Effect of the lateral substituent on the mesomorphic behavior of side-chain liquid-crystalline polymers containing a Schiff base ester

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Abstract New polymerizable macromers containing a Schiff base ester linkage have been synthesized. These macromers were used to synthesize side-chain liquid-crystalline polymers (SCLCPs) by radical polymerization. The chemical structures of the macromers and polymers were characterized by spectroscopic techniques (FTIR, $^1$H NMR, and $^{13}$C NMR). The mesomorphic properties of the macromers as well as the polymers were studied by polarized optical microscopy (POM) and differential scanning calorimetry (DSC) and confirmed by powder X-ray diffraction (PXRD). POM and DSC studies revealed that all of the macromers and polymers showed liquid crystal behavior, with their nematic phases occurring in different mesophase ranges. The macromer without a lateral unit in the mesogen (M1) showed a thermal transition at a relatively high temperature (181.4 °C), whereas the macromer with a lateral unit in the mesogen (M2) showed a thermal transition at a relatively low temperature (101.8 °C). The SCLCP from macromer M1 (HPM1) also showed a comparatively high-temperature thermal transition compared to that of the polymer from macromer M2 (HPM2). The thermal properties of the polymers were studied by thermogravimetric analysis (TGA). The polymer from the macromer with a lateral unit in the mesogen (M2) showed higher thermal stability than the polymer from the macromer without a lateral unit (M1).

Keywords Schiff base ester · Side-chain liquid crystal polymer · Mesomorphic properties · Thermal stability

Introduction

Polymers containing mesogenic side groups attached laterally in a main chain are known as side-chain liquid-crystalline polymers (SCLCPs) because of their liquid-crystalline bulk properties [1]. As well as their liquid-crystalline behavior, SCLCPs have attracted great interest in recent years due to other useful properties, such as their high heat resistance, flame retardance, chemical resistance, dimensional stability, heat-aging resistance, adhesion, low viscosity, and comparatively low cost [2, 3]. SCLCPs offer a relatively ordered structure because a flexible spacer decouples the mesogen from the polymer backbone and forces the mesogenic unit into an ordered structure [4]. As a result, SCLCPs show some enhanced thermal and mechanical properties [5, 6]. The properties of a particular SCLCP depend on several parameters, such as the nature and length of the spacer used [7], the nature of the polymer backbone [8], and the type of mesogen [9–11].

The core units in the mesogen normally consist of benzene rings that are connected by a linking unit. In the study described in the present paper, we linked the core units using ester and Schiff base groups, and then studied the mesomorphic and thermal properties of the resulting polymers. Using a combination of Schiff base and ester linking groups in the mesogenic structure leads to unique mesomorphic properties. Hence, many studies have focused on Schiff base ester liquid crystals due to their interesting properties and considerable applications in various temperature ranges [12–14]. Although Schiff base ester liquid crystals have been extensively investigated for different applications, research on SCLCPs with a Schiff base ester moiety as the side group is still limited. To
4.88 °C, 14.22 °C, and 6.73 °C higher, respectively, than those for HPM1. This may be explained by invoking bond energy values [32]. The presence of an extra methoxy group at the meta position of the HPM2 side group makes it more stable than HPM1 due to the higher bond energy of this group. As a result of their high decomposition temperatures, these polymers exhibit good thermal properties for practical processing and for possible use in devices. Decomposition of the polymers was observed to be almost complete at around 900 °C, with no further weight loss seen after that. The char yields of the polymers were less than 20 % when measured at 600 °C.

Conclusions

We have synthesized polymerizable macromers containing Schiff base ester liquid crystals with a lateral substituent on the mesogen in order to study the effects of these structural motifs on mesomorphism. Side-chain liquid-crystal polymers (SCLCPs) with different molecular weights were successfully prepared by radical polymerization. The macromers and polymers were characterized by 1H NMR, 13C NMR, and FT-IR. The liquid-crystalline behavior of the macromers and polymers were studied by DSC, POM, and PXRD. Due to the different mesogen structures of these synthesized macromers and polymers, they all showed nematic textures at different temperatures. TGA demonstrated that both polymers are thermally very stable, which is useful from the perspectives of practical processing and their possible use in devices. The thermal stability of polymer HPM2 was higher than that of polymer HPM1, which can be ascribed to the presence of the methoxy group as a lateral substituent on the mesogenic side group.

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References
