

---

# CONTENTS

---

<b>CONTENTS .....</b>	<b>xxii</b>
<b>LIST OF FIGURES.....</b>	<b>xxxiii</b>
<b>LIST OF TABLES.....</b>	<b>1</b>
<b>CHAPTER-1: Introduction .....</b>	<b>1</b>
1.1. Liquid crystals .....	1
1.2. Classification of liquid crystals .....	5
1.2.1. External controlling factors .....	5
1.2.1.1. Lyotropic Liquid Crystal .....	6
1.2.1.1.1. Colloidal lyotropic phases .....	7
1.2.1.1.2. Self-assembled structures .....	7
1.2.1.2. Thermotropic liquid crystals.....	9
1.2.2. Liquid crystals formed by the shape of the molecules .....	11
1.2.2.1. Calamatic liquid crystals .....	11
1.2.2.2. Discotic liquid crystals .....	13
1.2.2.3. Bowlic liquid crystals .....	14
1.2.2.4. Bent liquid crystals .....	15
1.2.2.5. Polymeric liquid crystals .....	15

## CONTENTS

---

1.2.2.6. Chiral liquid crystals.....	16
1.3. Types of orderings present in the anisotropic liquid crystalline phases .....	20
1.3.1. Order parameters .....	20
1.3.2. Orientational order.....	20
1.3.3. Translational order.....	21
1.3.4. Bond orientational order .....	22
1.4. Liquid crystalline phases .....	22
1.4.1. Liquid crystalline phases formed by thermotropic calamitic liquid crystals .....	22
1.4.1.1. Non-tilted phases .....	22
1.4.1.1.1. Nematic (N) phase .....	22
1.4.1.1.2. Smectic (Sm) mesophases .....	24
1.4.1.1.2.1. Smectic-A (SmA) phase .....	25
1.4.1.1.2.2. Smectic-B (SmB) phase .....	27
1.4.1.2. Tilted phases .....	28
1.4.1.2.1. Smectic-C (SmC) phase.....	28
1.4.1.2.2. Smectic-D (SmD) phase .....	30
1.4.1.2.3. Smectic-E (SmE) phase .....	30
1.4.1.2.4. Smectic-F (SmF) phase .....	31
1.4.1.2.5. Smectic-G (SmG) phase .....	32
1.4.1.2.6. Smectic-H (SmH) phase .....	34

## CONTENTS

---

1.4.1.2.7. Smectic-I (SmI) phase .....	35
1.4.1.2.8. Smectic-J (SmJ) and smectic-K (SmK) phases ..	35
1.4.1.2.9. Smectic-M (SmM) and smectic-O (SmO) phases .....	36
1.4.1.2.10. Smectic-Q (SmQ) and smectic-X (SmX) phases .....	37
1.4.2. Liquid crystalline meso-phases formed by thermotropic chiral liquid crystals.....	37
1.4.2.1. Cholesteric ( $N^*$ ) or chiral nematic mesophase .....	38
1.4.2.2. Chiral smectic- $A^*$ ( $SmA^*$ ) phase .....	41
1.4.2.3. Chiral ferroelectric Smectic- $C^*$ ( $SmC^*$ ) phase .....	42
1.4.2.4. Chiral anti-ferroelectric $SmC_A^*$ phase .....	45
1.4.2.5. Chiral ferrielectric $SmC_\gamma^*$ phase .....	45
1.5. Sequence rule and re-entrant behavior in calamitic liquid crystals.....	46
1.6. The concept and use of symmetry in liquid crystals .....	49
1.7. Concept of phase transitions.....	51
1.8. Physical properties of liquid crystalline materials .....	55
1.8.1. Optical anisotropy (Birefringence).....	55
1.8.2. Dielectric anisotropy.....	57
1.8.3. Dielectric spectroscopy.....	58
1.8.4. Spontaneous polarization.....	59
1.8.5. Viscosity .....	62

