

## Preparation and Characterization of New Side Chain Liquid Crystal Polymers

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### Introduction

Liquid crystalline polymers are being recognized for their potential application in recording and electrooptic devices such as digital and holographic storage, fast optical switches and non-linear optical materials.<sup>1,2</sup> Since Finkelmann et al. and Ringsdorf<sup>3</sup> introduced the flexible spacer concept, immense research efforts have led to a variety of novel liquid crystal polymers of various mesogenic groups such as phthalocyanines,<sup>4</sup> porphyrines,<sup>4</sup> and perylene.<sup>5</sup>

Various studies have shown that by varying the size and geometry of the mesogenic core of liquid crystalline monomers, the properties change dramatically. Increasing the size of the mesogenic core results in enhanced  $\pi$ - $\pi$  overlap, thus giving rise to larger phase widths and more stable mesophases. Vast differences for mesoscopic properties are also seen by changing the periphery, e.g. by changing the substituents on the perimeter of triphenylene disc from pentyloxy to butyloxy, one does not only proceed from a columnar hexagonal packing to the formation of so-called plastic discotic phase, but one also increases the mobility by an order of magnitude.<sup>6</sup> The study focussed on the role of interconnecting structural units between the side-chain mesogen and the polymer backbone. Here we present the report on the synthesis and characterization of polyacrylate-based side-chain liquid crystalline polymers containing rod-like azobenzene mesogenic groups in their side chains.

### Materials and Methods

The rod-like azobenzene mesogenic monomer was prepared from 4-aminoacetophenone, which was diazotized and coupled with phenol to give 4-(4-acetylphenylazo) phenol. Alkylation of this compound with 3-bromopropa-

mol and 11-bromoundecanol converted it into 4-[4-(3-hydroxypropyloxy) phenylazo]acetophenone (L2) and 4-[4-(11-hydroxyundecyloxy) phenylazo] acetophenone (L4). Esterification of the hydroxylated compounds with acyl chloride in the presence of dry triethyl amine (TEA) using tetrahydrofuran as the solvent to afford the polymerisable monomers 4-([4-(acryloyl-3-oxypropyloxy) phenyl] azo) acetophenone (L3) and 4-([4-(acryloyl-11-oxyundecyloxy) phenyl]azo) acetophenone (L5). The polyacrylates L9 or L10 were prepared from its corresponding monomer L3 and L5 respectively by free radical polymerization in THF using 2,2'-azobisisobutyronitrile (AIBN) as an initiator. All new precursors and monomers were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and UV-Vis spectroscopy, and GC-MS. Preliminary mesophase characterization of the monomers and polymers is carried out by differential scanning calorimetry (DSC) and polarized light microscopy.

### Results and Discussion

Differential scanning calorimetry (DSC) result shows upon cooling from isotropic state, polymer L-9 shows two exothermic peaks at 260 and 96°C, corresponding to isotropic-liquid crystalline and liquid crystalline-crystalline transitions, respectively. Polymer L9 also shows two endothermic peaks at 108 and 272 °C under heating cycle. On cooling, the phase transitions of polymer L10 were observed at 236 and 94 °C, corresponding to isotropic-liquid crystalline and liquid crystalline-crystalline transitions, respectively. On heating two endothermic peaks were observed at 107 and 254 °C. On cooling, the enthalpy changes of isotropic-liquid crystalline transitions are 2.51 and 2.62 Jg<sup>-1</sup> corresponding to polymers L9 and L10, respectively. The small enthalpy change indicated that both polymers (L9 and L10) exhibited

the nematic phase. Polymer L11 shows two exothermic peaks on cooling at 105 and 56 °C and two endothermic peaks at 69 and 124 °C under heating. The large enthalpy change (11.52 Jg<sup>-1</sup>) of isotropic-liquid crystalline transition of L11 indicated that polymer exhibited the smectic phase. No glass transition temperature ( $T_g$ ) was detected in the given temperature range for all monomers of the polymers. DSC results for all polymer compounds are summarized in Table 1. The melting and the nematic transition temperature for monomers and polymers are dependent on the number of n of CH<sub>2</sub>'s in the alkyl segment. Isotropic point ( $T_i$ ) decreased with the increase of the spacer length. The mesophase properties of the polymers (L9, L10, and L11) are marked contrast to those of polymers, in which the azobenzene unit substituted at 4-position by linear alkyloxy chain containing a variable number n of carbon atoms. The lower homologues (n=1-3) of the polymer series exhibited one nematic mesophase, while on further increasing n (n=4,5) an additional smectic phase formed; polymer became purely smectic for n>6 based on Angeloni et al.<sup>8</sup> The phase structures of monomer L3 and polymer L9 were observed by polarizing optical microscopy when cooling from the isotropic point to their liquid crystalline phases. A typical schlieren texture of monomer L3 and polymer L9 were observed at 140 and 259°C, respectively, which are assigned to nematic phases. The micrograph of monomer L-5 and corresponding L10 in their liquid crystal phases exhibits both typical nematic droplets upon cooling from isotropic state are observed at 114 and 234 °C. The monomer L8 and corresponding polymer L11 also showed schlieren texture at 56 and 104 °C, respectively, which indicated smectic phases.

Based on the result of DSC and polarizing optical microscopy analyses, it can be concluded those two members of monomer and polymer show nematic liquid crystalline behavior, one monomer and polymer show "pseudo" smectic phase. Polymers L9 and L10 possess a greater propensity to give rise to stable and persistent nematic mesophase. Thus indicating that the placement of an oxygen atom by a carbonyl group strongly enhances the nematogenic character of the azobenzene group in the side chain polymer.

### Conclusions

In conclusion, the liquid crystalline polymers containing azobenzene moieties in the side-chain are prepared by using conventional free radical process. The mesophase behaviors of the polymers were investigated with those of analogous monomers and it was observed that (L9 and L10) exhibited nematic phase near isotropic point. This study will be further extended to the optical data storage materials.

### Benefits from the study

The study provided first hand experience in synthesis and characterizing advance materials: side-chain liquid crystal polymers. It trained staffs in designing, synthesizing and characterizing side-chain liquid crystal polymers, and the findings of this study will shed more light into this area and pave a way for further study.

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