

PREPARATION AND CHARACTERISATION OF NEW SIDE-CHAIN LIQUID CRYSTAL POLYMERS

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Introduction

Side-chain liquid crystalline polymers (SCLCPs) are a new class of materials, which combine the anisotropic physical properties of the liquid crystalline state with the characteristic properties of polymers. In the past two decades, various and numerous types of SCLCPs have been studied for the purpose of many potential applications in display devices, light induced data storage, switching devices, and non-linear optical materials (Williams, 1995; Haridas and Radhakrishnan, 1995; LeBarny and Dubois, 1989; Perrin and Armarego, 1989). However the detailed structure-properties relationships of SCLCPs which is important in achieving the highly qualitative property for each application has not been fully understood until now. It seems necessary to synthesise new types of SCLCPs by introducing new type of mesogenic groups, spacers and polymer backbones to create new property combinations in order achieve these goals. The objectives of this study were to develop new series of thermotropic SCLCPs and to investigate their thermal behaviours by means of polarised optical microscopy and differential scanning calorimetry. Two types of mesogenic groups were synthesised: One based on 4-hydroxybenzoate and L-tartaric acid and the other based on esterification benzoic acid derivatives. The former used an allyl ether while the later used methacrylate as the polymer backbone, respectively.

Materials and Methods

All chemicals used were of analytical grade. Solvents (THF, DMF, EtOH, etc.) were dried according to standard procedures (Perrin and Armarego, 1989). Purification of intermediates and products were done either by recrystallization, solvent extraction or column chromatography techniques. The physical and chemical characterization of the monomers and their precursors were performed using GC-MS, UV-Vis, FTIR, ¹H-NMR. Thermal behaviours were studied by means of polarised optical microscopy and differential scanning calorimetry. The olefinic compounds were prepared via a Williamson reaction pathways. The typical procedures of each reaction to obtain methyl 4-(3-butanyloxy)benzoate are as follows: Methyl 4-hydroxybenzoate (3.95 g, 24.7 mmol) and 4-bromobutene (5.26 g, 37.1 mmol) were dissolved in 50 ml of acetone. Potassium carbonate (3.59 mmol, 24.7 mmol) and potassium iodide (0.4 g) were then added to the mixture.

After heating at reflux temperature overnight, the precipitated salts were removed by filtration. The solvent was removed by distillation, and the residue was purified by column chromatography on silica gel with diethyl ether/n-hexane (1:8 vol.) to afford a pale yellow liquid of the product. Subsequent hydrolysis of the allyl ester and condensation reaction with the esterified L-tartaric acid afforded the allyl monomer. Polymerisation of the monomers was attempted by means of ordinary radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) as an initiator in THF.

Results and Discussion

Until now we have successfully prepared two new monomers ((4*r*,5*r*)-2-(*p*-allyloxyphenyl)-4,5-di(carbomethoxy)-1,3-dioxolan, Ac_mOX, and (4*r*,5*r*)-2-(*p*-allyloxyphenyl)-4,5-di(carboethoxy)-1,3-dioxolan, AceOX. The monomers were synthesised through sequential reaction processes involving Williamson etherification reaction between methyl 4-hydroxy benzoate and ω-bromoaalkane in the presence of potassium carbonate base. The reaction gave a rather low yield of methyl 4-(3-butanyloxy) benzoate which then reacted further with esterified L-tartaric to afford the appropriate products. Initial thermal study of Ac_mOX indicated that the new SCLCP monomer showed some smectic and discotic phases. However DSC result showed only two peaks at 56.1 and 79.8 °C that were due to glass transition and melting point temperatures. Polymerisation of these monomers by ordinary radical polymerisation with 2,2'-azobisisobutyronitrile (AIBN) as an initiator in THF was unsuccessful. It could be due to the unsuitable solvent or the presence impurities that poison the reaction. The preparation of the second type of SCLCPs was still in the monomer chemical- and spectroscopical- characterisation stages. No thermal behaviour studies were done until now.

Conclusions

Two monomers of thermotropic SCLCPs were synthesised and the monomer showed liquid crystalline behaviour. Attempts to polymerise the monomers were unsuccessful. Monomer based on benzoate skeletal and methacrylate seemed promising and further work on this type of thermotropic SCLCPs need to be pursued.

References

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