## CONTENTS

---

---

<b>References</b> .....	63
<b>CHAPTER-2: Theoretical Background and Experimental Techniques</b> .....	<b>77</b>
2.1. Introduction .....	77
2.2. Theoretical background .....	77
2.2.1. Theories of liquid crystalline phases .....	77
2.2.1.1. Maier-Saupe Mean field theory of the nematic phase .....	78
2.2.1.2. McMillan's theory of the smectic-A Phase .....	83
2.2.2. Phase transitions in liquid crystals.....	86
2.2.2.1. Thermodynamics of phase transitions .....	87
2.2.2.2. Classification of phase transitions .....	89
2.2.3. Kobayashi-McMillan theory.....	91
2.2.4. The basic ideas of Landau theory .....	93
2.2.4.1. Isotropic to Nematic (I-N) phase transition.....	97
2.2.4.2. Phenomenological description of the N-SmA phase transition. ....	100
2.2.4.3. Theory behind the SmA-SmC Phase transition.....	104
2.2.4.4. Higher order smectic phases .....	108
2.2.4.5. Re-entrant nematic phase.....	109
2.2.4.6. Theory behind the anti-ferroelectric liquid crystals.....	116
2.2.4.6.1. Orihara and Ishibashi model.....	117
2.2.4.6.2. Zeks and Cepic model .....	121

---

---

## CONTENTS

---

2.2.4.6.3. Theory behind the birefringence suppression..	129
2.2.4.7. Chiral SmA <sup>*</sup> -SmC <sup>*</sup> phase transition .....	131
2.2.5. Critical exponent, universality class and renormalization group expression .....	133
2.2.6. Theory behind the physical properties.....	137
2.2.6.1. Optical birefringence .....	137
2.2.6.2. Study of dielectric permittivity .....	139
2.2.6.2.1. Maier and Meier (MM) theory of dielectrics for liquid crystals.....	139
2.2.6.3. Dielectric Spectroscopic study .....	142
2.2.6.3.1. Debye model.....	142
2.2.6.3.2. Cole-Cole model.....	144
2.2.6.4. Relaxation modes .....	145
2.2.6.4.1. The Soft Mode .....	146
2.2.6.4.2. The Goldstone Mode .....	146
2.3. Experimental techniques .....	147
2.3.1. Preparation of liquid crystalline mixtures .....	147
2.3.2. Texture studies.....	148
2.3.3. Differential scanning calorimetry (DSC) .....	149
2.3.4. Optical birefringence measurement.....	150
2.3.5. Optical Transmission (OT) method .....	151
2.3.5.1. Determination of orientational order parameter .....	153

## CONTENTS

---

2.3.6. Dielectric investigations .....	154
2.3.6.1. Static dielectric permittivity measurements .....	154
2.3.6.2. Dielectric spectroscopy measurements.....	156
2.3.7. Spontaneous polarisation measurement .....	158
2.3.7.1. Determination of torsional viscosity and activation energy .....	160
2.3.7.1.1. Torsional viscosity.....	160
2.3.7.1.2. Activation energy .....	161
2.3.7.2. Anchoring energy coefficients.....	161
<b>References .....</b>	<b>164</b>
 <b>CHAPTER-3: Critical behaviour in the vicinity of the Isotropic to Nematic and the Nematic to Smectic-A phase transitions of two polar- polar binary liquid crystalline systems.....</b>	
3.1. Introduction .....	179
3.2. Materials .....	184
3.3. Phase diagram.....	185
3.4. Optical birefringence .....	188
3.5. Critical behaviour in the vicinity of the I-N phase transition.....	193
3.6. Critical behaviour in the vicinity of the N-SmA phase transition.....	196
3.7. Conclusion.....	210
<b>References .....</b>	<b>213</b>

## CONTENTS

---

---

<b>CHAPTER-4: Critical behaviour of birefringence in the vicinity of the Nematic to Smectic-A and the Smectic-A to Re-entrant Nematic phase transitions of a binary system composed of 6OCB and 8OCB .....</b>	<b>219</b>
4.1. Introduction .....	219
4.2. Materials .....	231
4.3. Phase diagram.....	233
4.4. Optical birefringence .....	234
4.5. Critical behaviour in the vicinity of the N-SmA and the SmA- $N_R$ phase transitions .....	237
4.6. Conclusion.....	244
<b>References .....</b>	<b>247</b>
<b>CHAPTER-5: Study the nature of various mesophase transitions associated with two enantiomers R-MHPOBC, S-MHPOBC and their racemic mixture .....</b>	<b>254</b>
5.1. Introduction .....	254
5.2. Materials .....	260
5.3. Texture studies.....	261
5.4. Birefringence and specific heat capacity of R and S-MHPOBC .....	262
5.5. Critical behaviour in the vicinity of the I-SmA*, SmA*-SmC $_{\alpha}$ * and other tilted smectic sub-phase transitions of R and S-MHPOBC.....	266
5.5.1. Determination of critical exponent from specific heat capacity anomaly.....	266
5.5.2. Determination of the critical exponent from birefringence.....	267

