SYNTHESIS OF SMECTIC AND DISCOTIC LIQUID CRYSTALS DERIVATIVES BY FLOW INJECTION SYSTEM

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ABSTRACT

A novel synthesis method for Discotic Liquid Crystals (DLC) with 1, 4, 5, 8, 9, 12-hexaaza-triphenylene derivatives, and chiral Smectic (S_{c*}) mesophases derivatives was done by Flow Injection System (FIS). This method have the advantage over normal synthesis method as saving time-solvent and lowering synthesis cost of LC phases. Optimizing conditions (sample & reagent volumes, 0.1 ml/min flow rate, with 0.5 m coil length and 0.5 mm i.d) were used for increasing percentage yield of the product. CLC was identified by using optical polarizing microscopy in conjunction with differential scanning calorimetry (DSC).

KEYWORDS: Liquid Crystal, Flow Injection, Organic Synthesis, Discotic and Smectic, Mesophases

INTRODUCTION

In 1888, the Austrian botanist Friedrich Reintizer observed that the cholesterol derivative, cholesteryl benzoate, appeared to have two melting points when heated.¹

Many phases with more order than present in liquids but less order than typical of crystals are called liquid crystals with specific order parameter, since they share properties normally associated with both liquids and crystals.² A group of liquid crystals, called lyotropic liquid crystals, which differ from thermotropic liquid crystals in that the formation of mesophase is dependent upon the concentration of a mesogen in a given solvent.³ When the molecules are depicted as being rod-like in shape (i.e., one molecular axis is much longer than the other two), such thermotropic mesogens are known as nematic and calamitic.³ It is also possible for thermotropic liquid crystal to be disc-like discotic (D) with one molecular axis much shorter than the other two.⁴

Scheme 1 shows a general template that can be used to describe the structure of calamitic liquid crystal materials, including those that exhibit the nematic phase and smectic phases. A and B are the core units which are sometimes linked by a linking group (Y) but more often a direct link is used. Similarly, the terminal chains (R and R") can be linked to the core with groups X and Z but usually the terminal chains are directly linked to the core.

Scheme 1: General Template of Calamitic Liquid Crystal
Lateral substituents (M and N) are often used to modify the mesophase morphology and the physical properties of liquid crystals to generate enhanced properties for applications. The units that are used in this general structure and their combinations determine the type of liquid crystal phase and the physical properties exhibited by a compound.

A certain rigidity is required to provide the anisotropic molecular structure; this core of the structure is usually provided by linearly linked ring systems (A and B) that are often aromatic but can also be alicyclic. The ring can be directly linked or may be joined by a linking group (Y) which maintains the linearity and polarisability anisotropy ($\Delta\partial$) of the core (e.g., $\text{-CO}_2$, $\text{-CH}_2\text{CH}_2\text{-}$). The rigid core alone is not usually sufficient to generate liquid crystal phases and certain flexibility is required to ensure reasonably low melting points and stabilize the molecular alignment within the mesophase structure.

**Liquid Crystal Core (A, B)**

It is usually the case that the core of a calamitic liquid crystal consists of two or more ring units. Highly conjugated ring units give increased birefringence, dielectric anisotropy and viscosity in comparison to alicyclic ring units.

**Lateral Substituents (M, N)**

Commonly used lateral substituents include F, Cl, CN and CH$_3$. These may be attached to one or more of the ring units. Lateral substituents have a number of affects on the physical properties of mesogen. One of these is the disruption of molecular packing, which usually leads to a reduction in transition temperatures as well as a reduction in smectic phase stability. Another affect, particularly with polar substituent’s, is on the value of the dielectric anisotropy. In general, the larger the lateral substituent, the lower the transition temperatures and smectic phase stability.

**Basic Types of Discotic Liquid Crystals**

Nematic (a) and Hexagonal columnar (b), affected by factors as stability of D core broadening, core length and peripheral (symmetrical) as shown in Figure 1.

