

**SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES OF  
NEW TWIN DIGLYCIDYL ETHERS BASED ON AZOMETHINE  
GROUPS CURED BY AROMATIC DIAMINES**

**by**

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## LIST OF ABBREVIATIONS

CAD	Computer-Aided Drawing
DDS	4,4'-diaminodiphenyl Sulfone
DGEBA	Diglycidyl Ether of Bisphenol A
UF	Urea Formaldehyde
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transform Infrared
LC	Liquid Crystal
LCD	Liquid Crystal Display
LCE	Liquid Crystalline Epoxy
LMM	Low Molar Mass
LCP	Liquid Crystalline Polymers
LCER	Liquid Crystalline Epoxy Resin
LCT	Liquid Crystalline Thermoset
NMR	Nuclear Magnetic Resonance
POM	Polarized Optical Microscope
PPDA	1,4 - phenylene Diamine
TGA	Thermogravimetric Analysis
$T_g$	Glass Transition Temperature
$T_i$	Isotropization Temperature
$T_m$	Melting Temperature
UV-Vis	UV-Visible Spectrophotometer
WAXD	Wide Angle X-ray Diffractometer

**SINTESIS DAN SIFAT HABLUR CECAIR KEMBAR DIGLISIDIL ETER  
BARU BERASASKAN KUMPULAN AZOMETINA DIMATANGKAN  
DENGAN AMINA AROMATIK**

**ABSTRAK**

Dua jenis bisfenol yang mengandung kumpulan azometina iaitu 3,3'-dimetoksi-4,4'-dihidroksi-N-benzilidina-*o*-tolidina (I) dan 4,4'-dihidroksi-N-benzilidina-*o*-tolidina (II) telah disintesis melalui tindakbalas *o*-tolidina bersama vanillin dan *p*-hidroksibenzaldehid. Tindakbalas seterusnya dengan epiklorohidrin dalam kehadiran tetraheksilammonium bromida (THABr) sebagai pemangkin untuk menghasilkan kembar hablur cecair baru diglisidil eter iaitu 4,4'-di(2,3-epoksiropoksi)-N-benzilidina-*o*-tolidina (III) dan 4,4'-di(2,3-epoksiropoksi)-N-benzilidina-*o*-tolidina (IV). Struktur kimia hasil sintesis dikonformasikan melalui spektroskopi FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-Vis dan analisis elemen (CHN). Pematangan III dan IV dijalankan dengan dua amina aromatik yang berbeza iaitu 4,4'-diaminodiphenil sulfone (DDS) dan *p*-fenilindiamina (PPDA) dalam nisbah diglisidil eter / diamina 1:1, 2:1, 3:1 dan 4:1. Tindakbalas pematangan yang berlaku dikonformasikan melalui spektroskopi FT-IR. Darjah kristaliniti, sifat hablur cecair serta kestabilan terma bagi III, IV dan hasil yang termatang masing-masing dikaji melalui sudut lebar X-ray diffraktometer, imbasan berskala kalorimetri (DSC), mikroskop berpolar (POM) dan analisis terma gravimetrik (TGA). Ciri-ciri mekanikal bagi hasil yang termatang dikaji melalui pelekatan, kekerasan permukaan, kelenturan, serta impak hentaman.

**SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES OF NEW TWIN  
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AROMATIC DIAMINES**

**ABSTRACT**

Two bisphenols containing azomethine groups namely, 3,3'-dimethoxy-4,4'-dihydroxy-N-benzylidene-*o*-tolidine (I) and 4,4'-dihydroxy-N-benzylidene-*o*-tolidine (II) were synthesized by reaction of *o*-tolidine with vanillin and *p*-hydroxybenzaldehyde. Subsequent reaction with epichlorohydrin in the presence of a catalyst called tetrahexylammonium bromide (THABr) to produce new twin liquid crystalline diglycidyl ethers namely, 3,3'-dimethoxy-4,4'-di(2,3-epoxypropoxy)-N-benzylidene-*o*-tolidine (III) and 4,4'-di(2,3-epoxypropoxy)-N-benzylidene-*o*-tolidine (IV). The chemical structures were confirmed by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, UV-Vis spectroscopy and elemental analysis (CHN). Curing of III and IV were then carried out with two different aromatic diamines namely, 4,4'-diaminodiphenyl sulfone (DDS) and *p*-phenylene diamine (PPDA) in the ratio of diglycidyl ether / diamine 1:1, 2:1, 3:1 and 4:1. The occurrence of curing reaction was confirmed by FT-IR spectroscopy. Degree of crystallinity, liquid crystal behaviors as well as the thermal properties of III, IV and the cured new twin diglycidyl ethers were studied by wide-angle X-ray diffractometer (WAXD), differential scanning calorimetry (DSC), polarized optical microscope (POM), and thermogravimetric analysis (TGA), respectively. Mechanical properties of the cured new twin diglycidyl ethers were also studied via adhesion, hardness, flexibility, and impact tests.

