SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENCE PROPERTIES OF PHOTOCROSSLINKABLE BENZYLIDENE-CONTAINING POLYESTERS AND THEIR POTENTIAL APPLICATION AS CHEMOSENSOR

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UNIVERSITI SAINS MALAYSIA
2017

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by

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**Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy**

March 2017

ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude and appreciation to my main supervisor Dr. Oo Chuan Wei for his invaluable support, advices and encouragement throughout my whole candidature period. I am also grateful to the Dean of School of Chemical Sciences for providing the assistance and facilities throughout the period of my research. Apart from that, I would also like to convey my gratitude to the Dean of Institute of Postgraduate Studies for given the chance to enrol as a PhD candidate in USM as well as all the staff of School of Chemical Sciences for their technical support and assistance.

On the other hand, I would like to express my sincere appreciation to Prof. Takaomi Kobayashi and his fellow students from Nagaoka University of Technology of Japan for given a chance to share and expand my knowledge in my research especially in the application studies. Besides that, I would also like thank my fellow laboratory mates and friends for their encouragement during the period of my research studies. Furthermore, I would like to acknowledge the Ministry of Higher Education and MyBrain15 for the scholarship and FRGS funding (203/PKIMIA/6711317) provided throughout the period of my studies.

Last but not least, I would like to express my deepest gratitude to both my parents, Lim Eng Guan and Teh Saw Cheng, my husband, Heng Boon Teck, my sisters, Lim Wan Thing and Lim Wan Huay and my family members for being understanding and provide invaluable supports throughout my whole research.

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LIST OF ABBREVIATION

°C	Degree Celcius
^{1}H-NMR	Proton nuclear magnetic resonance
^{13}C-NMR	Carbon nuclear magnetic resonance
EtOH	Ethanol
HCl	Hydrochloric acid
nm	Nanometer
$CDCl_3$	Deuterated chloroform
CHN	Carbon, Hydrogen and Nitrogen
COSY	Correlation spectroscopy
$CuSO_4.5H_2O$	Copper sulphate pentahydrate
K_2CO_3	Anhydrous potassium carbonate
KI	Potassium iodide
kV	kilo Volt
DMF	Dimethylformamide
DSC	Differential scanning calorimetry
FT-IR	Fourier transform infrared
FT-NMR	Fourier transform nuclear magnetic resonance
HMQC	Heteronuclear multiple quantum correlation
HMBC	Heteronuclear multiple bond correlation
J	Coupling constant
s	Singlet

d	Doublet
m	Multiplet
q	quartet
t	Triplet
ppm	Parts per million
ϕ	Quantum yield
TMS	Tetramethylsilane
WAXD	Wide angle X-ray diffraction
δ	Chemical shift
v/cm^{-1}	Wavenumber in centimetre unit
T_g	Glass transition temperature
T_d	Decomposition temperature
%	Percentage
μM	Micro Molar
λ	Wavelength
π	Pi
A_o	Absorption before irradiation
A_t	Absorption after irradiation at time 't'

SINTESIS, PENCIRIAN DAN SIFAT KEFOTOPENDARCAHAYAAN POLIESTER YANG MENGANDUNGI BENZILIDENA BERANGKAI SILANG FOTO DAN POTENSI APLIKASINYA SEBAGAI KEMOSENSOR

ABSTRAK

Tesis ini merangkumi tujuh siri homolog poliester baru yang mengandungi kumpulan benzilidena dan bisbenzilidena. Poliester yang disintesiskan mempunyai keterlarutan dalam pelbagai jenis pelarut organik yang meningkatkan potensinya dalam kajian aplikasi. Struktur molekul monomer dan polyester yang disintesiskan telah disahkan dengan menggunakan teknik spektroskopi seperti FT-IR dan FT-NMR (1D dan 2D NMR). Analisis TGA dan DSC menunjukkan bahawa semakin pendek rantai fleksibel, semakin tinggi kestabilan haba mengikut turutan m= 10>12>14>16>18 yang mana m ialah panjang rantai. Selain itu, kestabilan haba poliester bergantung kepada jenis kumpulan seperti fluorescein, fluorene dan triazol pada tulang belakang dan rantai sisi. Ia juga dipengaruhi oleh jenis kumpulan tertukarganti pada rantai sisi seperti $-OCH_3$ dan $-Cl$. Poliester yang mengandungi gelang heterosiklik triazol (**PB** dan **PD**) menunjukkan kestabilan haba yang lebih tinggi berbanding dengan analog yang tidak ada gelang heterosiklik triazol (**PA** and **PC**). Poliester dengan kumpulan metoksi pada rantai sisi mempunyai kestabilan haba yang lebih tinggi berbanding dengan $-Cl$ dan poliester tanpa kumpulan pengganti. Peratusan kehabluran yang didapati daripada kajian WAXD telah menunjukkan bahawa poliester dengan peratusan kehabluran yang tinggi mempunyai kestabilan haba yang lebih tinggi. Yang mengunikkan, semua poliester yang disintesiskan

adalah aktif terhadap peningkatan pancaran teraruh agregasi (AIEE). Poliester, **PFX** yang mengandungi fluorescein dan mempunyai ketegaran yang tinggi menunjukkan AIEE yang paling tinggi berbanding dengan **PEX** yang mengandungi fluorene. Ini diikuti dengan poliester yang mengandungi atau tanpa gelang heterosiklik triazol dalam turutan **PD**> **PB**> **PC**> **PA**. Poliester yang disintesiskan menjalani tindak balas berangkai silang foto dengan penyinaran UV dan peningkatan dalam keamatan kefotopendarcahayaan telah diperhatikan. Hal ini mungkin disebabkan oleh interaksi susunan π-π yang berkesan yang disebabkan oleh pendimeran foto yang membentuk gelang siklobutana yang menyebabkan rangkaian polimerik lebih tegar dan akan menambahkan lagi agregasi. Imej TEM menunjukkan bahawa agregasi molekul poliester berlaku apabila didedahkan kepada cahaya UV untuk membentuk misel seperti yang diperhatikan dalam kajian AIEE. Selepas tindak balas berangkai silang foto, SEM telah menunjukkan bahawa poliester tersebut mempunyai tekstur yang kasar seperti gentian dan banyak lowong pada permukaannya berbanding dengan tekstur poliester asal yang mempunyai lapisan permukaan yang licin. Aplikasi kemosensor poliester juga dijalankan dengan menggunakan pelbagai jenis ion logam berat. Poliester yang disintesiskan menunjukkan kepekaan dan kepilihan terhadap suatu ion logam yang spesifik dengan sifat pendarflour 'hidup'. Sebagai contohnya, **PB3** dan **PD3** adalah terpilih terhadap ion Pb^{2+}, **PA3** adalah terpilih terhadap ion Cd^{2+}, **PC3** adalah terpilih terhadap ion Cu^{2+}, dan **PEH** dan **PFH** adalah terpilih terhadap ion Ni^{2+}.

SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENCE PROPERTIES OF PHOTOCROSSLINKABLE BENZYLIDENE-CONTAINING POLYESTERS AND THEIR POTENTIAL APPLICATION AS CHEMOSENSOR

ABSTRACT

This dissertation comprised of seven homologous series of new polyesters containing benzylidene and bisbenzylidene moieties. The synthesized polyesters were found to be soluble in various organic solvents which would enhance their potential in application studies. The molecular structures of the synthesized monomers and polyesters were confirmed via spectroscopic techniques such as FT-IR and FT-NMR (1D and 2D NMR). TGA and DSC analyses showed that polyesters with shorter flexible chain length were thermally more stable in the order of m= 10>12>14>16>18, where m is the chain length. Furthermore, the thermal stability of the polyesters was also found to depend on the types of moiety, namely fluorescein, fluorene and triazole on the backbone as well as the side chain. It was also affected by the types of substituents, like -OCH$_3$ and -Cl on the side chain. Polyesters containing triazole hetereocyclic rings (**PB** and **PD**) were found to be thermally more stable than those without which are **PA** and **PC**. Polyesters with -OCH$_3$ substituent on the side chain had a higher thermal stability than those with -Cl and unsubstituted polyesters. The percentage of crystallinity obtained from WAXD study showed that polyesters with higher percentage of cystallinity had greater thermal stability. Uniquely, all the synthesized polyesters were aggregation-induced emission

enhancement (AIEE) active. Polyesters with greater rigidity like **PFX** which contained fluorescein moieties showed greatest AIEE effect than that of **PEX** which contained fluorine moieties. This was followed by polyesters with and without triazole hetereocyclic rings in the order of **PD> PB**> **PC> PA**. The synthesized polyesters underwent photocrosslinking upon UV irradiation and an enhancement in their photoluminescence intensity was observed. This could be due to the effective π-π stacking interactions when photodimerization occurred that formed the cyclobutane ring thus resulting in a more rigid polymeric network which would further induced aggregation. The TEM images showed that aggregation of the polyesters molecules occurred after exposure to UV light to form micelles, which was similar to that observed in the AIEE study. The SEM showed that after photocrosslinking, the polyesters displayed a fiber-like, rough texture with more voids as compared to that of the virgin polymers that had smooth surface layer. The potential of the polyesters as chemosensors was investigated using various heavy metal ions. The synthesized polyesters illustrated sensitivity and selectivity towards specific metal ions with 'turn on' fluorescence behaviour. For instance, **PB3** and **PD3** were selective towards Pb^{2+} ions. **PA3** was selective towards Cd^{2+} ions, **PC3** was selective towards Cu^{2+} ions and **PEH** and **PFH** were selective towards Ni^{2+} ions.

1.0   INTRODUCTION

1.1   Polymers

Polymers, also known as macromolecules are built up from numerous smaller molecules called monomers which are linked together via covalent bonding through a chemical reaction called polymerization [Sperling L. H., 2006]. In the past, most of the studies were focussed on natural polymers. In the early years (before 1800), the first polymers discovered and used were from natural products such as cotton, starch, wool and proteins, while *Hevea brasiliensis* (natural rubber) was used by the early South American civilizations (Aztecs) for waterproofing fabrics and making elastic articles. After years of work in Yonkers, New York, in 1907, the early twentieth century, Leo Baekerland announced the first synthetic polymer, Bakelite, followed by Nylon 6,6 in 1928. To date, more and more polymers were synthesized in accordance to the advancement of technologies [Charles E. & Carraher Jr., 2013]. The concept of covalently bonded macromolecular structures was first proposed by Hermann Staudinger in 1920. After that, more polymers were synthesized and classified as homopolymers and copolymers. Homopolymers are made up of identical monomer units which can be obtained via radical reactions that take place on the alkene double bond of a single monomer. Copolymers are made up of two or more different monomer units which can be obtained through polycondensation reaction [Wade L. G. Jr., 2006].

1.1.2   Polymerization process

There are two methods of polymerization, namely additional polymerization and condensation polymerization. In fact, addition polymers are sometimes called chain-growth polymers due to the rapid addition of one molecule at a time at the end

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of the chain of a growing polymer chain. This type of polymer truly depends on the monomer and the initiator used wherein the reactive intermediates may be free radicals, carbocations or carbanions [Wade L. G. Jr., 2006].

The free radical polymerization usually involved an alkene with a radical initiator, for example a peroxide radical such as benzoyl peroxide in the presence of heat and/or high pressure. The mechanism involved three significant steps which were initiation, propagation and termination as shown in Figure 1.1 [Smith J. G., 2011].

Initiation step: Formation of a carbon radical in two steps

peroxide

styrene

Propagation step: Growth of the polymer chain by C-C bond formation

Termination step: Removal of radicals by formation of a sigma bond
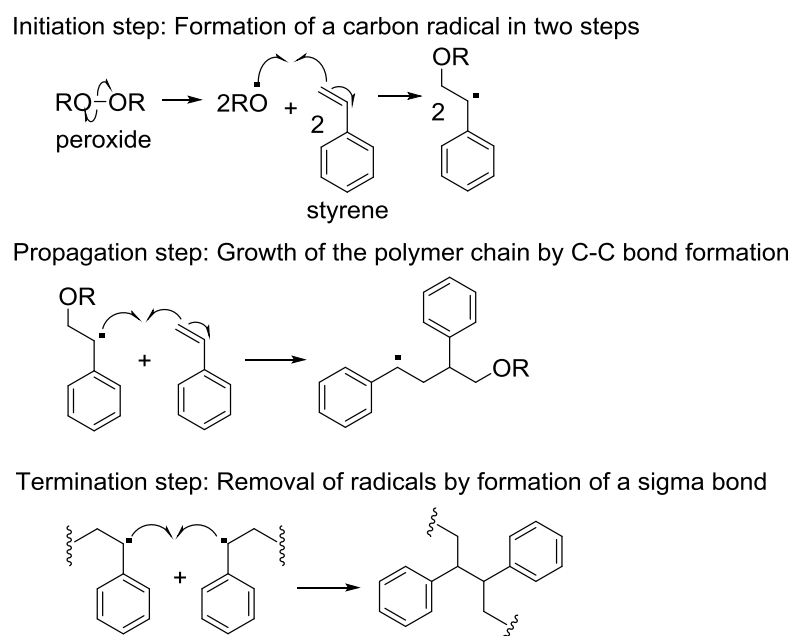
Figure 1.1 Mechanism of free radical polymerization of styrene [Smith J. G., 2011]

As for the cationic and anionic polymerization, their mechanisms are similar to that of the free radical process with the involvement of different intermediates of carbocation or carbanion. A cationic polymerization is initiated by a strong acidic catalyst like boron trifluoride, BF_3 in the presence of traces of water in methanol as a

co-catalyst while an anionic polymerization is initiated by a strong nucleophile like organolitium reagent or Grignard reagent. A cationic polymerization occurs in alkenes containing alkyl or electron donating groups, whereas an anionic polymerization occurs in alkenes containing electron withdrawing groups. Monotonously, both follow a three-step mechanism of initiation, propagation and termination as shown in Figures 1.2 and 1.3, respectively [Smith J. G., 2011].