**Synthesis and Studying Lateral Substituent’s Effect on Calamitic Liquid Crystals**

The three ring systems have a higher length to breadth ratio and accordingly have much higher liquid crystal phase stabilities than the two ring analogues. A lateral substituent is one that is attached off the linear axis of the molecule, usually on the side of an aromatic core (Scheme 2). Lateral substitution is important in both nematic systems and smectic systems; however, because of the particular disruption to the lamellar packing, necessary for smectic phases, lateral substitution nearly always reduces smectic phase stability (particularly the more ordered smectic phases) more than...
nematic phase stability. In general, the depression of \( T_{N-I} \) by a lateral substituent is directly proportional to the size of the substituent irrespective of its polarity.\(^\text{12}\)

The position of lateral chloro-substitution is crucial to the transition temperatures and phase morphology. If the outer-core position is chlorinated compound 1, the compound is very strongly discotic. This result is due to the polar chloro substituent filling vacant space on the edge of the core which strengthens the lateral intermolecular attractions. On the other hand, chlorination in the inner-core position compound 1 does not fill any vacant space and so the full effect of the molecular broadening is seen. In addition, the chloro substituent causes an inter-annual twisting which disrupts the polarisability of the core.\(^\text{13}\)

The six chloro substituents in this arrangement give a strong lateral dipole, which gives good molecular tilting and all of the smectic character is seen as the tilted \( S_C \) phase. Analogous materials to the chloro substituents in the end ring in compound 1 have a far greater discotic tendency that leads to a very wide \( D_C \) range.\(^\text{14}\)

![Scheme 2: 1, 4, 5, 8, 9, 12-Hexaaza-Triphenylene Derivatives Discotic Liquid Crystal](image)

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**Effect of Linking Groups (Y) and Terminal Groups(R, R')**

The affect of linking groups is to increase the length of the molecule, which in the case of rigid spacers, usually leads to increase in transition temperatures and polarisability anisotropy of molecular core in order to enhance LC phase stability by more than any increase in melting point. Terminal groups play an important role in the engineering of liquid crystal properties. They promote liquid crystal stability, often by dipolar and steric effects, by efficiency approximately following the order. The stereochemistry of the chiral unit is inverted during the reaction which occurs at the chiral carbon compound 3. Compounds 3 with azo- linking groups, have much higher nematic phase stability compared with the cyano-substituted parent system. The favourable transition temperatures of azo-linked materials generate room temperature nematic mixtures with chiral smectic (\( S_{C*} \))\(^\text{17}\) result by introducing of chiral 2-hexanol (\( n = 6 \)) through terminal chain as shown in Scheme 3. For short chain lengths, as butanol, the compounds possess a very rigid structure. Consequently, despite relatively high nematic phase stabilities, the melting points are sufficiently high for mesophases not to be seen on heating. For chain lengths of (\( n = 5, 6 \) and 7) the melting points are reduced considerably, owing to greater overall molecular flexibility and high van der waal intermolecular forces of attraction. At even greater chain lengths (\( n = 9 \)), the chains are sufficiently long to become efficient at filling space between layers of mesogens. At these chain lengths both smectic and nematic mesophases are expected. At even longer chain lengths (\( n = 10 \)), attractions between chains are greater, increasing the stability of the smectic phase. Thus, only smectics are seen at these chain lengths.

The azo- imine linking groups are used to connect two aromatic core units and the conjugation is extended over the longer molecule which enhances the polarisability anisotropy as in compounds 3. Compounds 3 with linking groups have much higher nematic phase stability but melting points are also higher. The favourable transition temperatures of imine- and azo-linked materials generate room temperature nematic mixtures but linking groups are a source of easy
decomposition through the action of light or moisture and are accordingly unsuitable for applications. Terminal alkyl chains lead to a more flexible structure to liquid crystals. This reduces melting points, thus enabling liquid crystal phases to form. Such chains also help to stabilize the molecular orientations associated with mesophase generation. The overall effect of terminal chains is not yet fully understood, but common trends can be distinguished through the analysis of a homologous series of compounds.