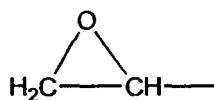


# CHAPTER 1

## INTRODUCTION

### 1.1 Epoxy Resin

Epoxy or epoxied resins are well known polymeric materials. It is defined as cross-linked polymers in which the cross-linking is derived from the reactions of epoxy group. The 'epoxy' name comes from a Greek prefix meaning 'over' or 'between' and the English suffix for oxygen. Therefore, epoxy materials are regarded as 'oxygen between compounds' [Saunders, 1988]. In general, epoxy resin is differentiated from other resins by the presence of epoxide functional group called oxirane group in its polymer chain. The oxirane group is capable to react with compound containing hydrogen active atoms for example amines, amides, carboxylic acid, phenol and mercaptan. Figure 1.1 shows the structure of the oxirane group that play an important role in the epoxy resin curing process [Mija *et al.*, 1996].



**Figure 1.1: Oxirane group**

Epoxy resin was first commercialized in 1946 and used in industries [Kaynak *et al.*, 2002]. Commercial epoxy resins are prepared by the reaction of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and epichlorohydrin. However, the developments of this type of epoxy resins were slowed down during the 2<sup>nd</sup> World War due to the high price of epichlorohydrin. At the end of the war, method of producing epichlorohydrin as an intermediate from glycerol was obtained. Therefore, it became commercially available and lead to a wider application of epoxy resins [Brydson, 1989].

Industrial sectors are the biggest consumer of the epoxy resins where most of the resins have been modified and enhanced by incorporating with additives. The modification are made due to several factors that restrict the uses of epoxy resins for instance the price of epoxy itself that is too costly, the compatibility with the end uses, environmentally friendly and to reduce the production cost and energy consumption [Milby, 1973].

### **1.1.1 Properties of Epoxy Resin**

Epoxy resin possesses properties that can be used in various applications. The properties are as follows;

- I. High tensile strength and tensile modulus [Joaquín *et al.*, 2002; Mikroyannidis, 1990]
- II. Good dimensional stability [Joaquín *et al.*, 2002; Mikroyannidis, 1990]
- III. Good rust and chemical resistance [Mikroyannidis, 1990]
- IV. Good thermal stability [Brydson, 1989]
- V. Brittle [Fernandez-Nogaro *et al.*, 1996], which is the limitation of its usage.

### **1.1.2 Utilization of Epoxy Resin**

The largest consumer of epoxy resin in the market is Germany which uses structural epoxy adhesives except for the epoxy film and paste which consume 25% of the worldwide demands and thus France is the biggest consumer for the epoxy film and paste. Structural epoxy is used in automotive industries in Germany while France use epoxy film and paste mostly in its aerospace industries. Other countries in Europe,

for example the United Kingdom and Ireland used epoxy resin in their marine industries.

Epoxy resin is utilized as listed below:

- I. Surface coating (high molecular weight resin)
- II. Lamination
- III. Adhesives
- IV. Composites
- V. Moulding
- VI. Construction
- VII. Engineering
- VIII. Electrical and electronics

Specifically, epoxy coatings are synthetic resins designed to provide a predetermined polymer structure. Epoxies are two-component, chemically cured paints. Since epoxies are synthetic, they are developed and used for a great variety of purposes. They form hard, abrasion-resistant films with excellent water, chemical, alkali and solvent resistance and are used on a variety of substrates from general purpose primers to high performance tank linings. Some epoxies present difficulties in overcoating due to hardness of cured film. In addition, they have a tendency to chalk and fade in direct sunlight. Therefore, epoxies are often modified with other binders to improve properties such as cathodic protection, surface tolerance, wetting, chemical resistance, gloss and color retention, abrasion resistance, and flexibility.

### **1.1.3 Types of Epoxy Resin**

The types of epoxies are differentiated by their structures and chemical compositions. Epoxy resins based on glycidyl ether includes epoxy resin based on bisphenol A, novolak, polyglycol, and halogenated epoxy resins.

#### **1.1.3.1 Epoxy Resin Based on Glycidyl Ether**

This type of epoxy resin is derived from the reaction between epichlorohydrin with polyhydroxyl compounds.

##### **1.1.3.1.1 Epoxy Resin based on Bisphenol A (DGEBA)**

Epoxy resins based on bisphenol A are the simplest epoxy resins and it is widely in commercial use [Mahesh *et al.*, 2006; Zhang and Wong, 2004; Sham and Kim, 2004]. In addition, it was the earliest commercialized epoxy resin. The preparation of liquid epoxy resin is by the reaction between bisphenol A and epichlorohydrin with molar ratio of 1:10 to 1:4 at 60 °C in presence of sodium hydroxide (caustic soda).