Initiation step: Formation of a carbocation

Z= electron donating group

Propagation step: Growth of the polymer chain by C-C bond formation

repeat step over and over

Termination step: Loss of a proton
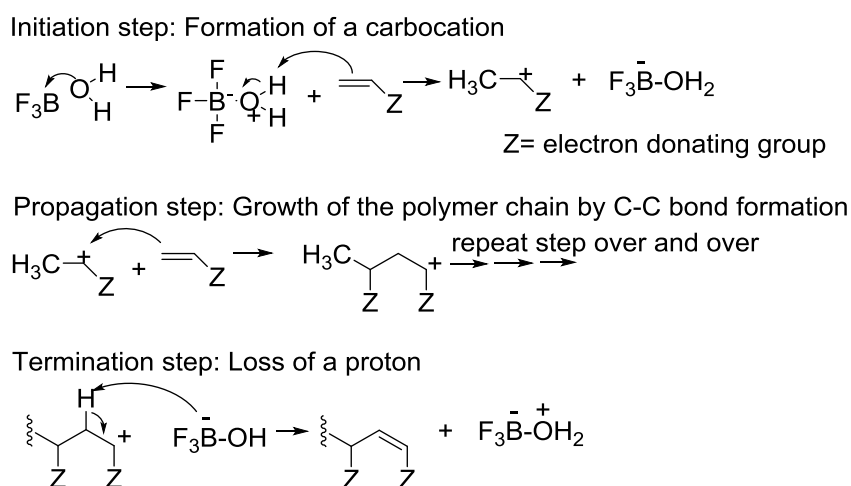
Figure 1.2 Mechanism of a cationic polymerization of $CH_2=CHZ$ [Smith J. G., 2011]

Initiation step: Formation of a carbanion

A= electron withdrawing group

Propagation step: Growth of the polymer chain by C-C bond formation

repeat step over and over

Termination step: Addition of a proton source to stop the chain
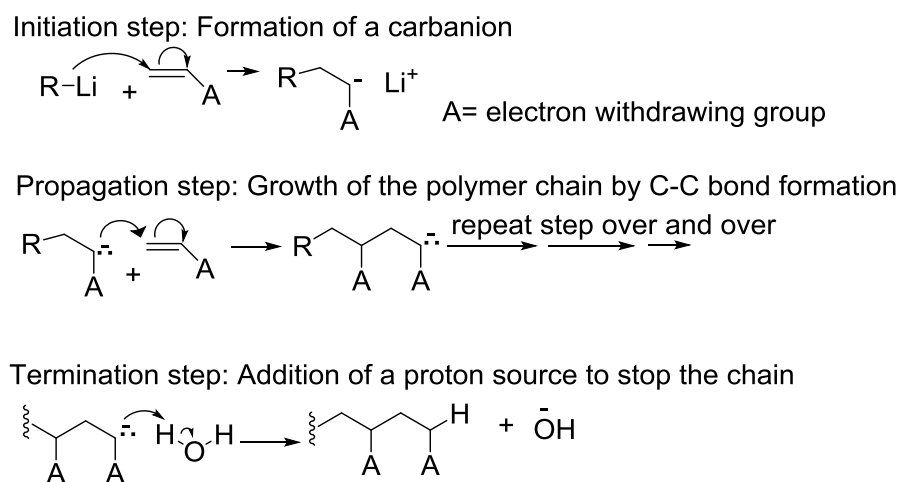
Figure 1.3 Mechanism of an anionic polymerization of $CH_2=CHA$ [Smith J. G., 2011]

Condensation polymers which are also known as step-growth polymers are actually formed by the reaction between two difunctional monomers, that result in

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the formation of a new bond in a separate step. There are in fact two common types of step-growth process, in which the first would involve two types of monomers, A-A and B-B to give –(A-A-B-B)$_n$– polymers while the second type would be the polymerization with its own monomer, also known as self–condensation of one type of monomer, A-B to give –(A-B)$_n$– polymers. Thus, it could be clearly seen that in each of these cases, functional group of A reacts exclusively with functional group of B and vice versa which results in the formation of a new covalent bond generally by polar reactions such as nucleophilic acyl substitution. There are several common types of condensation polymers, for instance, polyesters, polyamides, polyurethanes and polycarbonates as depicted in Figure 1.4 [Brown W. H. & Foote C. S., 2002].

Polyamide

hexanedioic acid   1,6-hexanediamine

Nylon salt

heat

Nylon 66

Polyester

1,4-benzenedicarboxylic acid   1,2-ethanediol   heat   + 2n H$_2$O

Polyurethane

2,6-toluene diisocyanate   low molecular weight polyester or polyether

polyurethane

Polycarbonate

disodium salt of bisphenol A   phosgene   lexan (a polycarbonate)   + 2 NaCl
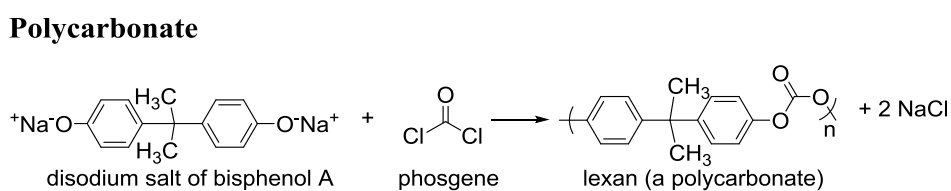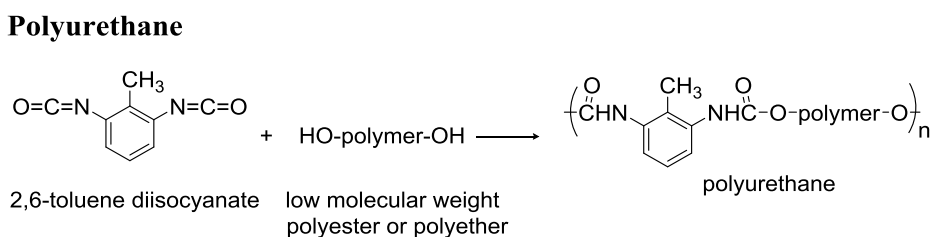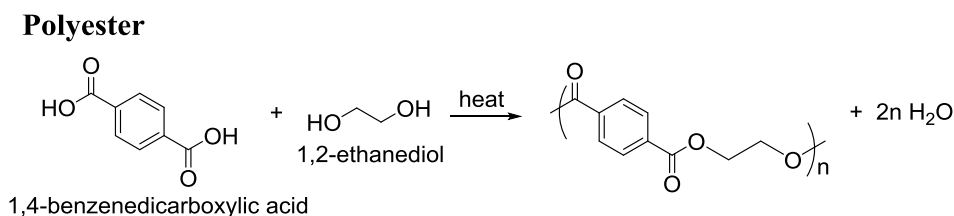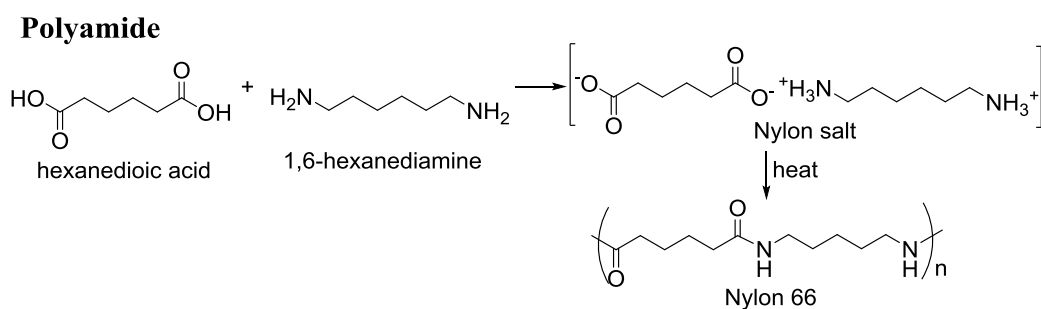
Figure 1.4 Formation of polyamide, polyester, polyurethane and polycarbonate

