

**SYNTHESIS AND PHYSICAL PROPERTIES OF
SOME MESOGENIC CHIRAL POLYSILOXANES**

*A thesis submitted to the
Bangalore University for
the degree of*

DOCTOR OF PHILOSOPHY

by

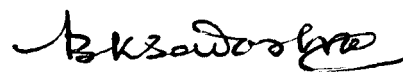
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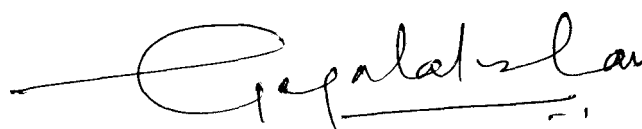
*I certify that this thesis has been composed by Mr. C. R. GOPALAKRISHNAN based on the investigations carried out by him at the Liquid Crystal Laboratory, **Raman** Research Institute, Bangalore - 560 080, under my *supervision*. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or any other similar title.*



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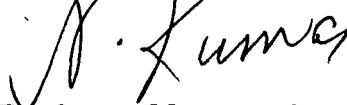
DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystal Laboratory, Raman Research Institute, Bangalore - 560 080, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship or any other similar title.



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ACKNOWLEDGEMENTS

I thank the almighty for this extraordinary world of awe and beauty and for having put me in it.

I thank Professor B.K. Sadashiva for his immense patience, able guidance and sustained encouragement through out this work, especially during the writing of the thesis. He provided a rare atmosphere of inquiry in the laboratory and backed it up with absolute freedom of choice of work for which I am greatly indebted.

I thank Professor N.V. Madhusudhana for his interest in this work and for useful suggestions during the preparation of this thesis.

I thank my senior colleagues Mr. M.R. Subramanya, Mr. K. Subramanya and Mr. P.N. Ramachandra and other laboratory colleagues Mr. N. Kasthuriah and Mr. G.R. Sheshadri for their help during various stages of this work and for maintaining a cordial atmosphere in the laboratory. I thank Mrs. Geetha Basappa for helping me with lively discussions in physics and metaphysics.

I appreciate the cooperation of all the colleagues from the workshop.

I thank Mr. A. Ratnakar, Mrs. Girija and the library staff for being patient with me and helping me in locating books, journals, and for the exceptional photocopying facility. This made the work seem lighter and made it quicker. This is easily one of the best maintained library that I have come across.

I thank Professor S. Ramakrishnan, Indian Institute of Science, Bangalore, for discussions and help at various stages of this work, especially for allowing me to do the **GPC** analysis of the polymers.

I thank my family members, for their love and encouragement. I thank my wife Mrs. K.Sritulasi for being there with me through thick and thin.

I thank the Director, **Raman** Research Institute, Bangalore, for providing me with financial help through out my stay here.

Finally, I thank the reader for going through this work and acknowledging the time and effort that I have put in. This, finally, makes it all most worthwhile.

List of abbreviations used in the text.

C	crystal
I	isotropic
N	nematic
N*	cholesteric
TGB _A	twist grain boundary smectic A
S	smectic
S _A	smectic A
S _C	smectic C
S _C *	chiral smectic C
S _{C_A} *	antiferroelectric smectic C
S _{C_γ} *	ferrielectric smectic C
S _{C_α} *	chiral smectic C _α
	phase exists
	phase does not exist
	<i>ortho</i>
p	<i>para</i>
n	normal
IR	infrared

NMR	nuclear magnetic resonance
ppm	parts per million
s	singlet
d	doublet
dd	doublet of doublet
t	triplet
q	quartet
m	multiplet
tlc	thin layer chromatography
DSC	Differential scanning calorimeter
TMS	Tetramethylsilane
DCC	N,N'-Dicyclohexylcarbodiimide
DMAP	N,N'-Dimethylaminopyridine
DEAD	Diethylazodicarboxylate
TPP	Triphenylphosphine
LAH	Lithium aluminium hydride
BBA	Benzoyloxybenzoic acid
THF	Tetrahydrofuran
LCP	Liquid crystalline polymer
SCLCP	Side chain liquid crystalline polymer
MCLCP	Main chain liquid crystalline polymer

PREFACE

Many organic compounds made up of geometrically anisotropic molecules have the inherent property to reveal a state of matter which can under different conditions display some properties of both crystalline solids and amorphous liquids. Such compounds have been classified as belonging to a new state of matter called **liquid crystals**. Based on the conditions necessary for obtaining the liquid crystalline property, liquid crystals have been classified as belonging to two broad classes:

1. **The thennotropic liquid crystals** which are formed by thermal effects.
2. **The lyotropic liquid crystals** which are formed from amphiphilic compounds and solvents.