##### **1.1.3.1.2 Novolak Epoxy Resin**

Produced from the reaction of novolak resin and epichlorohydrin, novolak epoxy resin has low molecular weight whereby the nuclei phenolic group is attached at ortho position.

### 1.1.3.1.3 Polyglycol Epoxy Resin

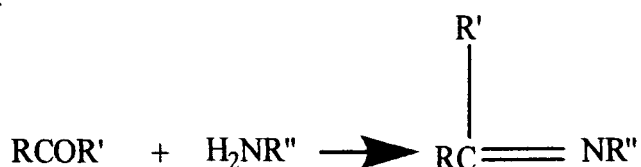
The polyglycol epoxy resin was synthesized by the reaction of epichlorohydrin and polyglycol. The polyglycol could be directly epoxidized through the terminal hydroxyl group that contained in the main chain. Generally, this type of resin is not used alone but incorporating it with 10-30% of epoxy resin based on Bisphenol A will result in better strength properties.

### 1.1.3.1.4 Halogenated Epoxy Resin

This type of epoxy resin is derived from the reaction of halogenated hydroxyl compound and epichlorohydrin. Either tetrabromobisphenol A or tetrachlorobisphenol A are the halogenated hydroxyl compounds, which are commonly used. The structure of epoxy resin produced is similar with the epoxy resin based on Bisphenol A except that halogen atoms are attached to its aromatic ring. The presence of halogen atom will result in fire retardant resin.

## 1.2 Azomethine

Azomethine or (Schiff base), is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. Azomethine is formed by condensation process between aldehydes or ketones with primary amines.



Where: R and R' are hydrogen, alkyl, allyl or aryl group; R'' is alkyl or aryl group.

**Scheme 1.1: Azomethine Reaction**

In the C=N group, the nitrogen atom is  $sp^2$  hybridized where it formed a sigma bond with the carbon atom, a sigma ( $\sigma$ ) bond with the substituent, the p orbital which form a pi ( $\pi$ ) bond with the carbon atom and a lone pair of electron. Schiff base are used in liquid crystals for electronics, as chemical intermediates and perfume bases, in dyes and rubber accelerators.

Azomethine compounds draw such wide interest in the chemistry field due to its ability to form aromatic poly(azomethine) compounds that are very high performance material. The polymers have high thermal stability, good mechanical properties and environmental resistance. However, the drawback is that poly(azomethine)s are generally infusible polymers and have poor solubility which leads to difficult processibility [Marin *et al.*, 2006]. Azomethine compounds have various applications and the most important are as following:

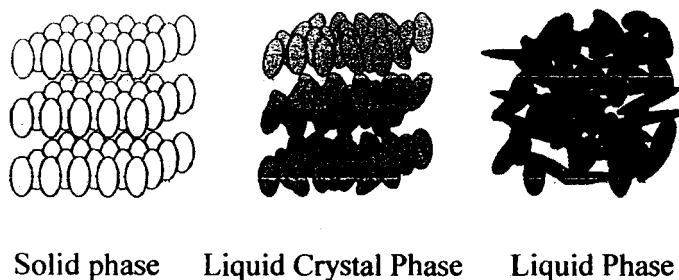
1. As a linker group in liquid crystal synthesis. [Kimura *et al.*, 2003]
2. Chelate forming ability in drug synthesis where azomethine polymer is able to bind with toxic and heavy metal. [Marin *et al.*, 2006]
3. In synthesis of high thermal stability polymers [Issam and Ismail, 2006]
4. Good optoelectronic properties [Issam and Ratnamalar, 2009]

By incorporating the azomethine linkage into the liquid crystalline polymer, it has been proved to maintain good thermal stability [Choi *et al.*, 2000]. Some of the polymer containing azomethine linkage had shown their thermal stability up to 400 °C [Morgan *et al.*, 1987; Wojkowski, 1987]. Thus, it is predicted that by the

presence of the azomethine linkage in the liquid crystalline epoxy resin, the thermal stability could be enhanced.

### 1.3 Liquid Crystal

The liquid crystal is another phase of matter. Liquid crystals are substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal. For instance, liquid crystals are the aggregate states of matter whose properties are intermediate between a crystalline solid and an isotropic liquid. There are three common states of matters that we are aware of which is solid, liquid and gas. The liquid crystal state is actually an intermediate state between crystalline solids and isotropic liquids states [Chandrasekhar, 1977].



