Thermo-Optical Properties of Polymer Dispersed Liquid Crystals

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

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March 2007
DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

Lu Guang Chen

March 2007
I would like to express my sincere thanks to my supervisor Prof. Robert A. Shanks for his inspiring supervision, assistance and time during my project. His professional experience and extensive contacts have contributed greatly to my research work.

I would like to thank the academic, technical and laboratory staff in the Department of Applied Chemistry, RMIT University for their support and assistant throughout the duration of this project.

I would like to thank Dr. Antonietta Genovese for all her technical advice, patience and specially her friendship.

Many thanks go to my colleagues in the polymer research group for their support and friendship without whose company and affable presence, the atmosphere at University would have been monotonous and not conducive to pleasant research. Special thanks go to Ashfaqur and Zynab for sharing their scientific expertise.

I would like to thank Daniel Kaminski for his patience, advice and his companion, which has made my experience at RMIT enjoyable and worthwhile.

I am indebted to my parents, Yonglian Chen and Yinhua Han, for their love, guidance and tremendous support during my study and in life generally. My sincere thanks also go to my uncle and aunt, Yongquan Chen and Changjun Ju, and my lovely cousin Dongping. I gratefully thank my family for their incredible supports during my studies from the past and present.
PUBLICATIONS FROM THIS RESEARCH

**Journal Paper**

L. Chen and R. A. Shanks; Thermoplastic polymer dispersed liquid crystals prepared from solvent induced phase separation with predictions of solubility parameters. Liquid Crystal; accepted

L. Chen and R. A. Shanks; Thermodynamic and kinetic processes in polymer dispersed liquid crystal phase changes. Thermochimica Acta; in preparation

L. Chen and R. A. Shanks; Melting and Isotropization of 4,4’-azoxyanisole Liquid Crystal Dispersed in Poly(vinyl chloride). Thermochimica Acta; in preparation

**Refereed conference paper**


L. Chen and R. A. Shanks; Thermoplastic dispersed liquid crystals from thermal induced phase separation. ACUN-5 International Composites Conference, Developments in Composites: Advanced, Infrastructural, Natural & Nano-Composites, Sydney, Australia; 2006, 57-64.

**Conference paper**

L. Chen and R. A. Shanks; Reversible and kinetic phase change events in polymer dispersed liquid crystals. International Conference on Polymer Physics Conference, Suzhaou, China; 2006, 437-438.
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<td>L-L-N</td>
<td>Two isotropic-nematic phases</td>
<td></td>
</tr>
<tr>
<td>L-N</td>
<td>Isotropic liquid-nematic phases</td>
<td></td>
</tr>
<tr>
<td>mA</td>
<td>MilliAmpere</td>
<td></td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
<td></td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
<td></td>
</tr>
<tr>
<td>mL·min⁻¹</td>
<td>Milliliter per minute</td>
<td></td>
</tr>
<tr>
<td>mm</td>
<td>Milliliter</td>
<td></td>
</tr>
<tr>
<td>MPa¹/²</td>
<td>Square root of Mega Pascal</td>
<td></td>
</tr>
<tr>
<td>MS</td>
<td>Maier-Saupe</td>
<td></td>
</tr>
<tr>
<td>M_w</td>
<td>Molar mass</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>Direction</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Nematic</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>Number of moles</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>$\bar{n}$</td>
<td>The statistical average direction of molecular orientation</td>
<td></td>
</tr>
<tr>
<td>N(D)</td>
<td>Number distribution</td>
<td></td>
</tr>
<tr>
<td>$n_d$</td>
<td>Average refractive index</td>
<td></td>
</tr>
<tr>
<td>$n_e$</td>
<td>Extraordinary refractive index</td>
<td></td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
<td></td>
</tr>
<tr>
<td>$n_o$</td>
<td>Ordinary refractive index</td>
<td></td>
</tr>
<tr>
<td>$n_p$</td>
<td>Polymer matrix of refractive index</td>
<td></td>
</tr>
<tr>
<td>ODSC</td>
<td>Oscillating DSC</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>Period</td>
<td></td>
</tr>
<tr>
<td>PDLC</td>
<td>Polymer dispersed liquid crystal</td>
<td></td>
</tr>
<tr>
<td>pHEMA</td>
<td>Poly(2-hydroxyethyl methacrylate)</td>
<td></td>
</tr>
<tr>
<td>PIPS</td>
<td>Polymerization induced phase separation</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate acid)</td>
<td></td>
</tr>
<tr>
<td>POM</td>
<td>Polarized Optical Microscope</td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>Smectic</td>
<td></td>
</tr>
<tr>
<td>SIPS</td>
<td>Solvent induced phase separation</td>
<td></td>
</tr>
<tr>
<td>SmA</td>
<td>Smectic A phase</td>
<td></td>
</tr>
<tr>
<td>SmC</td>
<td>Smectic C phase</td>
<td></td>
</tr>
<tr>
<td>SmC*</td>
<td>Chiral SmC phase</td>
<td></td>
</tr>
<tr>
<td>SmD</td>
<td>Smectic D phase</td>
<td></td>
</tr>
<tr>
<td>SmF</td>
<td>Smectic F phase</td>
<td></td>
</tr>
<tr>
<td>SmG</td>
<td>Smectic G phase</td>
<td></td>
</tr>
<tr>
<td>$T_0$</td>
<td>Initial temperature</td>
<td></td>
</tr>
<tr>
<td>$T_c$</td>
<td>Clearing temperature</td>
<td></td>
</tr>
<tr>
<td>$T_g$</td>
<td>Glass transition temperature</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
<td></td>
</tr>
<tr>
<td>TIPS</td>
<td>Thermal induced phase separation</td>
<td></td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature</td>
<td></td>
</tr>
<tr>
<td>TMDSC</td>
<td>Temperature Modulated Differential Scanning Calorimetry</td>
<td></td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>Molar volume</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Voltage</td>
<td></td>
</tr>
<tr>
<td>V(D)</td>
<td>Volume-weighted distribution</td>
<td></td>
</tr>
<tr>
<td>w/v</td>
<td>Weight per volume</td>
<td></td>
</tr>
<tr>
<td>W-52</td>
<td>Mixture of isothiocyanates</td>
<td></td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide angle X-ray diffraction</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Weight fraction liquid crystal</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Liquid crystal fraction in droplet</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>Instantaneous heating rate</td>
<td></td>
</tr>
<tr>
<td>$\beta_a$</td>
<td>The amplitude of heating rate</td>
<td></td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>The average heating rate</td>
<td></td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>The heating rate for the first (heat) segment of a heat-cool cycle</td>
<td></td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>The cooling rate for the second (cool) segment of a heat-cool cycle</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>Solubility parameter</td>
<td></td>
</tr>
<tr>
<td>$\delta_d$</td>
<td>Dispersion parameter</td>
<td></td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
<td></td>
</tr>
<tr>
<td>$\delta_h$</td>
<td>Hydrogen bonding parameter</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>Δn</td>
<td>Birefringence</td>
<td></td>
</tr>
<tr>
<td>δ_p</td>
<td>Dipolar parameter</td>
<td></td>
</tr>
<tr>
<td>ΔS</td>
<td>Entropy</td>
<td></td>
</tr>
<tr>
<td>δ_xP</td>
<td>Hansen component parameter for polymer</td>
<td></td>
</tr>
<tr>
<td>δ_xS</td>
<td>Hansen component parameter for solvent</td>
<td></td>
</tr>
<tr>
<td>η</td>
<td>Harmonic distortion of the instrument</td>
<td></td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
<td></td>
</tr>
<tr>
<td>μW</td>
<td>MicroWatt</td>
<td></td>
</tr>
<tr>
<td>φ</td>
<td>Volume fraction</td>
<td></td>
</tr>
<tr>
<td>χ</td>
<td>Parameter</td>
<td></td>
</tr>
<tr>
<td>ω</td>
<td>Frequency</td>
<td></td>
</tr>
<tr>
<td>γ_i</td>
<td>Surface tension of the isotropic phase</td>
<td></td>
</tr>
<tr>
<td>γ_N</td>
<td>Surface tension of the nematic phase</td>
<td></td>
</tr>
<tr>
<td>%wt</td>
<td>Weight percent</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>Phase angle</td>
<td></td>
</tr>
<tr>
<td>θ</td>
<td>The angle the long axis of the molecule with a particular direction or Bragg angle</td>
<td></td>
</tr>
<tr>
<td>μL</td>
<td>Microliter</td>
<td></td>
</tr>
<tr>
<td>Δ_T</td>
<td>Lyderson correction</td>
<td></td>
</tr>
<tr>
<td>ΔH</td>
<td>Enthalpy</td>
<td></td>
</tr>
<tr>
<td>ΔU</td>
<td>Internal energy</td>
<td></td>
</tr>
<tr>
<td>ΔT</td>
<td>change in temperture</td>
<td></td>
</tr>
<tr>
<td>μm</td>
<td>Micrometer</td>
<td></td>
</tr>
<tr>
<td>5CB</td>
<td>4-cyano-4’-n-pentyl-biphenyl</td>
<td></td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
<td></td>
</tr>
<tr>
<td>°</td>
<td>Degree</td>
<td></td>
</tr>
<tr>
<td>°·min⁻¹</td>
<td>Degree per minute</td>
<td></td>
</tr>
<tr>
<td>°C</td>
<td>Celsius degree</td>
<td></td>
</tr>
<tr>
<td>°C·min⁻¹</td>
<td>Celsius per minute</td>
<td></td>
</tr>
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</table>
Polymer dispersed liquid crystal (PDLC) films serve as the basis of a variety of high-efficiency electro-optical effects. In the most general sense, as PDLC materials consist of micro-sized domains of a liquid crystal, with the domain size determined by a continuous polymer matrix running through the film. Depending on the choice of liquid crystal and polymer, a variety of electro-optical effects have been demonstrated. PDLC materials do not require the use of polarizers and as such can offer advantages of high optical efficiency and wide viewing angles compared with the liquid crystal display. Therefore, the aim of this study is to prepare and characterize mesotropic liquid crystals and polymer dispersed liquid crystals by application of solubility parameters through solvent induced phase separation, followed by thermally induced phase separation to obtain the suitable morphologies of PDLCs.

The thermal properties of four low molar mass mesogens were studied by DSC and the morphologies were investigated by polarized optical microscope (POM). There were significant super cooling/heating effects on the first order phase transitions but not on the mesophase transitions, which are second-order or weak first-order transitions. The structural effects on the transition temperature were investigated. Between the two 4-alkoxybenzoic acids mesogens, the clearing temperature of 4-(octyloxy)benzoic acid was higher than 4-(decyloxy)benzoic acid because of the increasing chain length. Trans-4-methoxycinnamic acid had the highest melting temperature among the four mesogens despite the molar mass because the carboxylic acid termini of trans-4-methoxycinnamic acid gave rise to strong intermolecular attractions.

The different liquid crystal structures were captured by POM. Some typical mesophase structures, like Schlieren nematic texture, “focal-conic” and “threading” smectic textures, were discussed. The smectic phases of 4-(octyloxy)benzoic acid were classified as head-to-head bilayer orientational smectic structures, SmA₂ and
SmC$_2$, respectively, by wide angle X-ray diffraction through measuring the d spacing of the liquid crystal.

The total solubility parameter was used to evaluate matching a polymer-LC-solvent combination. However, the polar component of the solubility parameter was most important in predicting the solubility limit in a polymer matrix and the LC fraction in the droplets, while the other components, dispersive and hydrogen bonding were not critical.

PDLC films were prepared by the solvent induced phase separation method and suitable morphologies were achieved by thermal induced phase separation. The phase transition temperatures of PDLCs were shifted to a lower temperature due to the polymer dispersion effects. Different mesophases were observed in PDLC films when LC exhibited different mesophases.

There are different factors that affect the size of the droplet dispersed in the polymer matrix. The thermal cooling rate and the liquid crystal concentration in the PDLC composites were investigated in the PVC dispersed 4,4'-azoxyanisole. The results showed that fast cooling rate and low LC concentration more readily produced a smaller and narrower distribution size of droplet, which would be an advantage for commercial applications. The LC fractions in the droplets were calculated from the nematic to isotropic enthalpies through the Smith equation. The other phase enthalpies, such as crystallization and smectic to nematic, were not achieved because they were not sufficiently isolated from other endotherms to allow enthalpies to be determined accurately due to the complex sequences of solid transitions.

The phase transitions, first-order crystallization to smectic, second-order smectic to nematic and a weak first-order nematic to isotropic phase transition, of 4-(octycloxy)benzoic acid and its pHEMA dispersion were investigated by DSC, TMDSC and quasi-isothermal TMDSC. The TMDSC results were analysed by the two approaches, reversing and non-reversing heat flow and complex heat capacity. The C-S and N-I transition temperatures of the PDLC were shifted to lower temperature and the enthalpies decreased compared with those of the pure LC due to the effects of the polymer. However, the S-N transition temperature of the PDLC was almost the same as its pure LC and the enthalpies of the mesophase change decreased.
The 4,4’-azoxyanisole and PVC dispersed 4,4’-azoxyanisole were investigated by TMDSC. The non-reversible C-N transition and reversible N-I transition were investigated by DSC and TMDSC. The significant peaks in the loss heat capacity curve and the phase lag curve represented the C-N transition which was a non-reversing first-order transition. On the contrary, the N-I transition was reversing transition which proved that there were no obvious peaks could be observed in the loss heat capacity curve and in the phase angle curve. POM was employed to investigate the morphologies of the PDLC film and four different self-organized extinction patterns were found in the 4,4’-azoxyanisole dispersed PVC film caused by the different orientations of droplet axes, but not in the different internal structures.

The results of the phase transitions of the two PDLCs illustrated that PDLCs involved both non-reversing, melting, and reversing, clearing and the transition between two mesophases. In the non-reversing transition, the transition temperature would be affected by super cooling/heating and the results obtained in the experiments were dependent on the experimental conditions, such as the heating or cooling rate, sample size and purge gas flow rate. However, in the reversing transition process, there were no super cooling/heating effects observed and it seemed that the experimental conditions were not so critical. Results could be monitored by Lissajous figures obtained from the quasi-isothermal TMDSC. The plots of modulated heat flow versus the derivative of modulated temperature can be used to alert to unfavorable experimental conditions where loss of system linearity could be seen. The quasi-isothermal TMDSC were provided accurate results for phase transition temperature and the transition ranges in addition.
Chapter 1 Introduction

1.1 Overview

Liquid crystals (LCs) are substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal (Priestley 1974; Hans and Rolf 1980). The existence of liquid crystals has been known for more than a century; yet it is only in the last thirty years that their optical, electrical, electrooptic, and thermal properties have been exploited to any significant extent in such technological applications as digital displays and thermography. LCs have been the first electro-optical materials to find widespread commercial use.

Over the past decade, several new dispersions of LCs and polymers have been developed. One of these is the polymer-dispersed liquid crystal (PDLC), where the liquid crystal is trapped as 1~3 μm diameter drops embedded within a polymeric matrix. PDLCs are becoming increasingly interests as novel materials for display applications, candidate for flat-panel displays, switchable privacy windows, and switchable optical elements such as holographic films. This is because they offer a number of potential advantages over the well-established nematic devices (twisted and supertwisted) as well as over a number of other competitors (e.g., ferroelectric or emissive) (Vaz 1989; Lovinger, Amundson et al. 1994; Hakemi and Santangelo 1998): (1) They require no polarizers (which absorb more than half of the transmitted light), thus increasing brightness, minimizing heat-control problems, and reduced power and weight; (2) they require no alignment layers or stringent thickness control, thus greatly simplifying processing and enabling larger-size displays, like switchable privacy window.

Their scattering power can be modulated by an electric field. Typically, as the electric field aligns the liquid crystal in the drops, the scattering power of the film decreases substantially, bring the film from a highly scattering state to transparency. While twisted- and supertwisted- nematic displays gain their contrast through absorption at polarizers, PDLC films gain contrast through scattering. For this reason, they offer the potential for greater brightness.
1.2 Aim

To prepare and characterize mesotropic liquid crystals and polymer dispersed liquid crystals by application of solubility parameters through solvent induced phase separation, followed by thermal induced phase separation to obtain the suitable morphologies of PDLCs.

1.2.1 Objectives

- Characterization the transition temperatures, crystal melting, $T_{CN}$ and isotropisation, $T_{NI}$, and mesogenic textures of liquid crystals.

- Determination the mesophase structure by X-ray scattering method.

- Determination the suitable polymer-solvent combinations for the liquid crystals depending on their solubility parameters.

- Preparation of polymer dispersed liquid crystals by the method of solvent induced phase separation followed by the thermal induced phase separation.

- Characterization the thermo-optical properties of the polymer dispersed liquid crystals by differential scanning calorimetry and polarized microscope with hot stage.

- Investigation the varies effects, cooling rate and liquid crystal concentration on the mesogenic droplet size in the polymer dispersed liquid crystals

- Calculation the liquid crystal solubility limits and concentration in the droplets.

- Interpretation of the phase transitions of liquid crystals and their PDLCs using differential scanning calorimetry and temperature modulated differential scanning calorimetry.
1.2.2 Research Questions

This proposed research raises some questions that are important for meeting the objectives. The questions that need to be addressed are:

1. What type of polymer-solvent combinations can be used to form polymer dispersed liquid crystals for the selected liquid crystal?

2. What are the morphologies of polymer dispersed liquid crystals films?

3. How would variables such as thermal treating rate, liquid crystal concentration affect on PDLC formation?

4. How would the mesophase transition temperatures be affected by the polymers?

5. How to interpret the TMDSC results with total heat flow approach and complex heat capacity approach?

1.3 Thesis Outline

This thesis contains eight chapters. The Chapter 1 presents a general introduction describing the overall aim and objectives of the project. Chapter 2 presents a literature review of relevant published literature of interest for this project. It covers general aspects of LCs and PDLCs. The thermo-optical properties of PDLC are discussed. In addition, the various methods of preparation and the applications of PDLC are included in Chapter 2.

Chapter 3 contains the materials used in this project. This chapter contains a brief, general introduction to the analytical techniques utilized to characterize the LCs and PDLCs. A comprehensive outline of the parameters and conditions of the experimental techniques performed to obtain the results are presented in this chapter.

Chapter 4 will investigate the thermo-optical properties of the LCs used in the project. The transition temperatures are investigated by differential scanning calorimetry (DSC) and morphologies in different phases are observed by optical microscope. The mesophase structures were classified by wide angle X-ray diffraction (WAXD).
In Chapter 5, solubility parameters will be applied to choose suitable polymers and solvents for the LCs to make PDLC films, used the solvent induced phase separation method followed by the thermal induced phase separation, with controlled phase separation, suitable dispersed LC droplet size and stable phase structure. The PDLCs will be characterised using DSC and hot stage polarized optical microscope (POM) to study the thermal and optical properties of PDLC films. The solubility limits of LC in the PDLC will be calculated by the method described by Smith and co-workers to an analysis of the melting transition.

Chapter 6 will discuss the phase behaviour of thermoplastic polymer dispersed liquid crystal system. The extent of plasticization of poly(2-hydroxyethyl methacrylate) (pHEMA) by the 4-(octyloxy)benzoic acid along with several transitions of the liquid crystal was determined by differential scanning calorimetry and temperature modulated DSC (TMDSC). The influence of the polymer on the Crystalline to Smectic (C-S), Smectic to Nematic (S-N) and Nematic to Isotropic (N-I) was investigated by DSC, the standard TMDSC and quasi-isothermal TMDSC.

In Chapter 7, TMDSC and traditional DSC were used to study the melting and isotropization transitions for the small molar mass liquid crystal [4,4’-azoxyanisole] and its polymer dispersed liquid crystal [poly(vinyl chloride) dispersed 4,4’-azoxyanisole]. Quasi-isothermal TMDSC was used to analyse the thermodynamic reversibility of the transitions. The isotropic system was illustrated by polarized optical microscopy.

Chapter 8 provides the conclusion and recommendations for further research.
Chapter 2 Literature Review

2.1 Liquid Crystals

Although the phenomenon of liquid crystallinity was discovered in 1888 and the term of “liquid crystals” was first used in 1890 (Priestley 1974; Meier, Sackmann et al. 1975; Hans and Rolf 1980; Finkelmann 1987; Pavel, Ball et al. 2002), liquid crystallinity has attained prominence only in the last two decades. Liquid crystals can exhibit intermediate phases where they flow like liquids but possess some physical properties of crystals. Accordingly, they are also called mesogens and various intermediate phases in which they could exist are termed mesophases or mesomorphic phases. LCs are anisotropic materials whose flow properties strongly depend on their structures and molecular orientation. The mesomorphic phases appear as a more or less viscous fluid which can be identified visually by their characteristic turbidity or by optical birefringence. Whereas LCs exhibit a degree of macroscopic orientational order that is found between the boundaries of crystalline solid state and isotropic, ordinary liquid state, the properties of LCs are intermediate between those of an isotropic liquid and those of a crystalline solid. Many organic compounds, including macromolecules, would possibly form liquid crystals when they are heated above their melting temperatures. The well-known and widely studied liquid crystals are thermotropic and lyotropic (Priestley 1974; Meier, Sackmann et al. 1975; Hans and Rolf 1980). Thermoropic liquid crystals are of interest both from the standpoint of basic research and also for applications in electro-optic displays, temperature and pressure sensors (Meier, Sackmann et al. 1975). Lyotropic liquid crystals, on the other hand, are of great interest biologically and appear to play an important role in living systems (Meier, Sackmann et al. 1975). Depending on temperature, pressure, constitutes, concentration, substitutes, and so on, mesogens can exhibit rich mesophases, including nematic (N), smetic (S), cholesteric (Ch), and blue phase (Priestley 1974; Meier, Sackmann et al. 1975; Hans and Rolf 1980; Finkelmann 1987; Leadbetter 1987). They will be explained in details in the text.
2.1.1 Thermotropic Liquid Crystals

A mesogen is thermotropic if the order of its components is determined or changed by temperature (Priestley 1974; Hans and Rolf 1980; Pavel, Ball et al. 2002). If temperature is too high, the rise in energy and therefore in motion of the components will induce a phase change: the LC will become an isotropic liquid. If, on the contrary, temperature is too low to support a thermotropic LC phase, the LC will become a crystal. The liquid crystallinity of thermotropic LC appears only in a particular temperature range, as schematically shown in Fig. 2.1. Smectic, nematic and cholesteric are three main types of thermotropic LC phases (Pavel, Ball et al. 2002). There are a number of sub-classifications in smectic liquid crystals in terms of position and direction arrangements of molecules. In addition, the complicated textures of thermotropic LCs have been designated by the observations of columnar and blue phases.

![Thermotropic liquid crystalline transition diagram](image)

**Figure 2.1 Thermotropic liquid crystalline transition. (Pavel, Ball et al. 2002)**

I. Nematic Liquid Crystals

Nematic liquid crystals differ from ordinary liquids by a long range orientational order of the long molecular axes and the long molecular axes are aligned parallel to a preferred direction (Cladis and Kleman 1972; Cladis 1974; Priestley 1974), as seen in Fig. 2.2. The molecules are allowed to rotate freely about their long axes and the axes of symmetry are identical with the preferred axis of the structure. Although the molecules are directionally correlated, they are positionally random or the centers of gravity are randomly distributed like an ordinary liquid. The physical properties of nematic molecules are the same along the direction of alignment and optically
uniaxial direction. Apparently, as long as no ferroelectric effects can be detected, the alignment must be assumed to be nonpolar.

Characteristic "Schlieren" is observed in nematic textures (Fig.2.5 (a) and (b)) the dark threads that are observed throughout the colored regions correspond to molecular domains which are aligned with one of the optical polarizer.

![Figure 2.2 Schematic representation of molecular arrangements in nematic.](image)

**II. Smectic Liquid Crystals**

Smectic liquid crystals have a layered structure as presented in Fig.2.3. The position of smectic molecules is correlated in some ordered patterns. Unlike nematic liquid crystals, X-ray diffraction from smectic phase would exhibit diffraction peaks due to the position order. The centers of gravity of the elongated molecules are arranged in equidistant planes (Cladis 1974; Cladis 1976; Fayolle, Noel et al. 1979). The long axes of smectic molecules are parallel to a preferred direction that may be normal to the planes (smectic A) or tilted by a certain angle (smectic C). The arrangement of the centers of gravity within the plans may be at random or regular. Typical textures of smectic liquid crystals, such as fan-shaped, focal conic, and Schlieren textures, are presented in Fig.2.5.
III. Cholesteric Liquid Crystals

Cholesteric phase is often referred to as “twisted nematic” or “chiral nematic” phase but differs significantly in that the director (the unit vector describing the average direction of molecular long axes) is not constant in space (Candau, Le Roy et al. 1973; Saupe 1973; Bonnett, Jones et al. 1989). The cholesteric phase is characterized by layers of nematic molecules where each layer is twisted with respect to the ones above and below it. As a succession of layers is passed through, the director turns through $360^\circ$ (as shown in Fig.2.4) and the thickness of such a period represents a pitch length of the helix. The fingerprint texture of cholesteric phase is shown in Fig.2.5 (j). The cholesteric fingerprint texture is observed for samples with a helical pitch in the order of several micrometers. The helix axis basically lies in the plane of the substrate, i.e. in the plane of the image and the distance between adjacent dark lines is equal to the half the pitch of a helical superstructure.

The main chemical feature which distinguishes a cholesteric material from an N material is that its molecular structure is chiral and therefore not superimposable on its mirror image. The importance of structural optical activity and the special relationship between the N and Ch phases have been demonstrated by two noteworthy observations (Levine 1974; Priestley 1974).

1. N phases are made Ch by dissolving in their optically active enantiomers which themselves may or may not be LC materials.
2. A racemate exhibiting an N phase can be resolved into its enantiomers, each of which will exhibit a Ch phase. A further point to note is that the helical twist senses of the phases formed by the two enantiomers are opposite in sign, indicating a relationship of helical sense to molecular structure.

Figure 2. 4 Schematic representation of cholesteric liquid crystalline phase.
IV. Columnar Phase

Columnar phases are formed on heating/cooling of compounds composed of disc-shaped molecules that can pack together to form flexible cylinders or columns of different types (resembling stacks of coins) (Priestley 1974; Meier, Sackmann et al. 1975). The arrangement of disc-shaped molecules within an individual column can be either ordered or random in accordance with positional arrangements of disc-shaped molecules. The columns themselves can be grouped into hexagonal or orthogonal
lattices. A schematic representation of the ordered hexagonal structure of columnar phase is given in Fig. 2.6.

