

**THE SYNTHESIS AND CHARACTERIZATION OF
LIQUID CRYSTAL POLYMER**

EVELYN TEO YI MIIN

**INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH**

May 2008

PERPUSTAKAAN
UNIVERSITI MALAYSIA SABAH



UMS
UNIVERSITI MALAYSIA SABAH

**THE SYNTHESIS AND CHARACTERIZATION
OF LIQUID CRYSTAL POLYMER**

EVELYN TEO YI MIIN

**THIS PROJECT IS SUBJECTED IN PARTIAL FULLFILLMENT OF THE
REQUIREMENT FOR THE DEGREE OF BACHELOR OF SCIENCE**

**INDUSTRIAL CHEMISTRY PROGRAM
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH**

MAY, 2008



UMS
UNIVERSITI MALAYSIA SABAH

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS@

JUDUL: THE SYNTHESIS AND CHARACTERIZATION OF LIQUID
CRYSTAL POLYMER

Ijazah: SARJANA MUDA SAINS

SESI PENGAJIAN: 2008

Saya EVELYN TED DI MIN

(HURUF BESAR)

mengaku membenarkan tesis (LPS/Sarjana/Doktor Falsafah)* ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:

1. Tesis adalah hakmilik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. **Sila tandakan (/)

SULIT

(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)

TERHAD

(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)

TIDAK TERHAD

Disahkan oleh

DR

(TANDATANGAN PENULIS)

(TANDATANGAN PUSTAKAWAN)

Alamat Tetap: 61, LORONG 2R,
KINNEFISHER - PHASE 2,

DR. MD. LUTFEE RAHMAN

KOTA KINABALU

Nama Penyelia

Tarikh: 7/5/08

Tarikh: 7/5/08

CATATAN: * Potong yang tidak berkenaan.

** Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT dan TERHAD.

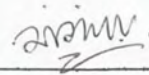
@ Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Laporan Projek Sarjana Muda (LPSM).



DECLARATION

I hereby declare that the work in this thesis is of my own except for the quotation and references, which have been properly acknowledged.

MAY 2008



EVELYN TEO YI MIIN

HS2005-4241




VERIFICATION

Name: Evelyn Teo Yi Miin

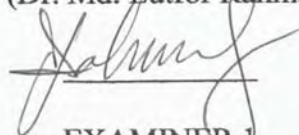
Title: Synthesis and Characterization of Liquid Crystal Polymer.

Signature



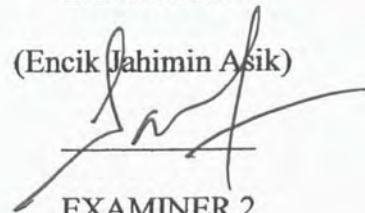
SUPERVISOR

(Dr. Md. Lutfor Rahman)



EXAMINER 1

(Encik Jahimin Asik)



EXAMINER 2

(Dr. Sazmal Effendi Arshad)

DEAN

(SUPT/KS Prof Madya Dr Sharif A.K. Omang)

May, 2008



ACKNOWLEDGEMENT

I would like to record my appreciation to Dr.Lutfor Rahman for opening the gate to the interesting world of liquid crystal and liquid crystal polymer. Even in the lab, the lessons you taught extend beyond the pages of book and even after university life, it will serve a purpose.

Molly, your patience and time are worth more than the most precious gems in the world. Let me wish you every success in your future endeavors. To all my dear family, fellow friends and staffs of the faculty of Science and Technology, thank you.

Here is a brief poem for all of us to enjoy:

Sadly, perhaps mark the last,
But hopefully, not the end,
This fond memory of the past,
Remain dear as long as can.



ABSTRACT

A liquid crystal polymer was synthesized by AIBN free-radical polymerization from an azobenzene mesogen rod-shaped monomer. The liquid crystal monomer was also synthesized by azo-decoupling reaction and Williamson ether synthesis. The thermal property of the LCP monomer was determined by DSC while the structure was determined by FT-IR. It is possible to further confirmed the structure of the synthesized compound if X-Ray diffraction was done. The presence of the azo linkage in both synthesized compounds showed potential for non-linear optic studies as well as photoswitching experiments concerned with cis-trans isomerization cycles.



