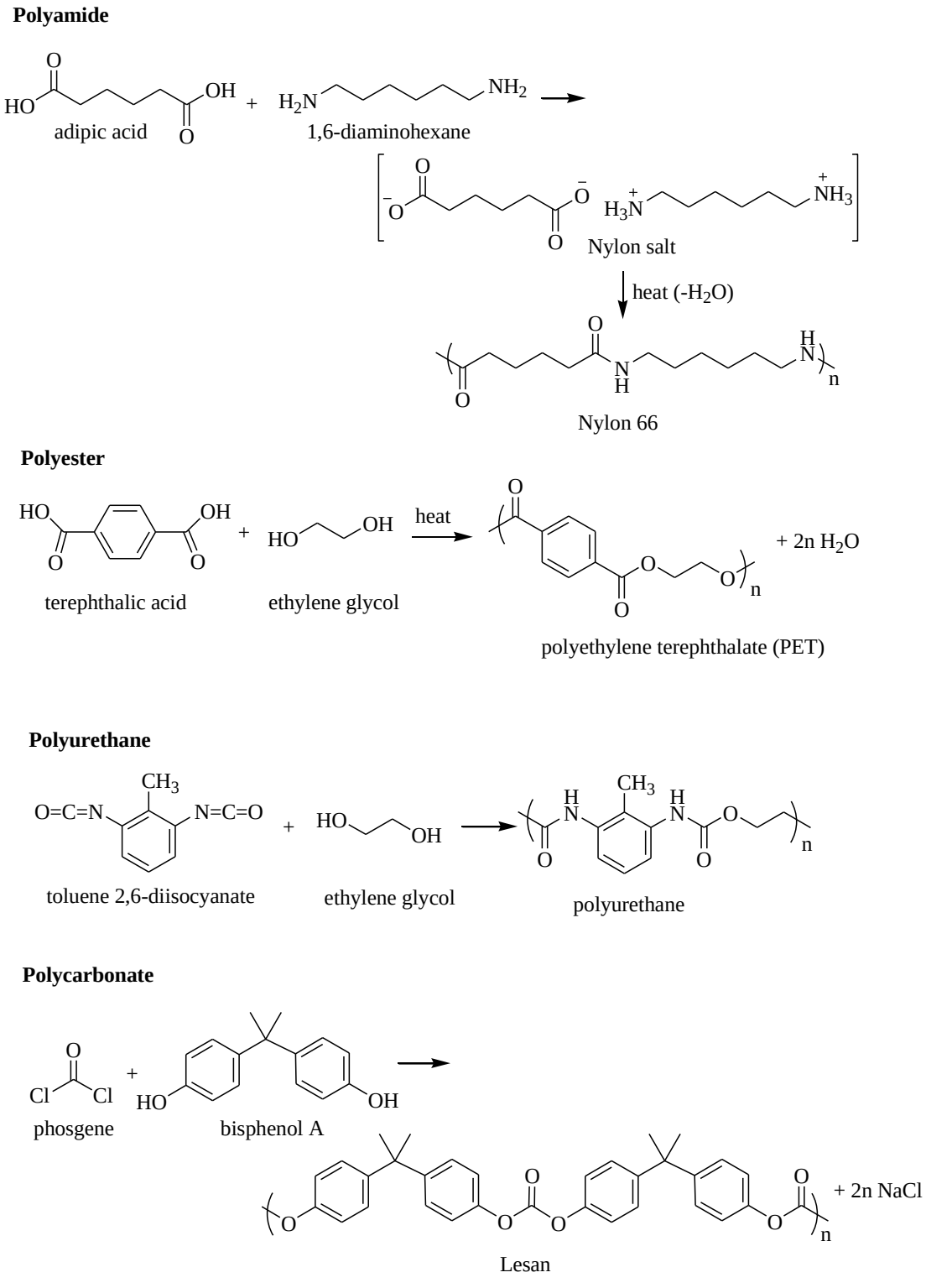


Figure 1.9 Formation of polyamide, polyester, polyurethane and polycarbonate [Smith J. G., 2011]