![Schematic representation of the ordered hexagonal structure of columnar phase.](image)

In some cases, compounds that form columnar phases do not have a disc-like shape by themselves, but may aggregate into disc-like formations. Therefore, the often used term ‘discotic phase’ is not quite correct for the columnar phase, since it refers to building blocks that are not necessary prerequisite for obtaining this two-dimensional order. The columns can be two-dimensionally ordered with nematic-like, hexagonal, rectangular or oblique packing. This distinct class of mesophase has only been recognized for a few years. In practice, columnar phases are relatively rare since a special disc-like geometry of mesogen is required. The research effort on this phase is still somewhat limited, but increasing steadily.

**V. Blue Phase**

For some cholesteric materials, the blue phases could appear as the temperature increases from that of cholesteric (helicoidal) phase but does not reach that of isotropic liquid phase (Levine 1974; Priestley 1974; Hans and Rolf 1980). They are called “blue” phase for historical reasons, so the adjective blue does not prevent them from looking bright yellow or red in some instances (Priestley 1974; de Gennes and Prost 1995). The blue phases occur in cholesteric systems of sufficiently low pitch, less than about 5000Å (Hans and Rolf 1980). The temperature region in which the blue phases are thermodynamically stable is very narrow, usually only about 1 K (Meier, Sackmann et al. 1975). This fact has limited the progress of study of blue phases in contrast to other mesophases.
Currently, three distinct blue phases have been identified: BP I (a body-centred cubic lattice), BP II (a simple cubic lattice) and BP III (probably amorphous) occurring in that order with increasing temperature (Priestley 1974). The details of molecular arrangements within the blue phases, however, remain unclear.
Table 2.1 Structural classification of thermotropic liquid crystals. (Levine 1974; Leadbetter 1987)

<table>
<thead>
<tr>
<th><strong>Rod-like molecules</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nematic (N)</td>
<td>Long-range orientational order but no long-range translational order</td>
</tr>
<tr>
<td>Cholesteric (Ch)</td>
<td>Chiral nematic</td>
</tr>
<tr>
<td>Smectic A (SmA)</td>
<td>Liquid-like types of SmB have been indentified: 3D crystal, hexagonal lattice, upright molecules; Stack of interacting ‘hexatic’ layers with in-place short-range positional correlation and long-range 3D six-fold ‘bond-orientational’ order</td>
</tr>
<tr>
<td>C (SmC)</td>
<td>Titled form of SmA</td>
</tr>
<tr>
<td>D (SmD)</td>
<td>Cubic</td>
</tr>
<tr>
<td>F (SmF)</td>
<td>Monoclinic (a &gt; b) with in-place short-range positional correlation and weak or no interlayer positional correlation</td>
</tr>
<tr>
<td>G (SmG)</td>
<td>3D crystal, monoclinic (a &gt; b)</td>
</tr>
<tr>
<td>Hz (SmH)</td>
<td>3D crystal, monoclinic (a &gt; b)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Disc-like molecules</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>D_{hd}</td>
<td>Columnar structure (D) with a hexagonal packing of the columns and a disordered or liquid-like arrangement of the discs in each column</td>
</tr>
<tr>
<td>D_{ho}</td>
<td>Hexagonal but with an ordered arrangement of the molecular cores in each column</td>
</tr>
<tr>
<td>D_{t}</td>
<td>Titled columnar structure</td>
</tr>
<tr>
<td>D_{D}</td>
<td>Nematic-like arrangement of discs</td>
</tr>
</tbody>
</table>
All LC compounds with rod-like molecules exhibit nematic, cholesteric, smectic and/or (in a few cases) cubic mesophases (shown in Table 2.1). In practice, only nematic cholesteric, smectic A and smectic C phases are commonly observed for polymer dispersed liquid crystals (PDLCs) (Amundson, Blaaderen et al. 1997; Hakemi and Santangelo 1998), other higher order smectic mesophases being comparatively rare.

2.1.2 Lyotropic Liquid Crystals

There is a class of materials that exhibit liquid crystal behaviour only when in solution with a solvent. Liquid crystalline phases formed in such solutions are said to be lyotropic (Priestley 1974; Hans and Rolf 1980). A lyotropic LC can consist of two or more components that exhibit liquid-crystalline properties in appropriate concentrations. Lyotropic liquid crystalline transition process is presented in Fig.2.7. In lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic LCs, the lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases.

A molecule which possesses immiscible hydrophilic and hydrophobic parts is called an amphiphilic molecule (Priestley 1974; Hans and Rolf 1980). Many amphiphilic molecules show lyotropic liquid-crystalline phase sequences depending on the volume balances between the hydrophilic part and hydrophobic part. These structures are formed through the micro-phase segregation of two incompatible components on a nanometre scale. Soap is an everyday example of a lyotropic LC (Finkelmann 1987; Drzaic 1995).
The content of water or other solvent molecules changes the self-assembled structures of amphiphilic molecules. At very low concentrations, amphiphilic molecules will be dispersed randomly without any ordering. At slightly higher (but still low) concentrations, amphiphilic molecules will spontaneously assemble into micelles or vesicles. This is done so as to ‘hide’ the hydrophobic tail of the amphiphile inside the micelle core, exposing a hydrophilic (water-soluble) surface to aqueous solution. These spherical objects do not order. A typical phase is a hexagonal columnar phase, where the amphiphiles form long cylinders that arrange themselves into a roughly hexagonal lattice or the middle soap phase. As the concentration is further increased, a lamellar phase may form, wherein extended sheets of amphiphiles are separated by thin layers of water. For some systems, a cubic (also called viscous isotropic) phase may exist between the hexagonal and lamellar phases, wherein spheres are formed that create a dense cubic lattice. These spheres may also be connected to one another, forming a bicontinuous cubic phase.

The objects created by amphiphiles are usually spherical (as in the case of micelles), but may also be disc-like (bicelles), rod-like, or biaxial (all three micelle axes are distinct) (Yang, Kikuchi et al. 2003). These anisotropic self-assembled nanostructures can then order themselves in much the same way as LCs do, forming large-scale versions of all the thermotropic phases (such as a nematic phase of rod-shaped micelles).

For some systems, at high concentration, inverse phases are observed. That is, one may generate an inverse hexagonal columnar phase (columns of water encapsulated by amphiphiles) or an inverse micellar phase (a bulk LC sample with spherical water cavities).

A generic progression of phases, going from low to high amphiphile concentration, is (Kronberg, Bassignana et al. 1978; Hans and Rolf 1980; Finkelmann 1987):

- Discontinuous cubic phase (micellar phase)
- Hexagonal columnar phase (middle phase)
- Bicontinuous cubic phase
• Lamellar phase

• Bicontinuous cubic phase

• Reverse hexagonal columnar phase

• Inverse cubic phase (Inverse micellar phase)

Even within the same phases, their self-assembled structures are tunable by the concentration: for example, in lamellar phases, the layer distances increase with the solvent volume. Since lyotropic LCs rely on a subtle balance of intermolecular interactions, it is more difficult to analyse their structures and properties than those of thermotropic LCs.

2.1.3 Polymorphism in Thermotropic Liquid Crystals

Many thermotropic materials have been observed to pass through more than one mesophase between the solid and isotropic liquid phases. Such materials are said to be “polymorphic” (Finkelmann 1987; Leadbetter 1987; Zhang, Hong et al. 1992). One can predict the order of stability of these mesophases on a scale of increasing temperature simply by utilizing the fact that raising temperature results in a progressive destruction of molecular order. Thus, the more ordered of mesophase, the closer in temperature it lies to the solid phase. From the description of the various types order, a number of conclusions can be immediately drown as follows (Hans and Rolf 1980; Finkelmann 1987; Agra, Amos et al. 1997):

1. For a material having nematic and smectic trimorphous phases, the order of mesophase stability with increasing temperature follows such a sequence:

   solid→smectic B→smectic C→smectic A→nematic→isotropic

   This order of stability is in complete agreement with experimental observations.

2. For a material having nematic and/or smectic phases, but not all those listed in (1), the order of stability can be obtained from that shown in (1) by simply deleting those phases not present. This is also confirmed experimentally.
3. Furthermore, for a material having cholesteric and smectic mesophases, the order of stability is identical to that of conclusion (1) except the word “nematic” is replaced by “cholesteric”. The following have been experimentally observed

a) solid→cholesteric→isotropic

b) solid→smecticA→cholesteric→isotropic

Finally, there are no known examples of polymorphism involving both nematic and cholesteric mesophases. It is found, however, that the cholesteric liquid crystal can be forced into a nematic structure in the presence of an external electric or magnetic field.

2.2 Polymer Dispersed Liquid Crystals

Due to their numerous and important electro-optical properties, LCs play a very important role in a wide variety of applications, particularly, in the most popular being displays (Meier, Sackmann et al. 1975; Hans and Rolf 1980; Poetsch, Jubb et al. 1992; Kato, Tanaka et al. 1993). However, the main drawbacks of LCs applications for a large screen are the thickness which must be carefully checked and the polarizer which reduces the light transmission. Novel materials composed of LCs and polymers are accordingly considered to meet such a challenge. The combinations of LCs with polymers can be divided into two types: polymer dispersed liquid crystals (PDLCs) and liquid-crystalline polymers (LCPs) (Amundson, Blaaderen et al. 1997; Park, Ahn et al. 1997; Magagnini, Paci et al. 1999; Liu and Wang 2004). Liquid crystal dispersions were first studied by Lehman in 1904 (Bloisi and Vicari 2003; Mucha 2003), when he suspended liquid crystal droplets in glycerine. It was not until 1980s, however, that this class of materials became a candidate for practical applications (Vaz 1989; Simoni 1992). Polymer dispersed liquid crystals were pioneered by Doane and co-workers (Arora, Ziemnicka et al. 1985; Doane, Vaz et al. 1986). PDLCs consist of birefringent liquid crystal droplets dispersed in an otherwise optically transparent polymer matrix, whereas the mosogens are bonded to the polymer in LCPs. The resulting PDLCs are a sort of “Swiss Cheese” polymers with liquid crystal droplets filling in the holes. In PDLCs, the tiny droplets (a few microns across for
practical applications) are responsible for the unique behavior of materials. For example, the tiny droplets can afford much needed electro-optical properties. By changing the orientation of the liquid crystal molecules with an electric field, it is possible to vary the intensity of transmitted light (Aliev, Baushev et al. 1980; Pan, Yang et al. 1994; Bloisi, Ruocchio et al. 1996; Bloisi, Ruocchio et al. 1996; Crawford, Jr. Whitehead et al. 1998; Fuh and Lin 2004). The polymer matrix basically provides thermal and mechanical stability. A high level of activity has characterized the field of research on PDLCs, which are potentially useful for a variety of electrooptical applications including switchable windows, displays and other devices (Poetsch, Jubb et al. 1992). The properties of LCPs can be selectively manipulated by changing main-chain, side-chain, combined main-chain/side-chain, and Cross-linked (Park, Cho et al. 2000; Pavel, Ball et al. 2002; Trongsatitkul, Aht-Ong et al. 2004; Zhang, Zhang et al. 2004).

2.2.1 The Developments of the Studies of PDLCs

Dispersed liquid crystals have been the object of study in the literature for many decades.

- Liquid crystal tactoids (cigar-shaped droplets) were noted in the first half of last century by Zöcher and others (Zöcher 1925; Bernal and Fankuchen 1941). Candau et al. examined the effect of magnetic fields on bipolar, radial and spherulitic droplets in the early 1970’s (Candau, Le Roy et al. 1973). The structures of nematic and smectic liquid crystals in capillary tubes were reported in the same period of time.

- Liquid crystals dispersed in a polymer matrix, which was known as nematic curvilinear aligned phase, were first made by emulsifying a nematic liquid crystal into an aqueous solution of poly(vinyl alcohol) (PVA). Thin films are prepared by casting onto a conductive substrate, drying and laminating a second conductive substrate to form the device (Drzaic 1995).

- PDLC thin films with electrically controllable scattering can be obtained, in general, by a phase separation method. Such PDLC thin films were first successfully prepared by Doane et al. in 1985 (Doane, Vaz et al. 1986).
Briefly, an epoxy resin was used to mix with a liquid crystal in a selected solvent. Upon heating, the liquid crystal phase can be separated from growing polymer chains to form liquid crystal droplets distributed in a cured epoxy matrix.

- PDLCs materials initially prepared for electronic devices can normally stand voltages ranging from 60 V to 120 V (Drzaic 1995). In recent years, improvements in polymer materials have advanced to the point where PDLC thin films would be operated in a 5-10 V range (Drzaic 1995). Lower voltages have made active-matrix PDLC devices possible.

### 2.2.2 Methods of PDLCs Preparation

Polymer dispersed liquid crystals have been prepared in several different ways including: encapsulation (emulsification) (Huang and Zhu 1990; Hakemi and Santangelo 1998; Coates 2000), phase separation and other methods. Note that the phase separation process has become the primary method in manufacture (Hakemi and Santangelo 1998). Different methods can result in different properties and characteristics of PDLC materials. Among the factors influencing the properties of PDLC materials are the size and morphology (shape) of droplets, the types of polymers and liquid crystals used, and cooling and heating rates in preparation (Arora, Ziemnicka et al. 1985; Im, Jin et al. 1995; Hakemi and Santangelo 1998; Hong, Chen et al. 1998; Coates 2000; Park, Cho et al. 2000; Fan, Xie et al. 2002), which are detailed below.

#### 2.2.2.1 Encapsulation

Early attempts to produce PDLCs were made with a technique known as microencapsulation (Mucha 2003). In this method, a liquid crystal is mixed with a water soluble polymer dissolved in water. When the water is evaporated, the liquid crystal is surrounded by a layer of polymers. Thousands of these tiny “capsules” are produced and distributed through the bulk polymer. LC droplets produced with this method tend to be non-uniform in size and can even be interconnected with each other. Materials manufactured by encapsulation are referred to as NCAP or nematic curvilinear aligned phase.
2.2.2.2 Phase Separation

In order to obtain PDLCs by phase separation, a homogeneous mixture of a polymer and a liquid crystal is first prepared. The liquid crystal droplets are then formed by a progressive separation. The phase separation can take place in one of the following three ways:

I. Polymerization-Induced Phase Separation

Phase induced phase separation (PIPS) (Klosowicz 1994; Lovinger, Amundson et al. 1994; Maschke, Coqueret et al. 1995; Gyselinck, Mechernene et al. 2001; Mahinay, Davila et al. 2004) is useful when polymer materials are miscible with low molecular weight liquid crystal compounds. A homogeneous solution is made by mixing the polymer with the liquid crystal. Polymerization is achieved through a condensation reaction, as with epoxy resin (Park, Ahn et al. 1997), through free-radical polymerization, as with a vinyl monomer catalyzed with a free-radical initiator such as a benzoylperoxide; or through a photo initiated polymerization (Mucha 2003).

The solubility of liquid crystals decreases in the stiffening polymers until the droplets of liquid crystal form. These droplets grow until gelation of the polymer constrains change of the droplet morphology. Droplet size and morphology are determined during the time between nucleation of droplets and gelation of the polymer. The main factors that influence the size of the liquid crystal droplets in PIPS are the cure temperature, the relative concentrations of materials, and the type and proportions of liquid crystal and polymers used (Klosowicz 1994; Lovinger, Amundson et al. 1994; Gyselinck, Mechernene et al. 2001; Mahinay, Davila et al. 2004). It is worth noting, however, that the droplet size is also controlled by physical parameters such as viscosity of solution, rate of diffusion, and solubility of the liquid crystal (Lovinger, Amundson et al. 1994). The rate of polymerization is controlled by cure temperature for thermally cured polymers or by light intensity of photochemical polymerization. The different sizes of the liquid crystal droplets will translate into different macroscopic optical properties.

The most convenient method used for the preparation of PDLC film is the polymerization induced phase separation of mixtures composed of reactive polymer precursor and LC (Mucha 2003).
The curing by free-radical polymerization can be initiated by ultraviolet (UV), or electron beam (EB). Compared with the PIPS-UV process, EB-curing does not require the addition of initiator (Drzaic 1995; Mucha 2003). Hardening of polymers may take place also by thermal cure (polycondensation) using initiators (Drzaic 1995).

II. Thermally-Induced Phase Separation

Thermal Induced phase separation (TIPS) (Challa, Wang et al. 1995; Vorflusev and Kumar 1998; Hoppe, Galante et al. 2003) is useful for thermoplastics that melt below their decomposition temperature. In this method, a homogeneous mixture of a liquid crystal and a melted polymer is formed. The solution is cooled at a specific rate to induce phase separation. Liquid crystal droplets begin to form as the polymer hardens. The droplets continue to grow until the glass transition temperature of the polymer is crossed.

Droplet size is affected the most by the cooling rate of the polymer/liquid crystal solution (Smith and Vaz 1988; Lackner, Margerum et al. 1989; Smith 1990; Hoppe, Galante et al. 2003). Fast cooling rates tend to produce small droplets because there is not sufficient time for large particles to form. Therefore, droplet size and cooling rate are related inversely. Fig. 2.8 shows the TIPS process at different cooling rate in PMMA dispersed E7. The droplet size increased with the decrease of the cooling rate. The droplet size depends upon a number of material parameters, which include viscosity and thermodynamics. In general, larger concentrations of liquid crystals are required for these films as compared to PIPS.

Figure 2.8 The droplet size vs. the cooling rate in PMMA dispersed E7. (Lackner, Margerum et al. 1989)
TIPS methods, while simple, have been of limited use in PDLC film construction. The properties of TIPS films are often sensitive to the processing history and can be difficult to reproduce. The films formed by this method are also unstable at high temperatures where the liquid crystal and polymer phases have high solubility.

III. Solvent-Induced Phase Separation

Solvent induced phase separation (SIPS) (Klosowicz 1994; Mucha and Nastal-Grosicka 1999; Andreau, Sannier et al. 2001; Sumana and Raina 2004) is useful with thermoplastics which melt above the decomposition temperature of thermoplastics or liquid crystals, or where solvent coating techniques are used. The liquid crystal and polymer are dissolved in a common solvent forming a homogeneous solution. The solvent is then removed by evaporation, resulting in phase separation and polymer solidification. Liquid crystal comes continuously out of solution until the solvent has been completely removed. The main factor affecting droplet size in SIPS is the rate of solvent removal. Like TIPS, droplet size increases as the rate of solvent removal decreases.

Some common methods of preparation for PDLC are presented in Table 2.2 and typical recipes for preparation of PDLCs are given in Table 2.3.
Table 2.2 The various methods of preparation for polymers. (Mucha 2003)

<table>
<thead>
<tr>
<th>Methods</th>
<th>Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Emulsion</td>
<td>PVA</td>
</tr>
<tr>
<td>2 PIPS, thermosetting</td>
<td>Epoxy resins</td>
</tr>
<tr>
<td>3 PIPS, photocuring</td>
<td>NOA-65 Polyester resin</td>
</tr>
<tr>
<td>4 TIPS and SIPS</td>
<td>PMMA Polycarbonate</td>
</tr>
</tbody>
</table>

Table 2.3 Examples of recipes for preparation of PDLC. (Coates 2000; Bloisi and Vicari 2003; Mucha 2003)

<table>
<thead>
<tr>
<th>PIPS method</th>
<th>Weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid prepolymer</td>
<td>Epon 828</td>
</tr>
<tr>
<td>Curing agent</td>
<td>Capcure 3-800</td>
</tr>
<tr>
<td>Liquid crystal</td>
<td>E7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TIPS method</th>
<th>Weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer melt</td>
<td>Epon 828 (50%) + t-butyl amine (50%)</td>
</tr>
<tr>
<td>Liquid Crystal</td>
<td>E7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SIPS method</th>
<th>Weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer</td>
<td>Poly(methyl methacrylate) (PMMA)</td>
</tr>
<tr>
<td>Liquid Crystal</td>
<td>E7</td>
</tr>
<tr>
<td>Solvent</td>
<td>Chloroform</td>
</tr>
</tbody>
</table>
2.2.2.3 Other Methods for PDLC Formation

Most of the PDLC systems described to date have been produced by methods that fall within the broad definition of emulsion or phase separation processes described above. Nevertheless, a few other schemes that fall outside these broad categories have been reported to make dispersed nematic systems.

I. Glass-dispersed Systems

Organosilicon sol-gel chemistry has been used to create dispersed nematic systems within a silica glass matrix (Levy, Pena et al. 1992; Levy, Serna et al. 1992). Sol-gel chemistry is a step-polymerization process which allows soluble and reactive organosilicon species to form a highly crosslinked silica network. Initially, the organosilicon reactants are dissolved into water (or into water/alcohol solutions). Alkoxy substitutes on silicon hydrolyze to form crosslinkable hydroxyl-substituted species. These hydroxyl-substituted molecules can react to form a gelled silica network. Further densification of the gel through loss of water leads to a silica glass.

If a liquid crystal is mixed into the system at the sol stage, dispersed droplets are trapped by the glass matrix after completion of the reaction. Heavy metal alkoxides (like titanium isopropoxide) can be added as a dopant to the aqueous solution, which can improve the refractive index of the glass matrix.

II. Dispersed Silica Systems

Kreuzer et al. (Neubecker, Kreuzer et al. 1991; Bittner and Kreuzer 1996) have reported a liquid crystal composite system formed by mixing fumed silica with a nematic liquid crystal. Fumed silica consists of agglomerates of silicon oxide particles with typical particle diameters on the order of 10-40 nm. Typically, the silica makes up 2-3% of the liquid crystal weight. The silica may be used with its native hydroxyl-rich surface or can be derivatized with various organic groups prior to mixing with the liquid crystal. After dispersing the silica in the liquid crystal, the mixture is placed between parallel indium tin oxide (ITO)-coated plates. These devices show bistable scattering and transparent states.
III. Mixtures of Microspheres and Liquid Crystals

Mixtures of nematic liquid crystals and micro-sized spheres have been used to create a liquid crystal composite system (Nomura, Suzuki et al. 1990; Nomura, Suzuki et al. 1991). Microspheres can be made only from a polymer. Alternatively, microspheres can be glass particles coated by polymer film, which would enhance adhesion and liquid crystal alignment. These microsphere systems show a highly-scattering low-field state and a weakly-scattering high-field state, analogue to standard-mode PDLC films.

2.2.3 Materials for PDLC Preparation

2.2.3.1 Polymer

Polymers are formed by the connection of numerous repeat units or monomers. To form a polymer, each monomer must be able to connect to at least two other species to form a link in a continuous chain. Polymer molecular weights span a wide range, from a few hundred to many million, and exhibit a polydispersity. Low molar mass polymers possess properties bridging those of monomers and polymers; these compounds are usually referred to as oligomers. The number of repeat units is often referred to as the degree of polymerization.
Figure 2.9 Schematic examples of different polymer structures.

The polymer chain can be relatively simple, with a linear structure and no variation in type of monomer (a homopolymer). Alternatively, different types of monomers can be used to form a chain where the monomer type is mixed (a copolymer). Except for the simplest polymers, the monomers can connect in different orientations relative to each other to vary the stereochemistry of the polymer chain (the tacticity of the polymer). If the monomers in a copolymer within the chain tend to segregated by type (so that monomer type A tends to react with type A and type B reacts preferentially with type B) the polymer chain can possess long stretches AAA...A and BBB...B. These are coined block copolymers. The polymer chains can be linear, branched, or crosslinked, where different linear chains are connected to each other (Fig.2.9).

If the chain structure is sufficiently regular, the polymer could tend to crystallize. These polymers consist of small crystalline domains connected by amorphous regions. The relative amount of crystalline and amorphous domains depends on both structure of the polymer and the processing conditions used to create the material. Polymers containing crystalline regions can exhibit a melting transition at a temperature $T_m$. Depending on the size and density of the crystallites, semicrystalline films strongly scatter light, and undesirable proper in PDLC devices.
All polymers also exhibit a glass transition temperature $T_g$, which marks a second-order phase transition. This phase transition is often evidenced by a change in the mechanical properties of the polymer, or a change in the slope of a plot of specific volume vs. temperature. The glass transition results from the sudden onset of increased molecular motion of the polymer chains above a characteristic temperature. Increased rotation of the polymer chains is one such motion that increases above $T_g$. The glass transition temperature is always below the melting temperature. Depending on the ambient temperature, a polymer can exist in several physical forms, such as a semicrystalline solid, a glass, a rubber, or a viscous fluid.

Both $T_m$ and $T_g$ for polymer can be lower by plasticization, where an absorbed low molar mass species solvates the polymer chains. Most of the polymers used in PDLC systems will absorb liquid crystal. This is an important phenomenon in PDLC films, as liquid crystal absorbed into a polymer will both lose its mesogenic properties and alter the properties of the polymer. In phase separation films, the necessity of having the polymer and liquid crystal mutually soluble makes it virtually certain that the polymer in a PDLC film is heavily plasticized by the liquid crystal. It is likely that the polymers in most PDLC devices have strongly suppressed glass transition and melting temperatures.

Linear and branched polymers can be often be dissolved by solvents. Crosslinked polymers, on the other hand, have an effectively infinite molar mass and can not be dissolved in solvents. Rather, crosslinked polymers will swell as they absorb solvent, maintaining their network structure. Crosslinked polymers can be tough and durable, linear polymers, in contrast, can be deformed by the slippage of polymer chains or by deformation of the crystallite structure, and so are easier to distort. As will be discussed later, PDLC films containing crosslinked polymers can readily be formed using both emulsion and polymerization-induced phase separation methods, while solvent and thermal-based phase separation methods are restricted to linear or branched polymer. The most common polymers in PDLC chemistry are those derived from acrylate, methacrylate, or vinyl families.
2.2.3.2 Mesogens

There is no way of predicting with certainty whether or not a given molecule will exhibit liquid-crystal mesophases. However, the presence of common structural features in the majority of thermotropic liquid-crystal mesogens makes generalizations regarding the types of molecules most likely to show liquid-crystalline behavior. The two structural features that appear essential are (1) the constituent molecules must be elongated and (2) they must be rigid (Leadbetter 1987). It should be borne in mind that these are only generalizations, and exceptions do exist.

One group of structurally related compounds has been already encountered that often form liquid-crystal phases, viz. the substituted cholesterols. It is evident that these molecules are elongated and quite rigid, thereby satisfying the two criteria above. As mentioned earlier, all mesophases produced by molecules of these types have a finite pitch due to the optical activity of the parent cholesterol molecule.