ABSTRAK

Hablur cecair polimer disintesis melalui tindakbalas radikal bebas AIBN menggunakan monomer bentuk rod yang bermesogen azobenzene. Hablur cecair monomer pula dihasilkan dari tindakbalas azo-decoupling dan sintesis ether Williamson. Ciri-ciri termal hablur cecair monomer tersebut ditentukan oleh DSC manakala strukturnya ditentukan oleh FT-IR. Strukturnya dapat disahkan dengan lebih tepat dengan kaedah pembelahan sinar X . Kehadiran rantai azo dalam bahan yang disintesis menunjukkan potensi dalam kajian optik tidak linear serta penukaran foton berkaitan isomerasi cis-trans.



LIST OF TABLE

Table no.		Page
1.1	Application liquid crystal polymers in various fields.	21
2.1	Properties of liquid crystal polyesters (Deronzier & Bentolinit, 1997).	24
2.2	Description of chemical reagent used.	32
3.2	List of glassware/apparatus used.	33
3.3	List of analytical instrument used.	34
4.1	Percentage yield of compound 1, 2 and 3.	47
4.2	Melting point of compound 1, 2 and 3.	47
4.3	Band assignments of compound 1.	48
4.4	Band assignments of compound 2.	49
4.5	Band assignments of compound 3	50
4.6	Phase transition, peak temperature, area and enthalpy heat (ΔH) of Compound 2 of DSC scan.	52
4.7	NMR shift assignment for Compound 3.	52



LIST OF FIGURE

No. Figure		Pages
2.1	Molecular Structure of AIBN	10
2.2	The mechanism of statistical photo-orientation of azo molecules (Yager and Baret)	13
2.3	Schematic representation of a mesomorphic side-chain polymer (Davidson, 1996).	21
2.4	Structural formula of Vectra (Campbell, 2005).	25
2.5	Schematic representations of macromolecules of LC polymers	28
2.6	with rod- and disk-shaped mesogenic groups (Shioaev <i>et al.</i> , 2003).	
4.1	FT-IR spectrum of compound 1.	50
4.2	FT-IR spectrum of Compound 2.	51
4.3	FT-IR spectrum of Compound 3.	51
4.4	DSC thermogram of compound 2.	52



LIST OF SCHEMES

No.Scheme		Page
2.1	Coupling reaction by Gomberg Bachmann reaction.	6
2.2	Nucleophilic substitution reaction.	7
2.3	Vinyl halide undergo S_N1 reaction.	8
2.4	Formation of vinyl cation.	8
3.1	Reagent and conditions.	34
4.1	Diazo-coupling of compound 1.	43
4.2	Williamson Ether Synthesis of compound 2.	44



LIST OF PHOTOGRAPHS

Photo no.		Page
3.1	Pester and mortar.	39
3.2	Hand press for making KBr pellet.	40
3.3	FT-IR spectrometer.	40
3.4	Furnace with the lid removed with the disks on which the reference and sample are placed.	40
3.5	Perkin Elmer DSC 6 Differential Scanning Calorimeter.	41
3.6	Crimper.	42



LIST OF SYMBOLS

°C	= Degree Celcius
LC	= liquid crystal
LCPs	= liquid crsytal polymers
LC	= liquid crystal
mm	= milimeter
g	= gram
mmol	= milimol
MLCs	= monomer liquid crystal
Equiv	= equivalent
DSC	= differential scanning calorimetry
AIBN	= 2,2' -Azobis(isobutyronitrile)
FT-IR	= Fourier Transform Infrared
HPLC	= high performance liquid chromatography
T	= temperature
NMR	= nuclear magnetic resonance
¹³ C	= Carbon-13
¹ H	= hydrogen
IR	= Infrared
MCLCP	= main-chain liquid crystal polymer
SCLCP	= side-chain liquid crystal polymer
T _g	= glass transition temperature
HCl	= hydrochloric acid
%	= percent
THF	= tetrahydrofuran