Liquid crystals or mesophases have been classified further depending upon the degree of ordering of molecules. Thus rod-like molecules show **Nematic** and **Smectic** phases, while disc-like molecules show **Columnar** phase. In the nematic phase, molecules have long range orientational order, but no positional order. In the smectic phase the molecules have positional as well as orientational order within the phase, *i.e.* the molecules are arranged in layers. Smectic phase has been classified further into, smectic **A**, **B**, **C**, etc., depending upon the positional and directional correlations of a molecule with its neighbour, for example, in smectic **C** or smectic **G** phase the molecules in a layer are tilted with respect to the layer normal. In the columnar phase, discovered as recently as 1977¹, the molecules are arranged aperiodically one on top of other, resulting in liquid-like columns.

If the constituent rod-like molecules of a compound are chiral or if a chiral compound is added to a compound exhibiting a nematic phase, then the structure of

the obtained mesophase becomes helical in nature. Such a phase is called Cholesteric, in which a screw axis is superimposed perpendicular to the preferred molecular direction (director). In the case of chiral tilted smectic phases, there will be a helical precession of the tilt axis along a direction perpendicular to the layers. In both cases, the helical pitch is generally found to be of the order of wavelength of light. The smectic phase may be further subdivided depending upon the distortion that chirality can induce into the layered ordering of the molecules.

Vorlander postulated that 'infinitely long mesogens' would be compatible with supramolecular organisational constraints in liquid crystals.² Thus, the field of Polymeric liquid crystals was initiated as early as 1923. The above mentioned mesophase classification can be applied directly to the field of polymers too. Polymers have been classified into Main chain and Side chain polymers. In the main chain liquid crystalline polymers (MCLCPs), the mesogens are the monomeric units separated by a spacer. In the case of side chain liquid crystalline polymers (SCLCPs), the mesogens hang from the main polymeric backbone as pendants.³ If the backbone itself is liquid crystalline then this forms a novel class of liquid crystalline polymers under SCLCP.

The object of the present study was to investigate the relation between the molecular structure and the physical properties exhibited by chiral monomers and their polymers. The chiral smectic phases, of late have been widely investigated, and have become the focus of active research since the discovery of the chiral smectic C* sub-phases such as *antiferroelectric*, *ferrielectric* and $S_{C\alpha}^*$ phases in the late 1980's.⁴ The effect of polymerisation on the mesophase has been investigated by various authors.⁵ Several reviews have appeared since then, signifying the importance of this field.^{6,7,8} This thesis describes the synthesis and physical properties of a number of naphthalene

moiety containing liquid crystalline monomers and siloxane polymers in which these monomers are attached as pendants.

The thesis has been divided into three parts. Part I deals with a general introduction to the field of liquid crystals. Part II contains the results and discussion of investigations carried out on monomers and their polysiloxanes. Part III describes the experimental procedures that were used to prepare the various compounds as well as the measurement of various physical properties.

Part I : Introduction

The section begins with the customary introduction to liquid crystals as a distinct state of matter and continues to review this century old field which was revived about thirty years ago. A brief description of the various very well known phases, such as nematic, smectic and ferroelectric phases is followed by some recently discovered phases such as antiferroelectric and twist grain boundary (TGB_A) phases. A review of the synthesis and properties of polymeric liquid crystals begins with their classification. This is succeeded by a description of the main chain liquid crystalline polymers (MCLCPs), and synthetic strategies to achieve different types of MCLCPs.