![Scheme 3](image)

**FIS METHOD**

The heart of a flow injection analyzer (as shown in Figure 3) is the transport system that brings together the carrier stream, the sample, and any reagent that react with the sample. Each reagent stream is considered a separate channel, and all channels must merge before the carrier stream reaches the detector.

Because the sample must mix with carrier stream, a lower flow rate is used. The carrier stream consists of an acidic solution of HCl into the THF carrier stream as in Scheme 4. Sampling rates of approximately 6 samples per hour have been achieved with this system. The detectors for FIS is optical detectors or DSC.

**Advantages of Fis Method**

Injection of the sample into one reagent stream prior to mixing with the second reagent stream. The choice of manifold depends on the chemistry of the reactions between the analyte and the reagents. This system offered the following advantages: (1) increasing the yield of LCs, rather than other traditional methods, (2) saving time and lowering synthesis cost, (3) mixture of partial substitution of poly-functional core can be separated without chromatographic plate. (4) direct phase detection. The diazo samples was injected through a 30 ml valve into the carrier solution containing, the mixed reagent, pumped at a rate of 0.1 ml/min.

![Figure 3](image)

**Figure 3:** A Single-Channel Manifold of Flow Injection System with A Mixing Coil (0.5 M Long, 0.5 Mm I.D.). the Diazos Sample was Pumped at A Rate of 0.8 Ml/Min with Reagents: (1) thf and Phenol, (2) Chiral 2-Hexanol Terminal Chain and DEAD With Pph₃

Characterization techniques used in identification of liquid crystalline phases¹⁸
The following techniques was used to identify and detect different types of mesophase result from FIS:

**Polarising Optical Microscopy**

The most widely used technique of liquid crystal phase identification is optical polarizing microscopy, which reveals that each different LC phase has a distinct optical texture. Accordingly, the opaque appearance combined with some degree of fluidity signifies the presence of a liquid crystal phase in pure sample.

Such materials alter linearly polarized light, and hence some of this light may pass through the second polarizer, allowing optical textures to be seen, which are characteristic of the mesophase type.¹⁹

The nematic phase is close in order to the isotropic liquid and very fluid, non-viscous LC phase that is lightly opaque. Smectic phases are much more viscous and appear less transparent than the nematic phase.

The smectic Sₐ molecules are aligned homeotropically then polarized liquid is extinguished and the texture appears completely black because the polarized light is passing down the optical axis. Secondly, when the molecules are not aligned homeotropically, the phase structure adopts a focal-conic fan texture, which arises because of an energetically favorable packing of the lamellar structure to give a system of curved layers.

**Differential Scanning Calorimetry**

Differential scanning calorimetry (DSC) is nearly always employed as a complementary tool to optical microscopy and reveals the presence of mesophases and LC phases by detecting the enthalpy change that is associated with a phase transition. DSC was used as complementary technique to polarizing optical microscopy, confirming the temperatures of phase transitions, as well as providing values for the enthalpies associated with these transitions.

The level of enthalpy change (associated with phase transition) gives information about degree of order in mesophase as shown in Figure 4.

![Figure 4: Two Types of Phase Transitions: First Order and Second Order](image)

Two types of phase transitions: 1-Discontinuous first order. 2-Continuous second order. The cooling, curve shows a slight displacement of the NI transition, partially due to supercooling. The smectic A to crystal transition is depressed strongly due to super-cooling of the smectic A phase.