## CONTENTS

---

5.5.3. I-SmA* phase transition .....	268
5.5.4. SmA* - SmC $\alpha$ * phase transition .....	269
5.5.5. SmC $\alpha$ * - SmC* phase transition .....	271
5.5.6. SmC* - SmC $\gamma$ * phase transition .....	271
5.5.7. SmC $\gamma$ * - SmC $A$ * phase transition .....	271
5.6. Critical exponent from the birefringence suppression near the SmA* - SmC $\alpha$ * phase transition of R and S-MHPOBC .....	276
5.7. Birefringence and specific heat capacity of the racemic mixture of R and S-MHPOBC .....	279
5.8. Critical behaviour in the vicinity of the SmA-SmC and SmC-SmC $A$ phase transitions of the racemic mixture of R and S-MHPOBC .....	281
5.8.1. SmA-SmC phase transition .....	281
5.8.2. SmC-SmC $A$ phase transition .....	282
5.9. Comparison of the critical exponents extracted from the two different parameters .....	284
5.10. Conclusion .....	286
<b>References</b> .....	<b>289</b>
<b>CHAPTER-6: Investigation on the smectic-A* to smectic-C* and N* to smectic-C* phase transitions of some pure chiral ferroelectric liquid crystalline compounds and their binary mixtures .....</b>	<b>297</b>
6.1. Introduction .....	297
6.2. Materials .....	306
6.3. Preparation of binary mixtures .....	306

---

## CONTENTS

---

6.4. Texture studies.....	309
6.5. Modulated differential scanning calorimetry .....	311
6.6. Optical transmission (OT) method .....	312
6.7. Phase diagram.....	314
6.8. Optical birefringence of the investigated pure compounds and their binary mixtures .....	315
6.9. Critical behaviour in the vicinity of the investigated phase transitions .....	319
6.9.1. Order character of the I-SmA*, I-N* and N*-SmC* phase transitions .....	320
6.9.2. Critical behaviour in the vicinity of the SmA*-SmC* phase transition .....	322
6.10. Spontaneous polarization of the investigated pure as well as the binary mixtures .....	328
6.11. Conclusion.....	330
<b>References .....</b>	<b>333</b>
<b>CHAPTER-7: Effect of molecular structure on electro-optic and dielectric properties of some pure chiral ferroelectric liquid crystalline compounds based on lactic acid derivatives having three aromatic rings connected by ester groups.....</b>	<b>339</b>
7.1. Introduction .....	339
7.2. Materials .....	344
7.3. Mesomorphic behaviour.....	345

## CONTENTS

---

---

7.4. Spontaneous polarization .....	347
7.5. Response time and torsional viscosity.....	352
7.6. Activation energy .....	355
7.7. Anchoring energy co-efficient.....	357
7.8. Static dielectric permittivity and dielectric anisotropy .....	359
7.9. Frequency dispersion of complex dielectric permittivity.....	363
7.10. Temperature dependence of dielectric strength and relaxation frequency .....	369
7.11. Conclusion.....	372
<b>References .....</b>	<b>376</b>
<b>CHAPTER-8: Study of the electro-optic and dielectric properties of some ferroelectric liquid crystalline binary mixtures.....</b>	<b>385</b>
8.1. Introduction .....	385
8.2. Materials .....	387
8.3. Phase identification .....	388
8.4. Spontaneous polarization .....	390
8.5. Response time and torsional viscosity.....	394
8.6. Activation energy .....	396
8.7. Static dielectric permittivity and dielectric anisotropy .....	398
8.8. Dielectric spectroscopy .....	403
8.8.1. Frequency dependence of complex relative dielectric permittivity .....	403

## **CONTENTS**

---

---

8.8.2. Dielectric loss due to Soft Mode contribution.....	411
8.9. Conclusion.....	413
<b>References .....</b>	<b>415</b>
<b>CHAPTER-9: Summary and Conclusions.....</b>	<b>421</b>
<b>LIST OF PUBLICATIONS .....</b>	<b>441</b>
<b>PAPER PRESENTED IN CONFERENCES .....</b>	<b>443</b>
<b>INDEX .....</b>	<b>445</b>