An enumeration of the salient features of side chain liquid crystalline polymers (SCLCPs) follows the above. There is an emphasis on the siloxane based side chain polymers as this thesis describes the preparation and properties of some polysiloxanes. A brief description of the different types of SCLCPs, the synthetic strategies to prepare them, novel ways of coupling a mesogen to the backbone and the types of mesogenic units that can be used is also given. Some aspects of copolymers form the last part of this sub-section.

Some applications of liquid crystals have been mentioned at the end of this section. This includes only the latest advances in low molar mass liquid crystals (LMMLC) and the conventional uses of LMMLC are touched upon very briefly. The uses of polymeric liquid crystals, especially the **SCLCPs**, are given in more detail.

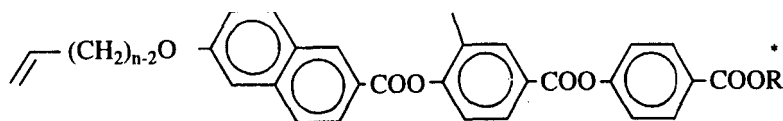
Part II : Results and Discussion

This section begins with a discussion of the structure and properties of chiral smectic C phase. The physical properties of the ferroelectric as well as other chiral sub-phases has been discussed briefly and emphasis has been laid on the ferroelectric properties of the chiral smectic C phase.

The synthetic approaches adopted for the synthesis of the monomers is described. The reaction sequence used to synthesise each compound is also given.

Polarising optical microscopy is one of the most important ways of identifying and characterising a mesophase. This technique was used to characterise mesogenic property of the monomers synthesised and is described in detail. Photomicrographs of the textures of mesophases of a few compounds is also appended.

It is well known that investigation of structure property relationship may be studied by a systematic variation of the structure. The modifications carried out on the parent compound should neither be too less, as to make the properties very similar, nor too much as to make the structure completely different from that of the parent molecule. Keeping this in mind, the following general structure of the mesogenic system was chosen.



General structure of the mesogenic system chosen.

The molecular structure was systematically varied in every respect except for the naphthalene moiety in order to study the effect of various modifications on the thermal stability and appearance of different mesophases. **Fig.i** shows the different series of compounds synthesised, changes effected and their effect upon the mesophases is described.

It was observed that a longer spacer increased the possibility of formation of a S_C^* phase. Also monomers with a longer spacer showed lower thermal stability and lower transition temperatures. With a shorter spacer, TGB_A phase over a narrow range of temperature was observed in series 'R' and 'K'. An important requirement for obtaining a TGB_A phase is a smectic A phase over a small range of temperature. The compounds of series reported here have a fairly wide temperature range for the smectic A phase, and still exhibited a TGB_A phase. This has been attributed to the ability of the chiral centre, which has a strong dipolar chloro group, to induce enough fluctuation for the cholesteric phase to penetrate the smectic A phase.

The structure was next varied by removing a phenyl ring from the parent molecule. Thus the compound now contained a three ring system as its core. As expected the mesophase thermal stability was drastically lowered (compare series I vs S and N vs H), by about 100-120°C.