**Alignment**

Homogeneous alignment was obtained by coating the substrate with a polymer layer (for example, unidirectional rubbed polyimide coated glass plates). Homeotropic alignment was obtained by coating the glass substrate with a monomolecularly applied surfactant as shown in Figure 5.
Figure 5: (A) Focal–Conic Fan (Layer in Curve) Energetically Favourable Packing of Lamellar Structure to Give Curved Layers. (B) Smectic A Phase

Experimental

Materials and Methods

All the chemicals were of reagent grade purity and used without further purification. The dry solvent THF with water content less than 0.005% was purchased from Aldrich Co. The finely grounded anhydrous potassium carbonate was used after further drying at 200 °C. $^1$H-NMR spectrum (400 MHz) of monomers were recorded on a Bruker DPX 400 Spectrometer using CDCl$_3$ as the solvent and tetramethylsilane as the internal standard. Solid state $^{13}$C-NMR measurement was carried out on a Bruker Avance 300 spectrometer equipped with a cross polarization magic angle spinning (CP/MAS) probe and a fully automated pneumatic unit for sample spinning. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) equation. The micropore area was calculated using t-plot method. The pore size distributions were calculated from the adsorption isotherm using the Horvath-Kawazoe (H-K) and Nonlocal Density Functional (NLDFT) calculations. The heats of adsorption for H$_2$ was calculated using the ASAP 2020 software (Micromeritics, Norcross, GA).

1,4,5,8,9,12-Hexaaza-Triphenylene (1) Analysis

A yellow solid obtained was further refluxed in DCM for 12 h. After cooling, the precipitated product was filtered and washed with petroleum ether to give a light yellow solid.

$^1$H NMR (DMSO-[$D_6$], 400 MHz, 25°C) δ ppm: 7.68 (d, 6H), 8.12 (m, 6H), 8.51 (d, 6H); $^{13}$C NMR (100MHz) (DMSO-$d_6$) δ ppm: 159.28, 151.84, 139.54, 132.58, 128.64, 125.32, 68.49, 58.56; IR (KBr)/cm$^{-1}$: $\nu$ = 1066 and 1170 (O-C), 2019 and 2123 (N=N), 1511 and 1499 (C=C), 845 (C-Cl); Elemental analysis calcd (%) for C$_{70}$H$_{72}$Cl$_6$N$_{12}$O$_{12}$ (1482.35) requires C, 56.57; H, 4.88; N, 11.31%; found C, 56.21; H, 5.03; N, 10.71%; MS (EI); m/z (%) 1482 (M$^+$, 100%).

Chiral Smectic Liquid Crystal ($S_c$*) (3) Analysis

A white solid obtained was further refluxed in acetic anhydride for 1 h. After cooling, the precipitated product was filtered and washed with petroleum ether to give a light yellow solid.
Synthesis of Smectic and Discotic Liquid Crystals
Derivatives by Flow Injection System

$^1$H NMR (DMSO-[D$_6$], 400 MHz, 25°C) ppm: 2.08 (s, 12H), 6.86 (m, 2H), 7.21 (m, 4H), 7.57 (m, 2H), 7.68 (m, 8H);
$^{13}$C NMR (100MHz) (DMSO-d$_6$) ppm: 139.54, 132.58, 128.64, 125.32, 68.49, 24.56, 22.89; IR (KBr)/cm$^{-1}$: $\nu =$2260 (CN), 1050 and 1150 (C-O), 2092 and 2231 (N=N), 1560 and 1523 (C=C), 935 (C-O); Elemental analysis cal cd (%) for C$_{21}$H$_{27}$N$_3$O (337.23) requires C, 74.77; H, 8.01; N, 12.46%; found C, 74.31; H, 7.93; N, 12.07%; MS (EI): $m/z$ (%) 337 (M$^+$, 100%).

CONCLUSIONS

Flow injection method was used for synthesis of Liquid crystal. This method have advantages over the normal synthesis method as lowering cost and time of both discotic and calametic LC synthesis. Controlling the length of the coil, flow rate and reaction temperature was used for improvement the yield percentage of LC. LC was identified by using optical polarizing microscopy in conjunction with differential scanning calorimetry (DSC).

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APPENDICES

Figure 6