1.1.4 Polyesters

In 1847, Berzelius synthesized the first laboratory made polyester from tartaric acid and glycerin. A new era of polymer science began when Wallace Carothers formally reported his brilliant works about condensation polymerization and synthetic polymers including glycol ester [Dodiuk H. & Goodman S. H., 2013]. Polyesters contain repeating units of ester functional group which is derived from dicarboxylic acid and diols. Polycondensation, ring-opening polymerization, and polyaddition processes are the reactions that could be carried out to form polyesters [MacDonald J. P. *et al*, 2016; Dong B. T. *et al*, 2012]. Polyesters are classified into thermoplastic polyesters and thermoset polyesters.

The invention of textile fiber is the first commercial application of polyesters and subsequently, the use of thermally stable products made of thermoplastic polyesters derived from isophthalic acid, terephthalic acid with bisphenol-A. They were hard to process due to their low solubility in organic solvents as well as high glass transition temperature. These were attributed to the rigidity of the aromatic backbones and high molecular weights which increased the crystallinity of the polymers. Therefore, nucleating agents and plasticizers are blended with aromatic polyesters to lower the glass transition temperature of the latter for injection molding. Besides that, polyesters can be reinforced by carbon and glass fiber, and consequently utilized in a diverse array of applications such as automotive, electronics and recreation. Carbon and glass-reinforced polyesters have better mechanical strength without an increase in molecular weights that could result in molding difficulties but good thermal stability [Scheirs J. & Long T. E., 2003]. On the other hand, low molecular chains of polyglycolic acids, polylactics and polycaprolactones are the aliphatic thermoplastic polyesters that show high solubility

in organic solvent, but low thermal resistance due to their flexible backbone. Despite of that, they are biodegradable due to the high flexibility of their backbones which are capable to fit into the enzyme active sites [Huang S. J., 1989].

Unsaturated polyesters are one type of thermoset polyesters. Unsaturated polyesters contain C=C bonds that will cross-link with another monomer such as methyl methacrylate which also contains C=C bond. Unsaturated polyesters are versatile as their physical properties can be tailored for the manufacturing resins. Several types of organic acid anhydrides are reacted with diol to form the rigid general-purpose resins whilst unsaturated polyesters with better tensile strength and ductility are produced when adipic acid is used as the monomer [Dodiuk H. & Goodman S. H., 2013]. Polyunsaturated esters can combine with fiber glass or mineral filler prior to cross-linking. This type of polymers are commonly used in construction, marine and land transportation industries due to their lightweight and durability [Mittal V., 2013].

1.1.5 Photoluminescent polymers

In the past several decades, research on photoluminescent polymers was enormous and that had brought significant developments to the semiconductor and light emitting diode (LED) industries. High photoluminescence (PL) quantum efficiency is one of the vital requirements in the preparation of efficient polymer light emitting diodes (PLEDs). Photoluminescence in these polymers is attributed to the spatially extended π-bonding in their structures. Photoluminescent polymers are also known as conjugated polymers. In conjugated polymers, an extended conjugated network of sp^2 hybridized atoms gives rise to an energy difference between the π molecular orbital and π* molecular orbital [Adam P. & Patrice R, 2002]. An

example of a conjugated polymer is poly[2-methoxy-5-(2'- ethylhexyloxy)-1,4-phenylenevinylene] (Figure 1.20) synthesized using the Gilch's method and its photoluminescence was due to π- π* transition as reported by Lin and coworkers in year 2006