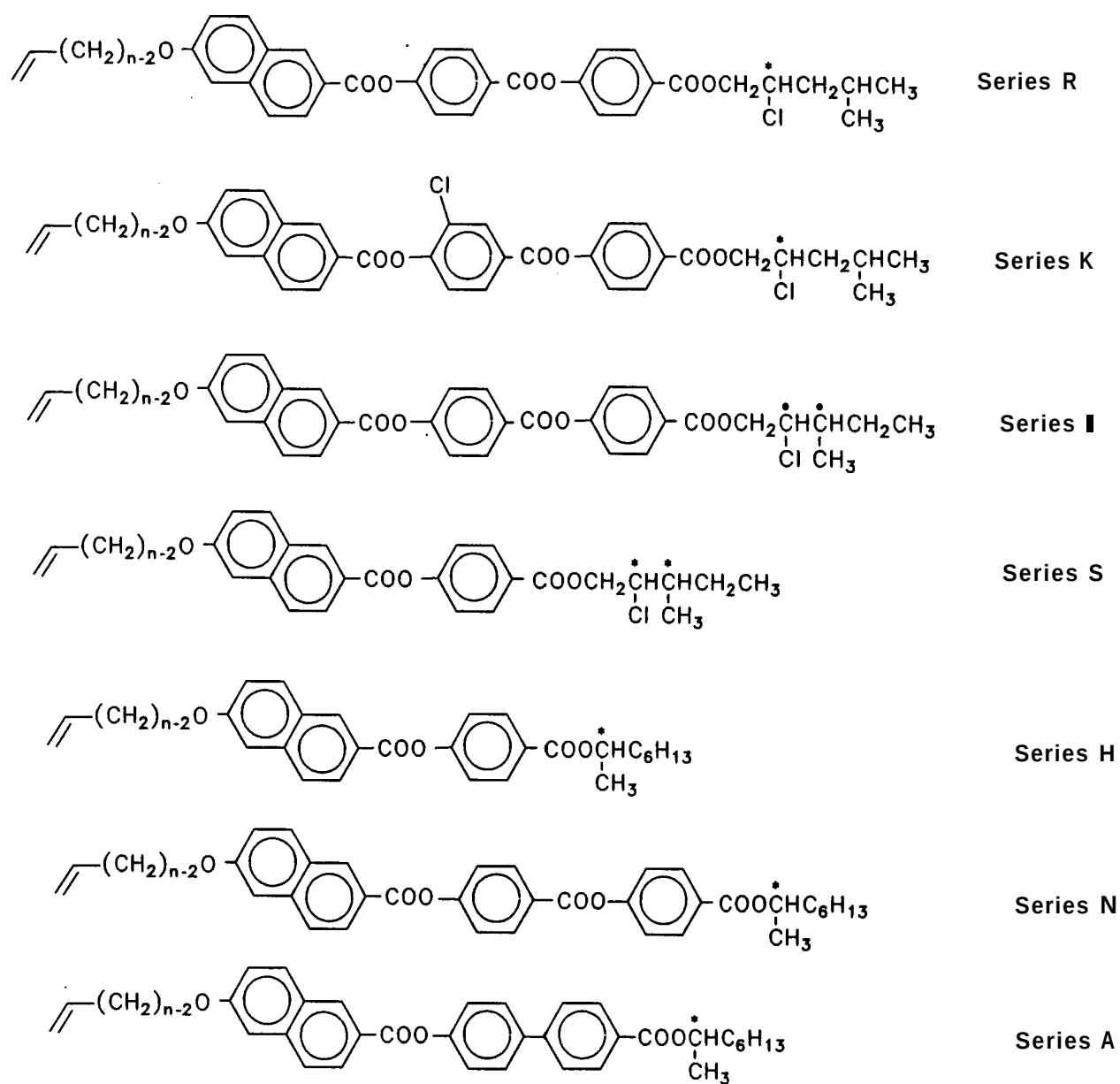


Fig. i

Then, keeping the three ring core constant, the chiral centre was changed. Chiral octan-2-ol based phenyl ester (series H) was prepared instead of the 2-chloro 3-methylpentyl phenyl ester (series S) system. This new series of compounds showed even lower thermal stability. In fact, in the case of lower homologues, the normally stable smectic A phase became metastable.

An additional phenyl ring was added to this system, resulting in series N. This new series showed the novel antiferroelectric phase in addition to the ferroelectric phase. It was clear that the stability of the chiral smectic C phase observed in case of series R and I could be attributed to the influence of the terminal double bond. This was causing an antiferro-like arrangement of molecules in the adjacent layers and consequently stabilising the tilted smectic phases. The antiferroelectric phase exhibited by compounds of series N, which contain a naphthalene moiety, was stable over a much wider temperature range as compared to compounds containing a phenyl ring⁹ (series P, Fig.ii).

The central ester linkage between the two phenyl groups was effectively removed by the introduction of a biphenyl moiety. This major structural change did not bring about much change in the transition temperatures, or the spontaneous polarisation value or the optical tilt angle measured.

