SYNTHESIS OF LIQUID CRYSTALLINE AZOBENZENE CONTAINING POLYMER

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DECLARATION

I hereby declare that this dissertation is based on my original work, except for quotation and summaries each of which have been fully acknowledged.

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ABSTRACT

The objective of this thesis is to synthesis of liquid crystalline azobenzene containing polymer. The starting material for the synthesis is 4-Aminoacetophenone. The initial process is diazonium salt coupling reactions which react with sodium nitride and phenol to obtain 4-(4-hydroxyphenylazo)acetophenone. The compound then reacts with 3and potassium carbonate to obtain 4-(4bromoprop-1-ene allyloxyphenylazo)acetophenone. This reaction is called Williamson synthesis reaction. The synthesized compound then undergoes radical polymerization reaction and purification. These reactions are reacted by AIBN as initiator and dried THF as the solvent. The final compound was 4-(4-propoxyphenylazo)acetophenone. This final compound is purified by methanol and crystallization. The final compound has a melting point at the range of 92°C to 105°C. By compare the functional group in the FT-IR 4-(4-hydroxyphenylazo)acetophenone, spectra 4-(4allyloxyphenylazo)acetophenone, and 4-(4-propoxyphenylazo)acetophenone, these compounds are indicated that the functional groups are in molecular structure as projected. The DSC analysis showed the compound has 110.69°C endothermic peak and 80.74 J/g enthalpy changes. The compound also has exothermic peak at 106.05°C and 81.76 J/g enthalpy changes.



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ABSTRAK

Objektif tesis ini adalah untuk menyintesiskan azo-benzena krystal cecair yang mengandungi polimer. Langkah permulaan dalam sintesis ini ialah menggunakan 4aminoasetofenon melalui tindak balas penduan garam diazonium dengan fenol untuk menghasilkan 4-(4-hidroksifenilazo)asetofenon. Bahan yang diperoleh bertindak balas dengan 3-bromopropena dan kalium karbonat untuk memperoleh 4-(4aliloksifenilazo)asetofenon. Tindak balas ini dipanggil tindak balas Williamson sintesis. Bahan ini kemudian mengalami tindak balas pempolimeran radikal dan pembersihan. Tindak balas ini bertindak dengan AIBN sebagai pemula dan THF kering sebagai larutan. Bahan terakhir ialah 4-(4-propoksifenilazo)asetofenon. Bahan ini akan dibersihkan oleh metanol dan pengristalan. Bahan ini mengandungi takat lebur pada lingkungan 92°C-105°C. Dengan membandingkan kumpulan berfungsi dalam imbasan FT-IR 4-(4-hidroksifenilazo)asetofenon, 4-(4-aliloksifenilazo)asetofenon dan 4-(4propoksifenilazo)asetofenon mempunyai sumua kumpulan berfungsi yang dijangkakan. Analisis DSC menunjukkan bahan terakhir mempunyai 110.69°C puncak pada endotermik dan 80.74 J/g entalpi. Bahan ini juga ditunjukkan pada 106.05°C pada puncak eksotermik dan 81.76 J/g entalpi.



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CHAPTER 1

INTRODUCTION

1.1 Introduction

The first liquid crystal (LC) materials were discovered in May 1888 by Dr. Friederich Reinitzer. The systematic study of main chain liquid crystalline polymers began only about ten years ago, and the first publications in the open literature on such polymers were apparently those by Roviello and Sirigu in 1975 (Chiellin *et al*, 1990).

Since the discovery that high performance polymeric fibers could be obtained from rigid-rod polymers forming liquid crystalline mesophases in solution, an enormous research effort has been addressed to the study of liquid crystal polymers containing rigid anisometric segments (Demus *et al*, 1998). At the end of the 1970's, innovation allowed high molecular weight polymeric systems to behave like low molecular weight systems finally helped to make durable temperature sensitive cholesteric systems possible (Demus *et al*, 1998).