CONTENTS

	Page
DECLARATION	ii
CERTIFICATION	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
ABSTRAK	vi
LIST OF TABLES	vii
LIST OF FIGURES	viii
LIST OF SCHEMES	ix
LIST OF PHOTOS	x
LIST OF SYMBOLS	xi
CONTENTS	xii
CHAPTER 1 INTRODUCTION	
1.1 Introduction	1
1.2 Objective of study	5
CHAPTER 2 LITERTURE REVIEW	
2.1 A brief history of Liquid Crystal Polymer.	5
2.2 Organic Synthesis Reactions.	6
2.3.1 Coupling reaction by Gomberg Bachmann reaction.	6
2.3.2 Williamson 's Ether Synthesis.	7
2.3.3 Free radical reaction in polymerization.	9
2.2 Experimental methods to study liquid crystal polymer.	10
2.2.1 Differential Scanning Calorimetry.	10
2.2.2 Phase Diagrams.	10
2.2.3 Examples of DSC application.	10
2.2.4 FT-IR	13
2.2.5 NMR	1



2.4	Azobenzene Mesogen Core.	16
2.4	Types of LCP and their application.	18
2.4.1	Thermotropic Liquid Crystal Polymers.	18
2.4.2	Side Chain liquid crystal polymers.	19
2.4.3	Main chain liquid crystal polymers.	24
2.4.4	Lyotropic liquid crystal polymers.	26
2.5	Characterization of LCP Based On Mesophase.	28
2.5.1	Nematic.	29
2.5.2	Cholesteric.	29
2.5.3	Smectic.	30
CHAPTER 3 METHOLOGY		
3.1	Materials.	31
3.2	Synthesis scheme.	33
3.3	Synthesis of 4-(4-ethyl-diazobenzoate) phenol (compound 3) via formation of diazonium salt (compound 2).	35
3.4	Synthesis of azobenzene-derived monomer (compound 3).	36
3.5	Synthesis of azo side-chain polymer (compound 3).	36
3.6	Calculation of percentage yield.	37
3.7	Determination of melting point of each synthesized compound.	37
3.8	Instrumental analysis	
3.8.1	FT-IR.	38
3.8.2	DSC.	39
3.8.3	NMR	41



CHAPTER 4 RESULT AND DISCUSSION	
4.1 Organic Reactions.	43
4.1.1 Diazo-Coupling Salt Formation.	44
4.1.2 Williamson Ether Synthesis.	45
4.1.3 Synthesis of azo side-chain polymer (compound 3).	45
4.2 Melting Point.	46
4.2.1 Comparison between the melting point of compound 1 and 2.	46
4.2.2 Comparison between the melting point of compound 2 and 3.	46
4.3 FT-IR Spectrum.	47
4.3.1 FT-IR Spectrum comparison between compound 1 and 2.	47
4.3.2 FT-IR Spectrum comparison between compound 2 and 3.	47
4.4 DSC Thermogram of compound 2.	51
4.5 NMR Spectrum of compound 3.	53
CHAPTER 5 CONCLUSION	55
REFERENCES	56
APPENDIX	



CHAPTER 1

INTRODUCTION

1.1 Introduction

Polymers which exhibits a combination of long range motion and fluidity together with a degree of order measurable by optical and scattering technique in the quiescent state and over characteristic temperature and concentration range intervals are termed liquid crystal polymers (Aharoni & Edwards, 1994). These materials are receiving more and more interest nowadays because of their unique properties compared with ordinary polymer (Zhong, 1998), for example cooperative behaviour and liquid crystallinity (Aharoni & Edwards, 1994).

Such polymers are of technical interest since they combine the elasticity of polymers and the liquid crystalline properties of the liquid crystal monomers (Li *et al.*, 1996) as anisotropic fluids (Davidson, 1996) to give an overall better mechanical property (Brostow *et al.*, 1999). As cited by Kurihara *et al.* (2007), polymeric LCs are well known to show excellent storage stability in contrast with low molar mass LCs. Also, corrosion resistance of LCP is in general very good with all chemical products



although very few experimental data are available. In general terms, liquid crystal polymers are known to possess very high tensile strength and tensile modulus, high heat deflection temperature and very low coefficient of linear thermal expansion (lower than metallic material coefficient) (Deronzier & Bentolinit, 1997; Wang *et al.*, 2006) as shown from the data in Table 1.1. Similarly, Wang *et al.* (2006) recognizes liquid crystal polymers as important materials for moulded interconnected devices due to their excellent properties, e.g. high temperature resistance, chemical stability, low-thermal expansion coefficient as well as excellent flow properties for the fabrication of fine structures by moulding techniques.

