SYNTHESIS OF BENT SHAPED LIQUID CRYSTAL HAVING POLYMERIZABLE MONOMERS

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DECLARATION

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

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ABSTRACT

The objective of this study is to synthesize a bent shaped liquid crystal that exhibit mesogenic properties. It focuses only on the organic synthesis of bent shaped liquid crystal and the determination of mesogenic behaviour of polymer liquid crystal. The starting material for the synthesis is ethyl-4-aminobenzoate. The initial step of the synthesis involves diazonium coupling reaction with phenol to obtain ethyl-4-(4-hydroxyphenylazo) benzoate. The compound undergoes Williamson ether synthesis to obtain [4-(4-ethyl-diazobenzoate)phenyloxy]prop-1-ene. Then, the compound was hydrolyzed by potassium hydroxide to produce 4-(4-allyloxyphenylazo) benzoic acid. Finally, the benzoic acid was reacted with DCC and DMAP in dry dichloromethane to yield 1,3-phenylene bis [4-(4-allyloxyphenylazo)benzoate. From the FT-IR spectrum, it indicates that the compound synthesized has all the functional group in the molecular structure. It indicates functional groups that present such as alkyl group, benzene rings, carbonyl group of an ester, ester and ether. NMR analysis determined molecular structure of the final compound where types of protons attached to the carbons can be clearly identified through downfield readings. Differential Scanning Calorimetry (DSC) used to determined crystallization temperature of the final product.

SINTESIS HABLUR CECAIR BERBENTUK LIKU YANG MEMPUNYAI MONOMER BERCIRI POLIMERIK

ABSTRAK

Objektif projek akhir tahun adalah untuk mensintesis hablur cecair yang berbentuk liku yang menunjukkan ciri-ciri mesogenik. Ini hanya menfokuskan kepada sintesis organik bagi hablur cecair yang berbentuk liku dan penentuan perangai mesogenik polimer hablur cecair. Bahan permulaan bagi sintesis ini ialah etil-4-aminobenzoat. Langkah permulaan bagi sintesis ini melibatkan tindak balas penduaan garam diazonium dengan fenol untuk mendapatkan etil-4-(4-hidroksifenilazo) benzoat. Sebatian ini menjalani tindak balas penghasilan ester Williamson untuk mendapatkan [4(4-etil-diazobenzoat)feniloksi]prop-1-ena. Kemudian, sebatian ini dihidrolisiskan oleh kalium hidroksida untuk menghasilkan asid 4-(4-alliloksifenilazo) benzoik. Akhirnya, asid benzoik ini telah bertindak balas dengan DCC dan DMAP dalam diklorometana kering untuk menghasilkan 1,3-fenil bis[4-(4-alliloksifenilazo) benzoat]. Melalui spektrum FT-IR, didapati bahawa sebatian yang disintesis mempunyai semua kumpulan berfungsi dalam struktur molekul. Spektrum FT-IR menunjukkan kumpulan berfungsi yang wujud seperti kumpulan alkil, gelang benzena, kumpulan karbonil daripada ester dan eter. Analisis NMR menentukan struktur molekul bagi sebatian akhir di mana jenis proton yang diikat kepada karbon ditentukan dengan jelas. Kalorimeter pengesan kebezaan(DSC) digunakan untuk menentukan suhu penghabluran bagi hasil akhir.

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CHAPTER 1

INTRODUCTION

1.1 Liquid Crystal

Liquid crystal is a substance that flows like a liquid but has some order in its arrangement of molecules (Collings and Hird, 1997). The discovery of liquid crystals is thought to have occurred nearly 150 years ago although its significance was not fully realised until over a hundred years later. Around the middle of the last century Virchow, Mettenheimer and Valentin found that the nerve fibre they were studying formed a fluid substance when left in water which exhibited a strange behaviour when viewed using polarized light. They did not realise this was a different phase but they are attributed with the first observation of liquid crystals.

Later, in 1877, Otto Lehmann used a polarizing microscope with a heated stage to investigate the phase transitions of various substances. He found that one substance would change from a clear liquid to a cloudy liquid before crystallising but thought that this was simply an imperfect phase transition from liquid to crystalline. In 1888, Reinitzer conducted similar experiments and was the first to suggest that this cloudy fluid was a new phase of matter. He has consequently been given the credit for the discovery of the liquid crystalline phase. In 1890, the first synthetic liquid crystal, p-azoxyanisole, was produced by Gatterman and Ritschke (Petrov, 1999).

In 1968, scientists from RCA first demonstrated a liquid crystal display (LCD). It become the subject of interest in considerable researches due to the enormous commercial interest and the importance of liquid crystal displays (LCD) (Huang, 2004).

There are a few types of classification for liquid crystals mesogen, namely rod like molecules, discotics, and the bent core mesogen that are also known as banana shaped mesogen depending on the shape of the mesogen. It is quite difficult to create polymer liquid crystals that show mesogenic behaviour over temperature ranges because many times the temperature of the crystalline behaviour is actually above the point where the polymer begins to decompose (Baron and Stepto, 2002).