**Figure 1.2: Molecule arrangement of solid, liquid and liquid crystal phase**

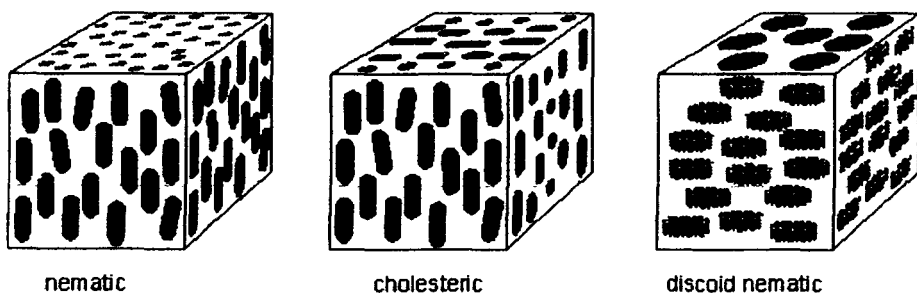
Liquid crystals flow like a liquid, but due to their anisotropy, they may have positional and/or orientational order as the solids. The optical, magnetic and the mechanical properties of a liquid crystal depend on the direction in which these quantities are measured. The transition of these states can be brought about by purely thermal process (thermotropic) or by the influence of solvent (lyotropic).

### 1.3.1 Types of Liquid Crystal Phases

Friedel had proposed that the nomenclature of thermotropic liquid crystal can be classified broadly into several types namely: nematic, smectic, and cholesteric [Chandrasekhar, 1977]. Hence, there are basically three types of liquid crystal (LC) phase based on the amount of order of the substance.

#### 1.3.1.1 Nematic Phase

The nematic phase generally has no positional order but tend to align in the same direction (along the director  $n$ ) [Baron, 2001]. The nematic liquid crystal has a high degree of long range orientational order of the molecules, however inadequate range translational order. Thus, it differs from the isotropic liquid because the molecules are spontaneously oriented with their long axes approximately parallel. The name of nematic is derived from the Greek words for thread where it can be observed from the polarized microscope that the shape of the crystal is just like a thread [Collings, 2002]. Figure 1.3 below illustrates the arrangement of the molecules of nematic phase.



**Figure 1.3: The arrangement of the molecules in nematic phase**



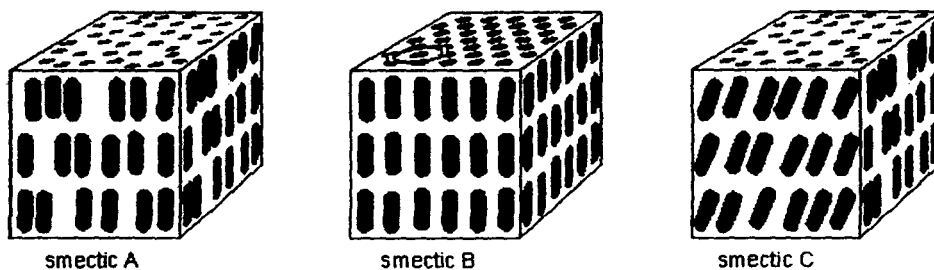
This phase also have the highest degree of fluidity but have the lowest degree of order when compare to the other mesophase [Collings and Hird, 1997]. The molecules in nematic phase consist of intermolecular phase to keep itself parallel to the other molecules [Collings, 1990]. However the center of gravity of the molecules in the volume is randomly distributed.

### **1.3.1.2 Smectic Phase**

The difference between smectic phase and nematic phase is that in smectic phase possessed a certain degree of translational order. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. The motion is restricted to within these planes, and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic. The smectic phases always represent the low-temperature modifications in systems where both nematic and smectic phases coexist [Kelker and Hatz, 1980]. Two of the most common smectic phase is smectic A phase and smectic C phase. The smectic A phase is a two dimensional with no correlation between layer.

The smectic C phase is similar to the smectic A phase in molecular distribution other than the director is at a constant tilt angle measured normally to the smectic plane. The smectic B phase however orients with the direction perpendicular to the smectic plane, but the molecules are arranged into a network of hexagons within the layer.

The molecular distribution of smectic A, B and C phase is shown Figure 1.4.



**Figure 1.4: The arrangement of molecules in smectic phase**

### 1.3.1.3 Cholesteric Mesophases (Chiral)

The cholesteric mesophases is also known as the chiral liquid crystal phase. It is because that the first material exhibiting this phase was cholesteryl benzoate [Collings and Hird, 1997]. This mesophases generally no difference than the nematic mesophases other than it is composed of optically active molecules. In other words, it is actually a nematic type of liquid crystal except that it is composed of optically active molecules. It is deemed that the structure has a screw axis superimposed normal to the preferred molecular direction [Chandrasekhar, 1977].

In order for a compound to have liquid crystal properties, the molecules of the compound needs to possess the criteria below;

- i. The molecule must be elongated in shape; it is significantly longer than its width.
- ii. The molecule must have some rigidity in its central region.
- iii. Ends of the molecules are flexible.

