ABSTRACT

The objective of the present investigation is to synthesize two series of novel dual functional main chain liquid crystalline polymers containing photocrosslinkable chalcone and photoisomerizable azobenzene group from p-hydroxybenzaldehyde and vanillin respectively (Series I & II). The highlight of this work is the synthesis of the hitherto unreported benzilidene containing alkanone polyesters carrying the azomoiety in the main chain. The photocrosslinking behaviour of these polymers is compared with that of the vanillylidene containing alkanone polyesters. The influence of the main chain azo moiety and the effect of the methylene spacer in both these cases are also assessed. The chalcone moiety was prepared by the reaction of cycloalkanones (pentanone and hexanone) with p-hydroxybenzaldehyde (I) and vanillin (II) separately in absolute ethanol with a Lewis acid catalyst to yield four different monomers.

The methylene spacers were introduced into the chalcone derivative by the nucleophilic displacement of bis(benzylidene) and bis(vanillylidene) with various m-bromoalkanols (m=6,8,10) in dry DMF. 4,4’-azobenzenedi carboxylic acid was prepared from 4-nitrobenzoic acid and α-D-glucose in the presence of sodium hydroxide. The acid synthesized was converted to acid chloride on reacting with thionyl chloride and purified by vacuum distillation. The polymers were synthesized by the solution polycondensation method by reacting with the 4,4’-azobenzendicarbonylchloride and the arylidene monomers at ambient temperature in chloroform in good yield.
The polymers were soluble in chloroform, dichloromethane, chlorobenzene, DMF and insoluble in methanol, ethanol, benzene and toluene. The inherent viscosity was determined using the Ubbelohde viscometer using chloroform as the solvent. The viscosity measurement indicated that the polymers were of moderate molecular weight.

The FT-IR spectroscopic investigations for all polymers showed strong absorption bands at 1683, between 1602-1590, 1730-1710, 2939-2919 and 3431-3370 cm\(^{-1}\) for carbonyl group (C=O), olefinic double bond of benzylidene, ester carbonyl, asymmetric stretching of the methylene spacers and the azo linkage respectively.

The \(^1\)H-NMR spectra of the polymers showed a doublet between 6.9 - 7.54 ppm. The aromatic protons of the azobenzene unit resonate at 8.3, 8.2 and 8.0 ppm. Methylene proton of the chalcone unit resonates at 3.7 ppm. \(^{13}\)C-NMR spectra of the polymers showed a signal at 112 - 114 ppm corresponding to the aromatic carbons of the azobenzene unit. The methylene carbons in the methylene spacer resonated at 280 - 290 ppm.

Polarizing Optical Microscopy (POM) is a technique that is used for the identification of liquid crystallinity. All the polymers exhibited thermotropic liquid crystalline properties and were found to show enantiotropic nematic mesophase. However, as the methylene spacer length was increased a dilution in the liquid crystalline texture was observed. Thermal studies reveal that the benzylidene series of polymers exhibit fairly high clearing points (Ti) than the polymers belonging to the vanillylidene series. The benzylidene series displayed mesophase stability between 60-153\(^\circ\)C where as the mesophase stability of the vanillylidene series was
between 56-103°C. Also, as the main chain flexible spacer flexibility increases as the Tg value decreases. The incorporation of the azobenzene moiety in the main chain increases the Tg. Hence, the polymers belonging to the vanillylidene series have higher Tg values than the polymers of the benzylidene series.

UV-Visible photolysis studies revealed that all polymers showed completely reversible photoisomerization in dilute solutions. It was observed that in the benzylidene series the photoisomerization predominates over the crosslinking reaction.

The cyclopentanone containing polymers showed higher rate of crosslinking than the cyclohexanone containing polymers. Studies also showed that the rate of photocrosslinking decreases as the methylene spacer was increased. This may be due to the presence of \(-\text{N=N-}\) in the main chain which induces rigidity.

Finally, it may be concluded that incorporation of the azobenzene moiety into the main chain induces rigidity in the polymer chain which in turn increases the glass transition temperature and thermal stability. In addition to this, the synthesized arylidene and azobenzene polymers possess high thermal stability, mesophasic property, photocrosslinkability and photoisomerization. All these properties can be exploited for various applications like optoelectronics devices, photoresists and photochromic multifunctional arrays.