The aim of the present investigation is to bring the two entities viz., azobenzene and phosphorus into the main chain and various terminal substituted azobenzene in the side chain units in the polymer backbone to have interesting features like high char yield, mesophase stability, reduced glass transition temperatures and type of mesophase produced. More over different dipolar moment due to the polarity imbalance of the pendant unit have its own effect owing to their nature. The main chain azobenzene monomer namely 4,4'-bis(6-hydroxyhexyloxyazobenzene) is prepared from 4,4'-dihydroxyazobenzene with 6-bromo-1-hexanol under Williamson ether synthesis conditions. The later was prepared by reductive coupling of p-nitrophenol using molten alkali. Various 4-hydroxy-4'-substituted (X) azobenzene were (X= H, CH$_3$, OCH$_3$, F, Cl, Br, I, NO$_2$, CN) prepared from corresponding p-substituted anilines and phenol. The anilines were diazotised using NaNO$_2$ and HCl at below 5°C. Subsequent reaction with phenol under basic condition yields the target compounds. 4-hydroxy-4'-substituted (X) azobenzenes were O-alkylated under Williamson ether conditions with 6-bromo-1-hexanol and it was used as side chain monomer. All the polymers were prepared by room temperature solution polycondensation method in NMP using 4-substituted(X)phenylazo-4'-phenyloxyhexyloxyphosphorodichloridate and 4,4'-bis(6-hydroxyhexyloxy) azobenzene.

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 are soluble in DMF, DMSO and NMP whereas insoluble
in chloroform, dichloroethane and THF. GPC analysis showed the average molecular weight parameter and suggests that these polymers are moderate molecular weight materials.

The proton and carbon NMR of the polymers were in accordance with structure of the polymers. Phosphorus NMR shows two signals due to two different environment of phosphate group. Since there is a possibility of forming copolymer terminated with phosphate ester. Hence the terminal phosphate linkage in the main chain will experience and resonates at two different environments. The phosphorus atom in the main-chain was deshielded and appears at downfield, whereas the phosphorus atom at the end of the chain appeared at upfield.

TGA analysis shows that the electron donating substituent increases the polarity nature of the molecule, leads to more stable and ordered effect. In the case of withdrawing substituent it is less polar so that the conjugation is less effective and hence the packing efficiency of the molecule is weak. The char yield was very high for Polymer VI may be due to the bromine substitution.

Microscopic analysis reveals that all the polymers are exhibiting liquid crystalline behavior. Polymer I, VI, VII & X were exhibiting grainy textures and all other polymers exhibited nematic textures. It is observed that the terminal groups of the polymers promote the liquid crystalline stability, and is in the following order.

CN > OCH₃ > NO₂ > Cl > Br > CH₃ > F > I > H

DSC analysis reveals that, Tg and Tm of polymers were considerably low when compared to similar liquid crystalline polymers that does not contain phosphate ester moiety. This may be due to abnormal sp³ hybridized bond angle of phosphorus, which produces more entanglement and hindrance to the
packing efficiency of the liquid crystalline monolayer. In addition, the bulkiness of the phosphorus atom in the chain also causes the reduction in transition temperature. The liquid crystalline mesophase duration is depend on nature of the substituent and follows the trend as given below.

\[ H < CH_3 < F < Cl < Br < I < OCH_3 < NO_2 < CN \]

All the polymers show intense absorption around 360 nm due to the \( \pi - \pi^* \) transition of the trans isomer on UV irradiation studies. It decreases during UV irradiation and the absorption maxima at 430 nm increases due to cis conformation is increased which may be due to \( n - \pi^* \) transition. But in the case of cis isomer there is no marked increase in absorbance. The absorption around 360 nm decreases considerably with increase in time of irradiation. The time taken for complete cis transformation for all the polymers is in the following order,

\[ IX > VIII > VII = VI = III > II > V > I = IV > X \]

It shows that time taken for total cis transformation depends on nature and size of the terminal substituent in the side chain mesogen. In addition, photoisomerization is also dependant on the dipolar moment of the pendant group. The relationship between the time taken for photoisomerization depends on both dipolar moment and size of the substituent in the pendant along with other factors viz., viscosity, cross-link density, crankshaft motion and rigidity of the polymer chain.

Finally, it may be concluded that these combined type liquid crystalline polymers containing azobenzene in both main and side chain can be suitably exploited for developing polymer blends, composites and display devices where thermal stability, liquid crystallinity and flame retardancy are collectively required, thereby proving to be potential futuristic material.