Optical Properties of Azo-Benzothiazole Side Chain Liquid Crystalline Polymers: Effect of Solvents, Substituents and Temperatures

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Abstract
The optical properties of a series of side chain liquid crystalline polymers (P1–P3) containing azo-benzothiazole mesogen with different terminal substituents (–H, –CH₃ and –OCH₂CH₃) in four organic solvents of varying polarity have been investigated by absorption and fluorescence spectral analysis. Solvatochromic studies of P1–P3 did not show any regular variation on the absorption and emission intensities with changing the polarity of solvent. Theoretical studies were performed based on different solvent correlation methods such as Dimroth-Reichert and Kamlet-Taft methods to investigate the solute-solvent interactions. Both absorption and emission maxima of investigated polymers were bathochromically shifted with the replacement of sixth position hydrogen atom by electron donating groups in benzothiazole moiety. The emission intensities of the studied polymers showed decreasing trend with increasing temperature.

Keywords Azo-benzothiazole · Side chain liquid crystalline polymer · Solvatochromism · Thermochromism

Introduction
Organic fluorescent materials that exhibit a fluorescence response to external stimuli such as pressure and heat have received tremendous attention because of their potential practical applications as sensors [1], in optical recording [2] photonic [3] and optoelectronic devices [4, 5]. In recent years, these stimuli-responsive photoluminescent materials, including those that are thermochromic, photochromic, mechanochromic, solvatochromic and electrochromic, have been developed widely as they have been extremely “smart” materials, since the external force can be easily controlled or modulated [6].

Solvatochromic molecules are a class of compounds which show spectral shift (absorption and/or emission maxima) with changing polarity of its surrounding environment. Both of intra- and intermolecular interactions between the solute and solvent exhibit a profound effect on the geometric, electronic and vibrational properties of aromatic molecules in their excited states [7]. These interactions can be classified into: (i) non-specific solute-solvent interaction caused by polarity-polarizability effects and (ii) specific solute-solvent interaction such as hydrogen bonding or electron donor-acceptor interaction [8].

Several theoretical models such as Lippert-Mataga, Weller’s, Rettig’s, McRay’s plots, Kamlet-Taft [9], and Dimroth-Reichert’s methods [10] have been proposed to describe the preferential solvation phenomenon. Jiang et al. [11] reported that the variation of Stock shifts with solvent polarity on napthalimide-carbazole dyes using Lippert-Mataga plot was mainly due to the large change in dipole moment upon excitation. In another work, Alphonse and co-workers [12] described that both absorption and emission spectra of their investigated compounds were red shifted by controlling hydrogen bond donor strength (α) of solvent and the theoretical calculations were made by using Kamlet-Taft method.

Besides solvatochromism, a study of thermochromic effect on the optical and electrical properties would also result to an intriguing and interesting phenomenon that could make the materials useful for electronic and optoelectronic devices [13]. The underlying theory to the spectral shifts involves...