Compounds forming small molecule thermotropic liquid crystals usually have the following molecular structural features (Priestley 1974):

- High length: breadth (axial) ratio is no less than 4.
- Rigid units such as 1,4-phenylene, 1,4-bicyclooctyl, 1,4-cyclohexyl, etc.
- Rigid central linkages between rings such as –COO-, -CH=CH-, -N=NO-, -N=N-, etc.
- Anisotropic molecular polarization.

The vast majority of compounds exhibiting liquid crystalline properties may be regarded as possessing a central linkage and end groups (shown in Fig. 2.10). When the central linkage is small, such as –C=N- or -C≡C-, aromatic nuclei are nearly always present. Mesogens containing both carbocyclic and heterocyclic aromatic residues are known. Central groups that require no highly polyarizable aromatic residues are exemplified by the carboxylic acid dimmers. Fig. 2.11 shows the more common central linkages.
Figure 2.10 Common structure of mesogenic compounds. (Priestley 1974)

Figure 2.11 Common central linkages of mesogenic compounds. (Priestley 1974)
Chapter 2 Literature Review

Figure 2.12 Common terminal groups of mesogenic compounds. (Priestley 1974)

Terminal groups vary widely in chemical nature. Fig. 2.12 presents those most frequently encountered. The terminal group frequently determines which mesophase will be observed.

There are exceptions to each generalization above, but the list can serve as a rough guide to predicting liquid crystalline (mesomorphic) potential of a given compound. In general the nematic phase is predominant for compounds having short flexible tails and the smectic phase is dominant for compounds with long tails. Both phases are often seen when tail length is of intermediate length. Lyotropic liquid crystals result from very specific interactions between an amphiphilic solution and solvent(s). Typical low molar mass lyotropic combinations are sodium dodecyl sulfate-water-1-alkanol and phospholipids-water. Table 2.4 presents more often used LC compound–nematic mixture known as E7.
Table 2. 4 Chemical structure of E7. (Vaz, Smith et al. 1991; Challa, Wang et al. 1995; Agra, Amos et al. 1997; Bedjaoui, Gogibus et al. 2004)

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Weight [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₁</td>
<td>51</td>
</tr>
<tr>
<td>C₇H₁₅</td>
<td>25</td>
</tr>
<tr>
<td>C₇H₁₉O</td>
<td>16</td>
</tr>
<tr>
<td>C₈H₁₇</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 2.5 presents some examples of materials used for PDLC preparation by polymer curing method (PIPS).

An advantage of acrylate chemistry is that the starting materials can be highly purified and the free-radical cure chemistry need not involve any ionic compounds (Mucha 2003). The resulting films can have high volume resistivity if used with high resistivity liquid crystal mixtures, a necessary requirement for display applications.
<table>
<thead>
<tr>
<th>Primer</th>
<th>LC</th>
<th>Paper</th>
<th>Cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligoester resin + styrene or diacrylate + UV initiator</td>
<td>W-52 (mixture of isothiocyanates), 6CB</td>
<td>(Mucha and Kyszewski 1992; Mucha and Nastal 1997; Nastal, Zuranska et al. 1999)</td>
<td>UV</td>
</tr>
<tr>
<td>Aromatic polyester acrylate dilute in tripropyleneglycol diacrylate + photoinitiator (Lucirin TPO)</td>
<td>E7 (cyano-paraphenylene derivatives)</td>
<td>(Vaz, Smith et al. 1991)</td>
<td>EB, UV</td>
</tr>
<tr>
<td>Photocurable acrylic thermalcurable epoxy + diglycidyl ether of polypropylene glycol (DER736)/dicyandiamide (DICY) (various fractions)</td>
<td>E7</td>
<td>(Roussel, Buisine et al. 1998; Vaia, Tomlin et al. 2000)</td>
<td>UV, thermal</td>
</tr>
<tr>
<td>Diglycidyl ether of bisphenol A (DGEBA) aliphatic triglyceride (EPON 812) + hardeners: Capture 3-800, Capture EH-30, Devcon 5B</td>
<td>5CB, 7CB, E7, E8</td>
<td>(Park, Ahn et al. 1997)</td>
<td>Thermal</td>
</tr>
<tr>
<td>Three component mixture Devcon 5A resin, Epon 812 resin and Capture 3-800 hardener in 1:1:2 volumetric proportions</td>
<td>E7</td>
<td>(Smith and Vaz 1988)</td>
<td>Thermal</td>
</tr>
<tr>
<td>Monofunctional acrylate monomer: ethylene glycol phenyl ether acrylate (EGPEA, Aldrich) + 2 wt% Darocur 1173</td>
<td>E7</td>
<td>(Allouchery, Roussel et al. 1999)</td>
<td>UV</td>
</tr>
<tr>
<td>Photocurable polymer NOA-65 (thiolene-polymerization)</td>
<td>E7</td>
<td>(Lovinger, Amundson et al. 1994; Zhou, Petti et al. 2004)</td>
<td>UV, EB</td>
</tr>
<tr>
<td>Various acrylate systems (monomeric, oligomeric and multifunctional)</td>
<td>Various LC</td>
<td>(Challa, Wang et al. 1995; Allouchery, Roussel et al. 1999; Bouchaour, Bennouna et al. 2000; Gyselinck, Mechemene et al. 2001; Fan, Xie et al. 2002)</td>
<td>UV, EB</td>
</tr>
<tr>
<td>Acrylic acid + benzoic acid initiator</td>
<td>W-52</td>
<td>(Mucha and Nastal 1998)</td>
<td>UV, Thermal</td>
</tr>
</tbody>
</table>
2.3 Aspects of Film Structure

The microstructure of dispersed liquid crystal embedded in an optically isotropic polymer matrix is a critical aspect in the electro-optical performance of the PDLC film devices. Despite the large number of methods available to create PDLC systems, the resulting films possess several common structural features of interest. These important aspects include:

- The PDLC film thickness
- The liquid crystal droplet domain sizes and shapes
- The polymer morphology
- The degree of cure in polymerized PDLC systems
- The volume fraction of liquid crystal dissolved into the polymer matrix
- The composition and refractive indices of the polymer and liquid crystal
- Any preferential alignment of the liquid crystal director field

2.3.1 Film Thickness

One of the fundamental parameters of a PDLC film is its thickness. PDLC films are field-effect devices, so that the voltage required to activate a film increases linearly with thickness. PDLC light scattering also depends strongly on the film thickness. Control of film thickness can be achieved in TIPS and PIPS methods through the use of film spacers of known dimension dispersed into the PDLC film. Spaces are less useful in emulsion-based and SIPS process film, which required a coating and drying step followed by lamination. Here, solid film thickness is determined during deposition of the fluid coating.

2.3.2 Microscopy of PDLC Film

Optical microscopy is usually of value in characterizing practical PDLC films. For isolated droplets, optical microscopy is useful in mapping droplet configurations.
Polarization microscopy can be useful in determining if the film possesses any preferential alignment of the droplets’ director fields. For example, Golovataya et al. have reported an interesting set of photos showing a cooperative alignment pattern in clusters (chains) PDLC droplets (Golovataya, Kurik et al. 1990).

### 2.3.3 Liquid Crystal Domain Size

PDLC Film scattering and reorientation fields depend strongly on droplet size, as do other properties like response time and hysteresis. Even for films that do not possess a distinct droplet structure it is usually appropriate to discuss an average liquid crystal domain size (i.e., the distance separating neighboring polymer-rich domains). Characterizations of both average droplet size and droplet size distribution are important in relating film microstructure to macroscopic device properties (Teixeria and Mulder 1996).

The value of the average droplet size will depend on how the droplet size distribution is counted. The simplest is the number distribution $N(D)$, which is simply the number fraction of the distribution at each diameter $D$. Some film properties, however, are better characterized using a volume-weighted distribution $V(D)$. To calculate a volume-weighted distribution, the number fraction at each droplet size is multiplied by the relative volume of sphere at that size and normalized, leading to

$$V(D) = \frac{N(D)D^3}{\sum N(D)D^3} \quad (2.1)$$

For example, a droplet at 5µm is weighted 1000 times more heavily than a droplet at 0.5 µm. Properties that are sensitive to the volume fraction of liquid crystal (like absorbance of light by a dye) are better represented by the volume distribution than the number distribution. Area –weighted and diameter-weighted distributions can be determined in a similar method.

### 2.3.4 Droplet Size Distributions

The distribution of LC droplet size embedded in a polymer matrix is associated with the way by which PDLC films are prepared. In emulsion-based film, the distribution of droplet sizes can be controlled so that over 80% of the droplets are within a range
of 4× in diameter. For example, for a volume-weighted mean of 2 µm most droplets lie within the range of 1 µm to 4 µm. Fig.2.13 shows the volume-weighted size distribution for emulsified liquid crystal mixtures.

![Volume-weighted size distribution](image)

**Figure 2.13 Volume-weighted size distribution. (Drzaic 1995)**

Phase separated PDLC films can show a great variety of droplet size distributions. Phase separation processes are highly sensitive to different parameters, so a small change in experimental conditions during the formation of films can lead to a significant change in film structure and properties. As a result, there is a poor reproducibility of distribution in phase separated films.

### 2.4 Properties of PDLCs

Much of the interest in LC dispersions is associated with the rich variety of thermo-optical effects seen with these materials. LC dispersions lend themselves towards construction of films which can be easily fabricated between transparent electrodes. Such films have been used to build devices with a variety interesting characteristics. Among the thermal properties which have been explored and exploited are transition temperatures and phase diagrams. Besides these thermal characteristics, other important film characteristics include optical properties, morphology, refraction and electrical properties.
2.4.1 Thermal Properties

Starting from the homogenous solution, the polymeric components of PDLCs eventually become sufficiently incompatible with the LC to induce formation of separate fluid and polymer phases. The thermal properties, such as phase diagrams, phase transition temperatures, determine the morphology of the PDLC film, which ultimately controls the electro-optical properties of PDLC devices (Kihara, Kishi et al. 2001; Kihara, Kishi et al. 2001). Differential scanning calorimetry provides valuable transition temperatures and the enthalpies of the different phases which are help for the determination of the LC solubility limit in the PDLC and the calculation details will be discussed in Chapter 5.

![Figure 2.14 Typical thermograms for the pure 5CB and a LC-polymer blend including 77 wt% 5CB as obtained by DSC. (Bouchaour, Benmouna et al. 2000)](image)

Typical DSC thermograms are given in Fig.2.14 for the pure 4-cyano-4’-n-pentyl-biphenyl (5CB) and one polymer-LC blend with 77 %wt 5CB. The phase transition temperatures of both pure liquid crystal and PDLC were shown in the diagram. The DSC trace illustrates that the nematic phase appears at about 23 ºC and followed by
isotropic phase at about 35 °C for both pure 5CB and the mixtures. In comparison with the pure LC, however, the heat flow of the mixtures is slightly lower. The basic phase transition information, transition temperatures and enthalpy changes, is illustrated by DSC and the information is useful for calculation on LC solubility limit in PDLC and drawing phase diagrams, which are helpful to understand the phase separation process in PDLC.

Many studies on the phase behavior of PDLCs have been reported. Kronberg and Patterson developed a simply theory for the nematic isotropic equilibrium in the region of high LC concentrations (Kronberg and Patterson 1976; Kronberg, Bassignana et al. 1978). Ballauff and Orendi (Orendi and Ballauff 1989) used the extended Flory lattice theory to describe the phase behavior of polymer-LC blends, including liquid-liquid phase separation in the isotropic phase. Kelkar and Manohar (Kelkar and Manohar 1986) and Shen and Kyu (Shen and Kyu 1995) extended the Flory-Huggins (FH) lattice theory of regular solution to describe mixtures of nematic liquid crystals with polymeric solutes. The nematic phase was described in terms of the Maier-Saupe (MS) approximation. The combined FH-MS theory predicted a complex phase diagram that consisted of isotropic, liquid-liquid, liquid-nematic and pure nematic regions. The theoretical calculation accorded well with the experimental cloud point phase diagram of poly(benzyl methacrylate) and PMMA of various molecular weights with nematic mixtures E7 and PS with 7CB (Riccardi, Borrajo et al. 1998) and E7 (Lin, Zhang et al. 1999), respectively.
Phase diagram of polymer-LC blend including the boundaries for L-L (liquid-liquid isotropic phases), L-N (isotropic liquid-nematic phases) and L-L-N (two isotropic-nematic phases) equilibria can be predicted.

Phase diagram (Fig.2.15) of PS ($M_n = 152,000$ g·mol$^{-1}$)-7CB blend shows experimental values of L-L phase separation, appearance of a nematic phase and vitrification, and predicted L-L, L-N, and L-L-N equilibria using $\chi$ versus $T$ (the shadow curve for the L-L equilibrium is represented by the dashed line at high LC concentrations).

The study of phase separation in binary systems is important for understanding the formation of final morphology of polymer-liquid crystal blends.

2.4.2 Order Parameter

The director $n$ determines only the direction of the preferred orientation of the molecules and indicates nothing about the degree of orientational order in the liquid crystalline phase. The degree of the orientational order is quantified and characterised by a scalar quantity $S$, which is called an order parameter, also known as Hermans orientation function (Holliday and Ward 1975; Suga and Takahama 1996), and it is calculated using the following equation (Bloisi, Ruocchio et al. 1996; Schmidt-Rohr and Hong 1996)
\[ S = \frac{(3\cos^2 \theta - 1)}{2} \] (2.2)

The square of the cosine term in Eq. 2.2 denotes a thermal average over all of the unit molecules and \( \theta \) is the orientational angle between the structural unit vector of the polymer chain and the director \( n \).

For all the molecules in the sample, where \( \theta \) is the angle the long axis of the molecule makes with a particular direction, \( n \). Averaging this function of \( \theta \) instead of just \( \theta \) alone conveniently gives a value between zero and one for the degree of orientation order. This order parameter is highly dependent on the temperature of the material. See Fig. 2.16 for a typical order versus temperature relationship. The order parameter is temperature dependent, decreasing with the increasing temperature in the mesophase. The values of \( S \) in the range of 0.6 ~ 0.8 are typical for many nematic LCs (Bloisi, Ruocchio et al. 1996; Kiselev, Yaroshchuk et al. 2004; Loiko and Konkolovich 2004). The value of \( S \) is zero, which indicates an isotropic fluid, while an order parameter of 1 means perfect alignment (Das and Rey 2004; Ongo 2004).

![Figure 2.16 Order parameter S vs. temperature for a typical liquid crystal. \( T_{N-I} \) is the temperature of transition between the liquid crystal and liquid.](image)

When the brackets around the cosine term in Eq. 2.2 are equal to 1/3, the value of \( S \) is equal to 0, which indicates total absence of orientation order – isotropic. The value of \( S \) equal to 1 corresponds to the case of the perfect order with all molecules strictly
parallel to director n. This ideal order would be possible near to absolute zero temperature if the material would not freeze.

Possible topologies (molecular arrangements) about point singularities are given in Fig. 2.17 and Fig. 2.18. The strength of the disclination, S, is connected with the number of dark brushes meeting at one point:

\[ S = \text{number of brushes}/4 \]  \hspace{1cm} (2.3)

From the observation of singularities with \( S = \pm \frac{1}{2} \) (Bittner and Kreuzer 1996; Park, Ahn et al. 1997; Das and Rey 2004), the mesophase can be identified unambiguously as a nematic phase since these singularities occur nowhere else. Smectic C phases, which can exhibit the Schlieren texture (Cladis 1974; Cladis 1976; Fayolle, Noel et al. 1979; Coates 2000; Dumon, Achard et al. 2000), only form singularities with four brushes corresponding to \( S = \pm 1 \).

![Figure 2.17 Schematic diagram of molecular trajectories associated with disclinations of strength ±½ or ±1. (Cladis and Kleman 1972; Williams, Pieranski et al. 1972)](image-url)
Figure 2.18 Nematic Schlieren texture. Schematic diagram of molecular trajectories associated with disclinations of strength $\pm 1/2$ or $\pm 1$ (strength of the points: No. 1: $S = +1/2$; No. 2: $S = -1$; No. 3 and No 4: $S = +1$; No. 5: $S = -1/2$). (Hans and Rolf 1980)

In some preparations, the declination lines do not lay perpendicularly, but more or less horizontally, their ends being attached to the glass surfaces and the other parts floating freely in the LC. The term ‘threads’ is usually used to describe these declination lines and the corresponding texture is the threaded texture.

### 2.4.3 Refractive Property

PDLC films typically use nematic liquid crystals that exhibit positive dielectric anisotropy. This type of mesophase is usually comprised of calamitic (pencil shaped) molecules, which have a larger dielectric permittivity along the extended axis than across the breadth. Thus, applications of a suitable alternating electric field, typically of frequency 1-10 kHz, causes a bulk material reorientation as the long axes of the molecules realign parallel to the field. This ordering is manifest at optical frequencies as optical anisotropy in the bulk LC and the mesophase demonstrates an ordinary refractive index, $n_o$, and an extraordinary refractive index, $n_e$, where $n_e > n_o$ and the birefringence, $\Delta n$, defined as $n_e - n_o > 0$. The optical axis coincides with the director, $\hat{n}$, the statistical average direction of molecular orientation. Light passing through the mesophase along the director experiences $n_o$, whilst light incident perpendicular to the director experiences $n_e$. Light incident at some intermediate angle experiences an appropriate refractive index, $n_i$, between $n_e$ and $n_o$, given by
where $\theta$ is angle between the Poynting vector of the incident light and the optical axis of the mesophase (Wu, West et al. 1987).

The average refractive index, $n_d$ (Drzaic and Gonzales 1992), of each randomly oriented liquid crystal droplet is

\[
n_d = \sqrt[3]{\frac{1}{3} n_e^2 + 2 n_o^2}
\]

Light incident normally upon a PDLC film passes through a polymer matrix of refractive index $n_p$, which is usually chosen to be similar to $n_o$, and is mainly forward scattered upon encountering the randomly oriented LC domains of refractive index $n_d$, hence the film appears opaque. Upon application of a sufficient electric field, the droplet directors realign along the field causing the apparent refractive index of the domains to change to $n_o$. The similar refractive indices of the two film media reduce the scattering and the light passes through without significant deviation and the film appears transparent. The LC molecules experience some anchoring attachment to the polymer enclosure at the mesophase-matrix interface and realignment at this boundary is often incomplete, although surface scattering tends to become less significant with increasing wavelength of incidence.

### 2.4.4 Morphology

The droplet morphology is the common morphology of PDLC films, as shown in Fig. 2.19 (top). The LC domains appear as relatively distinct droplets within the polymer matrix. The droplet structures have been found in many types of PDLC films, including emulsion systems, acrylate and epoxy-base PIPS systems, and in TIPS and SIPS phase separation systems. The droplets in this morphology may possess a varying sizes, shapes, and degree of interconnection.

A much different film morphology is the polymer ball morphology, first reported by Yamagishi et al. (Yamagishi, Miller et al. 1989). An example of polymer ball morphology is shown in Fig. 2.19 (bottom). It is seen that the matrix consists of small
polymer balls which merge to form a larger network structure. The liquid crystal exists in the irregularly shaped voids within the network. Polymer ball structures have been observed in both thiol-ene systems (Hoyle, Whitehead et al. 2000; Jr. Whitehead, Gill et al. 2000) and acrylate (Klosowicz 1994; Natarajan, Sutherland et al. 1997; Gyselinck, Mecherene et al. 2001) PIPS systems. Films with the polymer ball morphology tend to exhibit large memory effects.

Figure 2.19 Characteristic morphology of PDLC films; top: droplet morphology; bottom: polymer ball morphology. (Liu and Wang 2002)

Whether a system forms the droplet or polymer ball morphology can be dependent on subtle differences in the composition or the cure kinetics, like thermal treating rate...
and the degree of UV cure. Lovinger et al. (Lovinger, Amundson et al. 1994) have reported a detailed study of an NOA-65 dispersed in E7 and they found that the final PDLC film could exhibit several different morphologies, depending on the composition of the system and the cure temperature. The generalized diagram for this PDLC is reproduced in Fig 2.20. Several different morphological types were observed in this study:

- In low liquid crystal concentration, either an amorphous polymer phase or an amorphous polymer containing isolated nematic spherulites is observed.

- In intermediate concentrations and high temperatures, the PDLC formed a single phase “Spherulitic” texture. This phase appears as a collection of birefringent domains in which the nematic and polymer are mutually soluble. A variety of nematic defect structures (lines and walls) can be found in this spherulitic structure.

- In intermediate concentrations and low temperatures a droplet structure is observed. Most of the liquid crystal was contained in cavities.

- In high LC concentrations, the PDLC either separated into separate macroscopic nematic and polymer domains or formed a single nematic phase.
2.4.5 Droplet Configuration

The configuration of the liquid crystal droplets in a polymer matrix is the focus of much current research. Different configurations of LC have been experimentally observed, including radial, axial, and bipolar (Granqvist 1990; Ding and Yang 1994; Sousa, Qi et al. 2003). Regarding to PDLC, it has been found that the configuration of LC embedded in a polymer matrix depends on the droplet size, droplet shape, droplet surface anchoring, and applied fields (Ding and Yang 1994; Sousa, Qi et al. 2003).

The radial configuration occurs when the liquid crystal molecules are anchored with their long axes perpendicular to the droplet wall, as shown in Fig. 2.21(a). The axial configuration of the liquid crystal droplets occurs when the molecules are oriented perpendicular to the droplet wall, but only when there is weak surface anchoring. This configuration creates a line defect that runs around the equator of the spherical droplet, as seen in the Fig. 2.21 (b). When an electric field is applied to a radial droplet, the molecules adopt the axial configuration. The radial configuration is returned when the field is removed. The bipolar configuration is obtained by...
tangential anchoring the liquid crystal molecules. This created two point defects at the poles of the droplet and is shown in Fig. 2.21 (c).

![Droplet Configurations](image)

**Figure 2.21 Three common droplet configurations. (Ding and Yang 1994)**

In a typical PDLC material, there are many droplets with different configurations and orientations. When an electric field is applied, however, the molecules within the droplets align along the field and have corresponding optical properties, shown in Fig. 2.22.

![Electric Field Effect](image)

**Figure 2.22 The droplets align along the out-side electric field. (Kubono, Sato et al. 2003)**

- At zero fields, the symmetry axis of each droplet varies randomly from droplet to droplet. Light passing through the film will pass through a number of droplets and polymer walls. The refractive index of the medium varies rapidly from droplet to droplet and light is strongly scattered.

- At intermediate fields, some droplets will be totally oriented by the field, some partially oriented by the field, and others unchanged. For light entering the film the effective birefringence of these droplets is reduced. This reduced
birefringence results in a smaller variation in the refractive index for light passing through the film. Scattering is diminished.

- At high fields, each droplet’s symmetry axis is aligned with the external field. For light normal to the film, each droplet possesses a uniform refractive index. If this refractive index is close to the refractive index of the surrounding polymer, the film can appear transparent. If the nematic and polymer refractive index differ substantially, the film will weakly scatter light and appear hazy.

### 2.5 Applications of PDLCs

#### 2.5.1 Architectural Windows

An obvious application of PDLC is the construction of large-area devices which control the transmission of light. Since PDLC films can be switched between highly-scattering and nearly-transparent states, they can be used as electrically-controlled privacy windows in architectural applications. Figure 2.23 shows photographs of a large-area PDLC window.

![Figure 2.23 Examples of PDLC architectural windows in rest (left) and activated (right) states. (Drzaic and Muller 1989)](image)

The important issues in window applications of PDLC films are the nature of the zero-field scattering, the haziness of the high-field transparent state, and the extent that the transmission of solar radiation can be modulated.
2.5.2 Projection Displays

One of the more exciting applications of PDLC films is their use in projection displays. Presently, it is difficult to create large-area high-resolution displays using any direct-view method. Size, expense, and power requirements preclude present-day display technologies from easily creating large-area screens. Projection displays are an obvious method to create large-area displays using standard-size display components. Scattering-based PDLC films, when coupled with an active matrix substrate, possess many attractive features in creating high-performance projection displays.

2.5.3 Miscellaneous Applications

I. Encapsulated Cholesteric Liquid Crystals for Sensor Applications

Applications of encapsulated cholesteric liquid crystals attracted a great deal of attention in the 1970’s. Most schemes used a cholesteric liquid crystal in which the pitch (and thus the selective reflection wavelength) depended strongly on temperature. Thus, films of cholesteric liquid crystal could be used as temperature sensors. The work in this area is voluminous and mostly in the patent literature (Hans and Rolf 1980).

More recently, cholesteric liquid crystals have been used as shear sensors for both wind-tunnel and air-borne analysis of air flow (Bonnett, Jones et al. 1989). In these experiments airflow changes the orientation of the helical axes and provides a color change. Parmar has investigated scattering PDLC films for similar applications (Parmar and Holmes 1993; Parmar and Singh 1993; Parmar and Singh 1993).

II. Holographic Reflection Devices

Several groups have constructed holographic gratings from photopolymerizing PDLC devices with interfering laser beams (Lackner, Margerum et al. 1989; Sutherland 1991; West and Ondris-Crawford 1991; Sutherland, Natarajan et al. 1993). The intensity of light diffracted from these gratings can be controlled with an applied field. These devices have the potential for creation of active optical elements and direct-view reflective displays.
Chapter 2 Literature Review

III. Modulation of Long Wavelength Radiation

PDLC films have been used to modulate light outside the visible range. Liquid crystal materials possess birefringence at long wavelengths, so that the variable scattering properties of the films will extend outside the visible. Reports include work on infrared (West and Ondris-Crawford 1991) and millimeter (radar) wave modulation (Lim, Margerum et al. 1993).

IV. Thermal Switch

While the PDLC films are normally made clear by application of an electric field, they become transparent when the system is heated above the liquid crystal clearing temperature. As such, they can be used as a temperature-dependent switch. Alive et al. have discussed this effect in porous glasses (Aliev, Baushev et al. 1980; Aliev, Baushev et al. 1983). Jain and Thakur have noted that the exact transition temperature can be varied by several degrees by changing the drive frequency applied to the cell (Jain and Thakur 1992). Fuh has discussed the temperature dependence of several properties with respect to temperature sensing application (Fuh, Tsai et al. 1996; Fuh and Lin 2004).

V. Stacked Devices

Several examples have appeared where a PDLC film is a part of an optical stack. Kato et al. (Kato, Tanaka et al. 1993; Kato, Tanaka et al. 1993) have described stacks of either scattering based or cholesteric (colored) PDLC films. Devices where images from different “pages” are either selected or overlaid can be created with this approach. A drawback of this approach is that multiple layers of Ito (or other interfaces) will cause high levels of reflectivity within the stack, which will degrade the image contrast.