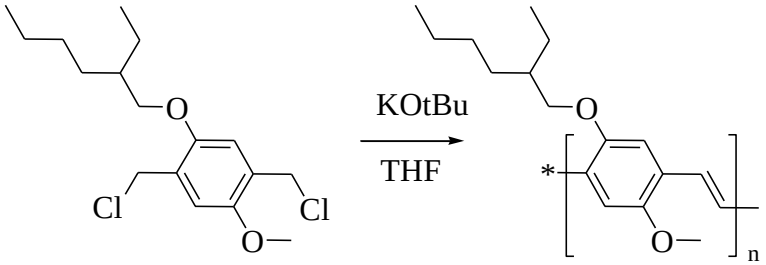


Figure 1.10 Synthesis of the conjugated photoluminescents poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene][Lin K.F., Fan Y. Y., Chow H. L., 2006]

Besides that, conjugated polymers were functionalized by varying the electron-hole pairs or photo-emissive units as illustrated in Figure 1.21 [Sekine C. *et al*, 2014]. Eventually, these modifications changed the conductivity (band gap energy) and caused either a red shifted or blue shifted emission. This has sparked global interest as these changes result in electroluminescence in the light emitting polymer and their use in PLED [Sekine C. *et al*, 2014].

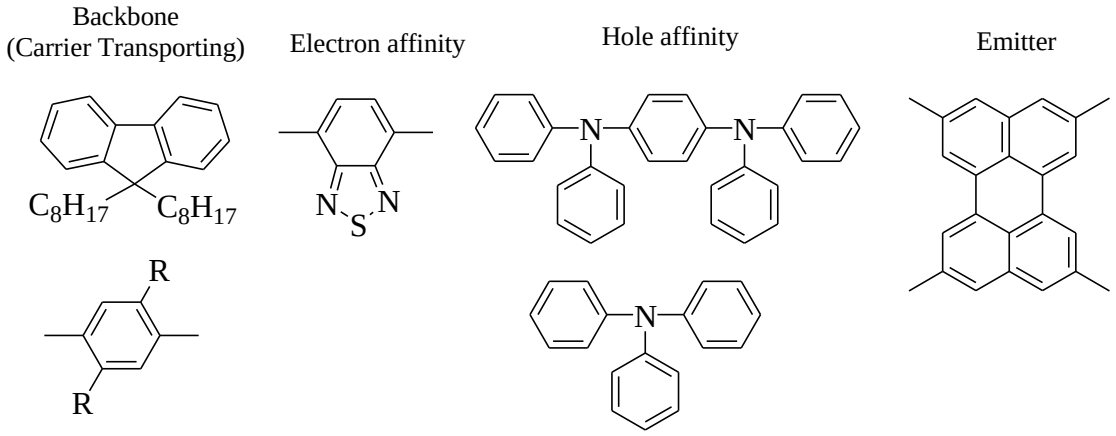


Figure 1.11 Functional units of typical light-emitting polymers [Sekine C. *et al*, 2014]

Non-conjugated polymers such as polyethyleneimine (Figure 1.22) also show enhanced photoluminescence by chemical cross linking where polymer chains were physically immobilized, known as crosslink enhanced emission effect as reported in the work of Zhu and co-workers in year 2014.

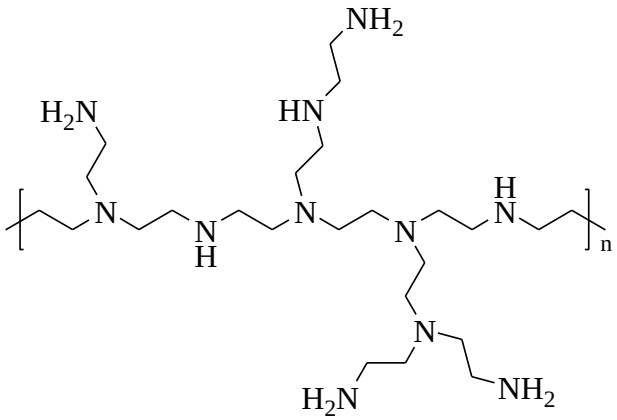


Figure 1.12 The non-conjugated photoluminescent polymer, polyethyleneimine [Zhu S. *et al*, 2014].

