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Temperature and frequency dependent dielectric properties of electrically conducting oxidatively synthesized polyazomethines and their structural, optical, and thermal characterizations

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ABSTRACT

Three azomethine diol monomers were synthesized by condensing with methanolic solution of aromatic aldehydes with ethylenediamine. These monomers were oxidatively polymerized using NaOCl as an oxidant. The structures of the monomers and polymers were confirmed by various spectroscopic techniques. Spectral results showed that the repeating units are linked by C–C and C–O–C couplings. The polyazomethines have fluorescent property with high stokes shift. Solid state electrical conductivity of polymers both in I_2 doped and undoped states, temperature and frequency dependent dielectric measurements were made by two probe method. The electrical conductivities of polyazomethines were compared based on the charge densities on imine nitrogens obtained from Huckel calculation. The conductivity of polymers increases with increase in iodine vapour contact time. Among the synthesized polymers PHNAE has shown high dielectric constant at low applied frequency of 50 Hz at 393 K due the presence of bulky naphthalene unit in polymer chain.

1. Introduction

Polyazomethines (PAMs) have received increasing scientific and technological interest of researches due to their importance in many fields like chemical gas sensors, light emitting diodes, photovoltaic devices etc., [1–3]. Recently, azomethine oligomers and polymers containing hydroxyl group have had usefulness in semiconductivity, paramagnetism and high energy resistance materials. Azomethine polyphenols were used to prepare high temperature resistance inhibitors, thermostabilizers, graphite materials, epoxy oligomers, block copolymers, adhesives and photoresists [4–6]. But, their poor solubility making them as less processable. To improve their solubility polar groups containing PAMs like polyazomethine ethers [7], polyacrylate-azomethines [8], polyazomethine carbonates [9], polyamide-azomethine-esters [10], and polyazomethine sulfones [11] have been synthesized. Also, PAMs containing alkoxy substituents have been presented with good solubility and high thermal stability [12]. Additionally, optical and semiconducting properties of these PAM have also been widely investigated for many years because of wavelength dependent photo and electroluminescence and non-linear optical properties. The conductivities of PAMs are increased by dopants [13], so they have been widely used in the field of opto electronics [14–16]. Synthesis of several PAMs using azomethine monomers were accomplished oxidatively using oxidants like NaOCl, H_2O_2 and air O_2[17,18]. The possibility to produce polymers in aqueous ambient conditions provides an important option in green chemistry aspects. Kaya et al. and others [18,19] have synthesized several PAMs by oxidative polymerization and characterized them for various properties. The electrical properties such as iodine doped conductivity of oxidatively polymerized PAMs have been studied widely. But very few reports only are found in the literature dealing with the dielectric property of PAM.

So, the present study is focused on synthesis of polyazomethines with varying degree of substituents and ring size to explore optical and electrical properties with a special focus on dielectric property. The structural characterization of synthesized compounds were made by FT-IR, UV–visible, NMR techniques. Fluorescence of monomers and polymers, electrical conductivity of polymers and dielectric properties of polymers at different temperature and frequencies were carried out.

