CHAPTER 4

CONCLUSION

The investigation deals with synthesis and characterization of combined type photoreactive liquid crystalline polymers containing cinnamoyl moiety in the side chain with various terminally substituted phenyl/4-biphenylyl groups. All the polymers were characterized by various spectral and thermal techniques. It also includes the photocrosslinking studies by UV irradiation of the polymers.

Two series of liquid crystalline-cum-photocrosslinkable polymers that differs in their substituent attached to the cinnamoyl moiety were synthesized from the various monomers with good yield and characterized.

The salient results emerged in this study as follows:

4.1 SYNTHESIS OF PRECURSORS AND MONOMERS

- \( \omega \)-Bromo-1-alkanols were prepared by the azeotropic distillation of corresponding diols and 47% HBr.
- The methylene chain extension of cinnamoyl derivatives were obtained by the nucleophilic displacement reaction of p-hydroxycinnamic acid with various \( \omega \)-bromo-1-alkanols \( (\omega = 6,8,10) \) in ethanol under Williamson aryl ether synthesis conditions. All are white solids.
• All the precursors i.e. 4-(m-methacryloyloxyalkoxy) cinnamic acids were prepared by reacting the methacryloyl chloride with the corresponding 4-(m-hydroxyalkoxy) cinnamic acids (m = 6,8,10) in THF.

• All the monomers were prepared by condensation reaction of precursors with substituted phenols/4-biphenylols using DCC as coupling agents

• All the synthesized monomers were confirmed by FT-IR and NMR spectroscopic methods.

### 4.2 POLYMERIZATION

• All the polymers namely, poly[4-x-phenyl-4'-((m-methacryloyloxyalkoxy)cinnamate)s (Ia - IIi) and poly[4-(4'-x-biphenyl)yl-4''-(m-methacryloyloxyalkoxy)cinnamate]s (IIa - IIi) were synthesized by a free radical solution polymerization from corresponding monomers using AIBN initiator in THF at 60°C with good yield (70-80%).

### 4.3 CHARACTERIZATION

• All the polymers were soluble in chlorinated solvents such as CHCl₃, CH₂Cl₂, and in polar approtic solvents such as DMF and THF due to flexible methylene chains and polarity of the ester linkage.

• The inherent viscosity data revealed that all the polymers possess moderate molecular weight.

• FT-IR, ¹H and ¹³C-NMR spectral data of the polymers are in accordance with polymer structure.
• All the polymers were showed anisotropic behavior as observed by hot stage optical polarizing microscope. They were exhibited grainy and nematic textures depending on the nature of substitutions.

• Thermogravimetric analysis revealed that all the polymers were stable in between 236-355ºC and started to degrade thereafter.

• Thermal stability of the polymers decreased with increasing number of methylene chain in the polymer backbone.

• Char yield of the polymers increases with decreasing number of methylene chain in the polymer chain.

• The liquid crystalline behavior of the polymers was confirmed by DSC analysis. All the polymers showed two endothermic peaks corresponds to crystalline-liquid crystalline, liquid crystalline-isotropic transitions respectively.

• The melting temperature of all the polymers are in the range of 48-75ºC. It is found to decrease with increase in methylene spacer.

• The isotropic transition temperature of the polymers are in the range of 72-109ºC. It is found to decrease with increasing the methylene chain linking polymer back bone and mesogen.

• The photocrosslinking property of the polymer was investigated by UV light/UV spectroscopy, the crosslinking proceeds via 2π-2π cycloaddition reactions of the olefinic group of the pendant cinnamate ester.

• The photolysis studies of various methylene spacer-containing polymers revealed that, the rate of photocrosslinking is
depending the length of methylene chain and follows the order as below

Hexamethylene < Octamethylene < Decamethylene

- The photocrosslinking ability of substituted cinnamoyl esters containing (H, OCH$_3$, CN) polymers reveal that the crosslinking rates are in the following order.

\[
\text{CN} < \text{H} < \text{OCH}_3
\]

This may be due to the electron releasing nature of the OCH$_3$ group, which strengthen the electron density of olefinic bonds through extended conjugation.

- The phenyl substituted polymers (Ia-Ii) showed faster crosslinking than the biphenyl substituted polymers (IIa-IIi).

Finally, it may be concluded that these dual functional polymers namely, liquid crystalline-cum-photocrosslinkable polymers (LC-PCPs) can be suitably exploited to various applications such as, data-storage materials, non-linear optics, photorefractive materials, intermediate for the drug synthesis, photoresists, composites, opto-electronic devices, liquid crystalline display applications, where thermal stability, liquid crystallinity and photocrosslinkability are collectively required.

4.4 FUTURE WORK

Similar photoreactive liquid crystalline poly(arylcinnamoyloxy alkylmethacrylate)s will be prepared with incorporation of ketonic group inserted of ester group in the pendant will be studied. This modification may enhance the photocrosslinking behaviour due to C = 0 band.