Research show that non-conjugated polymers become photoluminescent when certain side groups were attached to the backbones of these polymers. This type of polymers are known as pendant-type, non-conjugated polymers [Sekine C. *et al*, 2014]. The emissive pendants with the characteristic of planar π-conjugated

molecules such as pyrene, 2,5-diphenylfuran and triphenylamine were incorporated into polymer. The photoluminescence of pendant-type, non-conjugated polymers was further enhanced by excimer emission due to the intermolecular aromatic π stacking interactions at higher concentrations or in solid state [Fehervari A. F. *et al*, 2003; You. J. *et al*, 2010].

Host-guest type is another kind of photoluminescent non-conjugated polymers. Chen and co-workers (2015) had prepared a supramolecular polymers by utilizing the host-guest interaction between crown ether and dibenzylammonium moieties, and tetraphenylethylene moiety acted as fluorescent linker between two crown ether units.

According to the above mentioned structural features, incorporation of photoactive chromophores is essential to form photoluminescent polymers. Fluorescein, fluorene and curcumin are the chromophores that show absorption in UV-Vis region. Fluorene and its derivatives are well known for their non linear optical properties which are used in two photon fluorescence microscopy for bio imaging [Yao S. *et al*, 2010]. A full π-conjugated polycyclic aromatic compound, fluorene had been introduced into the backbones of conjugated polymers that will emit high efficiency blue photoluminescence emission. Photoluminescence of fluorene is tunable across the visible light spectrum by incorporating it with another chromophore [Gong X. *et al*, 2003; Wallace. J. U. & Chen S. H., 2008]. Besides that, substituted C-9 in fluorene was found to reduce long wavelength emission and increase solubility of the corresponding polymers [Damaceanu. M. D. & Marin L., 2015; Liou G. S. *et al*, 2007]. Therefore, 9,9-bis(4-hydroxyphenyl)fluorene was selected as one of the monomers in this study.

Fluorescein dye, on the other hand, has high fluorescence quantum yield. Hence, fluorescein-based probes are used in cancer cell imaging. The fluorescein moiety acts as a fluorophore which is highly fluorescent after tagging or binding with the target bio-molecules in cell of cytoplasm [Yin W. *et al*, 2014; Rajasekar M. *et al*, 2011]. Curcumin, or bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione is a natural yellow compound extracted from the rhizome of *Curcuma longa*. Curcumin was also utilized in the development of fluorescent probe in the monitoring of drug delivery systems [Nguyen H. N. *et al*, 2016]. Hence, copolymer chains containing multiple fluorescein or curcumin moieties which serve as energy donors or acceptors are expected to have higher photoluminescence intensity.