Umezu et al. have discussed a PDLC film stacked over a twisted nematic display to produce a backlit direct view display (Umezu, Takatsu et al. 1993).
Chapter 3 Materials and Experimental Techniques

3.1 Introduction

In this chapter, the various materials and the preparation of the PDLCs are described. The instruments and experimental techniques utilized to characterize the mesogens and the PDLCs are discussed. The experimental parameters for each technique are explained. The specific thermal treatments of LCs and PDLCs, however, are described in their respective chapters.

3.2 Materials

3.2.1 Mesogens

![Chemical structures of mesogens](image)

4-(decyloxy)benzoic acid

4-(octyloxy)benzoic acid

4,4′-azoxyanisole

Trans-4-methoxycinnamic acid

Figure 3.1 The structures of the mesogens.
Four low molar mass mesogens are used throughout the work. They are 4-(octyloxy)benzoic acid, 4-(decyloxy)benzoic acid, 4,4′-azoxyanisole and trans-4-methoxycinnamic acid. They were purchased from Aldrich Australia (≥ 98 % purity) and used as received. Each mesogen is a benzene derivate, as shown in Fig. 3.1. Although the mesogenic group is identical, 4-(decyloxy)benzoic acid has a longer flexible constituent in a terminal substitute than 4-(octyloxy)benzoic acid; differing by the number of methylene groups. It has been known that some of 4-alkoxybenzoic acids can exhibit smectic and nematic phases in corresponding temperature ranges and two different crystalline structures, as well below melting temperature. 4,4′-azoxyanisole and trans-4-methoxycinnamic acids can exhibit crystalline, nematic and isotropic phases with variation of temperature.

### 3.2.2 Polymers and Solvents

Poly(2-hydroxyethyl methacrylate) (pHEMA) (M\textsubscript{w} = 20,000 g·mol\textsuperscript{-1}), poly(methyl methacrylate) (PMMA) (M\textsubscript{w} = 996,000 g·mol\textsuperscript{-1}) and poly(vinyl chloride) (PVC) (M\textsubscript{w} = 43,000 g·mol\textsuperscript{-1}) are selectively used in the preparation of PDLCs materials. Solvents used were chloroform (CHCl\textsubscript{3}), N,N-dimethylformamide (DMF) and tetrahydrofuran (THF). All these chemicals were purchased from Sigma-Aldrich Australia and used as received without further purity.

![Figure 3. 2 The structures of the polymers.](image-url)
3.3 Methodologies

3.3.1 Differential Scanning Calorimetry

3.3.1.1 General Introduction

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference (Schick and Hohne 1991), as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

There are two types of DSC systems in common use, power-compensation DSC (Menczel and Leslie 1990; Schick and Hohne 1991) (in Fig. 3.3) and heat-flux DSC (Gmelin 1997)(in Fig. 3.4). In power-compensation DSC, the temperatures of the material and reference are controlled independently using separate but identical furnaces. The temperatures of the material and reference are made identical by varying the power input to the two furnaces. The thermal energy required to vary the power input is a measure of enthalpy changes in the material relative to the reference. In heat-flux DSC, the material and reference are connected by a low-resistance heat-flux path. The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in a material cause a difference in its temperature relative to the reference. The temperature difference is recorded and related to enthalpy change in the material using calibration experiments.

![Temperature sensors](image)

Figure 3.3 Schematic diagram of power compensation DSC. (Gmelin 1997)
Figure 3.4 Schematic diagram of heat flux DSC. (Gmelin 1997)

DSC can be used to measure a number of characteristic properties of a material such as fusion, crystallization, and glass transition temperatures ($T_g$). For the present work, the analysis of DSC thermograms allows to obtain the phases and phase transition in PDLCs (Huang and Zhu 1990; Russell, Paterson et al. 1995; Borrajo, Riccardi et al. 1998; Dumon, Achar et al. 2000; Kihara, Kishi et al. 2001). A matter transition between solid and liquid exhibits through a third phase, mesophase, which displays properties of both phases. Using DSC, it is possible to observe the small energy changes that occur as matter transitions from a solid to a liquid crystal and from a liquid crystal to an isotropic liquid.

Heat transfer plays an important role in DSC, and imposes certain constraints. The larger the material mass, the greater will be the heat flow signal for a given heating rate. On the other hand, the larger is the material, the more non-uniform will be the material temperature, and the greater will be the temperature lag between average material temperature and programmed temperature. Thus, about 2-3 mg material was weighted for DSC measurements in this project.

3.3.1.2 Experimental Conditions

DSC measurements were performed on an apparatus of Perkin-Elmer Pyris 1 (Pyris Software version 7.0) instrument, as presented in Fig. 3.5. The apparatus cell was purged with nitrogen at a rate of 20 mL·min$^{-1}$. About 2-3 mg (measured by Mettler Toledo MX 5 Auto balance) of material was placed in a 10 µL aluminum pan and hermetically sealed. Indium was used for heat flow calibrations of the DSC and the furnace was calibrated according to the manufactures instructions. The indicated temperatures of the DSC were checked in the standard DSC mode with the onset of
melting of indium (156.59 °C) and zinc (419.48 °C) at scanning rates of 10 °C·min⁻¹, determined by extrapolating the linear portion of the melting peak to the baseline. The heat flow was checked with the heat of fusion of indium (28.45 J·g⁻¹) and the heat of fusion of zinc (108.37 J·g⁻¹).

Figure 3.5 Perkin Elmer Pyris 1 DSC instrument.

Figure 3.6 DSC program tab in the method editor.

The materials were first heated at a rate of 40 °C·min⁻¹ in order to remove any thermal history, and then cooled and subsequently heated at different rates depended by the different materials to allow phase separation and the formation of ordered liquid...
crystalline regions from room temperature, to 10 °C above the transition temperature leading to the isotropic phase (The temperature programs of different materials are described in Chapter 4 and Chapter 5, respectively). The materials were held for 5 min in both the isotropic and crystalline states. The DSC program for 4-(decyloxy)benzoic acid is presented in Fig. 3.6. Transition temperatures were recorded systematically during the cooling program and the second heating program. Baselines were obtained with a matched empty pan under the same experimental conditions and were used to calculate specific heat capacity. Phase transition temperatures, crystallization, melting, mesophase transition and isotropization temperature, were obtained at the peak temperatures. The heat of fusion was proportional to the area under the peak.

3.3.2 Temperature Modulated Differential Scanning Calorimetry

3.3.2.1 General Introduction

Temperature modulated differential scanning calorimetry (TMDSC) was introduced in 1993 by Reading under the name modulated DSC (Reading 1993; Wunderlich, Jin et al. 1994; Wunderlich, Boller et al. 1996; Hensel and Schick 1997). It differs from the conventional DSC in a way that a low-frequency sinusoidal or nonsinusoidal (eg. Sawtooth) perturbation is overlaid on the baseline temperature profile (Gmelin 1997). The linear heating program of conventional DSC is modulated by superimposing a periodic wave form of small amplitude on the linear temperature program. Essentially, TMDSC provides periodic ‘heating’ and ‘cooling’ within each cycle but the overall effect is the same as in conventional DSC – a linear change in average temperature with time. The resultant heat flow signal is a composite of the response to a thermal event occurring in the material and the response to the underlying heating program.

The signals thus derived from a TMDSC experiment can be schematically shown in Fig. 3.7. As can be seen, (1) the TMDSC signal is separated into two components: in-phase and out-of-phase components (Toda, Oda et al. 1997; Reading and Luyt 1998); (2) the storage or reversing heat capacity ($C_p'$) is the in-phase component that results from heat effects which reversible at the time and the temperature at which they are
detected (Hutchinson and Montserrat 1996); (3) the out-of-phase component, loss or kinetic heat capacity ($C_p^\prime$) comes from the heat flow that has resulted in irreversible phenomena at the time and temperature at which they are detected (Reading and Luyt 1998); (4) the total heat capacity ($C_p$) is obtained by dividing the average heat capacity by the average heating rate and similar to the heat capacity obtained from a conventional DSC; (5) non-reversing signal ($C_{p,non}$) is the difference between $C_p$ and $C_p^\prime$ and may contain information on irreversible processes. Hence, in the simplest terms, TMDSC is a description of the heat flow into the material resulting from the sinusoidal modulation of the temperature program. Two properties of the sample can be investigated by TMDSC: the heat capacity that is directly related to the ‘reversing component’ and kinetically hindered thermal event that is related to the ‘nonreversing component’.

Figure 3. 7 The component output signals from TMDSC. (Hill 2005)
A sawtooth wave is the most commonly applied in TMDSC. Fig. 3.8 shows typically a modulated temperature imposed by a sawtooth wave as a function of time. The use of a complex saw-tooth modulation or other complex temperature modulation allows the response to multiple frequencies to be measured at one time.
Figure 3.8 Typical modulated temperature profile vs. time in TMDSC; the dashed line shows the underlying heating rate. (Simon 2001)

The instrument cell arrangement does not require any change provided that the sample and reference calorimeters are symmetrically placed. They must be capable of maintaining an accurate control of the energy for heating and cooling of the sample during an oscillation. Although Reading and coworkers originally conceived the idea of applying a modulation to DSC in 1992 (Sauerbrunn, Crowe et al. 1992), modulations/oscillations have already been applied to many other instruments such as the force in dynamic mechanical analysis (DMA). The proposition of superposition of a sine wave imposed upon a linear heating scan, led to the first commercial instrumentation of a modulated DSC (MDSC) developed with TA Instruments. Since commercialization, other equipment manufacturers have developed variants upon the same theme, but different methods of modulation and data analysis have been introduced. Other instruments currently available are (Jiang, Imrie et al. 2002):

- Dynamic DSC (DDSC) from Perkin-Elmer
- Alternating DSC (ADSC) from Mettler Toledo
- Oscillating DSC (ODSC) from Seiko Instruments
Figure 3.9 Schematic modulations of temperature during heating. a) Linear time-temperature program as per conventional DSC, b) modulated DSC with a sinusoidal oscillation, c) dynamic DSC in iso/scan mode and d) dynamic DSC in heat/cool mode. Ta refers to the temperature amplitude of the modulation; $\Delta T = \text{change in temperature increment on heating}$; $p=\text{period of the modulation cycle}$.

All of these techniques have a controlled modulation of heating rate. Fig. 3.9 shows schematically modulations of the temperature for MDSC and DDSC. As mentioned previously, in MDSC (as well as ADSC and ODSC) the temperature program comprises of a sinusoidal oscillation superimposed upon a linear heating ramp (Fig. 3.9.b). The Perkin-Elmer Pyris 1 DSC enables the choice of two modes, namely the iso/scan and heat/cool mode, as shown in Fig. 3.9.c and d. The main difference for these profiles is in regards to the iso/scan mode. The temperature in an overall heating scan does not allow the sample to cool. It is maintained at a maximum temperature of particular step for the duration of isothermal segment. The heat/cool mode allows the sample to cool below the average underlying heating rate. Unlike a sinusoidal oscillation, the temperature varies in a saw-tooth manner (square-wave form). The duration of total step is divided into two parts, where for example the heating time is equal to the isothermal time for the iso/scan mode. This is the same for the heat/cool mode. When the sample is subjected to this type of step program (for heating), the
temperature increases by $\Delta T_1$ and then decreases by $\Delta T_2$ upon cooling, as shown in Fig. 3.10.

Figure 3.10 Dynamic DSC in heat/cool mode where changes in temperature are indicated as $\Delta T_1$ and $\Delta T_2$, and $T_1$, $T_2$ and $T_3$ are the initial, intermediate and final step temperatures, respectively.

The average heating rate, $\beta_0$ and temperature amplitude $A_T$ is given by Eq. 3.1 and 3.2, respectively. The period of modulation is determined by Eq. 3.3. The scan rate modulation is defined by the variables: $\beta_0$, $A_T$ and $p$.

\[
\beta_0 = \frac{\beta_1(T_3 - T_1)}{2(T_2 - T_1)} \quad (3.1)
\]

\[
A_T = \frac{T_2}{2} - \frac{(T_1 + T_3)}{4} \quad (3.2)
\]

\[
p = \frac{\beta_1(T_2 - T_1)}{2} \quad (3.3)
\]

For the iso/scan mode, the temperature increases at the heating rate ($\beta_1$) specified ($\Delta T_1$) and then it remains constant for the duration of the isothermal segment ($\Delta T_2 = 0$). The variables in this case are not independent. The average heating rate (average of one modulation period) and temperature amplitude is given in Eq. 3.4 and 3.5, respectively.

\[
\beta_0 = \frac{\beta_1}{2} \quad (3.4)
\]
The amplitude of the heating rate ($\beta_0$) is related to the temperature modulation for both heat/cool and iso/scan modes. It is given by Eq. 3.6,

$$\beta_0 = \frac{4A_T}{p}$$  \hspace{1cm} (3.6)

Not only do these techniques provide the same information as the heat capacity of various transitions in conventional DSC, they also can provide more details about these thermal events.

### 3.3.2.2 Data Analysis

In TMDSC, a temperature modulation of amplitude $A_T$ and frequency $\omega$ is superimposed on the underlying heating rate $\beta_0$. If the initial temperature is $T_0$, then for a sinusoidal modulation the temperature at any time $t$ is given by

$$T = T_0 + \beta_0 t + A_T \sin \omega t$$  \hspace{1cm} (3.7)

$$\omega = 2\pi v = \frac{2\pi}{p}$$  \hspace{1cm} (3.8)

$$\beta = \beta_0 + A_T \omega \cos(\omega t)$$  \hspace{1cm} (3.9)

where $\beta$ is the instantaneous heating rate and $p$ is the period. It is evident then that there is a periodic modulation of the heating rate between maximum and minimum values given by, respectively (from Eq. 3.9)

$$\beta_{\text{max}} = \beta_0 + A_T \omega$$  \hspace{1cm} (3.10)

$$\beta_{\text{min}} = \beta_0 - A_T \omega$$  \hspace{1cm} (3.11)

### I. The approach of separating the reversing and non-reversing components

The most common TMDSC data analysis involves separating the total heat flow or apparent heat capacity into reversing and non-reversing components. This method, which was first suggested by Reading, has been used by Wunderlich et al. and some instrument manufacturers as well (Wunderlich, Jin et al. 1994; Kamasa, Merzlyakov
et al. 2002). The reversing component of heat flow is obtained from the amplitude of the first harmonic of the heat flow, $A_p$, using a Fourier transform of the data (or an approximation thereof). Dividing by the amplitude of the applied heating rate, $A_T$, gives the reversing component of the apparent heat capacity

$$C_{p, rev} = \frac{A_p}{mA_T}$$

(3.12)

where $m$ is the mass of the sample. $A_p$ can be measured directly in a power-compensated DSC and calculated from a temperature difference between sample and reference in heat flux.

Corrections to the heat capacity when the sample is unable to follow the program temperature, for example, due to the effects of thermal resistances and/or finite diffusivity, will be addressed in a later section. The non-reversing heat flow is defined as the difference between the average heat flow ($Hf$) and the reversing heat flow, whereas the non-reversing heat capacity is the difference between the normalized averaged heat flow divided by the underlying heating rate ($\beta$) and the reversing heat capacity

$$C_{p, non} = \frac{Hf}{m\beta} - C_{p, rev}$$

(3.13)

In the absence of thermal events, the reversing heat capacity is simply the frequency-independent heat capacity, $C_p$, and the non-reversing heat capacity is zero. In the presence of thermal events, the reversing heat flow is initially considered to only reflect reversible sensible heat effects (i.e. those due to changes in the heat capacity), and likewise, the non-reversing heat flow is considered to reflect primarily irreversible kinetic effects. The assumption that the sensible heat and kinetic effects can be equated to the reversing and non-reversing heat capacities (or heat flows) is valid only if the kinetics associated with the process being measured is linear and the kinetic response does not have contributions to the first harmonic as well.

II. The approach of resolving the complex specific heat

Another approach to analyzing TMDSC data, suggested by Reading and coworkers and advocated by Schawe (Schawe 1995), involves a dynamic heat capacity analysis
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comprised of the complex, real (storage), and imaginary (loss) heat capacities ($C_p^*$, $C_p'$, and $C_p''$)

\[
C_p^*(\omega) = C_p'(\omega) - iC_p'' = \frac{A_p}{A_T} \tag{3.14}
\]

\[
C_p' = \frac{A_p}{A_T} \cos \delta \tag{3.15}
\]

\[
C_p'' = \frac{A_p}{A_T} \sin \delta \tag{3.16}
\]

where $\delta$ is the phase angle between the sinusoidal heat flow and the sinusoidal heating rate. This would appear to a more logical approach than separating the total heat flow into reversing and non-reversing components. An apparent heat capacity can be obtained from an underlying heat flow and a frequency dependent complex heat capacity, with components in-phase and out-of-phase with respect to the heating rate and determined by a phase angle, can be obtained from a modulated heat flow. The in-phase component may be considered as the thermodynamic heat capacity, ($C_p'$ at zero frequency) since it is directly related to the heat flow that is in phase with the heating rate.

The problem with this approach is that, at present, there is no universally acknowledged interpretation of the meaning of the out-of-phase component $C_p''$. If the phase angle is small, the in-phase component is very nearly equal to the complex component and hence very nearly equal to the reversing heat capacity. On the other hand out-of-phase $C_p''$ should not be approximated to a non-reversing heat capacity. This problem is more of fundamental interest than of practical interest since, as is shown elsewhere, the measurement of the phase angle experimentally is severely complicated by another problem, that of heat transfer, which introduces an additional “instrumental” phase angle. Thus, the accurate experimental evaluation of the phase angle is an issue that is still unresolved for most transitions, indeed for any other than the glass transition, and hence it is not possible to investigate experimentally the out-of-phase heat capacity for different materials and different transitions.
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3.3.2.3 Experimental Conditions

The experimental conditions for operating TMDSC depend on the transitions being measured and have an impact on the reproducibility and meaningfulness of the results obtained. The most important concepts for evaluating the appropriateness of experimental conditions are those of linearity and stationarity. When these conditions are met, the total heat flow in the TMDSC experiment is equivalent to the heat flow from a conventional DSC for the same underlying heating rate.

A linear TMDSC response is one in which doubling the amplitude of the temperature perturbation would double the amplitude of the heat flow. In such a case, the heat capacity given by either Eq.3.12 or 3.15 will depend only on frequency but not on the amplitude of the perturbation. It has been suggested that the temperature perturbation should be as small as possible to insure linearity (Ozawa and Kanari 1995; Wunderlich, Boller et al. 1996; Hohne, Merzlyakov et al. 2002). However, the increased precision of the TMDSC relative to DSC is due in part to the high instantaneous heating rates with the maximum in the heating rate being given by

\[
\left(\frac{dT}{dt}\right)_{\text{max}} = \beta + \omega A_T
\]  

(3.17)

Hence, a more quantitative criterion is warranted.

A criterion for linearity based on the harmonic distortion of the instrument, \( \eta \)

\[
\frac{\Delta C_p(\omega)}{C_p(\omega)} = \frac{1}{C_p(\omega)} \frac{dC_p(\omega)}{dT} A_T \leq \eta
\]  

(3.18)

or in terms of the amplitude of the rate of temperature change

\[
\frac{\Delta C_p(\omega)}{C_p(\omega)} = \frac{1}{C_p(\omega)} \frac{dC_p(\omega)}{dT} A_T \leq \eta
\]  

(3.19)

Where \( \eta \) is approximately 1 % for heating rate amplitudes \( A_T = \omega A_T \) from 2 to 60 °C·min\(^{-1}\). According to these criteria, the maximum allowable amplitude of the temperature perturbation was reported to be in the millikelvin range for the sharp liquid crystal transitions and approximately 0.1 °C for the melting transition for polymers.
Stationarity, on the other hand, refers to the sample not changing during a measurement cycle. It is not possible to obtain physically meaningful results from TMDSC (without detailed knowledge of the kinetics of the transformations taking place and mathematical modeling of the response) if stationarity is not maintained. It has been suggested that the underlying temperature rate should be low such that the temperature does not change significantly (relative to the temperature perturbation) during a single period (Simon 2001; Hohne, Merzlyakov et al. 2002). However, since it is not known how low is low enough, a quantitative criteria is preferable.

In addition to insure that linearity and stationarity are met by determining the maximum allowable values of the experimental parameters, $A_T$, $\omega$ and $\beta$, a steady state should be reached before the collection of data. For quasi-isothermal measurements (in which $\beta = 0$), the steady state can be confirmed by insuring that the Lissajous loops are reproducible (Chen, Dadmun et al. 1998; Hohne, Merzlyakov et al. 2002). Lissajous loops can be made by plotting modulating heat flow versus the modulating heating rate. For quasi-isothermal experiments, the loops should be invariant after the steady state is reached. For non-isothermal experiments, the loops should be elliptical and symmetric about the axes. In addition, there are instrumental limitations for the minimum values of the experimental parameter of $A_T$ related to the sensitivity of the instrument. For example, heat flow amplitudes of $<100$ $\mu$W are generally not recommended because this heat flow minimum corresponds to a minimum temperature amplitude of approximately 0.1 °C when the period is 60 s for the most of polymers.
Figure 3.11 TMDSC program window in method editor.

Figure 3.12 The quasi-isothermal method window.

(1) Standard TMDSC runs were performed with underlying heating rates $\beta_0 = 0.25 \, ^\circ\text{C} \cdot \text{min}^{-1}$, modulation period $p = 120 \, \text{s}$ and modulation amplitude $A_T = 0.375 \, ^\circ\text{C}$. The maximum and minimum heating rates are $1.428 \, ^\circ\text{C} \cdot \text{min}^{-1}$ and $-0.928 \, ^\circ\text{C} \cdot \text{min}^{-1}$, which
were calculated from the Eq. 3.10 and 3.11, respectively. Fig. 3.11 shows the window of the TMDSC method for pHEMA dispersed 4-(octyloxy)benzoic acid.

(2) Quasi-isothermal TMDSC $\beta_0 = 0$ was carried out with a modulation amplitude $A_T = 0.1$ °C, coupled with a modulation period $p = 240$ s, and step-wise temperature-increments of 0.2 °C. The quasi-isothermal scans lasted 20 min each. The last 10 min were used for data collection. Fig. 3.12 displays the quasi-isothermal program for pHEMA dispersed 4-(octyloxy)benzoic acid at 135 °C.

These conditions were chosen to provide at least 6-7 temperature oscillations over the transition temperature range.

### 3.3.3 Morphology Property

#### 3.3.3.1 Polarized Optical Microscope

Polarized optical microscope is a most familiar tool for the study of the morphology of materials (Fayolle, Noel et al. 1979; Lovinger, Amundson et al. 1994; Natarajan, Sutherland et al. 1997; Magagnini, Paci et al. 1999). The external view of the microscope is shown in Fig. 3.13. Plane polarized light is used and an analyzer is placed between the specimen stage and the eyepiece, and it is rotated to the crossed position (zero light transmission) before inserting the specimen. This equipment is useful for a quick observation. After equipping with a camera, it is convenient to record observations in high resolution.
Figure 3.13 Schematic diagram of a microscope.

Unlike isotropic materials which have only one refractive index and no restriction on the vibration direction of light passing through them, anisotropic materials, which include liquid crystals and PDLCs studied in the present work, have optical properties that vary with the orientation of incident light. Polarized light microscopy is well known for its applications in semicrystalline polymers, liquid crystals, and polymer dispersed liquid crystals (Park, Lee et al. 1998; Loiko and Konkolovich 2004). For the systems studied, polarized light microscopy can provide rich information which is simply not available with other techniques. In particular, polarized light microscopy not only can provide information on absorption color and boundaries between differing refractive indices but also can distinguish between isotropic and anisotropic materials. Such an optical property of anisotropy is invaluable for revealing detailed information about structures, phases, and phase transitions of the systems studied.

3.3.3.2 Experimental Conditions

The thermo-optical studies were performed on a Nikon Labophot 2 optical microscope equipped with a Mettler FP-82 hot stage and Mettler FP90 temperature programmer. The temperature can be accurately controlled to within ±0.1 °C in the hot stage. As shown in Fig. 3.14, the system consisted of a Nikon digital camera,
Coolpix 5000 camera, an optical microscope and a hot stage, connected with a computer system, which included image capture, image processing and quantitative analysis software packages. The magnification of the microscope could be varied between 50 and 400×. The central processor in the hot stage enabled both isothermal and non-isothermal experiments to be performed. The hot stage, a very important part of this research, allowed visual study of a sample under heating, cooling and isothermal conditions. The camera was used to capture higher resolution images. The devices were used to observe the thermal transitions and to analyze the textures of the mesophases.

Figure 3.14 Hot stage microscopy equipments.
Material was heated from room temperature until it was melted at the rate of 20 °C·min⁻¹ and then quenched to room temperature at the same rate. After that, the LC film was heated from room temperature to isotropic temperature then cooled to room temperature at the rate of 5 °C·min⁻¹. The LC was held at different phase temperature for 10 min to be captured the structure changes by digital camera under polarized and transmitted light using a magnification of 100×.
3.3.4 Wide Angle X-ray Diffraction

3.3.4.1 General Introduction to Wide Angle X-ray Diffraction

Wide angle X-ray diffraction (WAXD) is an analytical technique used to determine the identity of crystalline phases in a multiphase powdered material and the atomic and molecular structures of single crystals.

WAXD employs a monochromatic beam of X-rays. The x-ray beam strikes the crystal surface of the material at an angle, \( \theta \). Part of the X-ray beam is scattered by the layer of atoms at the material surface. The unscattered X-ray beam penetrates to the second layer of atoms where further scattering occurs. The remainder of the X-ray beam passes through to the next layer. Diffraction occurs when the wavelength of radiation is comparable with the characteristic spacing between layers of the atoms and the scattering centers are distributed in a highly regular configuration. If the above requirements are satisfied, then the cumulative effect of the scattering results in diffraction of the beam and produces a diffraction pattern (diffractogram). The diffractogram provides a unique “fringerprint” of a material. Analysis of the angle positions, peak intensities, and shapes in WAXD diffractograms is used to give information on crystal structure and physical state.

