

CHAPTER 9

Summary and conclusions

The dissertation entitled “*Phase transitions in binary mixtures of calamitic and bent-core mesogens*” submitted for the degree of Doctor of Philosophy (Physics) of the University of North Bengal is principally devoted to comprehensive study and understanding of several phase transitions in binary liquid crystal mixtures consisting of calamitic and bent-core mesogens using different experimental techniques. The investigation of various physical parameters influenced by variation of temperature provides precious information about mesophase properties. The detailed investigation of these mesophase behavior and their transitions emerged a field of significant interest in liquid crystal (LC) research. Since extensive research works have been utilized so far to describe the nature of mesophase transition involving isotropic (*I*), nematic (*N*), smectic-*A* (*Sm-A*) phases in a number of pure calamitic compounds and their mixtures, it should be an appropriate formalism for the study of phase transition in liquid crystalline mixtures involving bent-core mesogens exhibiting a number of exotic mesomorphic features, finding no trace in classic calamitic compounds. Despite the success of qualitative explanations about the nature of transitions among these mesophases, an unsolved controversy still persists in ascertaining the exact nature of the smectic-*A* to smectic-*C* (*Sm-A–Sm-C*) phase transition. The bulk of this dissertation is mainly representing a clear scenario about the phase behavior and experimentally characterization of the order character for the isotropic–nematic (*I–N*), nematic–smectic-*A* (*N–Sm-A*) phase transitions and most importantly the smectic-*A* to smectic-*C* (*Sm-A–Sm-C*) phase transition in some binary mixtures comprising of calamitic and bent-core compounds. The influence of bent-core molecules on the phase character of rod-like and chiral mesogenic environment has also been discussed from the experimental point of view. Additionally, the molecular dynamics and the nature of the mesophases have been studied in some homologous symmetrical pure bent-core liquid crystal compounds. A brief summary and conclusions of eight various chapters are described as follows:

Chapter 1 deals with a brief introduction and basic concept of liquid crystal materials as well as their basic classification scheme, particularly the thermotropic liquid crystals. Associated molecular arrangements and general behavior of different mesophases for both the calamitic and bent-core LC system have been discussed. The importance regarding formulation of liquid crystal mixtures and appearance of the induced phase has also been described. The chapter also includes a concise discussion about the phase transition along with the critical phenomena and critical exponents.

Chapter 2 describes the experimental techniques and relevant procedures employed to investigate pure LC compounds and binary mixtures. Moreover, the basic theories of the $I-N$ and $N-Sm-A$ phase transitions along with an extension to the $Sm-A-Sm-C$ phase transition in liquid crystal system have also been discussed in brief.

In chapter 3, an extensive optical investigation has been carried out in a binary system, consisting of a hockey stick-shaped liquid crystal, 4-(3-decyloxyphenyliminomethyl) phenyl 4-decyloxybenzoate (SF7) and the rod-like 4-cyano-4'-octyloxybiphenyl (8OCB). An enhancement of the concentration of hockey stick-shaped compound within the mixtures leads to a significant decrease in the nematic width of the rod-like sample, *i.e.*, it stabilizes the lower temperature smectic phase. The molecular bend of the angular mesogenic dopant reflects a stronger influence on the phase-character of mixtures and leads to a relatively stronger coupling between nematic and smectic order parameter. The temperature-dependent variation of optical birefringence (Δn) demonstrates a quite well consistency obtained from both the high-resolution optical transmission method and thin prism technique. The birefringence data has been found to be rather successful in describing the transitional behavior more precisely associated with both the $I-N$ and the $N-Sm-A$ phase transitions in all the investigated mixtures. The experimental Δn data demonstrates a clearly distinguishable pretransitional phenomenon near