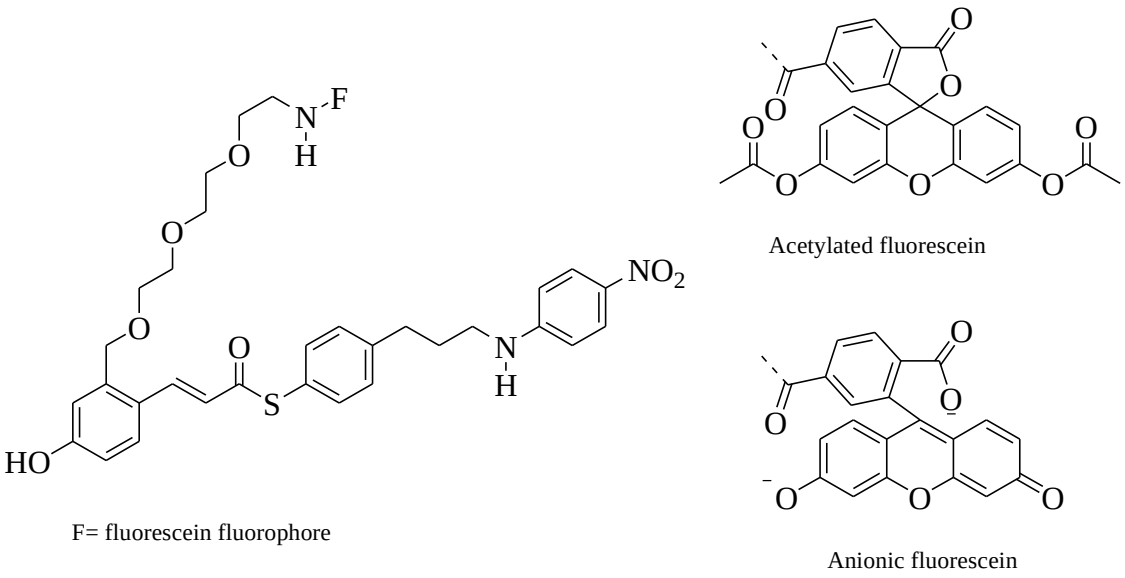
1.1.6 Chemosensors

Sensors are devices that respond to external stimuli and convert into recordable or measurable signals. Binding to a recognition unit, signal transduction and sensing readout are the three-step mechanism of a working sensor. Upon binding with specific analytes, it triggers a change in current, emission or absorption wavelength, fluorescent intensity and or temperature [Fegley M. E. A. *et al*, 2012].

Photoluminescent chemosensor are based on changes in fluorescence signal either in terms of emission intensity or emission wavelength. Receptor and fluorophore are the essential parts in photoluminescent chemosensors. There are two type of photoluminescent chemosensors: fluorescence ‘turn on’ and fluorescence ‘turn off’ [Fegley M. E. A. *et al*, 2012]. Photoluminescent chemosensors have been widely utilized in environmental, biology, physiology and pharmacology [Wu D. *et al*, 2017]. Explosive chemicals such as picric acid, 2,4,6-trinitrotoluene and 1,3,5-trinitroperhydro-1,3,5-triazine were detectable using photoluminescent chemosensor.

The explosive chemicals were deposited in soil in anionic forms after photolysis, especially in war affected area. Exposure to these substances may cause massive damages to the human eyes, respiratory system, skin, central nervous system and cardiovascular system [Jigyasa & Rajput J. K., 2018]. Jigyasa and Jaspreet Kaur Rajput had successfully developed a triaryl imidazole-based photoluminescent sensor for nitro-explosive trinitrophenol detection in 2018.

On the other hand, pyrene, fluorescein and coumarin are the photoactive moieties that had been used to develop photoluminescent chemosensors for biomacromolecules detection. For instance, chemosensors that are made of acetylated fluorescein, nitrobenzene and hydroxy cinnamic moieties (Figure 1.23) were membrane permeable. The fluorescence was 'turn on' upon binding with heterochromatin protein and hydrolysis of acetylated of fluorescein moiety by esterase. Apart from biomacromolecule, several photoluminescent chemosensors were designed for the detection of alkaline earth metals in cellular studies. 8-Hydroxyquinoline-based sensor was used in the fluorescent imaging of magnesium ions in living cells, which offered great help for early diagnosis, management and tracking of migraines, diabetes and Parkinson's disease progression [Wu D. *et al*, 2017].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polymers (Figure 1.24) were developed and they were able to detect different organic solvents, fluoride, chloride, bromide, nitrate and sulphate anions as reported by Zhang and co-workers in 2015.