It has been said that an organic chemist indiscriminately synthesizing compounds will find that one in every two hundred compounds synthesized possess the liquid crystal state [Collings, 2002]. This includes the polymer that has liquid crystal properties.

## **1.3.2 Applications of Liquid Crystals**

### **1.3.2.1 Liquid Crystal Display**

Liquid Crystal Display (LCD) is widely used in electronics application such as hand phone, laptop, electronic gaming devices and also flat screen LCD television. When compare to cathode ray tube, liquid crystal is lighter in weight and also significant reduction in power consumption. A mixture of liquid crystal is used because there is currently no single liquid crystal able to fulfill the simplest display requirement [Heckmeir, 2004]. Hence, a mixture of 10-20 liquid crystals was usually used to produce the liquid crystal display because the electronic devices require a large temperature operating range. Currently, most of the liquid crystal display used nematic liquid crystal mixtures.

Furthermore, there are two liquid crystal display available in the market, the active matrix display and passive matrix display. In active matrix display each matrix point (pixel) is driven by one to one related electronic switching device [Heckmeir, 2004]. In the passive matrix display, however, the pixel is not driven by using electronic switching device directly to one pixel. The passive matrix display is more economical (cost wise). However, the quality of optical and picture performance in large screen is not as good as in the active matrix display.

### **1.3.2.2 Liquid Crystal Thermometer**

The chiral nematic liquid crystal (cholesteric) reflects light with a wavelength equal to the pitch [Baron, 2001]. Since the pitch is dependent upon temperature therefore the color reflected is also dependent on the temperature. Hence we could identify the temperature by observing at the color exhibited by the thermometer. By mixing several different liquid crystals we can basically construct a thermometer where it could detect all range of temperature. In medical field, the liquid crystal thermometer is used to determine tumor. The temperature of the area of the tumor usually has a different temperature compare to the surrounding tissue. While in the electronic field, the liquid crystal thermometer is used to determine the bad connections of a circuit board by detecting the characteristic of high temperature [Baron, 2001].

### **1.3.2.3 Other Liquid Crystal applications**

LC is also used in optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. They are used for non-destructive mechanical testing of materials under stress test. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured. Low molar mass (LMM) liquid crystals have applications including erasable optical disks,

full color "electronic slides" for computer-aided drawing (CAD) and light modulators for color electronic imaging.

#### **1.4 The Problem**

Epoxy resins are one of the most widely used thermosetting materials due to their excellent adhesion [Luo and Wong, 2004], high strength [Rosu *et al.*, 2002], good thermal and chemical resistance [He *et al.*, 2001] and many others. Its primary applications include coating, adhesives, industrial tooling, structures and electronics packaging [Stefani *et al.*, 2001]. However, epoxy resins exhibit low fracture toughness, poor wear and crack resistance in real application due to its rigid and brittle nature [Ng, 1993; May, 1988; LeMay and Kelly, 1986].

To overcome these problems, considerable amount of works have been carried out in the direction of toughening epoxies, with some research focused on introducing appropriate amounts of rubbery and flexible components into epoxy networks. Researchers applied modifications that employ the use of functionalized reactive rubbers such as carboxyl-, amine- or epoxy-terminated butadiene acrylonitrile [Kunz *et al.*, 1897; Kirshenbaum, 1984]. The rubber modifications showed positive effect on toughness of epoxy but negative on the strength, stiffness as well as glass transition temperature range.

Other common modification routes include physical blending, interpenetrating polymer network and intercrosslink network formations and filler incorporation. Reports have shown that these modifications resulted in improved

physical, mechanical and thermal properties but at the same time posed further challenges with undesirable traits that need to be overcome. This continues to motivate research on epoxy as versatile core material of thermoset systems for decades to come.

Modification of epoxy further extends its applications which encompass some novel materials by the incorporation of rigid mesogenic groups into the epoxy network. Such materials with molecular order can also show anisotropic properties and are known as liquid-crystalline epoxy resins (LCERs) [Galina and Mossety-Leszczak, 2007].

Liquid crystalline epoxy resins can be synthesized from mesogens such as rigid rod molecules with epoxide groups (oxirane rings) directly attached to the mesogenic core, which were cured by reaction with aromatic amines thereafter. Liquid crystalline epoxy (LCE) networks are an important area of research given in their potential use in various applications such as electronics, advanced composites, non-linear optics, etc. The synthesis, development of texture, mechanical properties and influence of curing conditions has been examined for a number of LCEs [Balamurugan and Kannan, 2009; Wlodarska *et al.*, 2009; Harada *et al.*, 2009].