[Brown W. H. & Foote C. S., 2002]

1.1.3 Polyesters and Poly(azomethine)esters

Polyesters are synthesized by bifunctional monomers through step-growth polymerization to obtain the ester functional groups in the backbone. Such a polymerization reaction is also known as a polycondensation reaction (along with polyureas, polyamides and others) due to the outcome of producing small by product like water [Selvi R. S. et al, 2011]. The synthesis of polyesters was pioneered by Carothers and co-workers in 1930 but the synthesized polyesters were found to have low melting points and poor hydrolytic stability [Pang K. et al, 2006]. His research work involved straight chain polymerization of compounds like A-B ω-hydroxy-acids, lactones as well as esterification of A-A linear diols with B-B terminal aliphatic dicarboxylic acids [Carothers W. H., 1929]. In 1946, Whinfield and Dickson discovered and patented poly(ethylene terephthalate) (PET) having high melting temperature and good hydrolytic stability. The partial aromatic organic moiety was necessary to be incorporated the compound structure in order to increase its melting point, T_m above 250°C [Whinfield J. R., 1946; Whinfield J. R. & Dickson J. T., 1946].

Polyesters especially PET were then manufactured by ICI (UK, 1949) as industrial products, followed by Du Pont (USA, 1953) that used the trademark Mylar for the production of films [Edlund U. et al, 2003; Pang K. et al, 2006]. Years later, various aromatic polyesters such as poly(butylene terephthalate) (PBT) have been studied and produced commercially for more than 50 years [Pang K. et al, 2006]. In fact, the pure aromatic polyesters are not only well known for their naturally forming

film and fibre but also for their biodegradable [Zhang L. L. et al, 1995] and biomedical properties [Guo B. L. et al, 2013]. Thus, their applications in the field of both medical and non medical are highly acceptable [Vasanthi B. J. & Ravikumar L., 2007]. The broad spectra of both the aliphatic and aromatic polyesters in various application fields have been dependent on and well relevance to their structural designs and properties [Shenoy M. A. et al, 2005]. Therefore, it is of current interest towards the inclusion of various linking groups in the polyesters, either in the backbones or in their side chains [Kausar A. & Hussain S. T., 2013] of the polymer network.

The attempt of incorporating an azomethine linkage in a polyester backbone would lead to a new class of polyester called poly(azomethine)esters bearing both ester and azomethine functional groups on the polymer backbone. There are in fact two classes of poly(azomethine)esters. The first class was obtained from the reaction of two types of bifunctional monomers, for example, dicarboxylic acid and dialcohol monomers with the azomethine moiety in one of the monomers while the second class was obtained from the reaction of only one type of monomers consisting of both alcohol and acid functional groups on the terminal chain with the azomethine group on the backbone (HOOC-R-C=N-R-OH). These could be clearly seen in the example of an individual work reported by Bhuvaneshwari et al in 2015 for the first class of poly(azomethine)esters while the second class of poly(azomethine)esters was studied by Ravikumar et al in 2009. The detailed schematic works are as shown in Figure 1.5 and Figure 1.6, respectively.
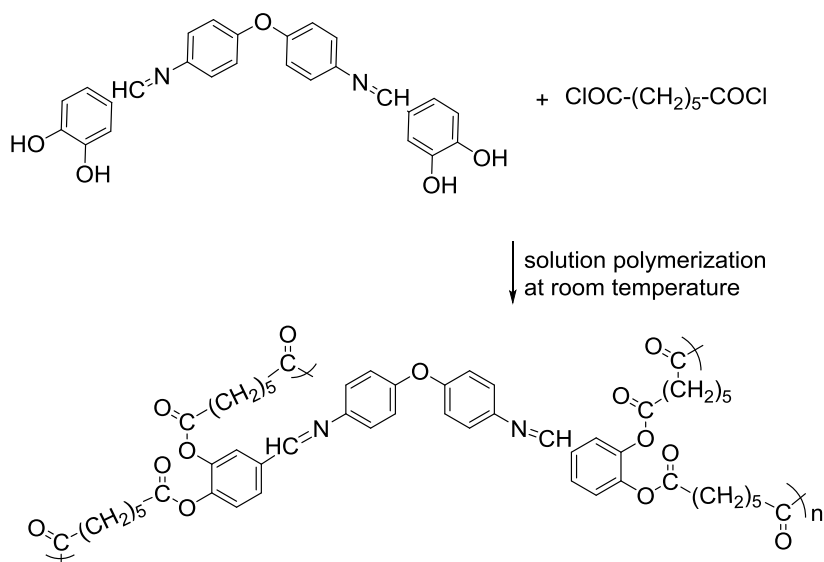
Figure 1.5 Poly(azomethine)esters formed from diacid and diol monomers

[Bhuvaneshwari B. et al, 2015]

X= H, OCH$_3$
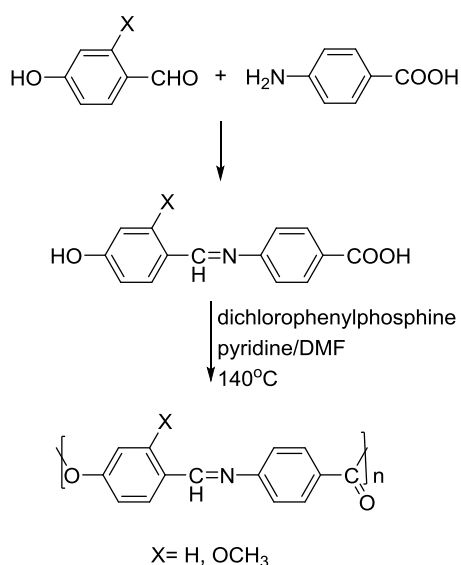
Figure 1.6 Poly(azomethine)esters synthesized from monomers consisting of both alcohol and acid functional groups on the terminal chain [Ravikumar L. et al, 2009]