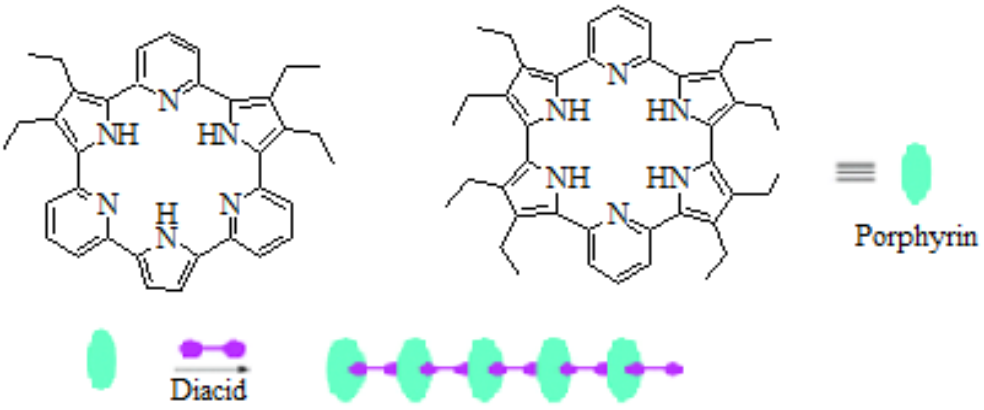

Figure 1.14 Top: Structures of expanded porphyrins; bottom: the formation of photoluminescent supramolecular polymer using porphyrins and diacid as the building blocks [Zhang X. *et al*, 2015].

1.1.7 Heavy metal ions

Though heavy metals were naturally found in the earth, heavy metal contamination has become our concern and they are mainly caused by mining and smelting activities, technological applications, agricultural pollution and industrial discharge [Tchounwou P. B. *et al*, 2014]. Water contamination is one of consquences of heavy metal exposure as most of the industrial and domestic waste water are drained to freshwater like rivers. The common heavy metals are cadmium, zinc, copper, lead and iron [Kumar J. & Kokil A., 2015]. Lead causes reduced bone density, low sperm count while increasing of abnormal sperm as well as cardiovascular system. The most detrimental effect of lead is in the central nervous system which results in the loss of cognitive ability in humans [Brochin R. *et al*,

2008]. High concentrations of iron affect the freshwater ecosystem. Aquatic plants will undergo necrosis, the growth of seedling and phytoplankton will be inhibited when the iron content in freshwater is above the threshold limit [Xing W. & Liu G., 2011]. However iron is an essential element in the biological system. Iron is needed for the well-functioning of all living cells and enzyme activity as well as in specialized storage and carrier proteins. Excess of iron in the human body will cause cancer and dysfunction of certain organs [Hasan S. *et al*, 2017]. Copper is commonly found in fungicides, herbicides, algaecides and insecticides. Hence, copper may be easily washed to freshwater. High exposure to copper causes the impairment of osmotic pressure and ion regulation in the gills of aquatic organisms [Kiaune L. & Singhasemanon N., 2011]. Besides that, high level of zinc or cadmium cause oxidative stress to cells and further inhibit many metabolic processes, especially in plants. However, zinc is an element that is essential to maintain good cell functionality, but the uptake of zinc is often interfered by cadmium. Therefore, it is important to constantly evaluate and monitor the concentrations of heavy metals in the environment and biological systems [Tkalec M. *et al*, 2014].

Several conventional methods such as total reflection x-ray fluorimetry (TXRF), anodic stripping voltammetry, inductively coupled plasma emission or mass spectrometry (ICP-ES or ICP-MS), and atomic absorption spectroscopy (AAS) have been used for the detection of heavy metals. These conventional techniques require considerable amount of time for pretreatment of samples, more so, they incur high instrumentation cost [Kumar J. & Kokil A., 2015]. On the contrary, photoluminescent chemosensors have high processability, they are simple, portable and cost effective. Several rhodamine-B and BODIPY derivatives were reported as photoluminescent chemosensors for copper, mercury and zinc ions [Wu D. *et al*,

2017]. However, polymer-based photoluminescent chemosensors are preferred because the chemical structures of the polymers can be tuned to obtain selectivity and increased sensitivity [Kumar J. & Kokil A., 2015].