A discussion of the above is followed by details of the experimental setup constructed for measuring the spontaneous polarisation and tilt angle of molecules in the ferroelectric phase. Tilt angle was also independently measured by X-ray experiments and their results compared with those obtained optically.

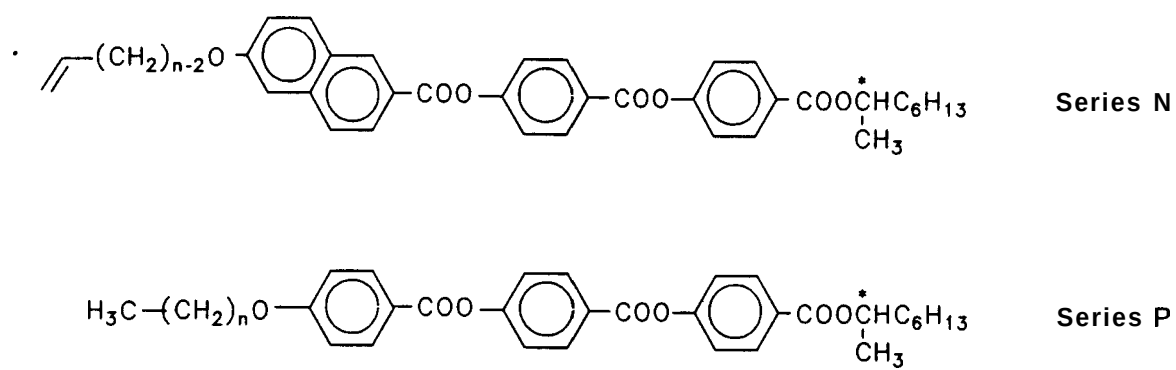


Fig. ii

Effect of polymerisation on mesophase formation and ferroelectric properties

Hydrosilylation with poly(hydrogendimethyl)siloxane was carried out using the terminal alkene monomers described above (Fig.iii.a, Fig.iii.b). The following observations could be made. The mesophases, such as TGB_A , antiferroelectric and chiral smectic C_α phases get suppressed on polymerisation while S_C^* phase gets stabilised as compared to the monomers. Transition temperatures as well as thermal stabilities of the polymeric liquid crystals were higher than the monomers from which they were derived, by about 30 to 40°C on an average. Most other influence seen in low molar mass (LMM) compounds were carried over, *e.g.* lowering of temperature by introduction of 'Cl' group or by removing the central ring. Copolymerisation (series MP, using N-8 and H-9, at increasing ratios of N-8, 0%, 25%, 50%, 75%, 100%) resulted in a lowering of phase as well as glass transition temperatures as expected, although no influence on the mesophase itself was seen. A possible explanation for the double glass transition temperatures observed in some series of polymers (NP, AP, MP) is also discussed. Briefly, the observation of double T_g implies an extensive decoupling of the motions of the main chain from that of the side chain, and possibly a microphase separation of the backbone and the side chain mesogenic groups. This fact is supported by observation of fairly good mesophase textures in the case of polymers showing double T_g .

X-ray diffraction data was used to study the temperature dependence of layer spacing in the monomers and the polymers synthesised. It was observed that the layer spacing in the S_A phase of the monomer was less than its corresponding siloxane polymer. This implies that the polymer backbone contributes to the net layer spacing that could be observed by X-ray methods.