Azomethine linkage in the backbone of polymers shows many desirable properties such as thermal [Issam and Jamil, 2006], liquid crystal [Mikroyannidis, 1989], etc due to the resonance of the poly-Schiff's base unit [Segal, 1967]. Stringent application requirements related to performance, processing and exposure to extreme conditions continue to increase demand for improved materials. Modification of

epoxy is indeed necessary to cope with such demands. Hence, azomethine reaction produces high yield, thus contributes to feasible processibility. Overall, many researches have been carried out on liquid crystalline epoxy resin, only few studies on liquid crystal epoxy resins containing azomethine groups have been reported so far. The incorporation of azomethine groups in various liquid crystal polymers that have been studied includes polyesters [Gaina *et al.*, 2001; Shukla *et al.*, 2003], polyurethanes [Sun and Chang, 1996; Stoica *et al.*, 1998], polyethers [Carter and Hedrick, 1994] and etc.

### **1.5 Objectives**

This research project aims to design new twin liquid crystalline diglycidyl ethers containing azomethine groups. It includes the synthesis, characterization, thermal and mesomorphic properties of the new compounds. Also of interest is the curing with two different aromatic diamines.

The above aims are achieved through fulfilling the objectives as follows:

- I To synthesize and characterize new twin liquid crystalline diglycidyl ethers containing azomethine groups.
- II To investigate the thermal behaviour and crystallinity of the new twin liquid crystalline diglycidyl ethers and epoxy resins.
- III To study the effect of different curing ratios of the new epoxy resins on the mechanical properties as well as on the liquid crystal behaviours.

## 1.6 Choice of Materials

It was realized that liquid crystalline polymers (LCPs) could not find wide diffusion on the market due to the costs of the raw materials in general, and to the synthesis that is often very expensive. Hence, in this research, the choice of vanillin as raw material was because of its low cost, safe and easy to crystalline. On the other hand, *p*-hydroxybenzaldehyde was chosen because it is composed of the similar structure as vanillin except for the absence of methoxy (-OCH<sub>3</sub>) group. As for the materials for epoxy curing, commonly used hardeners are amines, anhydrides, polyamides, phenols, isocyanates and polymercaptans [Strzelec, 2007]. The choice and stoichiometry of hardeners are application specific as it affects the properties of the cured thermosets. Amines are used for coating materials, amides for structural applications [Selvaraj *et al.*, 2006] and printed circuit board, for interior of food cans and anhydride [Wong and Bollampally, 1999] for urea formaldehyde (UF) material of the electronic packaging. Anhydride was the choice for microelectronic packaging materials because its resultant thermosets have the highest heat distortion values and the best aging stability. However, it has been subsequently phased out due to its tendency to absorb moisture [Chian *et al.*, 2000] and outgas [Zhang and Wong, 2004], as well as its sensitizing nature [Zhang *et al.*, 2002] that possess health hazard. Aromatic amines are the favored choice to replace anhydride [Blanco *et al.*, 2005; Sbirrazzuoli *et al.*, 2006; Merad *et al.*, 2009]. Its preference is attributed to the higher T<sub>g</sub> and rigidity [Zvetkov, 2002] as well as thermal and mechanical performances. The selection of 4,4'-diaminodiphenyl sulfone (DDS) was based on its high performance in the epoxy based composite materials [Wei-Fang *et al.*, 2002]. It is also interesting to note and compare the consequences of the biphenyl structure of DDS as to only single phenyl structure in 1,4-phenylene diamine (PPDA).



## **1.7 Thesis Layout**

This thesis consists of seven chapters. Chapter 1 is the introduction, which covers the progress and inherent issues, which is the problem statement, research goals and the scope of this research. Chapter 2 explains the literature survey whereas Chapter 3 details out the research methodology. Next, Chapter 4 presents the structural elucidation of the synthesized products by various spectroscopic techniques. Subsequently, the thermal properties and mechanical properties are discussed in Chapter 5 and 6 respectively. Lastly, Chapter 7 concludes this research and lists out suggestions for further investigation.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Liquid Crystalline Epoxy Resins

Liquid crystalline thermosets (LCT) particularly liquid crystalline epoxy resins (LCERs) show interesting properties due to the combination of a thermoset and liquid crystal (LC) formation capability [Punchaipetch *et al.*, 2002; Carfagna *et al.*, 1997; Giamberini *et al.*, 1995; Barclay and Ober, 1993; Earls *et al.*, 1993]. Epoxy compounds, which generally contain rigid-rod group, are particularly interesting as monomers for obtaining LCT. This is due to the fact that the formulations of epoxy resin and curing properties are highly versatile [Cai *et al.*, 2008]. In addition to the final properties of the thermosets obtained which includes low shrinkage upon cure, low thermal expansion coefficients, low dielectric constants and enhanced reaction rates [Carfagna *et al.*, 1997].

