The ferrocene containing organophosphorus polymers were prepared from two different monomers in which one segment containing ferrocene unit and the other segment containing organophosphorus unit. The starting material n-hydroxyalkyloxy-4-benzoic acid was prepared from corresponding n-bromo alkanol and p-hydroxybenzoic acid using Williamson aryl-alkyl ether synthesis method. The introduction of phosphorus heterogeneity along with methylene spacer has been achieved by reacting various aromatic/aliphatic-substituted phosphorus dichlorides by increasing size and aromaticity of the pendant groups with n-hydroxyalkyloxy-4-benzoic acid. The dicarboxylic acid thus obtained was converted into its corresponding bisacid chloride by refluxing with thionyl chloride. The ferrocene containing monomer was prepared by reacting benzyl protected quinol and 1,1'-ferrocenedicarbonyl chloride. Deprotection was done by reductive cleavage of benzylxoy group using Pd/C and cyclohexene. Cyclohexene was used for generating hydrogen \textit{insitu} during the reaction. The generation of hydrogen was achieved by refluxing the reactants in THF/methanol medium to get ferrocene-containing bisphenol. All the monomers were characterized by IR and $^1$H-NMR spectroscopy.

All the polymers were prepared by room temperature solution polycondensation method in dichloromethane using 1,1'-bis(p-hydroxyphenyl...
ferrocene dicarboxylate) with bis[4-chlorocarbonylphenyloxy alkyl(phenylphosphonate)] and bis[4-chlorocarbonylphenyloxy alkyl(methyl/arylphosphate)] where alkyl = ethyl, butyl, hexyl, octyl, decyl and aryl = phenyl, biphenyl. The polymers were characterized by Gel Permeation Chromatography, FT-IR, $^1$H, $^{13}$C, $^{31}$P-NMR spectroscopy. Liquid crystalline behavior of the polymers was examined by hot stage optical polarizing microscope. Thermal stability of the polymers was determined by DSC and TGA.

The polymers were soluble in chloroform, THF, DMF, DMAc and DMSO whereas insoluble in benzene, toluene and hexane. GPC analyses indicated the average molecular weight parameter suggests that these polymers are moderately high molecular weight.

IR spectra of the polymers exhibit absorption around 1013, 1062 and 1455 cm$^{-1}$ correspond to Ph-P stretching. The absorption around 919 and 2910 cm$^{-1}$ corresponds to P-O-C aliphatic stretching and aliphatic -CH$_2$- stretching respectively. The absorption around 1733, 3050 and 884 cm$^{-1}$ corresponds to -COO- ester linkage and 1,1'-disubstituted ferrocene ring respectively. Aryl-alkyl ether stretching appeared around 1280 cm$^{-1}$. All the polymers contain absorption around 1160 and 1075 cm$^{-1}$ are due to P=O stretching.

$^1$H-NMR spectra of the polymers show two 4H singlets appeared around 4.6 $\delta$ and 5.06 $\delta$ for the two-cyclopentadiene ring protons in ferrocene. The aromatic protons appeared as broad multiplet between 6.8-8.13 $\delta$. Two
unsubstituted phenyl protons adjacent to ferrocene moiety experiences more
deshielding effect and it appears in downfield than other two unsubstituted
phenyl protons. Ar-O-CH$_2$- protons appeared as triplet between 3.25-4.25 δ.
P-O-CH$_2$- protons appeared as triplet between 3.1-4.25 δ.

$^{13}$C-NMR spectra show the ferrocene carbon resonates at 68 δ and
72 δ and tertiary carbon of the same ring appeared at around 73 δ. All aromatic
carbon resonates between 110-118 δ. The alkyl carbon of aryl-alkyl ether
linkage appeared at 45 δ. All other methylene chain carbons were appeared
between 20-45 δ. $^{31}$P-NMR spectra of the polymers show two signals for all the
polymers except for polymer VI-X, which show only one signal around 9.8 δ.

Microscopic analyses show all the polymers were exhibiting liquid
crystalline behavior except for polymer XI. Thermal analyses of the polymers
reveals that the polymers possess high thermal stability with low glass
transition temperature. The Tm of the polymers was considerably low, Tg and
Tm were decreasing with increasing methylene spacer length for all the
polymers. The thermal stability as well as the char yield of the polymers were
comparatively increasing with increase in bulkiness of the side chain. The phase
duration of the polymers was increasing with decreasing the spacer length.

The energy minimized structures of the polymer shows, ferrocene
esters adopting a step like structure. The mesogen was stabilized with
conjugation arise from aryl-alkyl ether linkage and atomic steric repulsion of
carbonyl oxygen and ortho hydrogen of the aromatic diad esters. But the aspect ratio of the mesogen was disturbed and/or reduced by the free rotation of the ferrocene ring. The Tg of the polymers was much reduced due to this flexibility arise from the phosphorus incorporation. In addition to that, the lateral substitution of the phosphorus atom is also enhancing the effect of reducing the Tg of the polymers.

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.