the $I-N$ phase transition. The extracted order parameter critical coefficient β related to this transition has found to reveal a good conformity with the theoretically predicted tricritical value ($\beta = 0.25$) for all of the studied mixtures. Furthermore, a noticeable pretransitional behavior has been observed in Δn data at the $N-Sm-A$ transition. The divergence character of the differential quotient $Q(T)$ in the vicinity of that transition has found to be well described by a power-law expression including the scaling terms. The related effective critical exponent (α', β'), describing the critical fluctuations at that transition has appeared to be non-universal in nature representing the values in between the 3D-XY and tricritical limit. The obtained α' values demonstrates a strong dependency on the width of the nematic phase, while a crossover character of the $N-Sm-A$ phase transition from second order to first order nature for a McMillan ratio of 0.994 and an approximate nematic width of about 2.5 K which again reveals a close agreement with the reported value for the mixtures of similar mesogenic systems. Therefore, the modification in effective intermolecular interactions in the host medium demonstrates a sharp decrease in the nematic width and drives the $N-Sm-A$ phase transition towards the first order in nature.

Chapter 4 embraces the static dielectric and visco-elastic properties of the binary system reported in chapter 3. The value of longitudinal component of the dielectric permittivity exhibits a noticeable decrease with increase in dopant concentration due to a stronger dipole-dipole interaction within the mixture. All the investigated mixtures possess a large positive dielectric anisotropy ($\Delta\epsilon$), but found to diminish monotonically by increasing the hockey stick-shaped dopant concentration. The obtained values of the parameters ϵ_{avg} and $\Delta\epsilon$ exhibits a systematic temperature and concentration dependency. By analyzing the pretransitional fluctuation in the vicinity of $I-N$ phase transition, yielded critical coefficient assumes a value nearly equal to 0.5 within a valid error limit and independent of the concentration variation which clearly implies

a first-order character of the I - N phase transition. By the similar procedure as used in chapter 3, the critical anomaly in the vicinity of N - Sm - A phase transition has been investigated from the temperature-dependent dielectric anisotropy ($\Delta\epsilon$) data. The extracted critical exponent (α') divulges a systematic concentration variation and found to reveal a quite good consistency obtained from both the high-resolution optical birefringence and dielectric anisotropy measurements. Furthermore, the temperature-dependent value of the splay elastic constant (K_{11}) and the rotational viscosity (γ_1) in the nematic phase has been observed to enhance gradually by lowering the temperature due to increase in molecular ordering, while the slope of the increasing pattern for both the K_{11} and γ_1 becomes steeper with increasing the hockey stick-shaped mesogen. The obtained values of γ_1 for all of the mixtures have been found to be slightly higher than that of the usual calamitic compounds as well as comparatively lower value than the reported values of the bent-core compounds. The calculated activation energy (E_a) increases with the dopant concentration signifying an enhancement in intermolecular packing which affects the molecular motion within the system. Moreover, the strong dipolar correlation between dissimilar molecules within the mixture significantly affects the molecular motion.

Chapter 5 focuses on the investigations of the critical behavior at the nematic–smectic- A (N - Sm - A) and smectic- A –smectic- C (Sm - A - Sm - C) phase transitions from the optical investigation in a pure pyrimidine (PhP2) liquid crystal compound as well as in some binary mixtures of PhP2 with another homologous compound (PhP1) of the same series. The order character of these transitions has been explored by varying the temperature range of the Sm - A and N phases. However, an inspection carried out in this system concerning the dependency of critical exponent α' on the reduced temperature and observed that the transitional behavior of the Sm - A - Sm - C phase transition is really critical over the range 3×10^{-3} . The obtained values of the critical exponent α'

have been found to be non-universal in nature for both the N -Sm- A and Sm- A -Sm- C phase transitions and hence indicate a crossover character from second order to the first order transition. Moreover, the crossover character of these phase transitions from the second-order to weakly first-order in nature has been clearly explained on the basis of the width of the N and Sm- A temperature range linked with the N -Sm- A and Sm- A -Sm- C phase transitions respectively. Moreover, a comparative discussion has been accomplished concerning the similarity and dissimilarity of order nature for both the transitions. It has been seen that the origin of such critical behavior is a unique feature for both the N -Sm- A and the Sm- A -Sm- C phase transitions for all the studied compounds and they are seen to follow two distinctly different linear curves. Additionally, the critical behavior in the vicinity of isotropic-nematic (I - N) phase transition has been reported for all the studied mixtures including a pure compound. The critical exponent β , characterizing the limiting behavior of the nematic order parameter close to that transition, has come out to be close to 0.25 and hence in agreement with the tricritical hypothesis.

