CHAPTER 4

CONCLUSION

The present investigation deals with the synthesis and characterization of thermotropic liquid crystalline-cum-photocrosslinkable polyphosphate esters containing stilbene moiety. All the polymers were characterized by spectral and thermal studies. Further the photocrosslinking properties of all the polymers were investigated by UV and fluorescence spectroscopic techniques. The following results were emerged in this investigation.

4.1 SYNTHESIS OF PRECURSORS AND MONOMERS

Photocrosslinkable-cum-mesogenic trans-4,4'-dihydroxystilbene was synthesized by the condensation reaction of phenol and bromoacetaldehyde diethylacetal. It is white colored solid obtained with good yield. n-Bromo-1-alkanols (n=0,2,4,6,8) were synthesized by the azeotropic distillation of corresponding diols and 47% HBr.

4,4'-Bis(n-hydroxyalkyloxy)stilbene namely 4,4'-bis(2-hydroxyethyloxy)stilbene, 4,4'-bis(4-hydroxybutyloxy)stilbene, 4,4'-bis(6-hydroxyhexyloxy)stilbene, 4,4'-bis(8-hydroxyoctyloxy)stilbene and 4,4'-bis(10-hydroxydecyloxy)stilbene were synthesized from the corresponding mesogenic diols with n-bromo-1-alkanols under Williamson aryl ether synthesis conditions. All are pale yellow colored solids.

Arylphosphorodichloridates were synthesized by the condensation
reaction of phosphorous oxychloride with phenol, 1-naphthol and 4-phenylphenol. Phenylphosphorodichloridate was colorless liquid, whereas 1-naphthylphosphorodichloridate and 4-phenylphenyl phosphorodichloridates were brown colored and white colored low melting solids respectively.

All the synthesized monomers were confirmed by FT-IR, $^1$H-NMR and $^{13}$C-NMR spectroscopic studies.

4.2 POLYMERIZATION

All the three series of polymers namely, Ia-e; poly{bis (4, 4$'$-stilbeneoxy)alkylphenyl phosphates}, IIa-e; poly{bis(4,4$'$-stilbeneoxy)alkynaphthyl phosphates} IIIa-e; poly{bis(4,4$'$-stilbeneoxy)alkylbiphenyl phosphates}(alkyl: ethyl, tetramethylene, hexamethylene, octamethylene, decamethylene) were synthesized by solution polycondensation method at ambient temperature in CHCl$_3$ under nitrogen atmosphere.

4.3 CHARACTERIZATION

All the polymers were soluble in CHCl$_3$, DMF, DMSO, THF and insoluble in benzene, toluene, n-hexane and alcohols like methanol, ethanol, 2-propanol. The good solubility in polar organic solvents may be attributed to the flexibility and polarity of the methylene spacer and phosphorus linkage in the polymer backbone respectively.

The intrinsic viscosity data revealed that all the polymers have moderate molecular weight. FT-IR, $^1$H and $^{13}$C-NMR spectral data confirmed the structure of polymers. $^{31}$P-NMR spectroscopy confirms the incorporation of phosphorus linkage in the polymer backbone. HOPM observation revealed that the polymers containing ethylene and tetramethylene spacers have not exhibited LC texture, which is due to
the smaller microdomain and restricted movement of the mesogen. But, the polymers containing hexamethylene, octamethylene, decamethylene spacers exhibited LC textures, which is due to the larger monodomains and free movements of the mesogen. The liquid crystalline behavior of the polymers was confirmed by DSC analysis. All the polymers showed two endothermic peaks and one broad exothermic peak, which correspond to the crystalline-liquid crystalline, liquid crystalline-isotropic transition and thermal crosslinking respectively.

The melting temperature of all the polymers is within the range of 111-196°C. It is found to decrease with increase in methylene spacer. The isotropic transition temperature of the polymers is in the range of 178-257°C and also found to decrease with increasing the methylene chain in the polymer backbone. Tg, Tm and Ti, with respect to the pendent aryl groups, were found to decrease in the following order:

**Biphenyloxy > 1- Naphthyloxy > Phenyloxy**

Thermogravimetric analysis revealed that all the polymers were stable in between 273-367°C and started decomposition thereafter. Thermal stability of all the polymers was found to decrease with increase in methylene chain length in the polymer backbone.

Ethylene > tetramethylene > hexamethylene > octamethylene > decamethylene

Char yield of the polymers were found to increase with decreasing methylene chain in the polymer chain.

Ethylene > tetramethylene > hexamethylene > octamethylene > decamethylene.

The photocrosslinking property of the polymers were investigated by using UV spectroscopy, the crosslinking proceeding via 2π-2π cycloaddition reactions of the exo-cyclic double bond of the stilbene moiety. The photolysis
studies of various methylene spacer containing polymers revealed that, the rate of photocrosslinking of exocyclic double bonds of the polymers containing various methylene spacer is increasing in the following order.

Ethylene<tetramethylene< hexamethylene< octamethylene< decamethylene

The rate of photocrosslinking of all the polymers was found to be in the following order.

Biphenyloxy > Naphthyloxy > Phenyloxy

The pendant bipenyloxy containing polymers showed faster cross linking than the pendant naphthyloxy and phenyloxy containing polymers.

All the polymers exhibited the fluorescence properties in the range of 350-550nm, excited at 255-285nm.

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