Wide angle X-ray diffraction has played a decisive role in determining the structures, phases, and phase transitions in the phases and phase transitions of thermotropic LCs (Bernal and Fankuchen 1941; Dumon, Achard et al. 2000). The novel structure of the smectic A (SmA) phase was found and nematic-to-SmA transition was elucidated. The properties of SmA-to-smecticC (SmC) transition was characterized, where the molecules tilt with respect to the layer normal. In other experiments, the phase transition from SmA to chiral SmC (SmC*) was established. X-ray diffraction is also an important technique to explore some specific or more complex phenomena in LCs, including re-entrant phases, modulated phases, twist-grain-boundary phases, antiferroelectric phases, and phase transition under confined conditions. The alignment of LC molecules in PDLC has been investigated using microbeam of WAXD. It is worth noting that X-ray diffraction is particularly powerful to explore the translational order of mesophase.
3.3.4.2 Bragg Equation

The Bragg law as shown in Eq. 3.20 relates to the spacing between crystal planes, \( d_{(hkl)} \), in a material in relation to the particular Bragg angle, \( \theta \), at which refractions from these planes are observed

\[
n \lambda = 2d_{(hkl)} \sin \theta \quad (3.20)
\]

Where \( n \) is the order of reflection and is any integer such that \( \sin \theta \leq 1 \), \( \lambda \) is the wavelength of incident radiation in nanometer, \( d_{(hkl)} \) is the distance between two adjacent parallel planes (interplanar, interlayer or basal or d spacing), \( \theta \) is the incident angle of the X-ray beam to the planes of atoms. Fig 3.15 illustrates the case \( n = 1 \), which referred to the reflection of first order from the given phases.

3.3.4.3 Identification of the Phase Structures

The interlayer spaces of LCs were determined using a wide angle X-ray diffraction on a Brucker D8 Advance diffractometer using Cu-K\( \alpha \) radiation (\( \lambda = 0.154 \) nm) with graphite nomochromator to determine the structural information of materials. A hot stage was coupled with the diffractometer to study the structural information at different temperatures. The temperature was controlled to better than ± 0.1 °C. In order to obtain the characteristic profile of different phases, the materials were first heated above melting temperatures and then cooled to the measurement temperatures. Diffractograms were typically acquired in 20 ranges from 0 to 50° using a scanning rate of 5° min\(^{-1} \) at an acceleration voltage of 40 kV and current of 35 mA. Powdered and film materials were prepared on glass slides.
3.3.5 Solubility Parameters

3.3.5.1 Introduction

As mentioned above, the phase behaviour of LCs droplets or domains in polymers depends strongly on the thermodynamics and kinetics of phase separation via the diffusion and coalescence of LCs. For the present work, an understanding of thermodynamic of phases, phase separation and phase equilibrium would be essential to control the morphology of LCs droplets dispersion in polymers.

As early as 1916 Hildebrand laid the foundation for solubility theory in his classic work on the solubility of nonelectrolytes (Van Krevelen 1997). In 1931, Scatchard introduced a concept of “cohesive energy density” into Hildebrand’s theory to identify the solubility with a cohesive energy per unit volume (Van Krevelen 1997). In 1936, Hildebrand (Van Krevelen 1997) finalized his solubility theory with a comprehensive treatment by proposing the square root of the cohesive energy density as the solvency behavior of a specific solvent. The solubility parameter and its symbol $\delta$ were first introduced by Hildebrand and Scott (Hildebrand and Lamoreaux 1974).

The solubility of a given polymer in various solvents is largely determined by its chemical structure. As a general rule, structural similarity favors solubility. In terms of the above-mentioned quantities this means that the solubility of a given polymer in a given solvent is favored if the solubility parameters of polymer and solvent are equal. The solubility parameter of the polymer is defined as square root of the cohesive energy density in the amorphous state at room temperature.

\[ E_v = \Delta U = \Delta H_{vap} - p\Delta V = \Delta H_{vap} - RT \]  
(dimension: J mol\(^{-1}\))  \hspace{1cm} (3.21)

\[ \delta_i = (ced)^{1/2} = \left( \frac{\Delta E_v}{V} \right)^{1/2} \]  
(dimension: MPa\(^{1/2}\))  \hspace{1cm} (3.22)

Where, $E_v$ is the cohesive energy and $\Delta U$ is the internal energy. ced is defined as cohesive energy density.

In 1953, Small (Van Krevelen 1997; Hansen 2004) demonstrated that the combination $(E_{coh}V(298))^{1/2} = F$, the molar attraction constant, is a useful additive quantity for low-molecular as well as for high-molecular weight substances. These values are
frequently applied. Hoy in 1970 (Van Krevelen 1997) proposed group contributions to F, slightly different from those of Small.

### 3.3.5.2 Method of Hansen

**I. Hansen Method**

It has been well known that the cohesive bonds in a liquid, including “nonpolar” bonds, permanent dipole-permanent dipole bonds, and hydrogen bonds, are all broken in an evaporation process (Hansen 2004). These must all be accounted for within the energy of vaporization itself. This led to the division of the cohesive energy, i.e. the Hildebrand solubility parameter, into the three parameters, $\delta_d$, $\delta_p$, and $\delta_h$ to quantitatively describe atomic, nonpolar interactions ($d$), molecular, dipolar interactions ($p$), and molecular, hydrogen bonding interactions ($h$), respectively.

\[
(\delta_t)^2 = (\delta_d)^2 + (\delta_p)^2 + (\delta_h)^2
\]  

(3.23)

Where $\delta_d$, $\delta_p$ and $\delta_h$ are called Hansen solubility parameters. $\delta_d$ is found from corresponding states principles at 25 ºC, $\delta_p$ is found with the aid of dipole moments and other parameters, and $\delta_h$ is usually found by what is left over in Eq. 3.23 or by group contributions. Table 3.1 shows his parameters for some polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta$</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl chloride)</td>
<td>22.5</td>
<td>19.2</td>
<td>9.2</td>
<td>7.2</td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>23.1</td>
<td>19.0</td>
<td>10.2</td>
<td>8.2</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>23.1</td>
<td>18.8</td>
<td>10.2</td>
<td>8.6</td>
</tr>
</tbody>
</table>

**II. Hansen Model**

The method of Hansen has the disadvantage that three-dimensional structures are necessary for a graphical representation of the interaction between polymers and solvents. Hansen developed a three-dimensional model to plot polymer solubilities (Hansen 2004; Hansen 2004). He found that, by doubling the dispersion parameter axis, an approximately spherical volume of solubility would be formed for each polymer. This volume, being spherical, can be described in a simple way: the coordinates at the center of the solubility sphere are located by means of three
component parameters \((\delta_d, \delta_p, \delta_h)\), and the radius of the sphere is indicated, called the interaction radius \((R)\).

A polymer is probably soluble in a solvent (or solvent blend) if the Hansen parameters for the solvent lie within the solubility sphere for the polymer. In order to determine this (without building a model) it must be calculated whether the distance of the solvent from the center of the polymer solubility sphere is less than the radius of interaction for the polymer:

\[
D_{(S-P)} = 4[(\delta_{dS} - \delta_{dp})^2 + (\delta_{pS} - \delta_{pp})^2 + (\delta_{hS} - \delta_{hp})^2]^{1/2}
\]  

(3.24)

Where

\(D_{(S-P)}\) = Distance between solvent and center of polymer solubility sphere

\(\delta_{xS}\) = Hansen component parameter for solvent

\(\delta_{xp}\) = Hansen component parameter for polymer.

The figure “4” in the first term of Eq. 3.24 which doubles the dispersion component scale, is intended to create a spherical volume of solubility.) If the distance \(D_{(S-P)}\) is less than the radius of interaction for the polymer, the solvent would be expected to dissolve the polymer. This method avoids the reliance on graphs; maps of solubility behavior and can be used effectively in solely numerical form. The mathematics involved are inconvenient however, especially when solvent blends are concerned, and it is perhaps for this reason that the use of this excellent system is not more widespread. For practical applications a two-dimensional method is to be preferred.

III. Hansen Graphs

Hansen parameters are both reasonably accurate in predicting solubility behavior and concise in their representation of that information. Accurate because precise values for all three component parameters are utilized and concise because the entire solubility volume for a polymer can be numerically indicated by four terms: one set of parameters and a radius.

A two-dimensional graph sacrifices some of that accuracy and conciseness in return for a system that clearly illustrates the relative positions of numerous materials, and
can be easily used in practical applications. Prediction of whether a polymer is soluble in a mixture of two solvents, for example, while possible mathematically is accomplished on a graph by drawing a line between the two solvents and seeing whether that line passes through the area of solubility for the polymer.

Hansen’s three dimensional volumes can be similarly illustrated in two dimensions by plotting a cross-section through the center of the solubility sphere on a graph that used only two of the three parameters, most commonly $\delta_p$ and $\delta_h$, as shown in Fig. 3.16.

Hansen graphs are easy to use because solvent positions are constant and polymer solubility areas may be drawn with a compass; furthermore, solvent blending calculations can be done with a pencil and ruler. The accuracy of predicting solubility behavior is about 90 % (Hansen 2004), with solvent locations nearest the edge of a solubility area being the least predictable. This is due to the three-dimensional nature of the actual solubility sphere. Where reduced to two dimensions, solvents that appear near the edge inside the solubility area may in fact be outside it, in front or behind, in three dimensions.

![Hansen solubility parameters diagram](Hansen 2004)

**3.3.5.3 Method of Hoftyzer and Van Krevelen**

The Hoftyzer and Van Krevelen additive group contribution method allows the prediction of three solubility parameter components, using the following equations:

$$
\delta_d = \frac{\sum F_{di}}{V}
$$

(3.25)
This means that for the prediction of $\delta_d$ the same type of formula is used as Small proposed for the prediction of the total solubility parameter, $\delta$. The group contributions $F_{di}$ to the dispersion component $F_d$ of the molar attraction constant can simply be added.

The same method holds for $\delta_p$ as long as only one polar group is present. To correct for the interaction of polar groups, the form of Eq. 3.26 has been chosen.

The polar component is still further reduced, if two identical polar groups are present in a symmetrical position. To take this effect into account, the value of $\delta_p$, calculated with Eq. 3.27 must be multiplied by a symmetry factor of:

0.5 for one plane of symmetry;

0.25 for two planes of symmetry;

0 for more planes of symmetry.

### 3.3.5.4 Method of Hoy

Hoy solubility parameter method may be one of the best and the fastest methods to predict a solubility or compatibility. Essentially, this method is also a group contribution method: for each chemical group in the molecule, contributions are added to the total. Hoy’s method is special because it allows correcting specific contributions of structural features such as cis, trans, ortho-, meta-, branching, conjugation of double bonds, and rings.
Table 3.2 The equations to be used in the Hoy system for estimation of the solubility parameter and its components. (Van Krevelen 1997)

<table>
<thead>
<tr>
<th>Formulae</th>
<th>Low-molecular weight Liquids (Solvents)</th>
<th>Amorphous Polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive molar functions</td>
<td>( F_i = \sum N_i F_{i,j} )</td>
<td>( F_i = \sum N_i F_{i,j} )</td>
</tr>
<tr>
<td></td>
<td>( F_p = \sum N_i F_{p,i} )</td>
<td>( F_p = \sum N_i F_{p,i} )</td>
</tr>
<tr>
<td></td>
<td>( V = \sum N_i V_i )</td>
<td>( V = \sum N_i V_i )</td>
</tr>
<tr>
<td>( \Delta_T = \sum N_i \Delta_{T,j} )</td>
<td>( \Delta_T^{(p)} = \sum N_i \Delta_{T,j}^{(p)} )</td>
<td></td>
</tr>
</tbody>
</table>

| Auxiliary equations             | \( \log \alpha = 3.39 \left( \frac{T_b}{T_c} \right) - 0.1585 - \log V \) |
|                                 | \( T_b = \text{boiling temperature}; \ T_c = \text{critical temperature.} \) |
|                                 | \( \frac{T_b}{T_c} = 0.567 + \Delta_T - \left( \Delta_T \right)^2 \) |
| (Lyderson equation)             | \( \alpha^{(p)} = \frac{777 \Delta_T^{(p)}}{V} \) |
|                                 | \( n = \frac{0.5}{\Delta_T^{(p)}} \) |

<table>
<thead>
<tr>
<th>Expressions for ( \delta ) and ( \delta^{(p)} )-components</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_i = \frac{F_i + B}{V} ) (B = 277)</td>
</tr>
<tr>
<td>( \delta_i^{(p)} = \frac{F_i^{(p)} + B}{V} )</td>
</tr>
<tr>
<td>( \delta_p = \delta_i \left( \frac{1}{\alpha F_i + B} \right)^{1/2} )</td>
</tr>
<tr>
<td>( \delta_p^{(p)} = \delta_i^{(p)} \left( \frac{1}{\alpha^{(p)} F_i + B} \right)^{1/2} )</td>
</tr>
<tr>
<td>( \delta_h = \delta_i \left( \frac{\alpha - 1}{\alpha} \right)^{1/2} )</td>
</tr>
<tr>
<td>( \delta_h^{(p)} = \delta_i^{(p)} \left( \frac{\alpha^{(p)} - 1}{\alpha^{(p)}} \right)^{1/2} )</td>
</tr>
<tr>
<td>( \delta_d = (\delta_i^2 - \delta_p^2 - \delta_h^2)^{1/2} )</td>
</tr>
<tr>
<td>( \delta_d^{(p)} = (\delta_i^{(p)}^2 - \delta_p^{(p)}^2 - \delta_h^{(p)}^2)^{1/2} )</td>
</tr>
</tbody>
</table>

Table 3.2 gives a survey of the system of equations to be used in the Hoy system. It contains four additive molar functions, a number of auxiliary equations and the final expressions for \( \delta_{(\text{total})} \) and for the components of \( \delta \).

\( F_i \) is the molar attraction function, \( F_p \) is polar component (both as discussed earlier); \( V \) is the molar volume of the solvent molecule or the structural unit of the polymer. \( \Delta_T \) is the Lyderson correction for non-ideality, used in the auxiliary equations. The values for low molecular liquids were derived by Lydersen (1955) (Van Krevelen 1997); the corresponding values for polymers, which are slightly different, have been derived by Hoy \( (\Delta_T^{(p)}) \).

It must be emphasized that Hoy is the only one person who used a “base value” in the calculation of \( F_i \), whereas he neglects a base value in \( V \); it was mentioned earlier that Traube (1895) already proved that for the additive calculation of the molar volume of liquids a base value has to be used that of the others (Van Krevelen 1997). So there is difference in the values calculated by different methods. Table 3.3 shows the
solubility parameter poly(vinyl acetate) calculated by Hoy’s compared with the other values.

Table 3.3 The comparison of the solubility parameters of poly(vinyl chloride) calculated by different methods. (Hansen 2004)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Hansen</th>
<th>Hoftyzer-Van Krevelen</th>
<th>Hoy</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ₁</td>
<td>19.2-22.1</td>
<td>22.5</td>
<td>21.7</td>
</tr>
<tr>
<td>δ₂</td>
<td>_</td>
<td>19.2</td>
<td>17.7</td>
</tr>
<tr>
<td>δ₃</td>
<td>_</td>
<td>9.2</td>
<td>12.2</td>
</tr>
<tr>
<td>δ₄</td>
<td>_</td>
<td>7.2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The results of the two algorithmic methods for estimation of the solubility parameter and its components (Hoftyzer-Van Krevelen and Hoy) are of the same order in accuracy (10%). So the safest way for estimation is to apply both methods, taking the average results.

To conclude, the full equation which determines the solubility of a polymer in an organic liquid is as follow:

\[
\Delta \bar{\delta} = [(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2]^{1/2}
\] (3.28)

For a good solubility \( \Delta \bar{\delta} \) must be small (\( \leq 5 \)).

### 3.4 Preparation of PDLC Films

The preparation of PDLC films was made following a combination of SIPS and TIPS. In general, a selected polymer and a mesogen were dissolved in a common solvent at room temperature. Each solution was stirred for about 10 min until resulting a clear solution-state. A small quantity was then cast on a carefully cleaned glass substrate. The PDLC films were formed by a slow evaporation of the solvent (about 24 h). The films then were dried under vacuum, which allows complete evaporation of the solvent. A glass cover was placed over the PDLC films, and the dry films were pressed. The thickness of the films was determined to be 30 ~ 50 μm silicon spacer.


Chapter 4 Thermo-optical Properties of LCs

4.1 Introduction

LCs have experienced an explosive growth since the phenomenon of liquid crystallinity was discovered in 1888 (Priestley 1974). LCs are anisotropic materials whose flow properties strongly depend on their structures and molecular orientations. Molecules in the crystalline solid state are positional and orientation ordered in three dimensions, however, in the isotropic liquid state this ordering is completely destroyed. Whereas LCs exhibit a degree of macroscopic orientation order that is found between the boundaries of the crystalline solid state and isotropic, ordinary liquid, state. Consequently, the properties of LCs are intermediate between those of an isotropic liquid and those of a crystalline solid. LCs have been the first electro-optical materials among the widespread commercial use such as twisted nematic liquid crystal and super-twisted nematic liquid crystal flat-panel display because of their unique optical, electrical, electro-optical, and thermal properties.

In this chapter, the thermo-optical properties of the four small molar mass mesogens will be studied by DSC. The phase transitions, such as crystalline↔smectic ($T_{C-S}$), smectic↔nematic ($T_{S-N}$), nematic↔isotropic ($T_{N-I}$) and crystalline phase changes in the two 4-alkoxybenzoic acids will be investigated. The two different smectic phases of 4-(octyloxy)benzoic acid will be confirmed by WAXD.

4.2 Experimental

4.2.1 Measurements

4.2.1.1 Differential Scanning Calorimetry

DSC measurements were performed on a Perkin Elmer Pyris 1. The mesogens were firstly heated at the rate of 40 °C·min$^{-1}$ from room temperature and then cooled, followed by a heating at a rate of 10 °C·min$^{-1}$ to 10 °C above the transition temperature (155.0 °C for the two benzoic acids, 145.0 °C for 4,4’-azoxyanisole and
195.0 ºC for trans-4-methoxycinnamic acid) leading to the isotropic phase. After the first heating cycle, the mesogens were held for 3 min in order to remove the identical thermal histories of the mesogens before the cooling and second heating ramps. Transition temperatures were recorded systematically during the cooling ramp and the second heating ramp. Before measuring the mesogens, a baseline was run with two matching empty aluminum pans using the same temperature program. Curves were corrected using baselines recorded under identical conditions and converted to apparent specific heat capacity curves.

For the DSC measurements, the samples were prepared by introducing approximately 2 mg of the LCs into the aluminum pans and sealed by the covers. The two samples of the same composition were prepared independently, to check for the reproducibility of the results.

### 4.2.1.2 Polarized Optical Microscope

The mesogen was heated from room temperature until it was melted at the rate of 20 ºC·min$^{-1}$ and then cooled to room temperature at the same rate. After that, the mesogen film obtained in the first heat-cool circle was heated from room temperature to isotropic temperature then cooled to room temperature at the rate of 5 ºC·min$^{-1}$. The film was held at different phase temperatures for 10 min to be captured the structure changes by digital camera under polarized and transmitted light using a magnification of 100×.

### 4.2.2 Materials

Four low molar mass mesogens, 4-(octyloxy)benzoic acid, 4-(decyloxy)benzoic acid, 4,4’-azoxyanisole and Trans-4-methoxycinnamic acid were purchased from Aldrich (Australia) (≥ 98 % purity). The 3-D structures of these mesogens were shown in Fig. 4.1. The 4-alkoxybenzoic acids were chosen, differing from one another only by the number of methylene groups in a terminal substituent. The 4-alkoxybenzoic acids can show two mesophases, smectic and nematic, among the different temperature ranges. The other two mesogens contain nematic mesophase in appropriate temperature areas.
4.2.3 Preparation of LC Films

Thin films were prepared by casting a 1 % (w/v) of LC-chloroform solution onto a glass microscopic slide of 25 mm in width, 75 mm in length, covered with a 22 mm × 22 mm glass cover slip. Experiments were performed after the solvent had completely evaporated. The thickness of the film was about 10 µm.
4.3 Results and Discussion

4.3.1 4-Alkoxybenzoic Acids

I. 4-(octyloxy)benzoic Acid

Figure 4.2 shows the phase transformation of 4-(octyloxy)benzoic acid and its corresponding morphologies upon heating. The endothermic peak at 73.7 °C is attributed to the change of crystal structure from the long needle shape to the smaller needle, as shown in Fig. 4.2 (a) and (b). The enthalpy calculated from this peak was 58.5 J·g⁻¹. When the temperature was above the melting temperature, 101.2 °C, 4-(octyloxy)benzoic acid exhibited a smectic phase in about 7 °C temperature range. In this temperature range, the focal-conic fan shape texture was observed, as shown in Fig. 4.2 (c). As the temperature was increased, the second smectic phase (shown by Fig. 4.2 (d)) occurred. This phase transition was observed in the temperature range from 107.7 °C to 143.1 °C. As the temperature was further increased, the spherical-shape nematic structures formed, as seen in Fig. 4.2 (e), in the temperature range from 144 °C to 146.5 °C. The spherical-shape nematic structures dissolved once the temperature was higher than 146.5 °C at which the nematic-isotropic transition took place. The different smectic formation changing had an enthalpy of 4.66 J·g⁻¹ and the S→N required 2.67 J·g⁻¹ enthalpies. The isotropization process needed an enthalpy of 1.8 J·g⁻¹. The nematic phase only could be formed in a 2.5 °C narrow range.
Figure 4. 2 DSC traces and structures observed by POM of 4-(octyloxy)benzoic acid on heating; a) 50.0 °C, b) 85.0 °C, c) 103.0 °C, d) 120.0 °C and e) 144.1 °C.
Figure 4. 3 DSC traces and structures observed by POM of 4-(octyloxy)benzoic acid on cooling; a) 140.0 °C, b) 120.0 °C, c) 100.0 °C, d) 70.0 °C and e) 30.0 °C.
Fig. 4.3 presents selected DSC traces of 4-(octyloxy)benzoic acid on cooling. There were five exothermic peaks separating the area to six parts. Due to the super-cooling, the peaks moved to lower temperatures and the S→N peak separated from the N-I transition peak. The I→N transition appeared at 144.0 °C. The same spherical structure was formed as happened upon heating, as shown in Fig. 4.3 (a), followed by the S order forming at 135.3 °C, which shifted nearly 10 °C to the lower temperature compared with that in the heating. The focal-conic texture was observed, as shown in Fig. 4.3 (b), which clearly confirmed the formation of a SmA phase. It was found that the enthalpy of isotropic-nematic transition was 5.3 J·g⁻¹ and the nematic-smectic A was 2.5 J·g⁻¹, respectively. The smectic textures changed at 106.2 °C with ΔH = 4.7 J·g⁻¹. The morphology shown in Fig. 4.3 (c) was assumed to be a SmC phase. The crystallization took place at 95.8 °C with an enthalpy of 42.5 J·g⁻¹, shifting nearly 5 °C lower than the result obtained in heating. The crystallization structure change was at 53.5 °C with a similar enthalpy change as in heating. The temperature of structure change was significantly affected by the super-cooling, shifting almost 20 °C lower temperature. The two crystallization structures display in Fig. 4.3 (d) and (e), respectively.

Wide-angle X-ray diffraction (WAXD) was used to identify the mesophase structures of 4-(octyloxy)benzoic acid and the d spaces were calculated by applying the Bragg equation. Fig. 4.4 shows a set of WAXD patterns measured at three different temperatures, 140.0, 125.0 and 100.0 °C, in the 2θ range between 0 and 50º. Three intensity peaks were measured at 140 °C, as shown in Fig. 4.4 (a). The widest peak at 20.4º, with d = 0.435 nm, was assumed to be the distance between the molecules. The two sharp peaks at 38.4º and 44.7º were probably attributed to the atom distance in the molecule. A new intensity of reflection peaked at 2.8º with d = 3.212 nm, as shown in Fig. 4.4 (b), when the temperature arrived at 125.0 °C. This peak is assumed due to the space in a layered structure, which confirmed a smectic A phase formed because smectic phase appears to have one degree of translational ordering, resulting in a layered structure. When the temperature was at 100.0 °C, this peak shifted to 4º and d spacing decreased to 2.202 nm, which further confirmed that the smectic phase formed in the 4-(octyloxy)benzoic acid in this temperature range but another different smectic phase structure was formed since the length of the d spacing shorter than the value measured at 125.0 °C, which was classified as SmC phase.
In the cases of compounds containing strongly polar groups, an additional ordering appears which is based on a tendency to antiferroelectric ordered molecules, i.e. to an additional of the molecular long axes. Some the known smectic structures are illustrated in Fig. 4.5 and may be described as follows (Priestley 1974; Toyne 1987):

SmA₁, SmC₁ Conventional phases with completely random head-to-tail disorder

SmA₂, SmC₂ Bilayer phases with antiferroelectric ordering of the molecules

SmA₉, SmC₉ Semi-bilayers with partial molecular association

The maximum length of the molecule 4-(octyloxy)benzoic acid is 15.3 Å, calculated by the CS Chem 3D program. And the d spacing measured in SmA phase was 3.2 nm, which was slightly longer than the two times of the molecule length, therefore, 4-(octyloxy)benzoic acid displays a SmA₂ structure, which is a head-to-head bilayer orientational smectic structure and the schematic structure is displayed in Fig. 4.5. The d spacing was 2.2 nm for smectic C phase, whose value was between the molecule length and the SmA₂ d space. So it is assumed that the smectic C structure belonged to the SmC₂.
Chapter 4 Thermo-optical Properties of Liquid Crystals

Figure 4.4 The Diffractogram of 4-(octyloxy)benzoic acid at different temperatures during cooling; (a) 140.0 °C, (b) 125.0 °C and (c) 100.0 °C.
Chapter 4 Thermo-optical Properties of Liquid Crystals

The transition between nematic and isotropic is generally considered to be a weak first-order, which should occur at the same temperature on cooling and heating and the current observation of $T_{N\rightarrow I}$ in 4-(octyloxy)benzoic acid is in a good agreement with it though there was 1 °C difference between the cooling and heating, which is in an acceptable range compared with the significant shifting in crystallization. The nematic phase is more stable in the cooling and its nematic temperature range is broader because of the shift of $T_{N\rightarrow S}$. This is assumed because hydrogen bonding is formed among the molecules in the isotropic phase and these attractions are in determining nematic thermal stability and inhibited the molecules rotated freely to parallel with their neighbors in layers to form a more order S phase. The transition temperature between two smectic phases was not affected by super-cooling because it

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**Figure 4.5 Schematic of the three types of SmA and SmC structures. (Toyne 1987)**

The transition between nematic and isotropic is generally considered to be a weak first-order, which should occur at the same temperature on cooling and heating and the current observation of $T_{N\rightarrow I}$ in 4-(octyloxy)benzoic acid is in a good agreement with it though there was 1 °C difference between the cooling and heating, which is in an acceptable range compared with the significant shifting in crystallization. The nematic phase is more stable in the cooling and its nematic temperature range is broader because of the shift of $T_{N\rightarrow S}$. This is assumed because hydrogen bonding is formed among the molecules in the isotropic phase and these attractions are in determining nematic thermal stability and inhibited the molecules rotated freely to parallel with their neighbors in layers to form a more order S phase. The transition temperature between two smectic phases was not affected by super-cooling because it
is supposed to be the second-order transition that no nucleation is required, in contrast to the first-order transitions, like crystallization and melting.