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Liquid crystalline polymers are a new class of materials having unusual properties and represent one of the most exciting developments in high performance materials. Polymer liquid crystals combine the unique properties of low molecular weight liquid crystals and high molecular weight polymers with their ability to form films, fibers, coatings offers great promise in the field of data storage and display technology (Zentel and Mayer, 2002). They are characterized by the existence of mesophases that exhibit a pronounced anisotropy in shape. This generates organized fluid phases either on melting (thermotropic) or on dissolution (Lyotropic). The phase transitions between the crystalline, smectic, nematic and isotropic phases in liquid crystalline polymers (LCPs) are similar to those occurring in low molecular weight liquid crystals (LCs) (Pillai, 1998).

A number of LC polymers such as Xydar and Vectra have been commercialized, but it is reported that they still have processing problems because their transition temperatures are above 300°C. It is difficult to create polymer liquid crystals that show mesogenic behavior over temperature ranges which are convenient to work with (Saminathan and Pillai, 1997). In fact, many times the temperature of the liquid crystalline behavior is actually above the point where the polymer begins to decompose. The need for further studies in this line is indicated (Zentel and Mayer, 2002).

Liquid crystal main chain polymers are interesting, from an economic point of view, as materials for high strength fibers and self-reinforcing plastics, while LC side group polymers are of interest for optical components (Zentel and Mayer, 2002). Due to the low melt viscosity, high heat resistance and form stability, main chain LCPs are the



material of choice for applications in microelectronics whenever miniaturized devices are needed (Zentel and Mayer, 2002).

The most importance of the behavior of liquid crystals at surfaces is in normal flat panel electro-optical displays, and the subject of anchoring is an area of strong research activity (Demus *et al*, 1998). Polymer dispersed liquid crystals have attracted because sheets consisting of droplets of nematic liquid crystal in amorphous polymer matrix. The orientation in the nematic droplets can be manipulated by electric fields which changing the appearance of the sheet and opening up possibilities for electrically switchable windows and panels. The impact of such switchable panels has not been realized due to some problems in systems the liquid crystal is constrained in a confined geometry and the ratio of surface contact area to bulk volume is high. This has led to research on liquid crystal in confined geometries (Demus *et al*, 1998).

1.2 Research Objectives

The Objectives of this study are:

- 1. To synthesize polymer liquid crystals materials contains azo linkage.
- To determine the functional groups of the material using Fourier Transform Infrared Spectroscopy (FT-IR).
- 3. To determine the phase transition using Differential Scanning Calorimetry (DSC).



CHAPTER 2

LITERATURE REVIEW

2.1 Concept of Liquid Crystals

The liquid crystal (LC) phase is a well-known state of matter, which lies between the solid and isotropic liquid phases. By definition, the LC state (mesomorphic state) is characterized by having a long-range orientational order and possible partial positional order (Demus and Goodby, 1998). Different types of molecules can form liquid crystalline phases. The common structural feature is that these molecules are anisotropic: one molecular axis is much longer or wider than another one. The two major categories are (I) thermotropic LCs, whose mesophase formation is temperature (T) dependent and (II) lyotropic LCs, whose mesophase formation is concentration and solvent dependent. Liquid crystals are derived from certain macromolecules in solution but sometimes in the pure state. They are known as "liquid crystal polymers (LCPs)". The polymers are long-chain molecules formed by the repetition of monomers. (Robinson, 1996)



2.1.1 Thermotropic Liquid Crystals

The essential requirement for molecule to be a thermotropic liquid crystal is a structure consisting of a central rigid core and a flexible moiety. Thermotropic liquid crystals are the most widely used in nonlinear optical properties (Whinnery *et al*, 1977)

2.1.2 Rod-Like (Calamitic) Liquid Crystalline Compounds

Most of rod-like liquid crystalline compounds consist of two or more rings, which are directly connected by linking groups (L), and may have terminal (R) and lateral (Z) substituents. The major anisotropy of the molecules, which is necessary for their mesogenity, results from the cores, which are also the cause of the relatively high melting temperatures (Onsager and Ann, 1989).