The morphology of liquid crystal polymers are closely related to its molecular structure and processing histories to give each of this material its specific crystallization and multiphase behaviour resulting in different response time to stress and temperature. (Weiss, 1998). This phenomena of alignment and packing of macromolecules into an organization pattern of the molecules in the systems is due to (Weiss, 1998) inter- or intra- chain hydrogen bonding induced by the presence of mesogenic groups (Aharoni & Edwards, 1994). Mesogenic groups are stiff and elongated units in parallel arrays acting as pendants to chain backbones responsible for stiffness and shape anisotropy (Aharoni & Edwards, 1994).

Huang (1999) proved that molecular interactions between mesogenic moieties of liquid crystal polymer showed various patterns of changes during phase transition processes by studying intermolecular complex formation between mesogenic terohenyldiimide moieties of thermotropic liquid-crystalline (LC) polyimide using florescence technique. Below a glass transition temperature, T_g ,



molecular organization may be frozen (Davidson, 1996). Determination of the polymer chain conformation in the different mesophases is a problem because of the competition between the polymer entropy which leads the chain to adopt a random coil conformation and the long range order of the monomers in the mesophases (Li *et al.*, 1996).

Liquid crystal polymers are prepared through combinations of formanisotropic structural units (mesogenic groups) and polymer chains (Zentel, 1998). A characteristic feature of liquid crystal polymers is their ability to have a characteristic alignment according to the external field as they consist of anisotropic mesogens that are very sensitive to external fields such as stress, electric or magnetic field, making it highly valued in numerous applications such as high performance fibers, engineering plastics and functional materials (Zhong, 1989). Mesogenic groups can be incorporated into polymer chains forming liquid crystal main-chain polymer or attached to a flexible polymer chain as side groups forming liquid crystal side-chain polymer (Wittman *et al.*, 1998; Huang *et al.*, 1999; Zentel, 1989).

Liquid crytallinity in liquid crystal polymer is an anisotropic behaviour (Gedde, 1995) of which its properties vary with the measured direction whereby compared with true liquid, a restricted mobility of individual molecules is preserved (Campbell, 1994). The flexible, long chains of polymer molecules are readily compatible with liquid crystallinity where many chains can be aligned with relative ease in a bulk sample when the polymer chain is rather stiff and has limited mobility (Campbell, 1994). This orientational order is a nature feature of liquid crystal polymers in all their mesomorphic states ranging from nematic to smectic (Gedde, 1995).



Mesophases consisting of phase or phases between the low temperature crystalline or glassy state and the high temperature isotropic melt (Aharoni & Edwards, 1998) are differentiated from each other by the different ways by which the molecules pack. (Collyer, 1996). The number of mesophases through which polymer molecules pass is considerably less than those encountered in liquid crystals of low molecular mass (Collyer, 1996). Nematic mesophases shows molecular alignment without a special regularity (Gedde, 1995). The low viscosity exhibited is of interest to polymer processing as used in the spinning of lyotropic dopes to make fibres like Kevlar (Collyer, 1996). In the high viscosity smectic mesophases (Fried, 1995), molecules are aligned and stratified or layered (Wittold, 1994). Due to structural differentiation (Aharoni & Edwards, 1994), as a consequence of the different method in liquid crystal creation in liquid formation. Campbell (1994) indicated two primary classes of liquid crystal polymers, namely the thermotropic and lyotropic types.

Liquid crystal polymers are typically multiphase and contain at least one LC-rich phase which consists of islands (Brostow *et al.*, 1999) where three kinds of LCPs exist: lyotropic, barotropic and thermotropic. Three types of systems widely investigated in previous theory and experiment involved primarily the lyotropic solutions of stiff-chain polymer, thermotropic main-chain and side-chain liquid crystal polymers where the mesogenic group is respectively incorporated into the chain backbone or is pendant from the backbone and thermotropic solutions of LCPs dissolved in low-molar-mass solvent (Jamieson *et al.*, 1996).



1.2 Objective

1.2.1 To prepare liquid crystal polymers.

1.2.2 To identify the molecular structure by using spectroscopy method.

1.2.2 To determine the mesophase using differential scanning calorimetry.



CHAPTER 2

LITERATURE REVIEW

2.1 A brief history of Liquid Crystal Polymer.

In 1888, Austrian botanist Friedrich Reinitzer provided the first scientific description for liquid crystals. In 1888, the German scientist Otto Lehmann coined the term 'liquid crystals'. In 1900, Vorlander started a research group working on liquid crystals and this group continued to exist at Martin Luther University of Halle-Wittenberg up to today with constant contribution by Horst Sackmann, Dietrich Demus, Frank Kuschel, Horst Kresse and others.