II. 4-(decyloxy)benzoic Acid

The DSC heating scans and the morphologies of 4-(decyloxy)benzoic acid are presented in Fig. 4.6. The endotherm at 86.7 °C, with an enthalpy of 72.8 J·g⁻¹, is considered to be due to the change between two different crystallization forms, as the textures are displayed in Fig.4.6 (a) and (b). The S mesogen phase appeared from 96.2 to 120.6 °C and the characteristic “threading” texture of S phase (Fig. 4.6 (c)) was observed in this temperature range. The melting process had an enthalpy of 38.4 J·g⁻¹. This enthalpy value was only about half of the crystallization transition. Apparently, the thermal movement of molecules from solid to liquid is much easier than that between two solid phases. 4-(decyloxy)benzoic acid showed the second mesogenic phase, N phase, before the temperature reached the isotropic temperature at 141.2 °C. The typical nematic Schlieren texture is displayed in Fig. 4.6 (d), the $\Delta H_{N-I} = 6.1$ J·g⁻¹.

The DSC cooling scans and the morphologies of 4-(decyloxy)benzoic acid are presented in Fig. 4.7. It could be seen that the nematic Schlieren texture (Fig. 4.7 (a)) grew from isotropic at 139.9 °C. When the temperature was cooled to 119.7 °C, the mesophase changed to the S. The corresponding enthalpy was found to be 6.4 J·g⁻¹. The enthalpy changed in the N-S was 4.2 J·g⁻¹. The Schlieren texture was captured in S phase (Fig. 4.7 (b)), which shows only 4-fold singularities in contrast to the nematic phase exhibiting 2- and 4-fold singularities. The transition temperatures of mesophase did not shift notably to the lower sides because both I-N and N-S transitions are not the typical first-order transition which does not have strong super-cooling effects. The crystallization transition underwent at 92.0 °C with $\Delta H = 38.2$ J·g⁻¹. The change in crystallization structure occurred at about 75 °C, about 25 °C lower than the changing temperature in heating and the enthalpy decreased by two thirds times. The two different structures crystallizations are shown in Fig. 4.7 (c) and (d), respectively.
Figure 4. 6 DSC traces and structures observed by POM of 4-(decyloxy)benzoic acid on heating; a) 70.0 °C, b) 91.0 °C, c) 105.0 °C and d) 130.0 °C.
Figure 4. 7 DSC traces and the structures observed by POM of 4-(deceloxy)benzoic acid on cooling; a) 130.0 °C, b) 105.0 °C, c) 86.0 °C and d) 60.0 °C.
4-(octyloxy)benzoic acid and 4-(decyloxy)benzoic acid are homologues, only different from the number of the methyl. The mesophase-to-isotropic transition temperature usually decreases with the increase in chain length. The $T_{N,I}$ of 4-(octyloxy)benzoic acid is 5 ºC higher than that of 4-(decyloxy)benzoic acid since the 4-(octyloxy)benzoic acid has 2 methyl less than 4-(decyloxy)benzoic acid. But a few exceptions to this rule should be noticed that among compounds containing a biphenyl moiety which, due to the substitution, is restricted from adopting a coplanar conformation. When the two aromatic nuclei are not coplanar, it is possible that the termini of one molecule can interact strongly with one of the rings of another molecule, which would cause additional attractions, and as a result, the nematic phase becomes a more stable thermally as the terminus grows in length.

### 4.3.2 4,4′-azoxyanisole

Fig. 4.8 presents the DSC curve and the morphologies of 4,4′-azoxyanisole during heating. It could be seen that 4,4′-azoxyanisole only showed a N mesophase between the crystallization and isotropic phase. The tiny size crystallization structure (as shown in Fig. 4.10 a) was observed until the temperature reached 119.1 ºC with an enthalpy of 96.1 J·g$^{-1}$ for the crystal melting, and then the nematic marble structure formed before the molecules disordered becoming to liquid at 133.5 ºC, having $\Delta H = 1.6$ J·g$^{-1}$.

Fig. 4.9 shows the thermo-optical properties of 4,4′-azoxyanisole on cooling. The isotropic to nematic transition was observed at 133.0 ºC, which was only 0.5 ºC lower than the clearing temperature measured on heating, with $\Delta H = 1.6$ J·g$^{-1}$ for the molecules forming a N phase. The nematic marble structure appeared at 133.0 ºC but disappeared at 79.0 ºC, as shown in Fig. 4.9 (a). The more order crystallization structure (Fig. 4.9 (b)) formed at 79.0 ºC. In comparison with the heating process, the crystallization temperature decreased by about 40 ºC on cooling whereas the corresponding enthalpy decreased by about 50 J·g$^{-1}$.

Since the N→I transition is a weak first-order transition, the effects of the super cooling and heating on the transition of 4,4′-azoxyanisole are not significant and the clearing temperature measured is about 133.0 ºC, regardless of heating and cooling. The N→I transition can be used as a standard for temperature calibration for DSC on
heating as well as for I→N on cooling. However, the C→N transition is a classical first-order transition, which normally requires nucleation and the melting temperature and crystallization temperature to be at different positions, 119.1 °C on heating and 79.0 °C on cooling.
Figure 4. 8 DSC traces and the structures observed by POM of 4,4'-azoxyanisole on heating; a) 110.0 °C and b) 127.0 °C.
Figure 4. 9 DSC traces and structures observed by POM of 4,4'-azoxyanisole on cooling; a) 110.0 °C and b) 74.0 °C.
4.3.3 Trans-4-methoxycinnamic Acid

The melting temperature of trans-4-methoxycinnamic was 172.8 °C, as can be seen in Fig. 4.10. Above the melting temperature, the linear mesogen trans-4-methoxycinnamic acid exhibited only one nematic mesophase. When the temperature was higher than 188.5 °C, the molecules lost the N order. The enthalpies required were 123.0 J·g⁻¹ for the melting and 11.4 J·g⁻¹ for the N→I transition, respectively. The morphologies of different phases are presented in Fig. 4.10 (a) and (b).

Fig. 4.11 displays the DSC curve and the morphologies of trans-4-methoxycinnamic acid on cooling. The nematic order (Fig. 4.11 (a)) formed at 184.6 °C with an enthalpy of 11.0 J·g⁻¹ and the crystallization took place at 168.0 °C with the latent heat of 112.4 J·g⁻¹. This creation of crystallization structure is presented by Fig. 4.11 (b).
Figure 4. 10 DSC traces and structures observed by POM of Trans-4-methoxycinnamic acid on heating; a) 160.0 °C and b) 180.0 °C.
Figure 4. 11 DSC traces and structures observed by POM of Trans-4-methoxycinnamic acid on cooling; a) 178.0 °C and b) 156.0 °C.
4.4 Conclusion

For the 4-alkoxybenzoic acids mesogens, 4-(octyloxy)benzoic acid is two methylene groups less than 4-(decyloxy)benzoic acid. So the former clearing temperature is higher than the latter because of the increasing chain length.

The transition between the nematic liquid crystalline state and the isotropic liquid for the all four small molar mass mesogens is a weak first-order transition without superheating/cooling. The mesomorphic range should not be affected by the superheating/cooling. The $S\leftrightarrow N$ of 4-(decyloxy)benzoic acid occurred at the same positions no matter heating or cooling, which presented the properties of the second-order phase transition, however, the $T_{S\leftrightarrow N}$ of 4-(octyloxy)benzoic acid was shifted to the lower side in cooling because the hydrogen bonding, formed in the isotropic phase, inhibited the molecules arrange to S phase. The transition happened between two different S textures in 4-(octyloxy)benzoic acid exhibited no supercooling/heating effects. The structure changes among the crystalline solid state and the melting transitions are the first-order transitions and the transitions will shift to a higher/lower temperature depending on the heating/cooling.

Trans-4-methoxycinnamic acid has the highest melting temperature among the four mesogens despite of the molar mass. This is because the thermal stability of the solid state is principally influenced by attractive forces in the crystal lattice. The carboxylic acid termini of trans-4-methoxycinnamic acid gives rise to very strong intermolecular attractions which cause it to have high melting temperature and clearing temperature despite of its smallest molar mass among the four mesogens.

The d spacing measured by WAXD was utilized to classify the mesophases of 4-(octyloxy)benzoic acid. The layer spacing d in SmA of 4-(octyloxy)benzoic acid is slightly two times longer than the molecular length, which is unfamiliarly like the normal d spacing that somewhat shorter than the molecular length. Therefore, it is classified to the head-to-head bilayer SmA$_2$ structure and smectic C structure is classified to the SmC$_2$ structure because its d space is longer than the length of 4-(octyloxy)benzoic acid but shorter than the value d spacing for SmA$_2$.
Chapter 5 Thermo-optical Properties of PDLCs

5.1 Introduction

A new way to use LC: PDLC has been developed because of its unique character, where a low molar mass LC is dispersed within a polymer matrix. The optical response is based on the electrically controlled light scattering properties of the droplets. An applied electric field will align the nematic droplets to yield a non-scattering or transparent state.

PDLCs do not need polarizers as opposed to the traditional LC devices and they are easy to manufacture since the exact thickness of the film is not important. Xerox PARC has produced a 6.3 million pixel active matrix display with a resolution of 284 pixel per inch; near laser printer quality (Okabe, Abe et al. 1995). Most current notebook computer displays only have about 150 pixel per inch (Zmija, Klosowicz et al. 1993). Manufacturing this type of display in bulk would be futile given current imperfect fabrication processes, but at least it has been demonstrated that displays with these characteristics can be built and might even be commonplace in the future. Therefore, recently a high level of activity has characterized the field of research on PDLCs that are potentially useful for a variety of electro-optical applications.

These applications include large-scale flexible displays that do not require polarizers and are simple and cost effective to fabricate. Switchable coatings for windows to be used for controlling daylight or interior lighting, privacy, cosmetics, solar heat gains and security provide a totally new application for liquid crystal materials. The absence of polarizers coupled with the electrically controllable light scattering principle upon which these films operate make them useful for low-loss, high-intensity color projectors, thus expanding projection technology. PDLC materials can be optically switched with high intensity laser light as well, providing still other types of applications in such areas as optical sensor protection and optical processing and computing. Finally, thermally and mechanically responsive PDLC films make
possible thermal and strain sensors with applications in the medical and coatings industries. The formation of uniform liquid crystal droplets in a polymer binder may be achieved by several different phase separation processes which include phase separation: polymerization, thermal processes, and solvent evaporation. Each approach involves forming a homogeneous solution of polymer or prepolymer with a liquid crystal material followed by phase separation, droplet formation, and finally polymer gelation and solidification. These processes are a result of droplet nucleation and growth, on spinodal decomposition. Phase separation procedures can be applied to a broad range of polymers including thermoplastics, thermosets, or UV-cured systems. Phase separation methods are normally simple, one-step processes that can reduce fabrication costs in industry.

In the solvent induced phase separation (SIPS) process, solvents can be used to solubilize a liquid crystal and a thermoplastic polymer in order to create a single phase. As the solvent is evaporated, the liquid crystal phase separates as droplets in a polymer matrix. A suitable droplet size can be achieved by controlling the rate of solvent evaporation. However, in practice it is not easy to gain the desired droplet size using SIPS. Since the polymers used in SIPS processes are thermoplastic in most cases, it is possible to reset the droplet size of a SIPS film by a subsequent TIPS process. Usually, the PDLC film is heated to a temperature at which the liquid crystal molecules are dissolved throughout the polymer matrix. The liquid crystal phase can separate from the polymer matrix upon cooling. The LC droplet size will be better controlled by the cooling rate of TIPS. As can be seen, two steps are involved in the preparation of PDLCs with a controlled LC droplet size. Alternatively, the LC droplet size could be controlled using a one step approach, where the desired LC droplets with fine sizes form directly from phase separation of an initial uniform LC-polymer solution.

Apparently, the thermodynamics of mixing for two kinds of components plays an important role in understanding of phases and phase separation occurring in the preparation of PDLC. The thermodynamic equation for the Gibbs free energy ($\Delta G$) change accompanying mixing at constant temperature and (external) pressure is

$$\Delta G = \Delta H - T \Delta S$$  (5.1)
A change, denoted by $\Delta$, is the value of a variable for a solution or mixture minus the values for the pure components considered separately. The objective is to find explicit formulas for $\Delta H_m$ and $\Delta S_m$, the enthalpy and entropy increments associated with the mixing process.

The result obtained by Flory-Huggins is

$$\Delta G = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_1 \chi_12]$$  \hspace{1cm} (5.2)

The right side is a function of the number of moles $n$ and volume fraction $\varphi$ of mesogen (component $\phi_1$), the number of moles and volume fraction of polymer (component $\phi_2$), with the introduction of a parameter $\chi$ to take account of the energy of interdispersing polymer and mesogen. $R$ is the gas constant and $T$ is the absolute temperature. The volume fraction is analogous to the mole fraction, but is weighted to take account of the relative sizes of the molecules.

The key quantity is an interaction parameter between LC and polymer that in particular, would be a starting point in selecting a suitable polymer for a required mesogen. The solubility parameter ($\delta$), proposed by Hildebrand, provides an objective and quantitative predictor of PDLC combinations. This means that the solubility of a given mesogen in a given polymer is favoured if the solubility parameters of polymer and mesogen are equal.

In this chapter solubility parameters will be applied to the choice of materials to make PDLC films with controlled phase separation, suitable dispersed phase droplet size and stable phase structure. The PDLCs are characterized using differential scanning calorimetry (DSC) and hot stage polarized optical microscope (POM) to study the thermal and optical properties of PDLC films. The cooling rate and the LC concentration affecting on the droplet size in the 4,4'-azoxyanisole PDLC was investigated by POM. The melting endotherm was expected to be sufficiently isolated from the other thermal transitions to extend the method described by Smith and co-workers to an analysis of the melting transition.
5.2 Experimental

5.2.1 Materials

All chemicals used in the present work were purchased from Sigma–Aldrich, Australia. Three mesogens were 4-(decyloxy)benzoic acid, 4,4’-azoxyanisole, and trans-4-methoxycinnamic acid. The purity of the materials was 98%. The polymers were poly(2-hydroxyethyl methacrylate) (pHEMA) \( (M_w = 20,000 \text{ g mol}^{-1}) \), poly(methyl methacrylate) (PMMA) \( (M_w = 996,000 \text{ g mol}^{-1}) \), poly(vinyl chloride) (PVC) \( (M_w = 43,000 \text{ g mol}^{-1}) \). Chloroform \( (\text{CHCl}_3) \), N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were used without further purification.

5.2.2 Preparation of the PDLC Films

The preparation of PDLC films was made following a combination of SIPS and TIPS. The PDLC films were prepared as described by the method in Chapter 3.

5.2.3 Measurements

Phase transition temperatures were measured by DSC instrument. The equipment and the program were utilized as same as those used for LC. The details were described in Chapter 4.

A Nikon Labophot 2 optical microscope equipped with Mettler FP-82 hot stage and Mettler FP90 temperature programmer was used to explore the thermal transitions and morphologies. PDLC films were first heated at a rate of 10 °C·min\(^{-1}\) to 140 °C (for 4,4’-azoxyanisole dispersion) or higher (150 °C for 4-(decyloxy)benzoic acid dispersion; 200 °C for trans-4-methoxycinnamic acid dispersion) depending on the different components, to ensure that a homogenous isotropic state has been reached. PDLC films were cooled from above the isotropic temperature to room temperature at a cooling rate of 2 °C·min\(^{-1}\). The texture images were captured during the cooling process.

The morphology development of 4,4’-azoxyanisole dispersion in PVC was observed in the course of cooling and heating scans at 2 °C·min\(^{-1}\). The effect of the cooling rate
on the generated morphologies was assessed using three different cooling procedures: a) slow cooling: the PDLC was kept in the hot stage and the temperature was decreased from 130 °C to 110 °C at 2 °C·min\(^{-1}\); b) normal cooling: at the rate of 4 °C·min\(^{-1}\); c) fast cooling: at the rate of 8 °C·min\(^{-1}\); d) fastest cooling: at the rate of 16 °C·min\(^{-1}\). The morphologies were observed by optical microscope with and without crossed polarizers. The average sizes of the droplets were measured by the Image Processing Tool Kit (IPTK) software (Version 4.0).

### 5.3 Results and Discussion

#### 5.3.1 Solubility Parameters

The solubility parameters of materials were calculated by the method of Hoftyzer and Van Krevelen and the method of Hoy, as described in Chapter 3, moreover the final results were determined by the value of the average of these two methods because the results of the two algorithmic methods for estimation of the solubility parameter and its components are of the same order in accuracy (10 %). The results calculated with the two methods for mesogens are presented in Table 5.1. The average values for the materials are displayed in Table 5.2, respectively. Suitable polymers and solvents were chosen for the required LC, depending on the smallest difference in solubility parameter. LC-polymer pairs with small solubility parameter difference are expected to be miscible before solvent evaporation and immiscible after solvent evaporation and temperature decrease to form a PDLC film. So the matching pairs for PDLC materials are illustrated in Table 5.3.

<table>
<thead>
<tr>
<th>Liquid crystals</th>
<th>Hoftyzer and Van Krevelen</th>
<th>Hoy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta_1)</td>
<td>(\delta_d)</td>
</tr>
<tr>
<td>4-(decyloxy)benzoic acid</td>
<td>19.5</td>
<td>18.1</td>
</tr>
<tr>
<td>4,4'-azoxyanisole</td>
<td>23.2</td>
<td>20.3</td>
</tr>
<tr>
<td>trans-4-methoxycinnamic acid</td>
<td>23.4</td>
<td>20.7</td>
</tr>
</tbody>
</table>
Chapter 5 Thermo-optical Properties of PDLCs

Table 5.2 The average solubility parameter of the mesogens, polymers and solvents ($J^{1/2} \cdot cm^{-3/2}$).

<table>
<thead>
<tr>
<th>Mesogens</th>
<th>$\delta_i$</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(decyloxy)benzoic acid</td>
<td>19.4 (0.1)</td>
<td>16.6 (0.2)</td>
<td>4.7 (3.6)</td>
<td>8.4 (2.0)</td>
</tr>
<tr>
<td>4,4’-azoxyanisole</td>
<td>21.6 (0.9)</td>
<td>17.0 (2.2)</td>
<td>6.0 (3.2)</td>
<td>11.4 (4.2)</td>
</tr>
<tr>
<td>trans-4-methoxycinnamic acid</td>
<td>23.1 (0)</td>
<td>17.0 (1.8)</td>
<td>8.2 (2.2)</td>
<td>12.0 (3.4)</td>
</tr>
<tr>
<td>Polymer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PHEMA</td>
<td>19.5</td>
<td>16.4</td>
<td>8.3</td>
<td>6.4</td>
</tr>
<tr>
<td>PVC</td>
<td>22.5</td>
<td>19.2</td>
<td>9.2</td>
<td>7.2</td>
</tr>
<tr>
<td>PMMA</td>
<td>23.1</td>
<td>18.8</td>
<td>10.2</td>
<td>8.6</td>
</tr>
<tr>
<td>Solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>18.9</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
</tr>
<tr>
<td>THF</td>
<td>19.5</td>
<td>16.8</td>
<td>5.7</td>
<td>8.0</td>
</tr>
<tr>
<td>DMF</td>
<td>24.9</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
</tr>
</tbody>
</table>

The data in the brackets shows the difference of parameter in absolute value between the mesogen and its matching polymer.

Table 5.3 The matching pairs of PDLC materials.

<table>
<thead>
<tr>
<th>Mesogens</th>
<th>Polymers</th>
<th>Solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(decyloxy)benzoic acid</td>
<td>pHEMA</td>
<td>CHCl$_3$</td>
</tr>
<tr>
<td>4,4’-azoxyanisole</td>
<td>PVC</td>
<td>THF</td>
</tr>
<tr>
<td>Trans-4-methoxycinnamic acid</td>
<td>PMMA</td>
<td>DMF</td>
</tr>
</tbody>
</table>

5.3.2 Thermo-optical Properties of PDLCs

When the concentrations of LC were lower in the PDLCs, no discrete domains were observed in the PDLCs with decrease of the temperature, because LCs were completely miscible in the polymer matrix, therefore, no phase separation occurred.

Figure 5.1 a) the morphology of 25 %wt 4-(decyloxy)benzoic acid dispersed in pHEMA at 108 ºC; b) the two-phase morphology of 75 %wt 4-(decyloxy)benzoic acid PDLC at 125 ºC.
Chapter 5 Thermo-optical Properties of PDLCs

Fig. 5.1a shows that some tiny bâtonnets could be observed and no droplets were formed at 108 °C in the 25 %wt 4-(decyloxy)benzoic acid dispersed in pHEMA. As the LC concentration increases, the density and the size of the domains increases. However, when the LC concentration was greater than 70 %wt, the LC phase became continuous. Small polymer beads that have aggregated wind through the LC phase creating a co-continuous two-phase morphology, which is presented in Fig. 5.1b. Individual large pockets of 4-(decyloxy)benzoic acid existed in the 75 %wt PDLC in nematic phase and the dark area corresponded to the polymer matrix. The PDLCs with about 50 %wt LCs were synthesized in this project in order to create suitable LC droplets morphologies.
Figure 5. 2 DSC thermogram and polarized optical micrographs of pHEMA dispersed 4-(decyloxy) benzoic acid during cooling; a) 126 °C, b) 108 °C, c) 91 °C and d) 70 °C.
Fig. 5.2 shows the thermograph for pHEMA dispersed in 4-(decyloxy)benzoic acid prepared in CHCl$_3$ solvent. The concentration of mesogen was 54 %wt. The pure 4-(decyloxy)benzoic acid showed two mesophases, smectic (S) and nematic (N), in different temperature ranges. When this PDLC was cooled from the isotropic (I) phase, the I-N peak appeared at about 133 °C. As can be seen from Fig. 5.2a, the Schlieren texture of the N phase appeared and covered the whole field of view. This texture persisted until the temperature reached 119 °C at which the N phase changed to an S phase. A different texture from the N phase was observed at 108 °C, as shown in Fig. 5.2b. S phase appeared in the lower temperature range than N phase, which is attributed to the more ordered molecules of S phase. Because the more ordered the mesophase, the closer it lies to the crystalline phase. As shown in Fig. 5.3a, the molecular axes of the N molecules are aligned parallel to a preferred direction and the centres of gravity are distributed at random as in an ordinary liquid. All smectic LCs have a layered structure as shown in Fig. 5.3b. The centres of gravity of the elongated molecules are arranged in equidistant planes and the long axes of the S molecules are parallel to a preferred direction that may be normal to the planes ($S_A$) or tilted by an angle ($S_C$). The PDLC presents two different crystalline structures that are confirmed by both DSC curve and the morphologies observed by polarized microscope below the melting temperature ($T_m = 96$ °C). The change between the two different crystalline structures occurred at about 85 °C (Figs. 5.2c and 5.2d).
Figure 5. 4 DSC thermogram and polarized optical micrograph of PVC dispersed 4,4'-azoxyanisole during cooling; a) 124 °C and b) 108 °C.
Fig. 5.4 presents the thermal and optical properties of PVC dispersed 4,4’-azoxyanisole prepared in THF solvent. The concentration of LC is about 50 %wt. The droplets only show N phase between 129 °C and 120 °C. The evolution of droplets generated by cooling will be discussed later. The micrograph in Fig. 5.4a was taken at 122 °C, showing the N droplets. After continuing cooling, the fan-shaped focal conic texture of the liquid crystalline phase, shown in Fig. 5.4b, was observed.
Figure 5. DSC thermogram and polarized optical micrograph of PMMA dispersed trans-4-methoxycinnamic acid during cooling; a) 180 °C and b) 157 °C.
Fig. 5.5 presents the DSC curve and the textures of PMMA dispersed trans-4-methoxycinnamic acid prepared in DMF solvent. The concentration of mesogen is 57 %wt. The N phase of droplets was observed in the temperature range from 175 ºC to 190 ºC, as shown in Fig. 5.5a. The needle-like crystalline phase (Fig. 5.5b) appeared below 170 ºC.

5.3.3 Morphologies

5.3.3.1 Cooling Rate Effects

PVC dispersed 4,4’-azoxyanisole, containing 50 %wt 4,4’-azoxyanisole, were cooled from 130 ºC to 110 ºC, at fast and slow rates, as described in the experimental section. The resulting morphologies were observed by optical microscope at 110 ºC. The observed morphologies correspond to a dispersion of 4,4’-azoxyanisole droplets in the PVC matrix. These droplets were in a metastable nematic state at the time where the images were registered.
Figure 5.6 Micrographs obtained by transmission optical microscope without polarizers, showing 4,4'-azoxyanisole nematic droplets dispersed in PVC matrix at different cooling rates: (a) 2 °C·min⁻¹; (b) 4 °C·min⁻¹; (c) 8 °C·min⁻¹; (d) 16 °C·min⁻¹.

Fig 5.6 shows the resulting morphologies obtained with fast and slow cooling rates, respectively. The average size of dispersed droplets was estimated using Image Processing software for image analysis, presented by Table 5.4. As expected, the average size of the nematic droplets decreased when increasing the cooling rates. The average diameter of nematic droplets for the slowest cooling was 1.30 µm and decrease to 0.84 µm when the cooling rate increased to 4 °C·min⁻¹. The average size of the droplets was 0.72 µm at the rate of 8 °C·min⁻¹, however, the size decreased to 0.60 µm for the fastest cooling rate.
Table 5.4 The effects of cooling rate on the droplet size.