Figure 2.1 Figure representation of calamitic LCs, where I>>b.

The chemical structure of mesogen can be represented by the general formula I. The rings, represented in I by circles, and the linking group L form the core of the compound. The



core is usually a relatively stiff unit, compared to the terminal substituents, which is most cases are flexible moieties such as alkyl groups. The lateral substituents Z are small units such as halogens, -CN groups and acetal groups (Demus *et al.*, 1998).



Figure 2.2 Calamitic LCs can exhibit three common types of mesophases: nematic, smectic and cholesteric (chiral nematic)

a) Nematic Phase

The simplest liquid crystalline phase is the nematic phase. There are several types of nematic phases but all of them have only an orientational order (Oseen, 1933). The molecular long axis points on average in one favored direction. The various types of nematics have slightly different properties based on the details of their molecular structure and chemical behavior. The two primary types of nematic are unaxial and biaxial (Crawford and Zumer, 1996).





Figure 2.3 Figure representation of N phase. The molecules are oriented, on average, in the same direction referred to as the director, with no positional ordering with respect to each other.

b) Smectic phase

The next level of organisation is classified as smectic (S), where in addition to the orientational order the molecules possess positional order (Demus and Gray, 1998). The important feature which distinguishes smectic phases is that they have a layered structure. The simplest is the smectic-A phase made of non-chiral and non-polar molecules and characterized by a one-dimensional layered structure (Crawford and Zumer, 1996). This phase is uniaxial, the layers are incompressible, and the long axes of molecules within the layer, on average, are perpendicular to the layer (Demus *et al.*, 1998). In the basic state of the crystal the layers are planar, they can slip over each other and the molecules can diffuse within the layers. The director coincides with the layer normal and the



directions n and -n are equivalent. This explains the uniaxiality of the optical properties (Robinson, 1996).

The smectic-C phase is similar to the smectic-A phase in that it is a layered structure and each layer may be thought of as a two-dimensional liquid film. Most of the smectic-A to smectic-C transitions are second order but first order transitions in fluorinated compounds have recently observed (Jeffrey, 1997). The structure of the smectic-C phase exhibits the long-axes of the molecules which are tilted with respect to the planes of the layers. Thus the optical character is positive biaxial. As a result of tilt angle the layer spacing in smectic- phase is less than that of the corresponding smectic-A phase (Robinson and Singh, 2002).

Table 2.1Molecular arrangements in crystal and smectic LC phases (Demus *et al*,1998).

Orthogonal Phases	Tilled Ph	ases
		000 000 000 000 000 000 000 000 000 00
Smeetic A	Smectic C	Smeetic C _{all}
Hexatic B	Smectic I	Smectic F
Crystal B	Crystal J	Crystal G
Crystal E	Crystal K	Crystell H



c) Cholesteric (chiral nematic) phase

The structure of the chiral nematic or cholesteric phase is one where the local molecular ordering is identical to that of the nematic phase. This phase forms if the molecules which form the liquid crystal are either intrinsically chiral or if chiral dopants are added to a non-chiral (regular) nematic. The chirality of the system leads to a helical distortion, in which the director n rotates continuously in space along (Jeffrey, 1997). The director is uniformly twisted along a perpendicular axis called the helical axis. The distance along the helical axis for the director to twist 2π is called the pitch P (Blumstein *et al*, 1996). The pitch, P of the helix can vary to almost infinity (Demus *et al.*, 1998). The optic axis of the phase is along the helical axis can be positive or negative, corresponding to right or left handedness, and has a magnitude which can be strong function of temperature (Avraam *et al*, 1995). The pitch of a cholesteric can also be increased with the help of an applied electric field. It is important to note that for systems which have a small twist (long pitch), locally a cholesteric liquid crystal looks like a nematic (Jeffrey, 1997).



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