In 1923, after more than two decades of working on MLCs, Vorlander realized that PLCs must exist also. He questioned on whether the possibility of making molecules longer and longer would result in the disappearance of the liquid crystalline state. At that time, Volander had already speculated that there was no limit to the liquid crystalline state by chain elongation unless the substance could not melt any more without decomposition and could not be seen under a microscope.



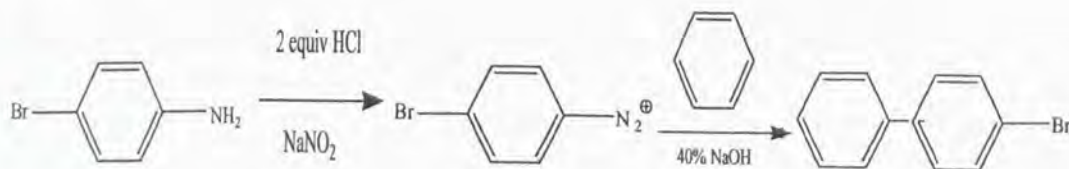
Klepl and later Emil Fischer already obtained long chains but did not realize their liquid crystalline character. Hermann Fischer gave some samples prepared by his father to Vorlander and Vorlander in turn found that they were liquid crystalline. Therefore, German researchers had already discovered liquid crystal polymers in the nineteenth century (Brostow, 1992).

2.2 Organic Synthesis Reaction in Preparation of LCP

2.2.1 Coupling reaction by Gomberg Bachmann reaction

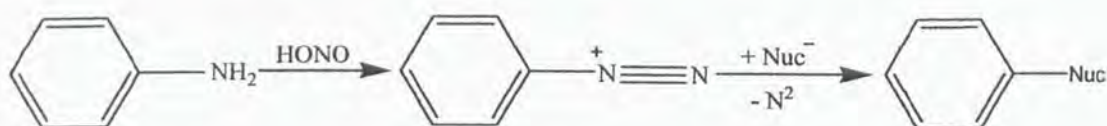
According to Smith (2002), there are many variations of aromatic diazonium salts used to join alkyl fragments or alkyl-aryl fragments in the coupling reaction. One example of generating the diazonium salt is treatment of an aromatic amine with nitrous acid. This reaction occurs through HONO via reaction of HNO_3/HCl or $\text{NaNO}_2/2\text{HCl}$. In the Gomberg-Bachmann reaction, diazonium salts are coupled to other aromatic compounds in the presence of a base.

A typical example is the treatment of 4-bromo-aniline with nitrous acid, giving a diazonium salt which reacted with benzene to give biphenyl derivative in 46 % yield as shown in Scheme 2.1. Hydrogenation of the nitrobenzene derivatives gives aromatic precursors.



Scheme 2.1 Coupling reaction by Gomberg Bachmann reaction.

In the example in Scheme 2.2, an aryl diazonium compound (benzenediazonium chloride) is formed when a primary amine such as aniline is treated with nitrous acid (HONO), generated by the reaction of sodium nitrite and HCl or H₂SO₄. The nitrogen fragments of a diazonium ion (Ar-N₂⁺) is a good leaving group and can be displaced by a variety of nucleophiles to give the substitution product. Many different nucleophiles can react with aryl diazonium salts through different mechanism, ranging from S_N1 type process to those involving radicals (Smith, 2002).



Scheme 2.2 Nucleophilic substitution reaction.

2.2.2 Williamson's Ether Synthesis.

The Williamson reaction is a very useful transformation in organic synthesis since the products are of value in both industrial and academic applications. The Williamson synthesis usually involves the employment of an alkali-metal salt of the hydroxy compound and an alkyl halide. These reactions are usually performed using organic solvents or with phase-transfer catalysts in the presence of a base followed by refluxing for several hours. Methods which involve alkylation of a phenol are usually highly efficient, although some care must be exercised in the choice of solvent in order to avoid formation of both C- and O-alkylated products (Paul & Gupta, 2004).