<table>
<thead>
<tr>
<th>Cooling Rate /°C-min⁻¹</th>
<th>Average diameter of droplet /µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.30</td>
</tr>
<tr>
<td>4</td>
<td>0.84</td>
</tr>
<tr>
<td>8</td>
<td>0.72</td>
</tr>
<tr>
<td>16</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Figure 5.7 The distributions of the droplets with different cooling rates; 2 °C-min⁻¹ (−); 4 °C-min⁻¹ (→−); 8 °C-min⁻¹ (→−) and 16 °C-min⁻¹ (→)

The distributions of the droplet sizes at four different cooling rates are shown in Fig. 5.7. The distribution variances calculated from the curve were 0.07 for 2 °C-min⁻¹, 0.03 for 4 °C-min⁻¹, and when the cooling rate increased to 8 °C-min⁻¹ and 16 °C-min⁻¹, the variance decreased to 0.006 and 0.002, respectively. A significant finding was the
fact that the distribution of particle sizes was distributed in a narrow range of sizes, which called unimodal, for fast cooling rates; and distributed in broad range of sizes, presenting a distribution of large droplets together with another distribution of small droplets, which called bimodal, for slow cooling rates. When PDLCs are used in electro-optical devices such as reflective displays, optical switches, and variable transmittance windows, it is convenient to generate unimodal distributions of dispersed droplets with sizes in the range of the wavelength of visible light. This may be achieved by combining an adequate selection of the initial composition with the use of a fast cooling process.

The different distributions generated with fast and slow cooling rates may be explained as follows. A fast cooling rate leads to a high nucleation rate followed by a limited growth/coalescence of dispersed droplets. A slow cooling enables a continuous nucleation during the whole cooling process. First nuclei are generated from a solution of low viscosity, high temperature and a 4,4’-azoxyanisole concentration close to the initial one. This leads to a rapid growth/coalescence process that generates the large droplets. But as the nucleation continues from solutions of increasing viscosities, at both lower temperatures and 4,4’-azoxyanisole concentrations, the new particles can only evolve limited growth/coalescence processes. This leads to a distribution of very large and small droplets (bimodal distributions).

In order to verify this phenomenon, the evolution of morphologies was followed by optical microscope between crossed polarizers, when cooling at 2 °C·min⁻¹ in the hot stage.
Figure 5.8 Evolution of morphologies generated by cooling PVC dispersed 4,4'-azoxyanisole with 50 %wt 4,4'-azoxyanisole at 2 °C·min⁻¹, observed by POM; a) 130.1 °C, b) 129.8 °C, c) 129.5 °C, d) 129.1 °C.

The evolution of the 4,4'-azoxyanisole N droplets separated from the PVC matrix is shown in Fig. 5.8. The appearance of the first generation of tiny droplets of 4,4'-azoxyanisole was observed at 130.1 °C (Fig. 5.8a) when cooling from the isotropic phase. At 129.8 °C (Fig. 5.8b), the initial droplets had significantly grown and a new generation of smaller particles was observed (the dark region correspond to PVC and the isotropic 4,4'-azoxyanisole phase). At 129.5 °C (Fig. 5.8c), an agglomeration of the large droplets of nematic domains was observed (initiation of phase inversion). Older particles continued their growth and new particles appeared. When the temperature reached 129.1 °C, the coalescence of the oldest droplets had significantly advanced (Fig. 5.8d). The phase inversion was evidenced by the appearance of a continuous nematic phase leaving dispersed domains of the isotropic solution.
5.3.3.2 LC Concentration Effects

![Micrographs](image)

**Figure 5.9** Micrographs obtained by microscope with polarizers at 120 °C, showing nematic 4,4’-azoxyanisole dispersed in PVC arising by a 2 °C-min⁻¹ cooling rate of PDLC from 130 °C; concentration of LC: (a) 30 %wt; (b) 40 %wt; (c) 50 %wt and (d) 60 %wt.

Fig 5.9 shows the nematic morphologies of 4,4'-azoxyanisole in the PVC dispersions with different LC concentrations. There tiny nematic 4,4'-azoxyanisole separated from the PVC matrix in Fig 5.9 (a). With the increasing of the LC concentration, the size of droplet increased. Fig. 5.9 (b) and (c) present the morphologies of the nematic droplets structures in the 40 %wt and 50 %wt PDLC, respectively. When the concentration arrived at 60 %wt, the size increased and some largest droplets (as shown in Fig 5.9 (d)) were obtained. The conclusion is that the LC droplet size was increased with the increasing LC concentration and that higher LC concentration can lead to bimodal distribution of droplet sizes, which is a disadvantage for commercial applications.
5.3.4 Liquid Crystal Solubility Limit in PDLC

Smith and co-workers (Smith 1993) have shown that the liquid crystal solubility limit, A, in the polymer matrix may be related to the ratio of the nematic isotropic enthalpy of the matrix, $\Delta H_{NI}(X)$, to that of the pure liquid crystal, $\Delta H_{NI}(LC)$, using:

$$\frac{\Delta H_{NI}(X)}{\Delta H_{NI}(LC)} = \frac{X - A}{1 - A}$$  \hspace{1cm} (5.3)

where $X$ is the weight fraction liquid crystal in the sample. So the fraction $\alpha$ of liquid crystal contained within the droplets is given by (as opposed to liquid crystal dissolved in the polymer).

$$\alpha = \frac{(X - A)}{X(1 - A)} \hspace{1cm} (X \geq A)$$  \hspace{1cm} (5.4)

$$\alpha = 0 \hspace{1cm} (X < A)$$  \hspace{1cm} (5.5)

Three assumptions are made in the derivation of these equations: (a) the liquid crystal dissolved in the polymer matrix did not contribute to the nematic-isotropic enthalpy and the phase-separated liquid crystal was contained wholly within droplets; (b) the amount of liquid crystal a given mass of the polymer matrix can dissolved is constant for $X \geq A$; (c) the presence of polymer in the liquid crystal droplets did not affect $\Delta H_{NI}$. As shown in Table 5.5, for the polymer-LC systems, the clearing temperature showed only a weak dependence on composition.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_m$ (°C)</th>
<th>$T_{NI}$ (°C)</th>
<th>$\Delta H_{NI}$ (J·g$^{-1}$)</th>
<th>A</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-(decyloxy)benzoic acid</td>
<td>Pure LC</td>
<td>96.3</td>
<td>141.2</td>
<td>5.08</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>PDLC</td>
<td>96.1</td>
<td>133.6</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>4,4'-azoxyanisole</td>
<td>Pure LC</td>
<td>119.1</td>
<td>133.7</td>
<td>1.99</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>PDLC</td>
<td>117.9</td>
<td>129.0</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>trans-4-methoxycinnamic acid</td>
<td>Pure LC</td>
<td>172.8</td>
<td>188.5</td>
<td>11.76</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>PDLC</td>
<td>173.0</td>
<td>188.3</td>
<td>1.81</td>
<td></td>
</tr>
</tbody>
</table>

Note that the values of $A$ determined from the data shown in Table 5.5 were slightly higher than the value reported in literature. However, these values are much higher than the typical values ranging from 10 to 20 measured for a thermally cured system. Table 5.5 shows the dependence of $\alpha$ on composition. The maximum value of $\alpha$ was
0.36 and observed for the 54 %wt 4-(decyloxy)benzoic acid mixture. The $\alpha$ values of 4,4'-azoxyanisole dispersion and trans-4-methoxycinnamic acid dispersion were 0.28 and 0.27, respectively. The smallest difference in polar solubility component between the trans-4-methoxycinnamic acid and the PMMA caused to the highest solubility limit (49) in the PMMA matrix and the smallest LC fraction.

The other phase transition enthalpy, $\Delta H_{CN}$ or $\Delta H_{SN}$, had been expected to be used to determine more reliable estimates of $A$ and $\alpha$. This expectation was not realized, however, because the endotherms, especially for lower concentration LC mixtures, for which the complete miscibility between the polymer matrix and LC was observed, were not sufficiently isolated from other endotherms to allow $\Delta H_{CN}$, or $\Delta H_{SN}$ to be determined accurately.

$T_{N-I}$ of PDLC shifted towards to lower temperatures compared to that of pure LC. This can be explained by Clausius-Clapeyron equation (Poniewierski and Sluckin 1987; Poniewierski and Sluckin 2006):

$$\frac{dT_{N-I}}{dD} = \frac{2}{D^2} \frac{(\gamma_N - \gamma_I)}{L} T_{N-I}(D)$$

(5.5)

In which D is the thickness of the film, $\gamma_N$ and $\gamma_I$ the surface tension of the nematic and isotropic phase relative to the substrate and L the latent heat of the N-I transition. From the Eq. 5.5, if the amounts to setting ($\gamma_N - \gamma_I > 0$), which means that the isotropic phase wets the solid surface more than the nematic phase, the $T_{N-I}$ of pure LC will be higher than the $T_{N-I}$ of PDLC. On the contrary, it could happen that a solid substrate promotes local nematic ordering in the isotropic phase which amounts to setting ($\gamma_N - \gamma_I < 0$) but which is only be observed for mica surfaces in lyotropic nematics. The nematic phase may then form above $T_{N-I}$ for thin enough films. This is the so-called capillary condensation.

### 5.4 Conclusion

The difference in solubility parameter between mesogen and polymer has been a useful parameter for predicting good dispersion. It provides a convenient approach to obtain the most uniform LC dispersion in a polymer matrix. That LC dispersion that
can be improved by selecting the most suitable polymer and solvent is proposed to be used for designing PDLC films and controlling the morphology of mesogen droplets in PDLC. The degree of phase separation in different PDLC systems using the melting, S-N phase transition and clearing enthalpies associated with the liquid-crystal component was investigated. Unfortunately, the melting enthalpy was not suited to this task because of complex sequences of solid transitions. The different mesophases are expected to be obtained in PDLC films when LC exhibits different mesophases between melting temperature and isotropization temperature.

The melting temperatures of the PDLC were lower due to the dispersion effects of polymer in the LC droplets. And the isotropic to nematic transitions of the three PDLCs were shifted towards to lower temperatures because the isotropic phase wets the solid surface more than the nematic phase.

The main factors controlling the morphologies generated were the initial liquid crystal concentration in PDLCs and the cooling rate. Cooling at a fast rate led to the generation of small nematic droplets with a narrow size distribution. Slow cooling rates led to a bimodal particle size distribution with a large extent of coalescence of the droplets first generated and nucleation of new generations of droplets in a medium of increasing viscosity. The use of fast cooling rate might be important for the generation of a narrow size-distribution of nematic droplets in PDLC to be used in electro-optical devices.

The total solubility parameter was used to evaluate matching a polymer-LC-solvent pair. However, the polar component of the solubility parameter is most important in predicting the solubility limit in a polymer matrix and the LC fraction in the droplets, while the other components, dispersive and hydrogen bonding were not critical.
Chapter 6 Thermodynamic and Kinetic Processes in PDLC Phase Changes

6.1 Introduction

In PDLC films formed by solvent induced phase separation (SIPS) followed by a thermal treatment for controlling the size of the droplets, the initial system consists of a solution of liquid crystal, solvent, polymer. A single phase is stable at high temperatures. Miscibility decreases with decreasing temperature, and phase separation can occur in the mixture at low temperatures. The temperature at which phase separation is allowed depends on the relative concentration of the liquid crystal and polymer solution, as well as on the relative solubility of the two components of the PDLC. At the extremes of concentration, the two components may be completely miscible and not phase separate upon forming the temperature.

Once phase separation occurring, the two phases do not simply separate into a pure liquid crystal phase and a pure polymer phase. Rather, the mixture separates into a liquid crystal-rich phase and a liquid crystal-poor phase. Phase diagrams for LC-polymer solutions have been mapped using optical and calorimetric means. West presented the first such diagram, using light scattering (turbidity) to determine the phase diagram of the liquid crystal E7 mixed with the reactants in an epoxy-type PIPS system. Hirai et al. (Hirai, Mitchell et al. 1990) examined the phase separation of the LC E8 and several different acrylate monomers and oligomers. Smith has used alorimetry to determine the phase diagram of the LC E7 with thiolene system NOA-65 (Smith 1990).

The solvent-induced phase separation followed by thermal-induced phase separation in the 4-(octyloxy)benzoic acid dispersion in pHEMA, particularly the several transitions that occur within the system, will be discussed in this chapter. The influence of the polymer on the Crystalline to Smectic (C-S), Smectic to Nematic (S-N) and Nematic to Isotropic (N-I) is investigated by DSC, TMDSC and quasi-isothermal TMDSC. TMDSC will be used to analysis the thermodynamic and kinetic events.
Chapter 6 Thermodynamic and Kinetic Processes in PDLC Phase Changes

6.2 Experimental

6.2.1 Materials

The liquid crystal material chosen for this study was 4-(octyloxy)benzoic acid obtained from Sigma-Aldrich (impurities < 2%). It is a typical, small-molecule liquid crystal with two mesogen phases, smectic (S) and nematic (N) and shows a two crystallization structures. Poly(2-hydroxyethyl methacrylate) (pHEMA) \((M_w = \text{20,000 g·mol}^{-1})\) and tetrahydrofuran (THF) from Sigma-Aldrich Australia were used without further purity.

6.2.2 Preparation of PDLC Film

The 4-(octyloxy)benzoic acid dispersion in pHEMA was prepared as the methods mentioned in Chapter 3. Two PDLC films of the same composition were prepared independently, to check for the reproducibility of the results.

6.2.3 Measurements

The transition temperatures were measured by a Perkin-Elmer power-compensation DSC (Pyris 1) with a saw-tooth modulation using the Perkin-Elmer DDSC software. The TMDSC and quasi-isothermal programs were carried out as described in Chapter 3.

6.3 Results and Discussion

6.3.1 Analysis of the Phase Transitions of 4-(octyloxy)benzoic Acid and Its PDLC

The phase transitions of 4-(octyloxy)benzoic acid were shown in Chapter 4 Fig. 4.2 for heating. The pure 4-(octyloxy)benzoic acid shows two crystalline forms before the melting temperature 101 °C. During heating, the crystalline structure changes at about 73 °C. A smectic (S) phase appears in the narrow temperature range of 7 °C until it
changes to nematic (N) phase at 107 °C. When the temperature reaches about 143 °C, the molecules lose order and the liquid becomes isotropic.

Figure 6.1 The phase transitions of pHEMA dispersed 4-(octyloxy)benzoic acid by DSC and TMDSC, heating rate for DSC, 10 °C\cdot\text{min}^{-1} (—); for TMDSC, \( A_T = 0.375 \, ^\circ\text{C} \), \( p = 120 \, \text{s} \), \( \beta_0 = 0.25 \, ^\circ\text{C}\cdot\text{min}^{-1} \) (—).

Figure 6.2 Diffractograms of pHEMA dispersed 4-(octyloxy)benzoic acid at (a) 103.0 °C and (b) 125.0 °C.
Fig. 6.1 presents the phase transitions of pHEMA dispersed 4-(octyloxy)benzoic acid measured by DSC and TMDSC. For DSC, at a heating rate of 10 °C min⁻¹, only four phases are observed as shown by the dark line. Compared with the pure LC, the smectic (S) phase is not formed during the DSC scanning, which is probably because the fast heating rate did not allow sufficient time for LC orientation during the narrow smectic temperature range (only about 7 °C). The phase transition temperatures of PDLC are almost as same as that of the pure LC as shown in Fig. 6.1, which are shifted about 1 °C to higher temperature, except $T_{N-I}$. The isotropic temperature of PDLC is about 138.4 °C, about 4.6 °C lower than that of the LC. The enthalpies of PDLC, decrease to nearly half of those of the pure LC since the 4-(octyloxy)benzoic acid concentration in the PDLC mixtures was only 53%. The enthalpy of crystallization to smectic transition of 4-(octyloxy)benzoic acid is 43.3 J g⁻¹ but that of pHEMA dispersed 4-(octyloxy)benzoic acid is only 26.0 J g⁻¹.

The phase transition temperatures measured by TMDSC shifted 2 °C to lower temperature, presented in Fig. 6.1 (solid line), which is caused by the lower underlying heating rate (0.25 °C min⁻¹) compared with 10 °C min⁻¹ for DSC. But the clearing temperature (144.5 °C) was higher than that measured by DSC. Meanwhile, the enthalpies of phase transitions increase due to sufficient time for the LC droplets to separate from the polymer matrix.

Fig 6.2 presents the PDLC’s WAXD results at 103.0 °C and 125.0 °C, respectively. The peak (Fig. 6.2 (a)) at $2\theta = 4^\circ$ was caused by the smectic layer structure. This layer structure disappeared with the increase of the temperature and the LC formed to another mesophase, nematic. As seen in Fig 6.2 (b), there was no significant peak could be observed at around $4^\circ$. 

6.3.2 Analysis of the C→S Transition

![Graph showing the crystallization to smectic (C-S) phase transition diagram of 4-(octyloxy)benzoic acid by TMDSC, AT = 0.375 °C, p = 120 s, β = 0.25 °C·min⁻¹; total heat capacity (—); storage heat capacity (→); non-reversing heat capacity (←); loss heat capacity (→).](image)

Figure 6.3 The crystallization to smectic (C-S) phase transition diagram of 4-(octyloxy)benzoic acid by TMDSC, AT = 0.375 °C, p = 120 s, β = 0.25 °C·min⁻¹; total heat capacity (—); storage heat capacity (→); non-reversing heat capacity (←); loss heat capacity (→).

The crystallization to smectic (C-S) phase transition of the LC, measured by TMDSC, is illustrated in Fig. 6.3. The total heat capacity curve (solid line) shows that the change from steady state before melting starts at 98.0 °C, the melting peak appears at 99.9 °C, and the return to the baseline from melting occurs at 101.5 °C. The enthalpy of the whole melting process is 77.2 J·g⁻¹. The same details for the melting transition are presented by the storage heat capacity curve (solid line with filled square markers); furthermore, it reveals that the enthalpy in the storage heat capacity curve is 23.0 J·g⁻¹. As melting proceeds, in any one “heat-cool” modulated cycle there is a rise in temperature causing further melting to occur, accompanied by both the heat capacity and the latent heat of fusion, followed by a fall in temperature allowing some recrystallisation to occur, itself accompanied by the heat capacity associated with the temperature reduction as well as any heat of crystallisation. The heat of fusion and...
crystallisation thus contribute to the amplitude of the heat flow modulation, appearing in the reversible heat capacities. Since not all the molecules recrystallise when the temperature was decreased in a modulated cycle, this part remained in the melting stage contribution to the non-reversing curve, as shown in Fig. 6.3 (solid line with square markers). The loss heat capacity curve (solid line with filled triangle markers) describes the out-of-phase component with respect to the heating rate and is determined by the phase angle. The melting peak in the loss specific is at 99.5 °C, near to that of the total and storage curves (99.9 °C), with $\Delta H = 11.3 \text{ J} \cdot \text{g}^{-1}$.

Fig. 6.4 gives the C-S phase transition of pHEMA dispersed 4-(octyloxy)benzoic acid by the heat-cool TMDSC and quasi-isothermal TMDSC. The transition peak shifts to a low temperature due to the effect of the polymer dispersion.
Chapter 6 Thermodynamic and Kinetic Processes in PDLC Phase Changes

The total heat capacity curve at 0.25 °C·min⁻¹ is displayed in the top of Fig. 6.4 (solid line). It depicts that the heat capacity of the mixtures gradually increase on approaching the transition temperature from the low-temperature side. A small shoulder that may be considered a pre-transition effect starts at about 98.6 °C. Close to the onset measured with traditional DSC (99.1 °C) a large jump occurs in the total heat capacity curve with ΔH = 14.3 J·g⁻¹, which is much smaller than that of pure LC because of the small concentration of LC in the mixtures and even smaller fraction of LC being able to be separated from the polymer matrix.

Taking the beginning of the transition at the increase in gradient of the heat capacity at 98.5 °C and at the end at 99.5 °C, as suggested by Fig. 6.3, the actual transition has a temperature range of about 1 °C, which is much narrower than that measured by DSC from 98.9 °C to 102.4 °C (in Fig.6.1) (about 3.5 °C). The storage heat capacity curve (solid line with filled square markers) illustrates the same peak position as does the total heat capacity curve. However, the enthalpy decreases to 11.5 J·g⁻¹.

The quasi-isothermal results (squares) give more detail about the melting process. The melting begins at 98.5 °C, the peak endotherm appears at 99.1 °C and the melting is completed at 99.5 °C. The results reveal that true reversibility during the process is even smaller than suggested by the storage heat capacity curve. There are two endothermal peaks in the loss heat capacity curve (solid line with filled triangle markers). The first small endotherm appears at 98.5 °C with a ΔH of 0.2 J·g⁻¹ and the main endothermic is at 99.1 °C with a ΔH of 1.3 J·g⁻¹. Integration of the total heat flow over the entire temperature range gives an out-of-phase endothermic response of 1.5 J·g⁻¹, which is much smaller than for the pure LC (11.3 J·g⁻¹).
6.3.3 Analysis of the S→N Transition

Figure 6.5 The smectic to nematic (S-N) phase transition diagram of 4-(octyloxy)benzoic acid by TMDSC, \( A_T = 0.375 \, ^\circ\text{C}, p = 120 \, \text{s}, \beta_0 = 0.25 \, ^\circ\text{C} \cdot \text{min}^{-1} \); total heat capacity (—); storage heat capacity (—-); non-reversing heat capacity (—-); loss heat capacity (—).

Fig. 6.5 illustrates the smectic to nematic mesophase transition in 4-(octyloxy)benzoic acid measured by TMDSC. The total heat capacity curve, presented by the solid line, shows an S→N peak at 105.7 \(^\circ\text{C}\) following a small exothermal peak at around 104.0 \(^\circ\text{C}\). The total enthalpies needed in this transition were 4.7 J·g\(^{-1}\). The reversing heat capacity curve contained the same trends as the total curve with an insignificant exothermal peak before the main peak. The transition temperature in the reversing was 105.6 \(^\circ\text{C}\) with an enthalpy of 4.1 J·g\(^{-1}\). A loss heat capacity curve, solid line with triangle markers in Fig. 6.5, was obtained in addition. The main peak appeared at 105.6 \(^\circ\text{C}\), followed by an upside down peak at 106.0 \(^\circ\text{C}\). A non-reversing heat capacity curve was calculated by subtracting the reversing part from the total curve. As
shown by the solid line with unfilled square markers in the Fig. 6.5, there was no obvious change in the non-reversing curve, which indicates that the smectic to nematic transition is a reversible phase transition. The quasi-isothermal TMDSC was utilized to investigate the S→N transition. The sharp transition peak happened at 104.2 °C in agreement with the exothermal peaks in total and reversing curves. It indicates the real transition range was only 1 °C, commencing from 104.0 °C and finishing at 105.0 °C.

Figure 6.6 provides the details of the S→N transition in pHEMA dispersed 4-(octyloxy)benzoic acid. The transition temperature shown in the total heat capacity curve was 105.4 °C with a small exothermal peak followed by a main endothermal peak. The enthalpy needed in the exothermal peak was 0.6 J·g⁻¹ and the enthalpy for
the endothermal peak was 4.1 J·g⁻¹. The peak temperature was shifted 0.2 °C to the lower temperature and the endothermic response decreased by 1.2 J·g⁻¹, compared with the results of the pure LC. The reversing heat capacity curve, the solid line with filled square markers, presents the transition temperature was 105.8 °C and the enthalpy change in the mesophase transition was 3.5 J·g⁻¹. There was no significant change in the loss heat capacity, as presented by the bottom line in Fig. 6.6, which illustrated that the measurements were completely kept in the phase. However, there was a double-peak curve appeared in the non-reversing signal. The first small peak appeared at 104.5 °C, followed by other sharp peak at 105.8 °C. In order to confirm the results from the TMDSC, a quasi-isothermal TMDSC measurement was run. The result was presented by the square markers. There was only one sharp peak at 105.6 °C in the quasi-isothermal curve. The real transition range measured by the quasi-isothermal TMDSC was much narrower than that shown by the total and reversing heat capacities curves.
6.3.4 Analysis of the N→I Transition

Figure 6.7 The nematic to isotropic (N-I) phase transition diagram of 4-(octyloxy)benzoic acid by DSC and TMDSC, heating rate for DSC, 2 °C·min⁻¹ (-----); for TMDSC, A_T = 0.375 °C, p = 120 s, β₀ = 0.2 °C·min⁻¹; total heat capacity (——); storage heat capacity (------); non-reversing heat capacity (-----); loss heat capacity (-----), quasi-isothermal measurements (■) with A_T = 0.1 °C, β₀ = 0, and ΔT₀ = 0.2 °C.

The DSC curve at 2 °C·min⁻¹ for the pure LC from nematic to isotropic (N-I) is given in the top of Fig. 6.7 (dark solid line). There are two peaks in the entire transition temperature range probably due to the LC showing two different nematic forms. The first peak appears at 143.1 °C with an enthalpy of 2.7 J·g⁻¹, followed by the second peak at 146.3 °C with an enthalpy of 1.8 J·g⁻¹. So the total heat flow over the entire temperature range gives an endothermic response of 4.5 J·g⁻¹.

The results for scanning and quasi-isothermal TMDSC measurements are plotted in Fig. 6.7. The curve trends from TMDSC are similar to the DSC curve. The total heat capacity curve (solid line) has a similar trend to the DSC curve but the peaks in the heat capacity curve seem to be narrower though the positions of the peaks are almost
in agreement with that determined from the DSC, 143.1 °C having ΔH of 1.6 J·g⁻¹ and 146.1 °C having ΔH of 1.6 J·g⁻¹, respectively.

The data for the storage heat capacity is presented by the solid line with filled square markers; illustrating most of the change is reversible during the clearing process. The peaks are shifted about 1 °C to lower temperature, with total enthalpy of 3.5 J·g⁻¹, which is more than that in the total heat capacity curve but nearly 1.0 J·g⁻¹ less than that determined by the DSC.

More details about the reversible information are presented by the results for quasi-isothermal TMDSC (squares in Fig.6.7). Only one endothermic peak appears at 143.1 °C in the curve of quasi-isothermal TMDSC. This reveals that probably only one nematic form is partly reversing but the other form is totally non-reversing. The positions of the peaks in the loss heat capacity are in agreement with those in the storage heat capacity, with a ΔH of 0.9 J·g⁻¹ and 0.3 J·g⁻¹, respectively. There are two peaks in the non-reversing heat capacity curve (solid line with square markers), which is maybe due to the N-I transition being insensitive to the experimental temperature modulation.
Figure 6.8 depicts the phase diagram of pHEMA dispersed 4-(octyloxy)benzoic acid from nematic to isotropic (N-I), measured by DSC and TMDSC. The endothermic peak is at 140.5 °C with an enthalpy of 3.72 J·g⁻¹, which is lower than that of the pure LC, revealed by standard DSC at a heating rate of 2 °C·min⁻¹ (presented by the dark solid line in Fig. 6.8). The transition temperature range is from 136.3 °C to 143.6 °C. The decrease of the T_{N-I} was because the isotropic phase wetted the solid surface more than the nematic phase.