In recent years, poly(azomethine)esters were studied owing to their noteworthy ability in overcoming the insolubility problem due to strong linearity of the polyazomethines chains. As according to the first synthesized polyazomethines

which was an insoluble and infusible polymer due to its strong chain-chain interaction whereby benzidine and dianisidine were treated with terephtaldehyde [Higuchi M. & Yamamoto K., 2002; Kaya I. & Culhaoglu S., 2008]. This shortcoming minimizes the feasibility of processing the polymers which later led to the approach of having ether or ester linkages in the polymeric compounds would help to impart chain flexibility, thus enhances solubility at the same time lowering the glass transition temperature [Marin L. et al, 2006; Suh S. C. & Shim S. C. et al, 2000]. In fact, the presence of ester groups does not only induce the flexibility, but also the charge carrier movement along the chain in the polymeric systems [Vasanthi B. J. & Ravikumar L., 2013; Balaji R. & Nanjundan S., 2010].

It is of great interest to investigate the various interesting and peculiar properties of polyesters in the presence of azomethine groups in their backbones. The azomethine linkages provide an extended spatial π-electron system that will increase the conductivity of the polymers [Kausar A. & Hussain S. T., 2013]. As reported by several researchers, these polymers belong to a class of high performance polymers well known for their excellent thermal stability [Kaya I. et al, 2011], ability to form chelation with metal complexes [Ravikumar L. et al, 2009], good environmental resistant and mechanical properties [Kimura K. et al, 2003], as conductive polymers [Kausar A. & Hussain S. T., 2013] and electron transporting layers (ETLs) or hole transporting layers (HTLs) [Fischer W. et al, 1996]. Moreover, this type of thermostable polymers is an interesting candidate in several potential applications in photonics and electronics, [Zaltariov M. F. et al, 2014] and as optoelectronics materials [Iwan A. et al, 2012] besides being a powerful alternative to nanofabrication and nanomanipulation for the development of nanotechnology as a

new perspective in material science [Kausar A. & Hussain S. T., 2013; Marin L. et al, 2009].

1.1.4 Photoluminescent polymers

The research studies on photoluminescent polymers have gathered great scientific attention due to their engrossing properties and applications in various fields of material and life sciences. Generally, there is an enormous demand for fluorescent materials in recent years. The latest research progress on photoluminescence polymers is on the development of new architecture. There are two approaches to prepare the photoluminescent polymers. The first approach involves polymerization of monomer containing a fluorescent chromophore with some other common monomers via chemical bonding. For instance, using the fluorescent compounds as initiator as well as chain transfer agents. The second approach involves chemical modification of commercially available polymers which consists of reactive groups like fluorescent dyes [Wang K. C. et al, 2002; Gao H. et al, 2004; Yuan J. et al, 2010]. In fact, most of the literatures of this research focus on the synthesis of polymers which incorporated rare earth metals such as work reported by Liu et al in 2009 on fluorescent 1,10-phenanthroline-based polymer complexes with Europium (Eu). Research on the luminescent rare earth metal complexes have attracted considerable attention in the past decades as they could be potentially used in organic electroluminescent (EL) devices and have high internal quantum efficiency. Besides, rare earth metal-incorporated materials can be used as optical microcavity emitters owing to their inherent extremely sharp emission bands. However, these types of rare earth metal containing materials have toxic effects on human health and the environment in addition to their high cost [Pagano G. et al, 2015]. Hence, conjugated polymers and non-conjugated polymers are of current

interest. An example of conjugated polymers is photoluminescence polybenzobisoxazoles (Figure 1.7), a polymer based on fluorene and benzoxazole which was reported by Xu and co- worker in 2010. Whilst, recently, Zhu and co-workers (2014) had worked out a non-conjugated photoluminescence polymer based on polyethyleneimine as shown in Figure 1.8.
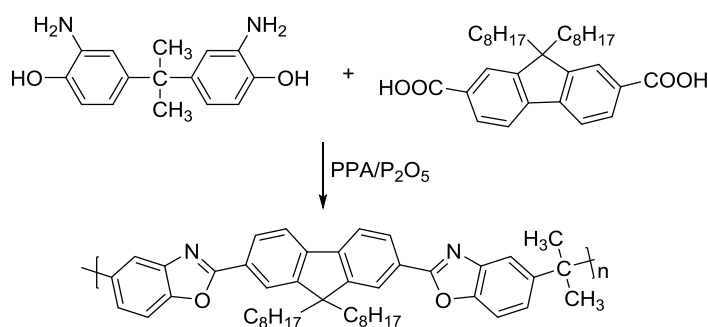
Figure 1.7 Synthesis of conjugated photoluminescence polybenzobisoxazoles [Xu X. et al, 2010]
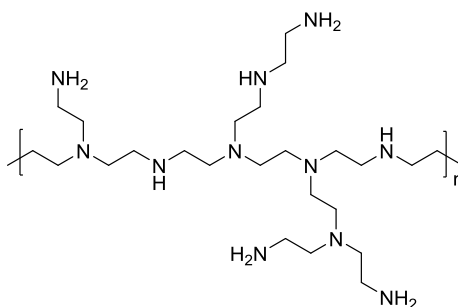
Figure 1.8 A non-conjugated photoluminescence polymer based on polyethyleneimine [Zhu S. et al, 2014]

Photoluminescence polymers have illustrated their importance in various emerging fields and photonics properties, especially as smart polymer machines, fluorescent chemosensors, fluorescent probes, in fluorescent imaging, drug delivery carrier, optoelectronics and etcetera. Polymeric compounds with fluorescence

properties have been ascertained as a convenient technology as they are easily formed into films that can be fabricated onto optical fiber waveguides in sensor studies [Yuan J. et al, 2010].

Thus the presence of the chromophore in the polymer is one of the utmost key factors towards the formation of photoluminescence polymers. Examples of chromophores are benzylidene and bis(benzylidene) moieties, 1,2,3-triazole moiety, fluorene as well as fluorescein moieties.