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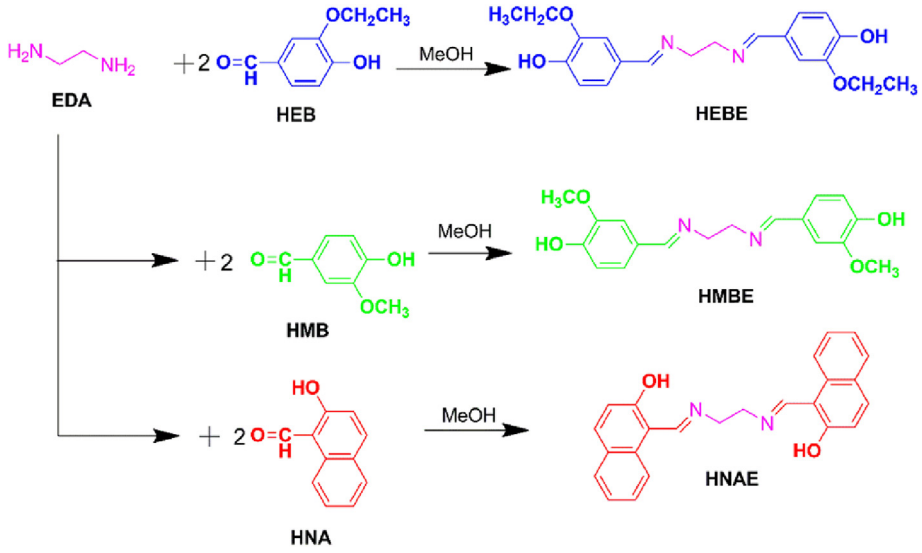
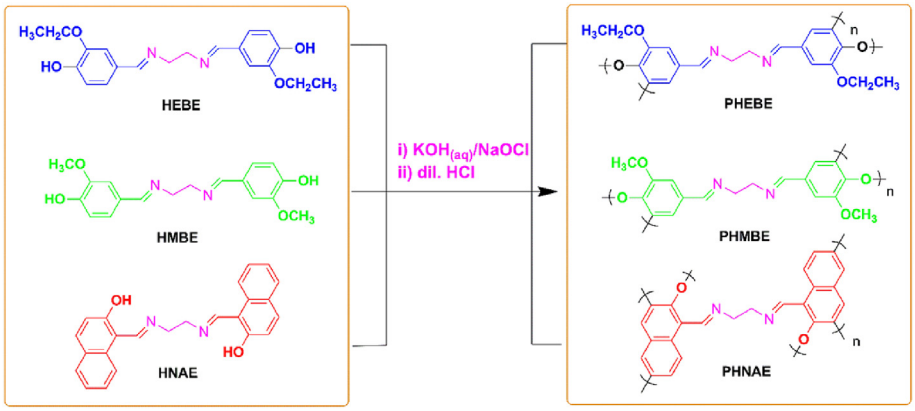


Scheme 1. Synthesis of monomers.



Scheme 2. Synthesis of polymers.

2. Experimental

2.1. Materials

4-Hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3-ethoxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, ethylenediamine were purchased from Sigma Aldrich. Sodium hypochlorite (6% aqueous solution), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), tetrahydrofurane (THF), methanol, ethanol, acetonitrile, acetone, toluene, ethyl acetate, heptane, hexane, CCl_4, $CHCl_3$, KOH and HCl were obtained from by Merck, India and used as received.

2.2. Synthesis of monomer

The azomethine diol monomers N,N′-bis(4-hydroxy-3-ethoxybenzylidene)ethylenediamine (HEBE), N,N′-bis(4-hydroxy-3-methoxybenzylidene)ethylenediamine (HMBE), and N,N′-bis(2-hydroxy-1-naphthalidene)ethylenediamine (HNAE) were synthesized by the condensation reaction of 4-hydroxy-3-ethoxybenzaldehyde (HEB), 2-hydroxy-3-methoxybenzaldehyde (HMB) and 2-hydroxy-1-naphthaldehyde (HNA) with ethylenediamine (EDA). The monomer, HEBE was synthesized by refluxing

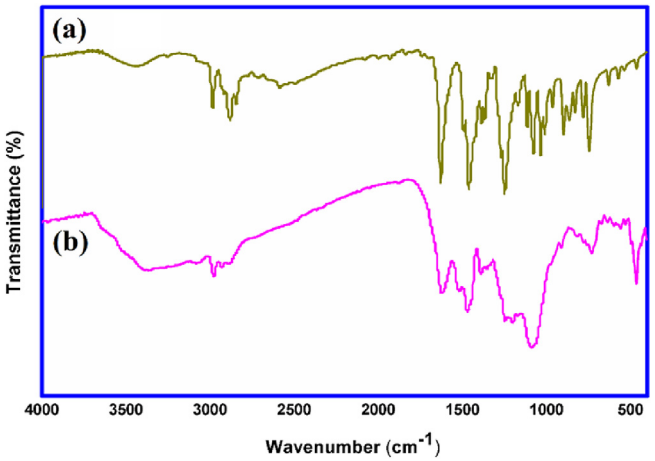


Fig. 1. FT-IR Spectra of a) HEBE and b) PHEBE.