The details of N-I transition are revealed by TMDSC. The heat capacity of the mixtures gradually increases on approaching the transition temperature (137.5 °C). The curves reach a peak at about 140.5 °C. However, the complex heat capacity curve (solid line) has a higher enthalpy which is approximately 1 J·g⁻¹ higher compared with that of the storage heat capacity curve (3.07 J·g⁻¹) (solid line with filled square markers). The quasi-isothermal results (squares) present the same trend with a larger
jump occurring at 140.5 °C, as expected for a sharp first-order transition. The actual transition temperature range estimated from the quasi-isothermal TMDSC is much narrower. Its width is merely 3 °C. The loss heat capacity curve (solid line with filled triangle markers) indicates the out-of-phase contribution during the N-I transition. A smaller endothermic peak appears at 137.5 °C before the main endotherm, which is probably because the existence of the polymer inhibits the mesogens from transferring from the nematic to the isotropic state and causes the transition temperature out of the modulation temperatures of the TMDSC.

6.4. Conclusion

C-S, S-N and N-I equilibrium transitions of a low molar mass 4-(octyloxy)benzoic acid and its pHEMA dispersions were measured by DSC, TMDSC and quasi-isothermal TMDSC. The two approaches namely reversing/non-reversing and complex heat capacity are used to discuss the phase transition diagrams. The C-S and N-I transition temperatures of the PDLC were shifted to a lower temperature and the enthalpies decreased compared with those of the pure LC due to the effects of the polymer. However, the S-N transition temperature of the PDLC is almost as same as its pure LC and the enthalpies needed in this mesophase change decreased.

WAXD was utilized to classify the droplet mesophases in pHEMA dispersed 4-(octyloxy)benzoic acid in addition. The peak at about 2θ = 4° was caused by the smectic layer structure and this peak disappeared with the increase of the temperature because the LC lost the layer structure and changed from smectic to nematic.

TMDSC is a powerful thermal analysis technique with the capability of giving more information than conventional DSC. The modulation gives better precision in heat capacity and the loss heat capacity signal can contain important information on irreversible processes, such as slow chemical reactions and non-equilibrium phase transitions.
Chapter 7 Melting and Isotropization of 4,4’-azoxyanisole LC Dispersed in PVC

7.1 Introduction

The thermally-induced phase separation of poly(vinyl chloride) dispersed 4,4-azoxyanisole, particularly the several transitions that occur within the PDLC will be discussed in this chapter. The influence of the polymer on the N-I (nematic to isotropic) and N-C (nematic to crystalline) will be investigated by TMDSC. The morphology of the PDLC will be studied by polarized optical microscopy to assist with interpretation of the DSC measurements.

7.2 Experimental

7.2.1 Materials

4,4’-azoxyanisole was purchased from Sigma-Aldrich (impurities < 2%) and was used as received., was chosen for this study. The molecular structure of 4,4’-azoxyanisole is shown in Fig. 1 poly(vinyl chloride) (PVC) (M_w = 43,000 g·mol^{-1}) was purchased from Sigma-Aldrich and was used without further purification. Tetrahydrofuran (THF) was from Sigma-Aldrich and used as received.

7.2.2 Measurements

7.2.2.1 DSC and TMDSC

The transition temperatures were measured by a Perkin-Elmer power-compensation DSC (Pyris 1) with a saw-tooth modulation using the Perkin-Elmer DDSC software. The TMDSC and quasi-isothermal programs were carried out as described in Chapter 3.
7.2.2.2 Optical Microscopy

Optical observations were made with a Nikon Labophot 2 optical microscope equipped with a Mettler FP-82 hot stage and Mettler FP90 temperature programmer. PDLC films were heated to 135 ºC at 20 ºC·min\(^{-1}\) to form an isotropic film and then cooled at 0.5 ºC·min\(^{-1}\) to 110 ºC. The images were recorded using a Nikon Coolpix 5000 digital camera under polarized and transmitted light with a magnification of 100×.

7.2.3 Preparation of the PDLC Film

The preparation of PDLC films was made following a combination of solvent induced phase separation (SIPS) and thermally induced phase separation (TIPS). PVC and 4,4’-azoxyanisole (62.2 %wt of PVC) were dissolved in THF at room temperature. The solution was stirred for about 5 min. A small quantity of the solution was then cast on carefully cleaned glass substrates. The solvent was first evaporated slowly at room temperature for about 24 h and then under vacuum until the films were completely dried.
7.3 Results and Discussion

Figure 7.1 The thermal properties of 4,4′-azoxyanisole and its dispersed PVC by DSC, for LC (—); for PDLC (—).

Fig. 7.1 shows the DSC heating thermograms of 4,4′-azoxyanisole and its dispersion in PVC. The dark line presents the thermal properties of pure 4,4′-azoxyanisole during the process of disordering. Three distinct regions are clearly identified. The peak at 118.9 °C indicates the transition from crystallisation to nematic (C-N). It is apparent that the C-N is a sharp first-order transition followed by a weak first-order clearing peak, from nematic to isotropic (N-I) at 133.4 °C. Note that this temperature is in good agreement with the data in the literature (\(T_{C,N}=118.8\) °C, \(T_{N,I}=134.9\) °C). The slight difference in \(T_{C,N}\) may be due to the difference in the heating rate. For the PDLC film, two phase transitions of 4,4′-azoxyanisole were observed at 119.3 °C and 135.7 °C, respectively, as shown by the thin line. It is found that both the melting temperature and the clearing temperature shifted about 1 °C to a higher temperature.
The nematic range of PDLC increased by 2 °C. The enthalpy of crystallization to nematic in the PDLC is 88.3 J·g⁻¹, which was 12.8 J·g⁻¹ lower than that of the pure 4,4'-azoxyanisole. However, the enthalpy of the isotropic transition is only 1.6 J·g⁻¹, which is much lower than that of the enthalpy of 2.1 J·g⁻¹ for pure LC.

The peaks of the PDLC were sharper than those of the pure LC because the PVC dispersion divided the volume of the LC into small droplets. The transition temperatures shifted to a higher position because the rigid polymer matrix constrained the LC molecules.

As the temperature was further increased, 4,4'-azoxyanisole in PVC matrix softened. As a result, phase separation took place, leading to the formation of droplets. It is worth pointing out that the phase separation does not necessarily mean the formation of two phases with pure components. A fraction of LC molecules remained within the polymer matrix and in LC rich droplets remaining as part of the PVC. This incomplete phase separation can affect the thermal properties of the material. The transition temperatures and enthalpies were reduced. The 4,4'-azoxyanisole solubility limit, A, in the polymer matrix was calculated to be 52.6 % and the fraction $\alpha$ of the LC contained within the droplets was 0.33 %. These two values for this system were calculated from the enthalpies of isotropic transition of the LC and its PDLC, using the equations given by Smith and co-workers. $\Delta H_{CN}$ could not be used to determine A and $\alpha$ because the melting endotherm was not sufficiently isolated from other endotherms associated with crystal-crystal transitions or exotherms associated with cold crystallization to allow $\Delta H_{CN}$ to be determined accurately.
7.3.1 The C→N Transition

Figure 7.2 The C-N phase transition of 4,4’-azoxyanisole by TMDSC and quasi-isothermal TMDSC, for TMDSC, $A_T = 0.15 \, ^\circ C$, $\beta_0 = 0.1 \, ^\circ C\cdot min^{-1}$, $p = 120 \, s$, total heat capacity (—), reversing heat capacity ( ——), non-reversing heat capacity ( ——), loss heat capacity ( ——); for quasi-isothermal TMDSC (■), $A_T = 0.1 \, ^\circ C$, $\beta_0 = 0$ and $\Delta T_0 = 0.2 \, K$; phase angle ( ——).

Fig. 7.2 presents the crystallization to nematic phase transition of 4,4’-azoxyanisole measured by TMDSC and quasi-isothermal TMDSC. The total heat capacity curve shows that the change from steady state before melting started at 117.5 °C. The peak appeared at 118.6 °C which is only 0.2 °C different from the result in the literature and is more accurate compared with the result measured by DSC; and the return to the baseline was at 119.2 °C. The enthalpy of the entire melting was 80.0 J·g⁻¹. The same peak temperature is illustrated by the reversing heat capacity curve (solid line with filled diamond markers). The enthalpy of the reversing endotherm was 60.4 J·g⁻¹ and 75 % of LC among the dispersed system was reversing. Some crystals melted when the program temperature increased and then recrystallised when the temperature was
decreased in “heat-cool” modulated temperature cycle. The heat of fusion and crystallisation thus contributed to the amplitude of the heat flow modulation, appearing in the reversing heat capacity curve. A proportion could not recrystallise when the temperature decreased, so this part remained in the melted stage contribution to the non-reversing curve, as shown in Fig. 7.2 (solid line with diamond markers). There was a small shoulder at 118.0 ºC before the main transition peak of 118.9 ºC, which is considered to be a pre-melting effect. The loss heat capacity curve (solid line with filled triangle markers) represents the out-of-phase component with respect to the heating rate and is determined by the phase angle. Two peaks appeared in the loss curve. The first peak appeared at 118.1 ºC, followed by the second peak at 118.9 ºC; the total enthalpy during melting was 13.0 J·g⁻¹. The quasi-isothermal curve (filled square markers) shows the thermal properties of the melting measured by quasi-isothermal TMDSC. It describes the detail of the 4,4’-azoxyanisole melting process. The actual transition range was only 1 ºC from 117.8 ºC to 118.8 ºC, much narrower than that measured by standard TMDSC.

As shown in Fig. 7.2 dark solid line, the phase angle curve followed the trend of the loss heat capacity curve. There was a small peak followed a significant change, near 1 rad, at around 119.0 ºC. The value changes of the phase angles described the kinetically controlled processes became larger between the LC and the reference with the proceeding of the order-disorder transition, caused by the components in the loss heat capacity curve.
The melting processes of 4,4'-azoxyanisole dispersed PVC are revealed in Fig. 7.3. Compared with the result measured by DSC, the transition peaks of PDLC in Fig. 7.3 are the same as those of LCs and close to the literature result. This is due to the much slower heating rate providing sufficient time for the LC droplets to separate from the polymer matrix and form the nematic phase. The C-N transition temperature is at 118.5 °C with ΔH = 79.2 J·g⁻¹, displayed by the total heat capacity curve. The reversing curve (solid line with diamond markers) depicts that the heat capacity gradually increased on approaching the transition temperature from the low-temperature side and a jump occurred at 118.4 °C with an enthalpy of 35.0 J·g⁻¹. Part of the LC was dissolved in the polymer matrix causing only 44 % reversible component. Most of the LC could not be recrystallised with decreasing of the modulation temperature. This part contributed to the non-reversing heat capacity curve.
Chapter 7 Melting and Isotropization of 4,4’-azoxyanisole LC Dispersed in PVC

(solid line with unfilled square markers). A sharp peak occurred at 118.4 °C in the non-reversing curve, as expected for the melting process. The loss heat capacity curve (solid line with filled triangle markers) had the same trend as the reversible curve but it was broader. The quasi-isothermal measurement (filled square markers) is much narrower than the reversible heat capacity of the standard TMDSC in the same figure. The main reason for this peak narrowing is the smaller modulation amplitude (A=0.1 K). The breadth of the melting was 0.9 °C (from 118.0 °C to 118.9 °C) measured by the quasi-isothermal TMDSC. Only one main peak appeared in the phase angle curve presented by the dark solid line in Fig. 7.3. The maximum angle was 0.9 rad, smaller than its pure LC indicating kinetic processes were less significant within the droplets than in the pure LC.
Figure 7. 4 Lissajous figures for eight quasi-isothermal TMDSC scans of 4,4'-azoxyanisole (from a to d) and its dispersed PVC (from e to h) at 117 °C, 118 °C, 119 °C and 120 °C different temperatures; the complete 20 min scans are displayed.
Fig. 7.4 illustrates the Lissajous figures of the heat flow rate versus temperatures for 4,4’-azoxyanisole and its dispersion in PVC at temperatures of 117 ºC, 118 ºC, 119 ºC and 120 ºC, respectively. The small deviation from true ellipses indicates the modulation cycle, but is otherwise largely reversible with increase of temperature. It is interesting to notice that, in Fig. 7.4 (f) and (g) sets of Lissajous figures, the initial large deviation from the ellipse, due to the contribution from the latent heat of the sharp transition, disappeared with increase of temperature. A new ellipsoid was reformed, indicating that the system seems to reach a new steady state where the LC remains in a nematic state.
7.3.2 The N→I Transition

![Graph showing heat capacity vs temperature for the N→I transition of 4,4'-azoxyanisole.]

The N-I transition is revealed by TMDSC. Fig. 7.5 depicts, with the quasi-isothermal results (filled squares), that the heat capacity of the 4,4'-azoxyanisole gradually increased on approaching the transition temperature from the low-temperature side. A large jump occurred at 134.6 °C, with an enthalpy of 1.5 J·g⁻¹, in the total heat capacity, reversing heat capacity and the quasi-isothermal heat capacity, as expected for a sharp first-order transition. The peak area of the reversing heat capacity (15.5 J·g⁻¹) is in an agreement with that determined from the total heat capacity (15.8 J·g⁻¹) but the high value of the baseline (4.8 J·g⁻¹·K⁻¹) in $C_p$ (solid line with filled diamond markers, the top curve in Fig. 7.5) causes a higher peak than that of the total heat capacity (represented by the solid line in Fig. 7.5), whose steady-state value started...
Chapter 7 Melting and Isotropization of 4,4’-azoxyanisole LC Dispersed in PVC

from 4.3 J·g⁻¹·K⁻¹ the same as the quasi-isothermal baseline value. That there was no significant change in the non-reversing heat capacity (solid line with unfilled square markers in Fig. 7.5) suggested that isotropization of the 4,4’-azoxyanisole was reversible and without need of nucleation. The transition occurs at the same temperature on cooling and heating. The DSC results (Table 7.1) confirmed that the isotropization of 4,4’-azoxyanisole is a non-nucleation process.

Table 7.1 The thermal properties of 4,4’-azoxyanisole in N→I transition by DSC (10 °C·min⁻¹).

<table>
<thead>
<tr>
<th>Process</th>
<th>Peak /°C</th>
<th>ΔH /J·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating</td>
<td>133.5</td>
<td>2.13</td>
</tr>
<tr>
<td>Cooling</td>
<td>133.2</td>
<td>-2.12</td>
</tr>
</tbody>
</table>

There was a small peak appearing in the phase angle curve in Fig. 7.5, which represented the thermal delay in the disorder process. The thermal lag caused to the out-phase components (solid line with filled triangle markers) with a peak at 134.4 °C and an enthalpy of 0.7 J·g⁻¹. The reason that the maximum value of the phase angle 0.3 rad is much smaller than that in the C-N transition is probably because it is easier for the heat transmission from the ordered-liquid state to the disordered-liquid state than from the crystallization to the N state.
The isotropization of 4,4'-azoxyanisole dispersed PVC measured by TMDSC and quasi-isothermal TMDSC is illustrated in Fig. 7.6. The peaks shifted about 0.5 °C to the lower temperature compared with those of the pure LC. The transition temperature in the total heat capacity was 134.1 °C with $\Delta H = 0.48$ J·g$^{-1}$. The reversing heat capacity had the same peak position with an enthalpy of 0.34 J·g$^{-1}$. Nearly 90 % among the PDLC was reversible during the disorder process. The remaining non-reversible part contributed to the non-reversible heat capacity (solid line with square markers). The value of the reversible component is 0.8 % lower than that in the pure LC (98 %). This may be because PVC dispersed in the LC droplets assisted the isotropic liquid to reform to the N state. The maximum value (0.39 rad) in phase angle (dark solid line in the bottom of Fig. 7.6) was 0.17 rad higher than that in the pure 4,4'-azoxyanisole (0.22 rad as shown in Fig. 7.5). The larger kinetic was because of
the dispersion of PVC potentially increasing viscosity and causing some diffusion control. The larger kinetic component caused a significant peak in the loss heat capacity (solid line with filled triangle markers). The transition temperature range of the PDLC was 0.6 °C, estimated from the quasi-isothermal TMDSC, which is 0.1 °C narrower than that of the pure LC.
Figure 7.7 Lissajous figures for six quasi-isothermal TMDSC runs of 4,4′-azoxyanisole (from a to c) and its dispersed PVC (from d to f) at different temperatures during the isotropization.

The occurrence of the N-I transition of 4,4′-azoxyanisole and its dispersion in PVC by quasi-isothermal TMDSC can be illustrated more clearly in the time domain using Lissajous figures, as shown in Fig. 7.7. The figures are the complete scans including the approach to steady state. The left column presents the process of the pure LC
during the isotropization. The right column presents the N-I transition of the PDLC. In the b and e sets of Lissajous curves in Fig. 7.7, the initial large deviation from the ellipse, due to the sharp transition, disappears with time. Then the new ellipsoid-like Lissajous curves (c and f) were re-formed, indicating that both the LC and the PDLC seem to reach a new steady state.
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7.3.3 Morphologies

Figure 7. 8 Evolution of morphologies generated by cooling PVC dispersed 4,4'-azoxyanisole with 62.2 %wt LC at the rate of 0.5 °C·min⁻¹ by polarized optical microscope (×100); (a) 134.5 °C, (b) 134.3 °C, (c) 134.1 °C, (d) 133.9 °C, (e) 133.5 °C and (f) 133.3 °C.

The morphologies of the PVC dispersed 4,4'-azoxyanisole on cooling are presented in Fig. 7.8. The nematic droplets generated and separated from the isotropic phase at 134.5 °C (Fig. 7.8(a)). The initial droplets grew and a new generation of particles was observed with temperature decrease, shown in Fig. 7.8(b). As the temperature was
further decreased, the new nematic droplets formed and covered the whole screen (Fig. 7.9(c) and (d)). When temperature arrived at 133.5 °C, the LC droplets completely separated from the polymer matrix and formed into nematic phase, as shown in Fig. 7.8 (e). Fig. 7.8(f) shows the morphology of the PDLC after nematic phase completely forming.

![Experimental](image1)

(a) Experimental

![Theoretical](image2)

(b) Theoretical

**Figure 7.9** (a) Polarizing micrograph of the PDLC film at 133.5 °C (×100); (b) corresponding birefringence patterns of a bipolar nematic droplet with different orientations of droplet axis.

Theoretical studies indicate that the director configuration of nematic droplets in a polymer matrix can be self-organised in four types, bipolar, axial, radial and equatorial. The different extinction patterns of nematic droplets were detected by polarized optical microscopy. The experimental photographs of the PDLC are presented in Fig. 7.9. The four type patterns from the PDLC with a united orientation of droplet axes were illustrated by the POM. The experimental graphs confirmed that the nematic droplets in the PDLC films show different orientations without external electric field. So the different extinction patterns given here correspond not to different internal structures, but to different orientations of the droplet axes with the same bipolar director configuration.
7.4 Conclusion

The melting and isotropization transitions of the low molar mass 4,4’-azoxyanisole and its dispersion in PVC were investigated by DSC, TMDSC and quasi-isothermal TMDSC. The C-N transitions of 4,4’-azoxyanisole and its dispersion in PVC are typical irreversible first-order transitions. Both the pure LC and the PDLC have shown a significant non-reversing heat capacity peak and a larger phase lag. In contrast to the melting process, the N-I transition is a reversible first-order transition without superheating effect. The PVC dispersion in the 4,4’-azoxyanisole caused a decrease of the phase transition breadth and the enthalpy required in the phase changes. Four different self-organized extinction patterns were found in the 4,4’-azoxyanisole dispersed PVC film caused by the different orientations of droplet axes but not the different internal structures.
Chapter 8 Conclusions and Future Research

8.1 Conclusions

The phase transition temperatures and mesophase morphologies of four low molar mass LCs, 4-(octyloxy)benzoic acid, 4-(decyloxy)benzoic acid, 4,4’-azoxyanisole and trans-4- methoxycinnamic acid, were investigated by DSC and POM. Supercooling/heating effects on the four mesogens were considered. However, for the clearing transition of LCs, there was no significant shifting between cooling and heating, which was in agreement with the theory that LC clearing transition is a weak first-order transition and does not involve nucleation during the transition. And the mesophase transition, like the S-N transition, was not affected by the cooling/heating because it is a second-order transition. On the contrary, the other transitions, such as the different crystallization transitions occurred in the two 4-alkoxybenzoic acids and the crystallization to mesophase transition shifted to a lower temperature in cooling scanning compared with the results in heating scanning. The carboxylic acid termini of trans-4-methoxycinnamic acid gave rise to very strong intermolecular attractions which cause it to have high melting temperature and clearing temperature despite its having the smallest molar mass among the four mesogens.

The mesophases of 4-(octyloxy)benzoic acid were investigated by WAXD. The mesophases were classified from the difference between d space and the length of the molecule during the transition process. During the heating, a SmC₂ structure was ordered first and then with increase of the temperature, mesogen disorder increased and another smectic phase was formed with, a head-to-head bilayer, SmA₂, before it formed a less ordered mesophase, the nematic mesophase. X-ray diffraction is a useful tool for characterization and mesophase identification and it can give more detailed information about the molecular organization of the liquid crystal phase.

The solubility parameters of the materials were calculated by the method of Hoy and the method of Hoftyzer-Van Krevelen. The final results were decided as the average
of the two methods. The LC-polymer-solvent combinations were matched by choosing the smallest difference of their solubility parameters. The total solubility parameter was considered when matching the polymer-LC-solvent combinations. Because the smallest difference in polar solubility component between the trans-4-methoxycinnamic acid and the PMMA caused to the highest solubility limit (49) in the PMMA matrix and the smallest LC fraction, therefore, the polar component of the solubility parameter is most important in predicting the solubility limit in a polymer matrix and the LC fraction in the droplets, while the other components, dispersive and hydrogen bonding were not critical. The PDLCs were prepared by SIPS and the structures were controlled by the TIPS process.

The thermal properties of the PDLCs were investigated by DSC. The $\Delta H_{N-I}$ was used to calculate the LC fractions in the droplets among the PDLC matrix. The other enthalpies, such as the melting enthalpy and S-N enthalpy, were intended to be used for the calculation of the LC fraction; however, this was not achieved because complex sequences of solid transitions prevented their accurate determination. The transition temperatures of the PDLCs were lower than their pure LCs due to the polymer dispersion effect in the LC droplets. The isotropic to nematic transition of the PDLCs were shifted towards lower temperature because the isotropic phase wetted the solid surface more than the nematic despite the dispersion effect.

The morphologies of the PDLCs were investigated by POM. Different mesophases were expected to be obtained in PDLC films when LC exhibited different mesophases between melting temperature and isotropization temperature. The cooling rate and LC concentration effects on the morphology were investigated in the PVC dispersed 4,4’-azoxyanisole PDLC system. Faster cooling rate and the lower LC concentrations lead to a small LC droplet size and a narrow size distribution, which is preferred for commercial purposes.

DSC, TMDSC and quasi-isothermal TMDSC were used to investigate the thermal properties in both pHEMA dispersed 4-(octyloxy)benzoic acid and PVC dispersed 4,4’-azoxyanisole. Two approaches, namely reversing/non-reversing and complex heat capacity, were used to discuss the phase transition diagrams.
The C-S, S-N and N-I equilibrium transitions of a low molar mass 4-(octyloxy)benzoic acid and its pHEMA dispersions were measured. The $T_{C-S}$ and $T_{N-I}$ were shifted to a lower temperature compared with those of the pure LC due to the dispersion effect of the polymer. However, $T_{S-N}$ was not affected, which might be because it was a second-order transition and did not require nucleation. However, the enthalpies involved in all the phase transitions, no matter C-S, S-N or N-I, were decreased due to the lower amount of LC in the droplets. There were no significant peaks observed in loss heat capacity of both pure LC and its PDLC in S-N and N-I transition, which proved that these two transitions were reversing transitions, on the contrary, there was an obvious endothermic peak appeared during C-S transition that confirmed that the C-S transition was a non-reversing transition. The non-reversing heat capacity was calculated from the total minus storage heat capacity and illustrated similar results to the loss heat capacity curves. The quasi-isothermal results showed the accurate transition temperatures and the enthalpies required in the reversing parts of the transitions. The quasi-isothermal TMDSC determined the accurate phase transition temperatures and the enthalpies involved in the reversing part of transition processes. It presented the actual phase transition ranges, which were narrower than the results measured by DSC and TMDSC.

WAXD was utilized to classify the droplet mesophases in pHEMA dispersed 4-(octyloxy)benzoic acid in addition. The peak at about $2\theta = 4^\circ$ was caused by the smectic layer structure and this peak disappeared with the increase of the temperature because the LC lost the layer structure and changed from smectic to nematic.

The melting and isotropization transitions of the low molar mass 4,4′-azoxyanisole and its dispersion in PVC were investigated by DSC, TMDSC and quasi-isothermal TMDSC. The non-reversible transition, C-N, and the reversible transition, N-I, of 4,4′-azoxyanisole and its dispersion in PVC were investigated. Both the pure LC and the PDLC had shown a significant non-reversing heat capacity peak and a larger phase lag curve in C-N transition. In contrast to the melting process, the N-I transition is a reversible first-order transition without superheating effect, therefore, the loss heat capacity curve was around zero and there was no change observed in the phase lag curve. The PVC dispersed 4,4′-azoxyanisole caused a decrease of the phase transition breadth and the enthalpy required for the phase changes. The Lissajous figures
demonstrated that before and after the transition the materials were in the steady state and no enthalpies were involved, however, with increase of the temperature the height of the oscillations increased markedly due to the increase in heat capacity during the phase transition and the distortion towards the bottom loop during the transition was evident due to large changes between the signals.

Four different self-organized extinction patterns were found in the PVC dispersed 4,4’-azoxyanisole caused by the different orientations of droplet axes but not the different internal structures.

8.2 Future Research

The thesis is concerned with the preparation and the characterization of the PDLCs and investigated the thermal properties. However, there are many external factors such as electronic field and magnetic field that are important to determine whether PDLC can be applied in commercial areas. Therefore, further studies of electro-optical properties: conductivity and dielectric constant, optical responses under the influence of an externally electronic field should be investigated in the future.

Secondly, PDLC materials are expected to be used as a way to study the fundamental effects of surfaces and confinement on nematics and other LCs. The large surface-to-volume ratio creates new physical effects that are extremely interesting to study. Measuring surface and confinement parameters that affect the droplet configurations will be the next challenge. And new techniques, such as neutron diffraction are proposed to be employed to investigate the structure and texture of PDLC system.

Finally, a study of PDLC should be carried out on the application of optical data storage, non-linear optical, stationary phases and gas separation membranes.
REFERENCES