REFERENCE

- Aharoni, S. M. & Edwards, S. 1994. *Rigid Polymer Networks*, Springer-Verlag, Berlin.
- Bahadur, P. & Sastry, N. V. 2005. *Principles of Polymer Science*. Second Edition. Alpha Science, United Kingdom.
- Bezoa, P., Pacreau, A. & Vairion, J. 1995. Synthesis of New Polarizable Liquid-Crystal Molecules, *Tetrahedron Letters* **36** (17): 2995-2998.
- Blackwood, K. M & Sage, I, C. 1998. Sidechain Liquid Crystal Polymers. *Current Opinion in Solid State & Material Science* **3**: 610-615.
- Brostow, W., Faitelson, E. A., Kamensky, M. G., Korkhov, V. P. & Rodin, Y, P. 1999. Orientation of a Longitudinal Polymer Liquid Crystal in a Constant Magnetic Field. *Polymer* **40**: 1441-1449.
- Bruice, P. Y. 2004. *Organic Chemistry*. Fourth Edition, Prentice Hall, United States of America.
- Busfield, W. K., Jenkins, I. D. & Van Le, P. 1996. Investigations into the AIBN Initiation Steps in the Free Radical Polymerisation of Acrylonitrile by the Aminoxyl Trapping Technique. *Polymer Bulletin* **36**: 435-441.
- Campbell, I. A. 1994. *Introduction to Synthetic Polymer*. Oxford Science Publication, New York, 193-195.
- Campbell, I. A. 2005. *Introduction to Synthetic Polymer*. Second Edition. Oxford University Press. New York. 176-183
- Collyer, A. A. Introduction to Liquid Crystal Polymer. 1996. Acierno, D & Collyer, A, A *Rheology and Processing of Liquid Crystal Polymer*. Polymer liquid



Crystal Series 2, Chapman and Hall, London. 5-7.

Correa, D. S., Gonzales, D.T., Mendonca, C. R. & Boni L.De. 2006. Induced Transparency in Polythiophene Bearing Azobenzene Moieties, *Polymer* **47**: 7436-7440.

Chen, X., Zhang, J., Zhang, H., Jiang, Z., Shi, G., Li, Y. & Song, Y. 2007. Preparation and Nonlinear Optical Studies of a Novel Thermal Stable Polymer Containing Azo Chromophores In the Side Chain. *Dyes and Pigments* **xx**:1e6.

Chiellini, E. & Lenz, R. W. 1989. Comprehensive Polymer Science: The synthesis, Characterization, Reactions & Applications of Polymers **5**. In: Eastmond, G.C., Ledwith, A., Russo, S & Sigwalt, P, *Polymers With Main-chain Mesogenic Units*. Pergamon Press. Oxford, 701-722.

Cui, Z. & Wang, Q. 2006. A continuum model for flows of cholesteric liquid crystal polymers and permeation flows. *Journal of Non-Newtonian Fluid Mechanics* **138** : 44-61.

Davidson, P. 1996. X-ray Diffraction by Liquid Crystalline Side-chain Polymers. *Progressive Polymer Science* **21**. 893-950.

Deronzier, J. C. & Bentolinit, G. 1997. Plate Heat Exchangers in Liquid Crystal Polymers. *Applied Thermal Engineering* **17** : 799-808.

Hirschfeld, T. 1982. Quantitative FT-IR A Detailed Look at the Problems Involved, In: Ferraro, J. R. & Basile, L. J. 1982. *Fourier Transform Infrared Spectroscopy: Applications in Chemical System*. First Edition, Academic Press, San Diego.

Fried, J. R. 1995. *Polymer Science and Technology*. Prentice Hall. Englewood Cliffs. New Jersey. United States of America, 364-366.