Benzylidenes or commonly known as chalcones are a group of yellow pigments of substituted benzalacetophenone derivatives with the presence of reactive keto vinylenic group [Iwan A. et al, 2012]. This moiety is a simple structure consisting of a α, β-unsaturated carbonyl group sandwiched between two aromatic rings and able to contribute to the various conformations, depending on the most suitable ring arrangement. The benzylidene moiety can exist as either *E*- or *Z*-isomer but in common case the chalcone will be isolated as the *E*-isomer as it is more stable thermodynamically as shown in Figure 1.9 [Borse S. L. et al, 2011]. While bisbenzylidene is a stilbenoid class of organic molecule but with an addition of one olefinic group as compared to the benzylidene moiety. Similarly, this moiety can also exist in various conformations with three isomeric structures: *EE*, *EZ* and *ZZ*. However, the *EE*-isomer has the most suitable and stable ring arrangement as shown in Figure 1.10 [Murali M. & Samui A. B., 2010].
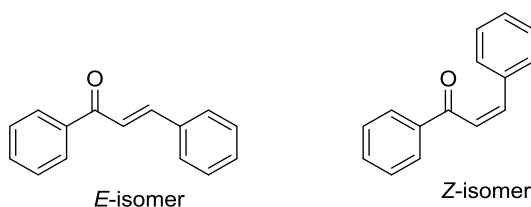
Figure 1.9 *E* and *Z* isomeric structures of benzylidene [Borse S. L. et al, 2011]
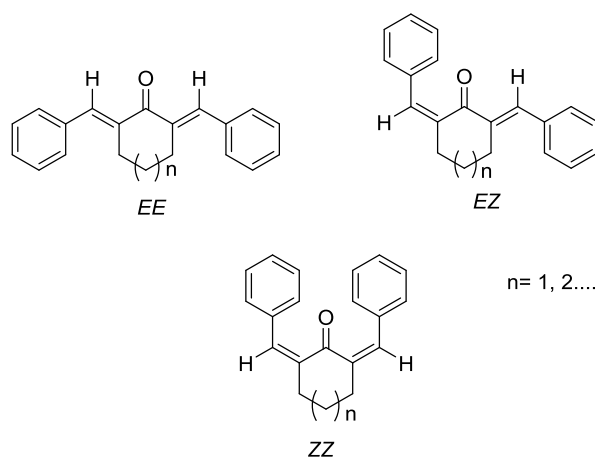
Figure 1.10 *EE*, *EZ*, and *ZZ* isomeric structures of bisbenzylidene cycloalkanone [Murali M. & Samui A. B., 2010]

Benzylidenes or chalcones are used as precursors of many naturally occurring pigments such as flavonoids and flavones [Borse S. L. et al, 2011]. In fact, these moieties have a unique template with diverse applications due to the presence of keto vinylenic group and their potential applications were reported as antioxidant, anti-angiogenic, analgesic, antimutagenic and anticancer agents besides possessing bactericidal, antifungal and insecticidal activity [Rehab A., 2003; Rehab A. & Salahuddin M., 2009]. Furthermore, bisbenzylidene or benzylidene moieties are a type of photoactive groups among other groups like cinnamoyl, coumaroyl, cyclic carbonate and stilbene derivatives which have been intensively explored for their photosensitive applications [Rami Reddy A. V. et al, 1996; Choi D. H. et al, 2001a]. The bisbenzylidene-containing polyesters would give the polyesters an outstanding photosensitive property which enables them to undergo photopolymerization reaction. This type of polymers has garnered remarkable interest among fellow researchers worldwide owing to their high processable properties such as good thermal stability, solubility, photosensitivity and as excellent adhesion [Rehab A., 2003; Rehab A. & Salahuddin N., 2009]. The photosensitive polymers are capable of changing their

chemical reactions through the induction of ultraviolet irradiation in obtaining new physical properties. There are several possible chemical reactions that may occur upon UV irradiation, such as crosslinking and chain scission [Horie K. et al, 2000]. Veritably, the presence of photosensitive moieties bearing the π electron density in the photoactive chromophores enables them to crosslink upon UV irradiation at ambient temperature, thus forming a highly crosslinked compound. Such polymers of which their structures could be changed by the action of just the exposure to UV light are valuable in the preparation of energy exchange materials, photocurable coatings and optical memory devices. Besides that, benzylidene and bis(benzylidene) would also afford photoluminescence properties in addition to giving photocrosslinkable ability to the polymers [Decker C. & Thi Viet T. N., 2001; Jayalatha D., 2009].

1,2,3-Triazole chromophore has been studied due to its crucial fluorescent properties besides being able to enhance the thermal stability of a material [Balamurugan R. & Kannan P., 2010; Li H. K. et al, 2011]. According to the hitherto reported work, the five membered [1,2,3]-triazole ring is formed via 'Click reaction' from the copper catalyzed [3 + 2] dipolar cycloaddition reaction between azides and terminal alkynes [Ozen C. & Tuzun N. S., 2012]. These triazole derivatives have received considerable attention owing to their ability to mimic peptide bonds, thus endowing them to be chemical materials in drug discovery as they showed their potential as anti-HIV [Alvarez R. et al, 1994], anti-bacterial [Genin M. J. et al, 2000], anti-histamine [Buckle D. R. & Rockell C. J. M., 1982] and anti-tumor [Pearson W. H. et al, 1990] agents. Along with that, they are also attractive materials in organic chemistry with interesting properties, for instance, they are chemically stable (inert to severe hydrolytic, oxidizing as well as reducing conditions at high temperature), have a good hydrogen-bond-accepting ability and a strong dipole moment [Srividhya D. et

al, 2009]. Hence the incorporation of triazole rings into polyesters will give fluorescent polymers with enhanced thermal stability.

Fluorene and its derivatives have attracted much attention owing to their wide energy gap as well as high luminescent efficiency [Liaw D. J. et al, 2009]. Fluorene incorporated polymers with relatively large band gaps were first developed as potential blue-light emitting materials in which the blue emission could be attained from the confinement of the conjugation length. Besides that, the fluorene polymers are also known as conjugated polymers that could emit a whole range of visible light [Lee J. et al, 2005]. Hence, the addition of fluorene moiety to the polyesters is expected to induce greater photoluminescence property.

Fluorescein dye was selected as one of the monomers in polyesterification due to the presence of two hydroxyl groups in its structure which could easily result in the formation of the ester linkages with the acid chloride groups. Furthermore, this dye is potent in inducing greater emission intensity with its high fluorescence quantum efficiency [Uthirakumar P. et al, 2005]. Moreover, fluorescein containing materials are promising candidates for nonlinear optics as inorganic glass filled with fluorescein illustrated third order nonlinear optical. In fact, making the fluorescent dye an integral part of a polymer is one of the extensive steps in the designation of fluorescent materials [Fomine S. et al, 1995].

1.1.5 Photocrosslinkable polymers

Photosensitive polymers have gained remarkable interests in current scientific research ever since they acquired significant importance in various industrial applications such as optical waveguide materials, liquid crystal display, photolithography, photoresist [Gayathri K. et al, 2009, Wen P. et al, 2011; Kumar G.

et al, 2013], energy exchange materials [Kim T. D. et al, 2002], cathode ray tubes, integrated circuits, compact discs and etcetera [Rehab A., 1998]. Furthermore, they have also been employed in applications, for example, as second harmonic generation materials in non-linear optics materials [Kang J. H. et al, 2002], as photorefractive polymers [Huang R. et al, 2010], holographic recording materials, fluorescent probes for sensing of metal ions, biological macromolecules and microenvironment in micelles [Rehab A., 1999; Murali M. & Samui A. B., 2010] as well as in medicinal prospects [Ferreira P. et al, 2011].