Although different treatments are employed for the removal of heavy metals, adsorption is one of the most effective method. Triazole moiety was used in development of different types of adsorbents for heavy metal ions removal due to its excellent cations binding motifs. Hence the 1,2,3-triazole moiety was incorporated into the ester oligomers in this study. Triazoles can act synergistically to provide receptor and sensor with suitable arrangement between triazole moiety and chromophores [Kim J. S. *et al*, 2010]. Triazole rings have high stability towards oxidation and acid hydrolysis. The incorporation of the triazole moiety into polymers increases the overall thermal and moisture resistance of the polymers due to its large dipole moment, and strong hydrogen acceptor [Kantheti S. *et al*, 2015].

1.2 Problem statements

Aromatic polyesters are widely used in electric, electronic and photonic fields due to their high thermal stability, interesting mechanical properties and chemical resistance. However, most of the reported aromatic polyesters showed low processability due to solubility problem. The poor solubility of aromatic polyesters in most organic solvents is attributable to the high regularity and rigidity of their backbones. On the other hand, several types of organic dyes and fluorene-based chromophores have been incorporated successfully as pendant groups to obtain photoluminescent polymers. Very few of them were integrated into the conjugated ester backbone as monomers. Moreover, the application of aromatic polyesters as photoluminescent chemosensors for heavy metal ions is not widely explored as most of the chemosensors are made up of simple molecules or supramolecules.

1.3 Research objectives

This research focused on the synthesis and characterization of photoluminescence ester oligomers with fluorene, fluorescein or curcumin as the backbone unit and a N-alkylated triazole pendant.

The objectives of this study are:

a) To synthesize new aromatic ester oligomers bearing alkyl side chains.
b) To investigate the solubility of the synthesized branched aromatic ester oligomers in various solvents, and their thermal stability using thermogravimetric analysis (TGA).
c) To investigate the photoluminescence properties of the ester oligomers using UV-Vis and fluorescence spectrophotometers.

d) To investigate the potential application of ester oligomers as chemosensors for different metal ions.

1.4 Scope of studies

a) The aromatic dicarboxylic acid and photoactive diol (9,9-bis(4-hydroxyphenyl)fluorene, fluorescein and curcumin) were used as monomers to synthesize aromatic ester oligomers bearing alkyl side chains. The synthesized ester oligomers were characterized using ATR-FTIR, 1D and 2D NMR spectroscopy. Their average molecular weights were analyzed using gel permeation chromatography (GPC).

b) The length of methylene chain m, ranged from 10-16 carbons in even parity, $(CH_2)_m$- introduced as side chain which was bridged by 1,4-disubstituted triazole ring to their respective backbones.

c) Cu^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Ni^{2+} were the metal ions used in the chemosensing studies.

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

The chemicals listed in Table 2.1 were used in the synthesis of monomers and oligomers. The chemicals were used without further purification unless otherwise noted.

Table 2.1. Chemicals used in the synthesis of monomers and oligomers

Chemicals	Purity	Manufacturers
5-Hydroxyisophthalic acid	>97%	TCI (TOKYO CHEMICAL INDUSTRY)
Propargyl bromide	>80%	TCI (TOKYO CHEMICAL INDUSTRY)
Fluorescein	NA	TCI (TOKYO CHEMICAL INDUSTRY)
9,9-Bis(4-hydroxyphenyl)fluorene	>97%	MERCK
1-Bromodecane	>98%	MERCK
1-Bromododecane	>98%	MERCK
1-Bromotetradecane	>98%	MERCK
1-Bromohexadecane	>98%	MERCK
Sodium azide	>97%	MERCK
Thionyl Chloride	>99%	MERCK
Sodium ascorbate	>98%	Sigma-Aldrich
Triethylamine	>99.5%	R & M Chemicals
Copper(II) sulphate pentahydrate	>99%	Qrec-Chemicals
Potassium hydroxide	85%	MERCK
Potassium iodide	>99%	Sigma-Aldrich
Curcumin	>97%	MERCK
Iron standard solution	NA	MERCK