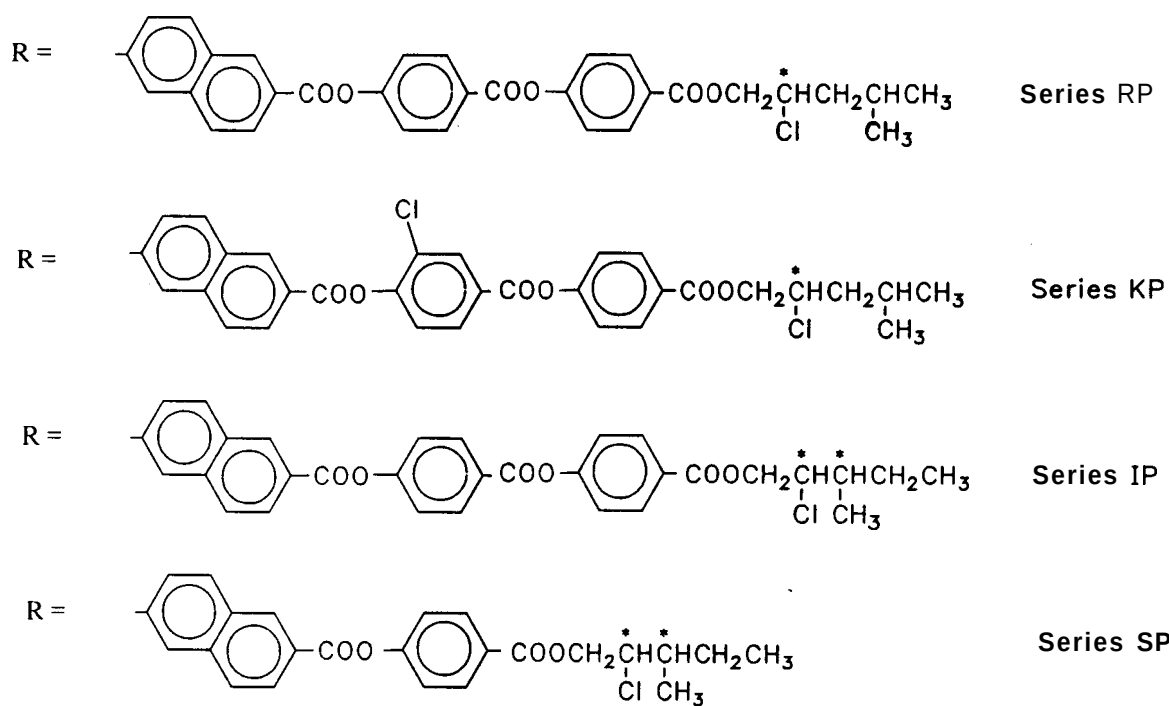
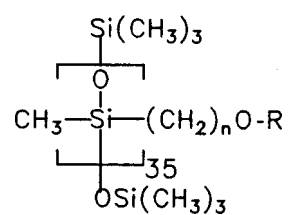
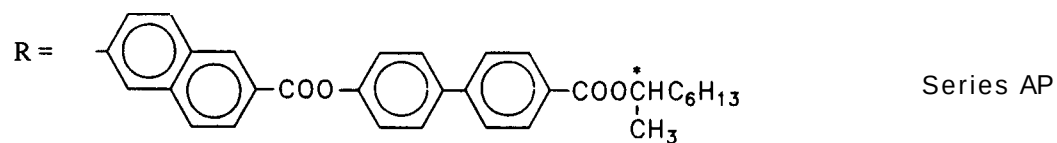
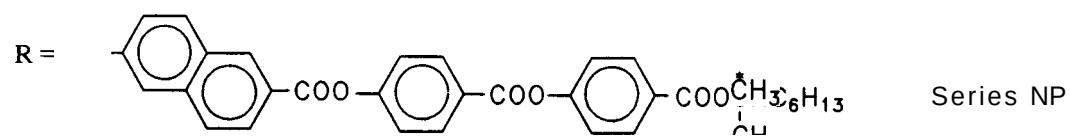
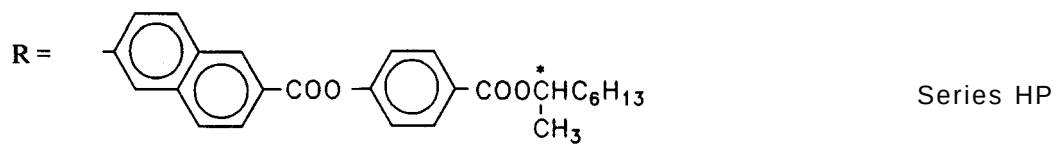
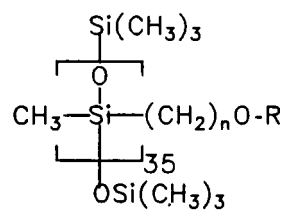