Furniss, B., Hannaford, A. J., Smith, P. W. G. & Tatchell, A. R. 1989. Fifth Edition,



- Vogel 's Texbook of Practical Organic Chemistry*. Longman. London.
- Gedde, U, W. 1995. *Polymer Physics*, First Edition, Chapman and Hall, London.
- Han, X., Shanks, A. R. & Pavel, D. 2005. The Synthesis and Thermal Properties of Polyeppichlorohydrin Side-chain Liquid Crystal Polymer. *European Polymer Journal* **41**: 984-991.
- Huang, H, W., Horie, K., Tokita, M. & Watanabe, J. 1999. Fluorescence Study On Intermolecular Complex Formation Between Mesogenic Biphenyl Moieties of Main-chain Thermotropic Liquid Crystalline Polyesters with 7-18 methylene units. *Polymer* **40**: 3013-3023.
- Huang, H, W., Kaneko, T, I., Horie, K. & Watanabe, J. 1999. Fluorescence Study on Intemolecular Complex Formation Between Mesogenic Terphenyldiimide Moieteis of a Thermotropic Liquid Crystalline Polyimide. *Polymer* **40**: 3821-3828.
- Hwang, D. K., Han, W. H. & Rey, A. D. 2006. Computational Rheooptics of Liquid Crystal Polymers. *Journal of Non-Newtonian Fluid Mechanics* **143**: 10-21.
- Jamieson, A, M., Gu, D., Chen, F, L. & Smith,S. 1996. Viscoelastic Behaviour of Nematic Monodomains Containing Liquid Crystal Polymers. *Progressive Polymer Science* **21**: 981-1033.
- Kosc, T, Z., Marshall, K, L., Trajkovska-Petkoska, A. & Kimball, E. 2004. Progress in the Development of Polymer Cholesteric Liquid Crystal Flakes for Display Application, *Display* **25**: 171-176.
- Kurihara, S., Moritsugu, M., Kubo, S., Kim, S., Ogata, T., Nonaka, T. & Sato, O. 2007. Photo-switching Properties of Photonic Band Gap Material Containing Azo-polymer Liquid Crystal. *European Polymer Journal*.
(accepted manuscript due for publication)



- Kruk, G., Vij, J. K., Karthaus, O. & Ringsdorf. 1995. Study of the Order Parameter of Thin Films of a Main-chain Discotic Liquid Crystalline Polymer using Fourier Transform Infra-red Spectroscopy. *Supramolecular Science* **2**: 51-58.
- Li, M. H., Brulet, A., Keller, P. & Cotton, J. P. 1996. Liquid Crystal Polymers: Evidence of Hairpin Defects in Nematic Main Chains, Comparison with Side Chain Polymers. *Journal of Molecular Structure* **383**: 11-18.
- Li, N., Lu, J., Yao, S., Xia, X. & Zhu, X. 2004. Synthesis and Fluorescent Properties of PAA-based New Side Chain Polymers. *Materials Letters* **58**, 3115–3118.
- Li, N., Lu, J., Xu, Q. & Wang, L. 2006. Synthesis and the Third-order Non-linear Optical Properties of New Azobenzene-containing Side-chain Polymers. *Optical Materials* **28**: 1412–1416.
- Liu, C., Liu, Y., Xie, P., Zhang, He, C., Chung, N.T. 2000. Synthesis and Characterization of a novel alcohol-soluble ladderlike polysilsesquioxane containing side-chain with amino terminal group, *Reactive and Functional Polymers* **46**: 175-184.
- Liu, J., Ni, P., Qiu, D., Hou, W. & Zhang, Q. 2007. Photochromism of Liquid Crystalline Dendrimer with Azobenzene Terminal Group in Solution, *Reactive & Functional Polymers* **67**: 416-421.
- Liu, Z., Srisanit, N., Ke, X., Wu, P., Song, S., Yang, J.J & Wang, M. R. 2007. An Azobenzene Functionalized Polymer for Laser Direct Writing Waveguide Fabrication, *Optics Communications* **273**: 94-98.
- Loudon, G. M. 1995. *Organic Chemistry*, Third Edition, Benjamin Cummings, London.
- Makaruk, L. & Furman, J. 1997. Mesophases Transition in Liquid Crystal Polymers.



Reactive and Functional Polymer **33**: 225-231.

Mishra, G. & Srivastava, A.K. 2007. Side-chain Liquid Crystalline Polymers with [α -terpineol-co-MMA] Main Chain: Synthesis and Characterization of Polymers with Phenyl Benzoate Mesogenic Group. *Polymer Bulletin* **58**: 351-358.

Pavia, D. L., Lampman, G. L. & Kirz, G. S. 2001. *Introduction to Spectroscopy: A Guide for Student of Organic Chemistry*. Thomas Learning Ltd, United States of America.

