ABSTRACT

Two series of liquid crystalline-cum-photocrosslinkable polymers were synthesized by the direct esterification reaction between various substituted phenols/4-biphenylols and 4-(m-methacryloyloxyalkyloxy)cinnamic acids. Electron releasing functional group like –OCH₃ and the electron withdrawing –CN group are introduced at the terminal para position of the phenyl/biphenylyl ring systems. The methylene chain extension of cinnamoyl derivatives were obtained by the nucleophilic displacement reaction of p-hydroxycinnamic acid with various o-bromo-1-alkanols (m=6,8,10) in ethanol under Williamson aryl ether synthesis conditions. Methacrylate monomers were prepared by the reaction between 4-(m-methacryloyloxyalkyloxy)cinnamic acid with various substituted phenols and 4-biphenylols. All the monomers were characterized by FT-IR, ¹H and ¹³C-NMR spectroscopy.

All the polymers namely, poly[4-x-phenyl-4’-(m-methacryloyloxyalkyloxy)cinnamate]s (Ia-Ii) and poly[4-(4’-x-biphenyl)yl-4’’-(m-methacryloyloxyalkyloxy)cinnamate]s (IIa - IIIi) were synthesized by a free radical solution polymerization from corresponding monomers using AIBN initiator in THF at 60°C. These polymers were characterized by inherent viscosity, FT-IR, ¹H, and ¹³C-NMR spectroscopy. Liquid crystalline behavior of these polymers were examined using the hot stage optical polarizing microscope. DSC and TGA were used to investigate the thermal properties of
the polymers. The photocrosslinking property of the polymers was investigated using the technique of exposing the polymer solution, to UV light and UV spectroscopy respectively.

All the polymers were found to be soluble in chlorinated solvents such as CHCl$_3$, CH$_2$Cl$_2$, chlorobenzene and in polar aprotic solvents such as DMF and THF. They were insoluble in alcohols like methanol, ethanol, 2-propanol and in hydrocarbons such as benzene and toluene. The inherent viscosity of these polymers was determined using Ubbelohde viscometer using chloroform as solvent. The inherent viscosity data revealed that all the synthesized polymers were moderate molecular weight materials.

The FT-IR spectra of the polymers showed a characteristic band at 2846 and 1716 cm$^{-1}$, belonging to the –CH$_2$ - and –CH=CH- double bond of the pendant cinnamate ester respectively. The aryl and alkyl ether stretching appeared around 1254 cm$^{-1}$.

All the $^1$H-NMR spectra of the polymers show multiplet in the region 6.9- 7.1 ppm for the aromatic protons, the pendant aryl group in the cinnamate ester appeared as a multiplet in the region of 7.11-7.6 ppm. The methoxy protons of the phenyl/biphenylcinnamate mesogen appeared as a singlet at 7.7-8.3 ppm. The - CH$_2$O- connected to phenyl ring of the mesogen appeared as a triplet around 4.1-4.4 ppm, while the methylene protons of the spacers resonated as multiplet in the region between 0.9–1.5 ppm.

$^{13}$C-NMR spectra of all the polymers show the carbon-carbon double bond (C=C) appeared at 118 and 143 ppm, aromatic carbons in the mesogenic
units resonated in the regions 113-130.51 ppm, aromatic carbons in the pendant units resonated in the region between 129-150 ppm and the methylene carbon of Ar–O-CH$_2$ group resonated at 102-115 ppm. The methoxy carbon of the phenyl/4-biphenylyl cinnamate mesogenic unit resonated at 54-58 ppm. The methylene carbon in the spacer (-CH$_2$-) resonated in the region 22-39 ppm.

The liquid crystalline properties of the polymers were examined by hot stage optical polarizing microscopy. All the polymers exhibited liquid crystalline behavior. The hexamethylene spacer containing polymers exhibited grainy textures and other polymers such as octamethylene and decamethylene spacer containing polymers showed nematic textures. As the increase in methylene chain in the pendant the LC texture of the polymers were more pronounced.

The differential scanning calorimetry studies indicated that the melting transition temperature (Tm) of the polymers lie between 54-74°C and the isotropic transition temperatures were in the range of 72-109°C. Thermogravimetric analysis revealed that all the polymers were stable in between 240-355°C in nitrogen atmosphere and underwent degradation thereafter. As the methylene chain increased in the polymer side chain, the thermal stability and char yield of the polymers decreased. The substitution on the terminal phenyl/4-biphenylyl ring affects the char yield and it observed the following trend:

$$CN > OCH_3 > H$$
The photocrosslinking property of the polymers were investigated by UV light/UV spectroscopy. The crosslinking reaction proceed via $2\pi-2\pi$ cycloaddition reactions of the –CH=CH- of the pendant cinnamate ester.

Rate of crosslinking increased with increase of methylene chain. Polymers containing decamethylene spacer showed faster crosslinking than octamethylene and hexamethylene substituted polymers.

The electron releasing substituents like –OCH$_3$ substituted polymers showed faster crosslinking than the unsubstituted and electron withdrawing like –CN substituted polymers. When comparing the two series of polymers (phenyl and 4-biphenyl), the phenyl substituted polymers (Ia-Ii) showing faster crosslinking than the biphenyl substituted polymers (IIa-IIi).

Finally, it may be concluded that these dual functional polymers such as liquid crystalline-cum-photocrosslinkable polymers (LC-PCPs) can be suitably exploited for various applications, such as non-linear optics, photorefractive materials, intermediates for the drug synthesis, photoresists, composites, opto-electronic devices and liquid crystalline display applications, whereas thermal stability, liquid crystallinity and photocrosslinkability are collectively required.