Fig. iiiia



Copolymer series MP

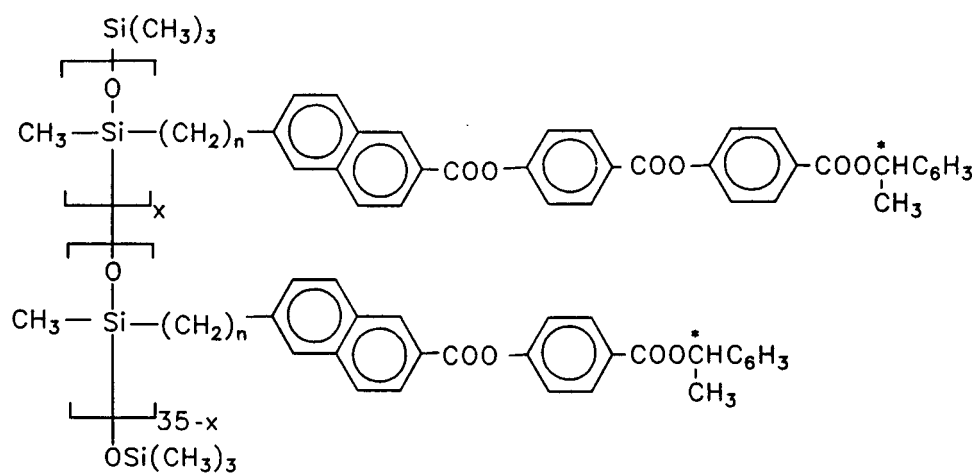


Fig. iiib

Part 111 : Experimental procedures and measurements

The experimental setup constructed and used for measuring the spontaneous polarisation and optical tilt angle has been described in this section. The setting up of the experiment involved the interfacing of three electronic equipments *viz.* a digital storage oscilloscope, a heating stage and a function generator with a 386 computer. The C programming language was learnt and used for the purpose of controlling the instruments. The oscilloscope had a built-in D-A convertor, which was used for the purpose of converting the analog output to digital and then retrieved back to the computer for further analysis. This instrument was interfaced *via* a National Instruments' GPIB card. The heating stage, Mettler FP-80, was interfaced through serial port by using RS-232 commands. Finally, the analysis of the data was done by a program written for the purpose in 'C'. Thus, in the process, the author learnt computer programming and interfacing of instruments with a PC *via* GPIB card and the serial port RS-232 routines.

X-ray studies were carried out on a 18cm image plate from Marresearch, Germany. A $\text{Cu-K}\alpha$ radiation at $1.54 \text{ \AA}$, monochromated with graphite monochromator was used. The sample was filled in capillaries and a magnetic field was used to align the samples. This was achieved by slow cooling across the I-S_A phase transition in the presence of the magnetic field. Temperature was controlled to an accuracy better than 0.1°C .

Synthesis

This section begins with a specification of the solvents, equipment and instruments used.

Monomers

The detailed experimental procedures used for synthesising and characterising the monomers has been described in this section. All the intermediates and the monomers synthesised were completely characterised by the standard methods of analysis using IR, UV, ¹HNMR, optical rotation and elemental analysis. The physical constants obtained for each of the monomer is given.

Polymers

The polymers were synthesised using the popular hydrosilylation reaction. The reaction conditions and the modification according to the requirements are given. This is followed by details of physical characterisation of the polymers synthesised. The analytical data for all the polymers synthesised is also given.

Some of results presented in this thesis are reported in the following publications.

1. Ferroelectric liquid crystalline polysiloxanes incorporating a naphthalene moiety. (C.R. Gopalakrishnan and B. K. Sadashiva) - Macromolecular Rapid Communications - accepted for publication.

2. Ferroelectric and antiferroelectric liquid crystalline phases in some naphthalene carboxylic acid derivatives. (C. R. Gopalakrishnan and B. K. Sadashiva) - accepted for presentation in the 6th International Conference on Ferroelectric Liquid Crystals, 18th-23rd July 1997, France.