In chapter 6, an extensive investigation has been carried out for the endorsement of tricriticality nature of the Sm- A -Sm- C phase transition in a binary system comprising of hockey-stick-shaped compound (H-22.5) and the calamitic compound (7OCB) from a high-resolution temperature scanning measurement of optical birefringence (Δn). A significant destabilization of the nematic phase along with an emergence of the Sm- A phase has been observed in the phase diagram due to the increase in the concentration of the calamitic nematogen. From a precise investigation on the temperature derivative of optical birefringence in the vicinity of the Sm- A -Sm- C phase transition, the yielded values of the effective critical exponent (α') have found to be non-universal in nature and exhibit a variation in accordance with the change of the Sm- A phase range. The values of α' are found to follow the same pattern in between 3D- XY and tricritical (TCP) limit as observed in chapter 5 for the

lower limit of Sm-A phase range of about ~ 10.5 K and further decrease in the Sm-A range drives the α' values to the tricritical limit ($\alpha' = 0.5$). The justification of such tricritical nature has been reanalyzed more elaborately with the aid of renormalization group expression including some precise modification. Interestingly, the extracted critical exponent (α') values suggesting a broad tricritical range for the Sm-A–Sm-C phase transition over a wide range of temperature ratio (from 0.972 to 0.994). Considering all experimental findings it has been ascertained that the order character of the Sm-A–Sm-C phase transition is strictly depends upon the Sm-A phase range and simultaneously it is independent on the molecular conformer of the mixture constituents. Based on the results obtained from both the chapter 5 and chapter 6, a conclusive discussion has been incorporated about the relative disparity between the *N*–Sm-A and Sm-A–Sm-C phase transitions.

Chapter 7 deals with optical, dielectric and electro-optical investigations in some binary mixtures of chiral ferroelectric compound (2H6R) with an achiral hockey stick-shaped compound (H-22.5). Noticeably, two stable TGB phases - TGBA and TGBC* with wide range of temperature have found to induce in these binary chiral-achiral mixtures. Introduction of small quantity of hockey stick-shaped compound in binary mixtures is sufficient to perturb the direction of the helical axis which can produce higher pitch length chiral twisted state, leading to the formation of such frustrated TGB phases. Several physical properties in these mesophases and related transitional phenomena have been discussed from the viewpoint of perturbation introduced by the achiral hockey stick-shaped compound. Dielectric studies reveal a sign inversion (positive to negative) of the dielectric anisotropy ($\Delta\epsilon$) for all of the investigated mixtures including the pure compound. However, the obtained temperature range of the positive dielectric anisotropy region has found to increase successively by increasing the achiral hockey stick-shaped compound. On the other hand, the field induced spontaneous polarization (P_S) value

decreases in TGBC* phase of the mixtures than the Sm-C* phase of the pure compound, while the response time (τ) and effective torsional bulk viscosity (η) exhibit a higher value than that of the pure compound. Moreover, the values of critical exponent β extracted from polarization data affirm that the weakly first order character of the N^* -Sm-C* phase transition transform towards the second order nature of TGBA-TGBC* phase transition by introduction of hockey stick-shaped mesogen in the mixtures. Additionally, the frequency-dependent dielectric spectroscopy measurement reveals that the relaxation frequency (f_R) and associated dielectric strength ($\delta\epsilon$) of the Goldstone mode in TGBC* phase slightly decreases with increasing the dopant concentration. However, the intermediate TGBA phase represents a transition from soft mode in N^* phase to a Goldstone mode in TGBC* phase with a greater value of activation energy.

