Thermal, optical and electrochemical study of side chain liquid crystalline polymers bearing azo-benzothiazole chromophore in the mesogen

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Abstract A series of new side chain liquid crystalline polymers (P1–P4) containing azo-benzothiazole mesogen in the side chain were successfully synthesized by conventional free radical polymerization. The chemical structure, thermal stability and mesophase behaviors of the synthesized polymers were characterized. All the polymers showed good thermal stability and revealed liquid crystalline property. The synthesized polymers exhibited blue photoluminescence and P1 exhibited highest intensity among P1–P4. The absorption maxima of UV–vis and photoluminescence spectra were influenced by the electron donating substituents located at the side chain of polymers. The HUMO and LUMO energy values of polymers were found in the range $-5.51$ eV to $-5.58$ eV and $-3.02$ eV to $-3.07$ eV respectively.

Keywords Azo-benzothiazole · Side chain liquid crystalline polymer · Optical properties · Electrochemical band gap

Introduction

Azo-chromophore containing polymers have extensively been studied due to the unique photochromic nature of azo group. The photoinduced reversible trans-cis isomerization of the azo chromophore makes azo polymers potential in variety of applications, for example, optical data storage [1, 2], nonlinear optical (NLO) materials [3–5], photo switching devices [6–9], liquid crystal displays [10–12], and so on. Generally, azo-polymers bearing heterocyclic moiety exhibit large molecular hyperpolarizability compared to benzenoid analogues. As a result, azo-polymeres comprising heterocyclic moiety have aroused much research interest among scientific communities because of the large molecular hyperpolarizability which is one of the desired criteria for NLO materials [13–16]. In recent years, fused ring heterocyclic compounds, e. g., benzothiazole incorporated compounds have attracted much research attention because benzothiazole derivatives are promising candidates as organic light emitting diodes (OLEDs) [17–19], photovoltaic cells [20] and memory devices [21–23]. However, the major challenge in device fabrication is to achieve favorable alignment of molecules to enable efficient charge transport through the semiconducting medium [24]. Liquid crystalline (LC) materials are possible candidates to resolve the difficulties by providing highly ordered or closely packed structures [25, 26]. In addition, side chain liquid crystal polymers (SCLCPs) offer more ordered structure because flexible spacer decouples the mesogen from the polymer backbone and renders the mesogenic unit into an ordered structure [27, 28]. As a result, SCLCPs show some improved thermal, mechanical and electro-optical properties [29, 30]. Although benzothiazole based compounds have extensively been investigated for different applications, research on SCLCPs having azo-benzothiazole moiety in the side chain is still limited. To the best our knowledge, SCLCPs bearing azo-benzothiazole mesogen in the side chain have rarely been reported.

In this connection, we describe the successful synthesis, spectroscopic characterization, thermal, mesophase, optical and electrochemical properties of a series of novel side chain...
where $E_{ox}$ is the onset oxidation potential and $E_{Fe/Fe^+}$ is the external standard potential of the ferrocene/ferriecinium ion couple and $E_g$ (opt.) is the optical band gap. The external standard potential of the ferrocene/ferriecinium ion couple ($E_{Fe/Fe^+}$), which was estimated under the same experimental condition and the value was located at 0.28 V to the Ag/AgCl electrode.

The onset potentials of P1-P4 were calculated from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammogram. The typical voltammogram of P1 is shown in Fig. 7 and HOMO-LUMO energies of P1-P4 and their corresponding band gap values are summarized in Table 3. All the polymers showed analogous redox behavior due to their structural similarities. The energy gap between HOMO and LUMO levels slightly decreased with the incorporation of the electron pushing groups ($\text{CH}_3$, $\text{OCH}_3$, $\text{OC}_2\text{H}_5$) on the benzothiazole unit in the mesogen. This observation indicates that the electron donating groups may extend the conjugation which could lower the energy levels between HOMO and LUMO. The obtained HUMO and LUMO values of polymers are in the range $\approx5.51$ eV to $\approx5.58$ eV and $\approx3.02$ eV to $\approx3.07$ eV respectively. These results indicate that the newly synthesized SCLCPs are conjugated p-type polymers and exhibit electron transporting properties [40].

Conclusions

In this article, we have described the synthesis and characterization of a series of new SCLCPs having azo-benzothiazole mesogen in the side chain. The synthesized polymers showed good thermal stability and exhibited liquid crystalline property. The $T_g$ values of polymers were found in the range 134–89 °C and influenced by the terminal tails situated in the side chain. All the synthesized polymers exhibited blue photoluminescence; however, polymer P1 showed highest fluorescence emission than P2-P4. The absorption maxima of UV–vis as well as PL spectra were red shifted by the influence of the electron donating substituents located at the sixth position on the benzothiazole ring. The band gaps of polymers were slightly shifted toward lower energy by the influence of the electron donating groups in the side chain. The band gap values of polymers (2.42–2.53 eV) revealed that the newly synthesized SCLCPs could be potential candidate in photovoltaic applications.

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References

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