As compared to ordinary epoxies, crosslinked LCERs exhibit higher fracture toughness [Giamberini *et al.*, 1995] and mechanical properties when oriented by magnetic fields [Barclay *et al.*, 1992]. This can be explained by their approximately overall isotropic properties, combined with localized anisotropy [Harada *et al.*, 2005; Choi *et al.*, 2004]. The inhomogeneties of the LC structure leads to the deviation of crack propagation, thus, an increase in fracture toughness. In addition, above glass transition temperature, liquid crystalline thermosets ensures greater mechanical resistance, fracture toughness and stiffness [Balamurugan and Kannan, 2009].

The excellent properties of LC thermosets stem from the preservation of molecular organization in the mesophase of LC precursors and monomers by means of crosslinking. The resulting highly crosslinked thermoset containing rigid rod molecules can offer improvement of rather poor properties in transverse direction to the chain orientation. Hence, of possible thermosetting polymers, epoxy resins are commercially important because of their superior adhesion, heat and corrosion resistance, mechanical and electrical properties than other classical thermosets. Incorporating LC structure into the epoxy network could enhance the properties.

LCER networks are an important area of research given in their potential use in a number of applications such as electronics, advanced composites, non-linear optics, etc. The syntheses, development of texture, mechanical properties and influence of curing conditions have been examined for a number of LCERs [Gaina, 2001; Carfagna *et al.*, 1997; Carter and Hedrick, 1994]. Over last years, several research groups have studied the synthesis and curing of LC diepoxides with a flexible spacer between epoxide moiety and mesogenic group [Mallon and Adams, 1993] with two mesogens linked by a central flexible spacer [Barclay *et al.*, 1992], and with substituents in mesogenic units [Mormann *et al.*, 1997; Carfagna *et al.*, 1997].

In general, LCT have been widely investigated in many research groups because of their unique properties, e.g. anisotropic orientation, low coefficient of thermal expansion and liquid crystalline phase development during curing. LCT can be prepared through many routes. It can be made through the self-cross-linking reaction of LC monomer or non-LC rigid rod monomer. The reaction between LC

monomer and non-LC curing agent, or LC curing agent can yield LCT. In addition, the possibility to obtain LCT through reaction of non-LC rigid rod monomer with non-LC curing agent is too low [Giamberini *et al.*, 1995].

It has also been reported that non-LC rigid rod oligomers can form a LCT through the cross-linking reaction with non-LC curing agent [Barclay *et al.*, 1992]. Curing reaction of liquid crystal epoxy (LCE) resin with curing agent can form highly orderly and densely crosslinked LC polymer networks under suitable curing conditions. As a result, the epoxy polymer may develop an LC structure during curing process [Jun-Gang *et al.*, 2009].

## 2.2 Azomethine

The azomethine group is of special interest due to its interesting properties such as syn-anti isomerism [Becker and Richney, 1967], good thermal stability [Issam and Ismail, 2006; Li and Chang, 1991; Roviello and Sirigu, 1979; Antoun *et al.*, 1901], non-linear optical activity [Yang and Jenekhe, 1991], ability to form metal chelates [Rudzinski *et al.*, 1988], fibre-forming ability [Yang, 1989], liquid crystalline property [Shukla *et al.*, 2003; Barbera *et al.*, 1992; Sek, 1984] and semiconductivity [Farcas *et al.*, 2001; Saegusa *et al.*, 1990]. The introduction of azomethine moiety in the polymer backbone will incorporate the above mentioned properties in the newly synthesized polymer due to the resonance stabilization of the Poly-Schiff's base unit [Segal, 1967].

Limited amounts of research articles have been published on epoxy resins containing azomethine mesogens. In 1989, Mikroyannidis reported the synthesis of

epoxy derivatives of bis(azomethine)s without flexible spacers, curing by 4,4'-sulfonyl dianiline and thermal stability of the resulting polymers. Soon later, Mormann *et al.*, 1997 reported the synthesis of azomethine-linked aromatic mesogenic epoxies with methyl and methoxy substituents as well as the phase behavior. Also, E-Joon *et al.*, 2004 and Gao *et al.*, 2007 reported the synthesis of azomethine epoxies and the curing behavior with diamines. According to their results, aromatic azomethine LCERs indeed possess advantages of high mesomorphic properties and can be obtained by a feasible and easy process with high percentage of yields [Mormann and Pokropski, 2005; Sadagopan, 2003].

### 2.3 Curing of Liquid Crystalline Epoxy Resin

Curing is a reaction between the epoxy group with other functional group that has an active hydrogen molecule to give linear, branched or cross-linked products [Sandler and Karo, 1992]. The excellent properties of LC thermosets stem from the preservation of molecular organization in the mesophase of LC precursors and monomers by means of crosslinking. The resulting highly crosslinked thermoset containing rigid rod molecules can offer improvement of rather poor properties in transverse direction to the chain orientation [Choi *et al.*, 2000].