Chapter 8 presents a comparative study based on the dielectric spectroscopy measurement and the electro-optical investigation of three pure homologous bent-core compounds (**1/7**, **1/9** and **1/10**) derived from 4-cyanoresorcinol bisbenzoates as a central core unit. The molecular conformations and their association impart a significant role in the mesomorphic behavior of the investigated compounds. The compounds **1/7** and **1/9**, exhibit a single molecular relaxation mode (P_1) in the planar-aligned N_{CyBC} phase and a couple of distinct relaxation modes (H_1 , H_2) in homeotropic (HT) cell. Both P_1 and H_1 modes are ascribed as molecular relaxation mode appeared due to molecular rotation around their short axis and long axis respectively within the tiny clusters of N_{CyBC} phase. Besides, the high frequency longitudinal relaxation peak (H_2) corresponds to the molecular mode, while it is associated with the influence of the anti-ferroelectric ordering of the molecular dipoles in adjacent layers of Sm-C₍₁₎ phase for compound **1/9**. The dielectric strength of the relaxation modes for the compound **1/9** is much sensitive to the externally applied bias field, confirms the influence of the effective dipole moment of the

molecules on these modes. Moreover, the higher homologous compound **1/10** exhibit only one longitudinal relaxation mode (H_2) and a transverse mode (P_1) throughout the mesomorphic region along with an additional relaxation mode (P_2) in planar aligned Sm- $C_{(I)}$ phase. This is due to the presence of a long terminal chain in compound **1/10**, the steric interaction between the molecules reorients the terminal chains parallel to the layer boundary and forms an interdigitation of the terminal chains. This in effect restricts the rotational motion of the molecules around the short axis in HT cell and found to be intensifies in planar (HG) cell. Moreover, owing to the elongation of chain length, a strong component of the effective dipole moment is being emphasized towards the direction of the field in the HG cell while it becomes weakened in the HT cell. The observed polarity of these mesophases has been confirmed by field reversal polarization technique and simultaneous observation of optical textures in polarizing optical microscope. On the basis of all investigated results, it is concluded that the N_{CybC} phase much differs from the usual nematics and consisting of tiny polar cluster which in effect reveals a ferroelectric polarization within the medium. Moreover, the lower temperature Sm- C phases (Sm- $C_{(I)}$ and Sm- $C_{(II)}$) representing an anti-ferroelectric type of ordering of the molecular dipoles in adjacent layers. The intermediate CybC phase accomplished the transition from the ferroelectric-type N_{CybC} phase to the anti-ferroelectric type of Sm- $C_{(I)}$ phase where the cybotactic clusters are being elongated. The Sm- $C_{(II)}$ phase is nothing but a Sm- C phase with enhanced packing density in comparison to Sm- $C_{(I)}$ phase, that seems like a more solid-like state or glassy state. Considering all the experimental findings it has been concluded that the Sm- $C_{(I)}$ phase should be designated as Sm- $C_S P_A$ phase (C_S stands for synclitic-type of molecular organization and P_A corresponds to anti-ferroelectric ordering of polar orientation in neighboring layers) where Sm- $C_{(II)}$ phase is nothing but a quite solid-like state or close-packed Sm- C phase with similar type of synclitic - anti-ferroelectric ordering (Sm- $C'_S P_A$ phase).

All of these findings presented in this dissertation demonstrate a basis for further qualitative research on transitional order and the universality class of the associated critical exponents for other liquid crystalline mesophases such as N - $Sm-C$, $Sm-A^*$ - $Sm-C^*$, transition between higher ordered smectic phases, transition to smectic mesophases from cybotactic nematic phase in bent-core mesogens etc. Investigation on these mesophase transitions necessitates further confirmation encompassing both the theoretical and experimental approaches by analyzing the heat capacity data (DSC study), tilt-angle measurement, dielectric study etc. Despite the success of proper explanation about phase transitional critical phenomena in binary mixtures, there exist several motivating investigations in multi-component mixtures involving bent-core compounds. In addition, continuous research efforts are required to increase the temperature stability of noble mesophases (blue phase, TGB phases etc.) by incorporating some achiral perturbation or nano-particle segregation in chiral environment. Moreover, the interest has grown up to extend the investigation towards the LC systems doped by polar or non-polar, conductive or non-conductive nano-particles which also contribute important information regarding the applicability of LC systems in several enhanced devices. Further work in this direction may be carried out to deal with the above mentioned problems.