In order for the polymers to possess photocrosslinking ability, the photosensitive groups or moieties should be able to undergo changes upon light irradiation. Past studies have been conducted in order to determine the irreversible transformation of the photosensitive polymers into a photocrosslinked network during the induction of light. The photocrosslinked polymers were first discovered when the pitch was photocrosslinked for some decorative purposes during the ancient days [Gersheim F., 1996]. In 1935, Louis Minsk of Eastman Kodak synthesized the first synthetic photopolymer from the dimerization of cinnamic acid [Reiser A., 1989; Kaniappan K. et al, 2014]. Thereafter, huge varieties of photocrosslinkable polymers were developed whereby photodimerization reaction was relied on inducing intermolecular cyclization between two reactive species [Ravve A., 2006]. Photocrosslinkable moieties can be in various functional groups like cinnamoyl, furan, stillbene, azides and azo groups.

However, this study will focus on polymers containing chalcone moiety as the pendant chalcone groups of polymers were found to behave similarly to pendant cinnamate groups. This class of polymers was initially synthesized by Unruh and co-workers of Eastman Kodak Company in 1960 involving acetylation of polystyrene to

obtain poly(p-vinyl acetophenone) which then underwent condensation reaction with benzaldehyde in the presence of an acid catalyst. The benzaldehyde with electron donating substituents in the *para-* position was observed to be more sensitive to light through investigation by ultraviolet spectroscopy. In fact, polymerization of photocrosslinkable polymers could be obtained via side chain polymerization as well as main chain polymerization. In 1971, side chain polymerization via cationic polymerization was demonstrated by vinyl monomers using BF_3-ethyl etherate catalyst to yield photosensitive poly[4'-(β-vinylethoxy)chalcone] and poly[4'-(β-vinyloxyethoxy) chalcone] [Kato M. et al, 1971]. Later, Watanabe et al (1986) synthesized photocrosslinkable polymer of poly(vinyl alcohol) with 4'-substituted-4-caboxychalcone in the presence of 2,4,6-trinitrochlorobenzene as a condensing agent in homogeneous dimethyl formamide solution. The crosslinking ability was then explained by the biradical formation (dimerization) of the olefinic group of the chalcone functionality.

Another method of side chain polymerization involved an initiator such as benzoyl peroxide in methyl ethyl ketone consisting of acrylate and methacrylate monomers containing the photodimerizable α, β-unsaturated ketone moiety as shown in Figure 1.11 [Rami Reddy A. V. et al, 1996]. However, these polymers were observed to be insoluble even in the absence of a photosensitizer.
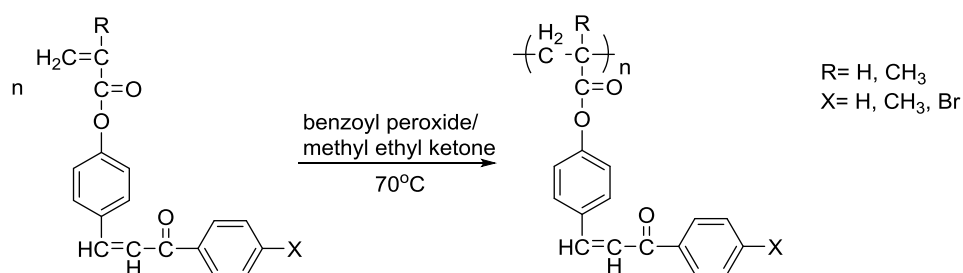
Figure 1.11 Synthesis of polymethacrylate using benzoyl peroxide at 70 ^{o}C [Rami Reddy A. V. et al, 1996]

In 1998, radical polymerization of vinyl–chalcone monomers in anhydrous toluene and tetrahydrofuran in the presence of N,N'-azo-isobutyronitrile (AIBN) as initiator was introduced by the work of Rehab in obtaining homo and comethacrylate chalcone polymers as shown in Figure 1.12.

homomethacrylate chalcone polymer   comethacrylate chalcone polymer
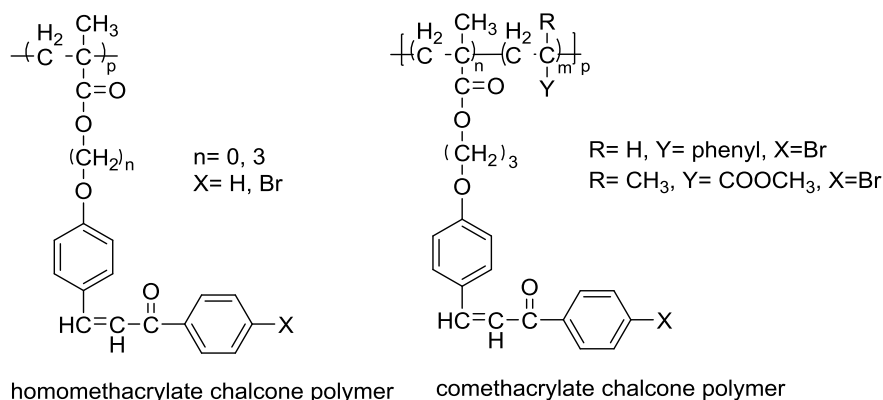
Figure 1.12 Synthesis of homo and comethacrylate chalcone polymers [Rehab A., 1998]

A few years later, in 2001, a modified polymer, poly(4-methacyloyl oxyphenyl-3'–methylstryl ketone) (MPMSK) with pendant chalcone moiety (Figure 1.13) was synthesized using ethyl methyl ketone solution and benzoyl peroxide as initiator. This polymer had very good thermal stability due to the presence of short side chains and rigid pendant chalcone units which could be potentially used for negative photoresists [Balaji R. & Nanjundan S., 2001].
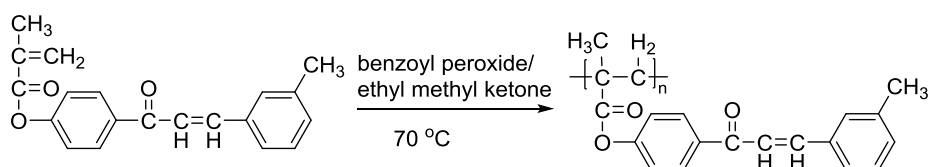
Figure 1.13 Synthesis of poly(4-methacyloyloxyphenyl-3'–methylstryl ketone) (MPMSK) with pendant chalcone moiety [Balaji R. & Nanjundan S., 2001]