Conventional thermotropic liquid crystal (LCs) are formed by anisometric molecules (mesogens) that are either rod-shaped (calamitic LCs) or disc-shaped (discotic LCs). By employing these two anisometric moieties, many conventional low molar mass (monomers) as well as high molar mass (polymers) liquid crystalline systems have been designed and synthesized. The thermal behaviour of such monomeric and polymeric LC's are generally well understood. LCs with rod-like molecules exhibit nematic (N) and /or smectic (Sm) mesophases whereas LCs with flat disc-shaped molecules show N and / or columnar (Col) mesophases (Yelamaggad *et al.*, 2004).

The ability to control the orientation of the molecules in a liquid crystal allows to produce materials with high strength or unique optical properties. High strength applications involve the use of extremely long molecules called polymers (Silberberg, 2003).

1.2 Applications of Liquid Crystal(LC)

The most common application of liquid crystal technology is liquid crystal displays (LCDs.) This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made.

An application of liquid crystals that is only now being explored is 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. This technique is also used for the visualization of RF (radio frequency) waves in waveguides. 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 (Collings and Hird, 1997).

1.3 Objectives

The objective of this thesis are:

- To synthesize a bent shaped liquid crystal that exhibit mesogenic properties.
- To determine the structure of the material that obtained by using Fourier Transform Infra Red Spectroscopy (FT-IR) and Nuclear Magnetic Resonance Spectroscopy (NMR).
- To determine the crystallization temperature of final product by using Differential Scanning Calorimetry (DSC).

1.4 Scope of Study

This project focuses only on the organic synthesis of bent shaped liquid crystal and the determination of mesogenic behaviour of polymer liquid crystal.

CHAPTER 2

LITERATURE REVIEW

2.1 States of Matter

Generally, matter is defined as anything which has mass or occupies space. Matters occurs commonly in three physical forms called states : solid, liquid, and gas. Each substance has a unique set of physical properties and chemical properties. Changes in matter can be physical or chemical. The observable features that distinguish these states reflect the arrangement of their particles. A changed in physical state brought by heating may be reversed by cooling. A chemical change can be reversed only by other chemical changes (Silberberg, 2003).

2.1.1 Solid

A solid is an object in the phase of matter characterized by resistance to deformation and changes of volume. It is in a three-dimentional regularity of structure, resulting from the proximity of the component atoms, ions, or molecules and the strength of the forces between them. True solids are crystalline. If a crystalline solid is heated, the kinetic energy of the components increases. At a specific temperature, called the melting point, the forces between the components become unable to contain them within the crystal structure. At this temperature, the lattice breaks down and the solid becomes a liquid (Sybil, 1993).

In a solid, the attactions dominate the motion to such an extent that the particles remain in position relative to one another, jiggling in place. The particles usually slightly closer together than in a liquid and their positions fixed, it has a specific shape. Consequently, solids compress even less than liquids, and their particles do not flow significantly (Silberberg, 2003).

2.1.2 Liquid

Actually, liquid is an amorphous or non-crystalline form of matter between of a crystalline solid and a gas. In a liquid, the large-scale three-dimentional atomic (or ionic or molecular) regularity of the solid is absent but, on the other hand, so is the total disorganization of the gas. Although liquids have been studied for many years, there is still no comprehensive theory of the liquid state. It is clear, however, from diffraction studies that there is a short-range structural regularity extending over several molecular diameters. These bundles of ordered atoms, molecules, ions move about in relation to each other, enabling liquids to have almost fixed volumes, which adopt the shape of their containers (Sybil, 1993).

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In the liquid, the attractions are stronger because the particles are in virtual contact. But, the kinetic energy still allows them to tumble randomly over and around each other. Therefore, a liquid conforms to the shape of its container, but has a surface. Since very little space between the particles, liquids resist an applied external force and thus, compress only very slightly. They flow and diffuse but much more slowly than gases (Silberberg, 2003).

2.1.3 Gas

Gas is a state of matter in which the matter concerned occupies the whole of its container irrespective of its quantity. In a gas, the energy of attraction is small relative to the energy of motions; so, an average, the particles are far apart. This large interparticle distance has several macroscopic consequences. A gas moves randomly throughout its container and fills it. Gases are highly compressible, and they flow and diffuse through one another easily (Silberberg, 2003).

2.1.4 Mesomorphic State

Mesomorphic or mesomorpheus state is a state of matter where the degree of molecular order is intermediate between perfect three-dimentional, long range positional order and orientational order of a solid or crystals and the absence of long range order of a isotropic liquids, gases, and amorphous solids (Baron and Stepto, 2002). The substance in the liquid crystal states are able to flow and form the droplets like those of a liquid, but at molecular level , the molecules are packed at a high degree of order (Silberberg, 2003).

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