CHAPTER 4

CONCLUSION

The investigation deals with the syntheses and spectral and thermal characterization of thermotropic ferrocene containing liquid crystalline phosphonates/polyphosphates. It also includes the conformational analyses of the polymers. The following salient results emerged in this study.

Phosphorus containing acid chlorides

- n-hydroxyalkyloxy-4-benzoic acids were prepared from corresponding n-bromo/chloroalkanols with 4-hydroxybenzoic acids under Williamson aryl-alkyl ether synthesis conditions. All are white colored solids.
- Phenylphosphonic dichloride was prepared from benzene and phosphorus trichloride using Lewis acid catalyst under Friedel-Crafts conditions. Alkyl/aryl substituted phosphorodichloridates were prepared from phosphorus oxychloride and corresponding alkanol and phenols. Phenylphosphonic dichloride and methoxy, phenyloxydichloridates are colorless liquids while biphenylphosphorodichloridate is a white solid.
- Bis[carboxy-4-phenyloxyalkyl(phenylphosphonate)] was prepared from phenylphosphonic dichloride and two moles of corresponding n-hydroxyalkyloxy-4-benzoic acids.
Bis[carboxy-4-phenyloxyalkyl(alkyl/arylphosphate)]s were prepared from various alkyl/arylphosphorodichloridates with two moles of corresponding n-hydroxyalkyloxy-4-benzoic acids.

- IR and $^1$H-NMR spectral analyses data are in accordance with structure of these monomers.
- Bis[carboxy-4-phenyloxyalkyl(phenylphosphonate)] and Bis[carboxy-4-phenyloxyalkyl(alkyl/arylphosphate)]s were converted to their corresponding acid chlorides by refluxing with thionyl chloride. The chlorofunctionalized compounds were used as such.

Ferrocene containing bisphenols

- Ferrocene was diacetylated under Friedel-Crafts conditions with acetyl chloride using aluminium chlorides as a catalyst.
- 1,1'-diacetylferrocene was oxidized under mild oxidizing conditions using 4% sodium hypochlorite aqueous solution to get 1,1'-ferrocenedicarboxylic acid.
- 1,1'-ferrocenedicarboxylic acid was converted to acid chloride using oxalyl chloride and pyridine.
- 1,1'-bis(p-benzyloxyphenyl ferrocenedicarboxylate) was prepared by condensing 1,1'-ferrocenedicarbonyl chloride and two moles of 4-benzoxyphenol.
- The deprotection of benzyl group was achieved by reductive cleavage of benzyl group using 10% palladium, charcoal and
cyclohexene as hydrogen resource to get 1,1'-bis(p-hydroxyphenyl ferrocenedicarboxylate).

- IR and $^1$H-NMR spectral analyses data are in accordance with structure of these monomers.

**Polymerization**

- All the polymers were prepared using various phosphorus containing diacidchlorides and ferrocene containing bisphenols by polycondensation method in dichloromethane at room temperature under nitrogen atmosphere.
- All the polymers were soluble in chloroform and other polar solvents like THF, DMF, DMAc due to flexibility and polarity nature of the phosphorus linkage.

**Characterization**

- The average molecular weights of these polymers are moderately high as evidenced by GPC data.
- Various spectral data of the polymers are in accordance with polymer structure.
- $^{31}$P-NMR spectroscopy confirms the incorporation of phosphorus in the main chain.
- All the polymers are showing anisotropic behavior as evidenced by the hot stage optical polarizing microscope photographs except for polymer XI. The polymers are exhibit grainy and nematic textures.
• Thermogravimetric analyses revealed that these polymers are stable up to 170-320°C and start to degrade thereafter.

• The thermal stability of the polymers were increasing with decreasing methylene chains in the polymers.

• The char yield of the polymers were found to increase with decreasing the methylene spacer and increasing bulkiness of the pendant group attached through phosphorus.

• The thermal stability and char yield of the polymers with respect to pendant groups in the phosphorus is in the following order. Biphenyloxy > Phenyloxy > Phenyl > Methyloxy

• Liquid crystalline behavior of the polymers were confirmed by the DSC analysis. All the polymers are giving three endothermic peaks at various temperatures corresponding to glass transition temperature, melting temperature and isotropic transition temperature respectively.

• The glass transition temperature of the polymers was in the range of 46-87°C. The Tg of the polymers were decreasing with increasing methylene spacer.

• The Tm of the polymers is in the range of 60-130°C. It is found to decrease with increase in methylene spacer.

• The isotropic transition temperature of the polymers is in the range of 115-255°C. It is found to decrease with increase in methylene spacer.
• The phase duration (ΔT) of the polymers is in the range of 42-125°C. It is found to decrease with increase in methylene spacer.

• Energy minimized structure of the model compound of the mesogen reveals that, the mesogenic activity of the diad ester groups were imparted by steric repulsion of the ester carbonyl and ortho hydrogen of the phenyl unit and conjugation effect made the unit rigid and rod like mesogen.

• Free rotation of the two-cyclopentadiene rings above and below the iron atom and induction of step like structure to the mesogen affect the rigidity and thereby it reduces the growth of monodomains and liquid crystalline domains. This could be the one of the reason for reduction in glass transition temperature.

• All the polymers irrespective of the different substituents show high char yield it is noteworthy to mention that the high char yield is an indication for these polymers to use as fire retardant materials.

• Energy minimized structures of the phosphorus moieties reveal that, the abnormal bond angle and flexibility of the phosphonate and phosphate group induces more entanglement and thereby reduces the Tg and Tm of the polymers.

• The rigidity due to conjugation and atomic overlapping effect on ferrocene made the unit as a solid mesogen. But the free rotation of the ferrocene ring destabilized the mesogenic behavior by acting the mesogen as just like two needles in a watch.
• The reduction in Tg provide a vide operation temperature for example just above to the ambient temperature to some of the polymers synthesized.

• The polymers are having considerably high ΔT. This results shows that these polymers could be processable in wide temperature ranges.

Finally, it may be concluded that these liquid crystalline ferrocene containing organophosphorus polymers can be suitably exploited for developing polymer blends, composites and opto-electronic devices where thermal stability, liquid crystallinity, low Tg, Tm and flame retardancy are collectively required. Thereby they can be explored as the potential futuristic materials.