In the aspect of main chain polymerization, photocrosslinkable polyesters were constructed via polycondensation reaction. According to the work reported by Kim and co-workers in 2002, step-reaction polymerization involving cinnamoyl group between the diol and diacid monomers and the photocrosslinking properties were documented (Figure 1.14). The high photocrosslinking behavior of this class of polymers ascertains its potential as photoresist as well as in photo-alignment applications of liquid crystals.
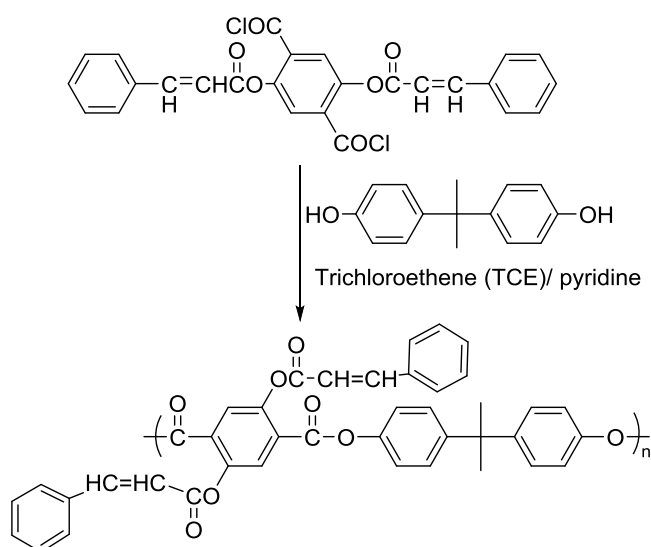
Figure 1.14 Synthesis of aromatic polyester with a cinnamoyl moiety [Kim T. D. et al, 2002]

The phase transfer catalyzed polycondensation method was used for synthesis of copolyester chalcone derivatives which was reported by Selvi and co-workers that involved the monomers of 1,3-bis(4-hydroxy-3-methoxyphenyl) propenone (BHMPP) and 1-(3, 5-dihydroxyphenyl)-3-(4-methoxyphenyl) propenone (DHPMPP) with aliphatic acid chlorides using tetra-n-butyl ammonium bromide as PTC catalyst as shown in Figure 1.15. These copolyesters were used in biological assays (anticancer properties) [Selvi R. S. et al, 2011].
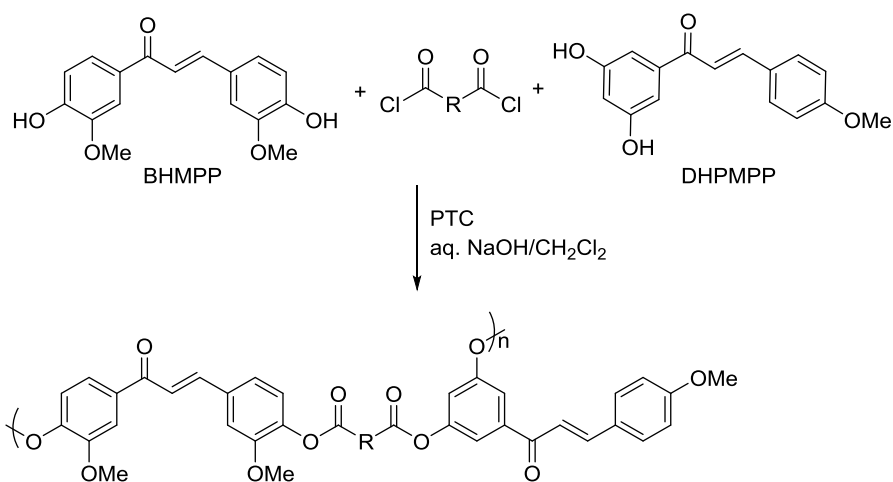
Figure 1.15 Synthesis of polyester using tetra-n-butyl ammonium bromide as PTC catalyst [Selvi R. S. et al, 2011]

As shown in Figure 1.16, Zhao and Wu have synthesized photocrosslinkable copolyesters based on ferulic acid and 9-hydroxy-9-fluorene-carboxylic acid by esterification-polycondensation method with acetic anhydride as the condensation reagent in the presence of magnesium acetate. They revealed that the photocrosslinked copolyesters depicted improved thermo-stability.

Figure 1.16 Synthesis of fluorene-based polyesters [Zhao Q. & Wu W., 2009]

1.1.6 Aggregation-induced emission enhancement (AIEE)

Fluorophores displaying aggregation-induced emission enhancement (AIEE) and aggregation-induced emission (AIE) have attained a powerful platform for the development of chemical and biological sens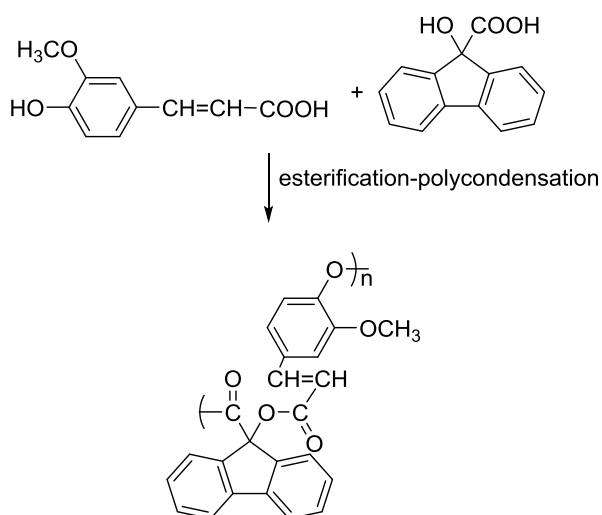ors. The concept of aggregation-induced emission (AIE) and aggregation-induced emission enhancement (AIEE) were first proposed by Ben Zhong Tang and his co-workers in 2001. It has been well known that most organic fluorescent materials give very strong fluorescence in dilute solution, but emission intensities decrease dramatically with increasing concentrations towards the formation of aggregates and this phenomenon is known as aggregation-caused quenching (ACQ). Literally, ACQ fluorophores have significantly confined the high-tech application of conventional fluorophores as compounds for practical applications that are usually used in the aggregated state. The phenomenon observed in AIEE was the exact opposite of aggregation-caused quenching (ACQ) effect whereby the fluorophore is weakly fluorescent in solution, but exhibited intense fluorescence in aggregation [Song P. et al, 2011]. Investigation shown that the AIE polymers adopt a non planar conformation leading to a restriction of intramolecular rotation (RIR) (Figure 1.17) which inhibits the face-to-face packing structure that will further minimize the likelihood of formation of the excimer. Nevertheless, it is amazing that an outwardly minor variation in the structure will elicit a great difference in the photophysical property from showing ACQ to AIE effect as illustrated in Figure 1.18. The incorporation of additional α-dimethyl group in 1,4-distyrylbenzene causes steric hindrance that will affect its molecular geometry, packed structure and molecular interaction which then gives it a complete reversion of planar to non planar conformation [Hong Y. et al, 2011].