

ABSTRACT

Main chain liquid crystalline polymers with photosensitive groups have attained special attention owing to the presence of dual functionalities. The mesogenic groups contributes to the LC properties and the photoactive groups in the polymer backbone, may facilitate photoisomerization, photocrosslinking, photodimerization, photodissociation and photoassociation of the polymer chains under the influence of UV irradiation.

Two photosensitive monomers namely, 2,6-bis[4-(3-hydroxypropyloxy)-3-methoxybenzylidene] cyclohexanone (BHPMBCH) and 2,5-bis[4-(3-hydroxypropyloxy)-3-methoxybenzylidene] cyclopentanone (BHPMBCP) were synthesized by reacting 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone (BHMBCH) and 2,5-bis(4-hydroxy-3-methoxybenzylidene) cyclopentanone (BHMBCP) with 3-bromo-1-propanol using anhydrous potassium carbonate catalyst in DMF medium. Three non-photosensitive monomers namely, 4,4'-diformyl- α,ω -diphenoxyalkanes, 4,4'-diformyl-2,2'-dimethoxy- α,ω -diphenoxyalkanes and 2,2'-diethoxy-4,4'-diformyl- α,ω -diphenoxyalkanes were prepared by reacting 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and 3-ethoxy-4-hydroxybenzaldehyde with dibromoalkanes respectively.

Two series of poly(benzylidene-ether)esters were synthesized by reacting photosensitive monomers with aliphatic and aromatic diacid chlorides by solution polycondensation technique using pyridine as a acid

scavenger catalyst in dioxane medium. Three series of poly(benzylidene-ether)s were synthesized by reacting non-photosensitive monomers with acetone, cyclopentanone, cyclohexanone, and cycloheptanone by solution polycondensation technique using a base catalyst in ethanol medium. The reaction parameters like catalyst, reaction time and reaction medium were optimized.

All the monomers and polymers were synthesized in good yield and the molecular structure was confirmed by elemental analysis, UV-Visible, FTIR, ^1H and ^{13}C -NMR spectroscopic techniques. The condensed phase characterization was carried out using DSC and HOPM and found that the monomers exhibit birefringence and stirred opalescence properties.

The synthesized poly(benzylidene-ether)esters were subjected to TGA analysis and found that the polyesters containing cyclopentanone moiety exhibit more thermal stability than cyclohexanone containing polyesters. It was noticed that the thermal stability initially increased with increasing spacer length, but further increases in the spacer length led to decrease in the thermal stability. This may be due to the opposing effects of the decoupling function of the spacer and the flexibility of the spacer on the thermal stability.

In poly(benzylidene-ether)s, the polymers containing cyclopentanone moiety exhibited more stability than the rest of the alkanones. Further, it was noticed that the increase in spacer length also decrease the thermal stability. The presence of methoxy and ethoxy substituent has the

impact on the methylene spacer units to vary the thermal stability order due to the negative effect of the spacer.

The DSC analysis results showed that the aliphatic poly(benzylidene-ether)esters are of multicrystalline and monotropic in nature. No endothermic peaks were observed in aromatic polyesters. Most of the poly(benzylidene-ether)s exhibited double melting and were enantiotropic in nature. The influence of the length of methylene spacer on phase transition was investigated and proved that the isotropic temperature decreases as the spacer length increases. The odd-even effect was also observed in these series of polyethers.

The presence of cyclohexanone and cyclopentanone groups in the polyesters backbone imparts rigidity and higher thermal stability to the polymer chain and showed uncleared texture in the hot stage optical polarizable microscope. Poly(benzylidene-ether)s exhibited double melting and showed well defined liquid crystalline properties. The presences of flexible methylene spacer units separate the mesogenic alignment, thus reducing the overall rigidity and showed nematic textures.

In fluorescence analysis, poly(benzylidene-ether)esters were unable to exhibit fluorescence due to the intramolecular quenching. On the other hand, all the synthesized poly(benzylidene-ether)s have a tendency to exhibit a fluorescence in the visible region. The length of methylene spacers and the presence of substituent have a significant influence on the fluorescence emission.

In photosensitivity study, all the poly(benzylidene-ether)esters showed absorption maximum at around 350nm due to $\pi \rightarrow \pi^*$ transition of the olefinic double bond present in the polymer chain. A decrease in the intensity of absorbance was observed in all the polymers during the successive irradiation with regular time intervals. This may be attributed to the disappearance of double bond leading to the formation of cyclobutane ring by the $2\pi+2\pi$ cycloaddition reaction of the olefinic double bond. Similarly, in poly(benzylidene-ether)s also during initial period of irradiation decrease in the intensity of absorbance was observed and at particular time interval an increase in intensity was noticed. The increase in intensity reverses on further irradiation and decreases regularly thereafter. This kind of disorder could be introduced by trans-to-cis photoisomerization of benzylidene chromophores on irradiation. The length of methylene spacers and the presence of substituent have a significant influence on the photosensitivity. Photoisomerization was further confirmed by solubility test, FTIR, DSC, and HOPM studies.

The results of this investigation indicate that the synthesized polymers can be used in optical switching applications, photolithographic and NLO applications.