3. Physical studies on side chain siloxane polymers with pendant **mesogens** containing naphthyl group in the core. (C. R. Gopalakrishnan and B. K. Sadashiva) - accepted for presentation in the 6th International Conference on Ferroelectric Liquid Crystals, 18th-23rd July 1997, France.

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CONTENTS

PART I

Introduction

Pages 1-32

I.1	Introduction
I.1.1	<i>Nematic liquid crystals</i>
I.1.2	<i>Cholesteric liquid crystals</i>
I.1.3	<i>Smectic liquid crystals</i>
I.1.4	<i>Ferroelectric liquid crystals</i>
I.1.5	<i>The twist grain boundary phases</i>
I.2	Introduction to polymeric liquid crystals
I.2.1	<i>Classification of liquid crystalline polymers</i>
I.2.2	Main chain liquid crystalline polymers
I.2.2.1	<i>Synthetic strategy for main chain liquid crystalline polymers</i>
I.2.2.2	<i>Rigid main chain liquid crystalline polymers</i>
I.2.2.3	<i>Semi-flexible main chain liquid crystalline polymers</i>
I.2.3	Side chain liquid crystalline polymers
I.2.3.1	<i>Side chain siloxane polymers</i>
I.2.3.2	<i>The backbone</i>
I.2.3.3	<i>Spacer</i>
I.2.3.4	<i>Mesogenic units</i>
I.2.4	Synthetic strategy for side chain liquid crystalline polymers
I.2.4.1	<i>Novel mesogenic units</i>
I.2.4.2	<i>Novel methods of coupling</i>
I.2.5	Copolymers
I.3	Applications
I.3.1	Applications of low molar mass liquid crystals
I.3.2	Applications of liquid crystalline polymers
I.3.2.1	<i>Application in electro-thermo-optical methods</i>
I.3.2.2	<i>Application in separation methods</i>
	References

PART II

Results and Discussion

Part IIa

Monomers

Pages 33-63

IIa.1	A brief survey of chiral smectic phases
IIa.1.1.1	<i>The ferroelectric-sub phases</i>
IIa.1.2	Influence of molecular structure on mesomorphism
IIa.1.2.1	<i>Variation in the hydrocarbon chain length</i>
IIa.1.2.2	<i>Variation in the core</i>
IIa.1.2.3	<i>Variation in the chiral moiety</i>
IIa.2	Synthesis and characterisation of monomers
IIa.2.1	<i>Liquid crystalline properties of monomers</i>
IIa.3	Physical measurements
IIa.3.1	Spontaneous polarisation
IIa.3.1.1	<i>Measurement of spontaneous polarisation</i>
IIa.3.2	X-ray studies
IIa.3.2.1	<i>Powder samples</i>
IIa.3.2.2	<i>Oriented samples</i>
IIa.3.3	Optical tilt angle
	References

PART II

Results and Discussion

Part II b

Polysiloxanes

Pages 64-84

IIb.1	A brief survey of side chain liquid crystalline polymers with special reference to polysiloxanes
IIb.1.1	<i>Structural types (homo- and copolymers)</i>
IIb.2	Methods of synthesis
IIb.2.1	<i>General aspects</i>
IIb.2.2	<i>Types of catalysts</i>
IIb.3	Synthesis and characterisation of side chain liquid crystalline siloxane polymers
IIb.3.1	<i>Ferroelectric liquid crystalline siloxane polymers</i>
IIb.4	Discussion
IIb.4.1	<i>Influence of spacer on phase transitions</i>
IIb.4.2	<i>Influence of polymer backbone on phase transitions</i>
IIb.4.3	<i>Influence of mesogenic unit on phase transitions</i>
IIb.4.4	<i>Naphthalene containing polymers</i>
IIb.5	Physical studies
IIb.5.1	<i>Spontaneous polarisation and tilt angle</i>
IIb.5.2	<i>X-ray studies</i>
	References

PART III
Experimental details
Pages 85-126

III.1 **General methods of investigation**

III.2 **Physical methods**

III.2.1 *Sample cell*

III.2.2 *Sample alignment*

III.2.3 *Experimental setup*

III.3 **Synthetic procedures**

III.3.1 *Monomers*

III.3.2 *Polymers*

References