Pragliola, S., Ober, C., Mattern, P. T. & Jeon, H. G. 1999. Mesogen-jacketed Liquid Crystalline Polymers Via Stable Free Radical Polymerization. *Macromolecular Chemistry Physics* **200**: 2338-2344.

Rahman, M. L., Tschierske, C., Yusoff, M. & Silong, C. 2005. Synthesis and Liquid Crystalline Properties of a Disc-Shaped Molecule with Azobenzene at the Periphery. *Tetrahedron Letters* **46**: 2303-2306.

Sandler, S. R & Karo, W. 1992. *Polymer Synthesis: Volume 1*, Second Edition. Academic Press, United Kingdom, 327-328.

Scaffaro, R., Pedretti, U. & La Mantia, F.P. 1996. Effects of Filler Type and Mixing Method on the Physical Properties of a Reinforced Semirigid Liquid Crystal Polymer, *European Polymer Journal* **32**: 869-875.

Shioaev, V., Bobrovsky, A. & Bako, N. 2003 . Photoreactive Liquid Crystal Systems with Light-controlling Structure and Optical properties. *Progressive Polymer Science* **28**: 729-836.

Solomons T. W. G. 1996. *Organic Chemistry*, Sixth Edition, John Wiley & Sons, New York.

Song, M, H., Shin, K., Park, B., Takanishi, Y,Y., Ishikawa, K., Watanabe.,



- Nishimura, S., Toyooku, T., Zhu, Z., Swager, T. M. & Takezoe, H. 2004. Polarization Characteristics of Phase Retardation Defect Mode Lasing in Polymeric Cholesteric Liquid Crystals. *Science and Technology of Advanced Material* **5**: 427-441.
- Snively, C. M. & Koenig, J. L. 2000. Structure/Property Relationships in Nematic Liquid Crystal/ Polymer Alignment Layer Interaction. *Journal of Molecular Structure* **521**: 121-126.
- Skoog, D. A., Holler, F.J & Crouch S.R. 2007. *Principles of Instrumental Analysis*. Sixth Edition. Thomson. Australia.
- Tibirna C. M & Diouf, P.N. 2008. Mixtures of Tertiary Amine Functionalized Azo-containing Mesogens With Acid-functionalized Polymers, *Polymer* **49**: 241-253.
- Wittman, J.G., Meyer, S., Damman, P., Dosiera, M. & Schmidt, H-W. 1998. Preparation and Characterization of Side-chain Liquid Crystalline Polymer Thin Films Aligned On PTFE Friction-transferred Layers, *Polymer* **39** (15): 3545-3350.
- Wang, B., Eberhardt, W. & Kuck, H. 2006. Plasma Pre-treatment of Liquid Crystal Polymer and Subsequent Metalization By PVD, *Vacuum* **81**: 325-328.
- Whitehead, K, S., Grell, M., Bradley, D. D. C., Inbasekaran, M. & Woo, E. P. 2000. Polarised Emission from Liquid Crystal Displays. *Synthetic Metals* **111-112**: 181-185.
- Wing, L.C., Hua, Y. & Yau, S.S. 2004. Synthesis of Mesoionic Side-chain Liquid Crystal Poly(siloxane)s, *Material Letters* **58**: 882-884.
- Yager, K. G & Baret, K. G. 2006. Novel Photo-switching Using Azobenzene Functional Materials, *Journal of Photochemistry and Photobiology A*:



Chemistry **182**: 250-261.

Yesodha, S. K., Sadashiva Pilai, C. K & Tsutsumi N. 2004. Stable Polymeric Materials for Nonlinear optics: A Review Based On Azobenzene Systems, *Progressive Polymer Science* **29**: 45-74.

Zentel, R.1989. *Comprehensive Polymer Science: The synthesis, Characterization, Reactions and Applications of Polymers* **5**. Eastmond, G. C., Ledwith, A., Russo, S & Sigwalt, P, *Polymer With Side-chain Mesogenic Units*. Pergamon Press, Oxford, 723-730.

Zhong, Y. Morphology of Thermotropic Longitudinal Polymer Liquid Crystals, Brostow, W. 1998. *Mechanical and Thermophysical Properties of Polymer Liquid Crystals*, Polymer Liquid Crystal Series 3, Chapman and Hall, London, 101-122.