In the case of LCERs, it is crucial to determine as to whether the cured resins will possess liquid crystalline properties or not. In addition, the amount of cross-linked involved during curing process also determine the properties of the cured LCER. It is reported that superior mechanical and thermal stability were obtained from highly cross-linked LCERs as compared to the lightly cross-linked LCERs [Ambrogi *et al.*, 2005].

The curing behaviour of LC thermosets are greatly influenced by the substituents on the mesogenic group, mesogenic structure and bridging group between the mesogenic group and the epoxide functional group [Lee and Jang, 2006]. Furthermore, LC epoxy networks have been obtained mainly through the crosslinking of epoxy monomers containing mesogenic groups. The long triaromatic ester mesogenic group in epoxy monomers makes the mesophase stable because of significant geometrical anisotropy. The synthesis and curing of monomers with these mesogenic groups have been widely studied [Mossety-Leszczak *et al.*, 2003; Lee *et al.*, 1999; Mallon and Adams, 1993]. Galina and Mossety-Leszczak, 2007 reported the synthesis of epoxy monomer based on a triaromatic mesogen and its cross-linking reaction with primary and tertiary aromatic amines have resulted to networks retaining anisotropic nematic mesophases with stability up to 300 °C.

Similar to the ordinary epoxy resin, LCER also need to undergo cross-linking process in order to become a cured resin. There are a wide variety of curing agents that can be chosen from and it can be classified into two main groups which are for room temperature curing and for elevated temperature curing [Miles and Briston, 1965]. Polyamines, polymecaptans and polyisocyanates are the example for room temperature curing while polycarboxylic acids, polyanhydrides, polyphenols and carboxy-functional polyesters only react with heating [Stoye and Frietag, 1996].

#### **2.4 Properties and Applications of Liquid Crystalline Epoxy Resin**

Researches on LC main chain polymers are mainly directed to high-strength fibers, high-modulus thermoplastic materials, and self-reinforcing polymers, which

in addition should have a better high temperature performance and resistance to thermal degradation [Mormann and Brahm, 1991].

Generally, the properties of LCER are actually a combination of properties of the epoxy resin and liquid crystal [Punchaipetch *et al.*, 2002]. By incorporating the liquid crystalline structure into the conventional epoxy resin network, it could enhance the epoxy resin properties such as good adhesion, heat and corrosion resistance as well as mechanical and electrical properties [(Choi *et al.*, 2000). Besides that, the thermal properties also reported have been enhanced [Carfagna *et al.*, 1997].

The amount of cross-linked involved during the curing process is crucial to determine the properties of cured epoxy resin. It is reported that in the case of highly cross-linked structures, superior mechanical and thermal stability epoxies were obtained compared to the lightly cross-linked structures [Ambrogì *et al.*, 2005].

Over the past years, LC epoxies have been extensively studied, since the simultaneous existence of rubber elasticity, due to the crosslinked backbone chains, and optical birefringence, related to the mesogens, lead to exceptional physical properties. An elastic deformation of the network influences the order of the mesogens and, therefore the optical properties. In particular, they can undergo stress-induced polydomain-to-monodomain transition [Ambrogì *et al.*, 2005]. Moreover, they exhibit many interesting features, and unique dynamic-mechanical properties [Ortiz *et al.*, 1998].

Most of the research conducted has studied the thermal behaviour of the liquid crystalline epoxy resin. Liquid crystalline epoxy resin exhibits high heat resistance [Lee *et al.*, 1999] and high thermal stability due to the improvement of the dimensional stability by the cross linking reaction [Litt *et al.*, 2003]. The cross linking agent plays an important role to determine the thermal stability of the cured resin. It is reported that most common epoxy resins undergo thermal decomposition at relatively low temperatures where it usually lose 10% of their mass between 250-300°C in air. However, researches using LCER had found that the mass loss is only 5% and this proved the good thermal stability of the cured liquid crystalline epoxy resin [Farren *et al.*, 2001].

Furthermore, by incorporating the azomethine linkage into the liquid crystalline polymer, it has been proved to maintain good thermal stability [Choi *et al.*, 2000]. Several polymers bearing azomethine linkage had shown their thermal stability up to 400°C [Wojkowski, 1987]. Thus, it is predicted that the thermal stability of LCER could be enhanced by the presence of the azomethine linkage in the polymer backbone.

Besides that, mechanical properties of liquid crystalline epoxy resin have become one of the main research interests in this exciting field. Numbers of paper published regarding the study of mechanical properties of cured liquid crystalline epoxy resin [Lee and Jang, 2006, Ochi and Takashima, 2001]. Compared to ordinary cured epoxy resin, cross-linked liquid crystalline epoxy resin exhibited higher mechanical properties when oriented by magnetic fields [Punchaipetch *et al.*, 2001]. Similar to the thermal stability properties, mechanical properties of cured resin