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Optical, dielectrical properties and conduction mechanism of copolymer (N,N′-bissulphinyl-*m*-benzenediamine-*p*-phenylenediamine)

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ABSTRACT

Copolymer N,N′-bissulphinyl-*m*-benzenediamine-*p*-phenylenediamine (SMBD-PPD) is synthesized by using Michael addition on reacting of N,N′-bissulphinyl-*m*-benzenediamine (SMBD) with *p*-phenylenediamine at 180–200 °C and characterized with various physical and chemical techniques. The number average of molecular weight of SMBD-PPD copolymer is estimated using ^{1}H NMR spectroscopy to be about 3160 g/mole. The absorption properties of SMBD-PPD copolymer showed two main absorption peaks at λ = 247 and 303 nm in methanol solution and at λ = 238 and 299 nm in ethanol. The energy gap is found in the range of 2.1–2.5 eV. SMBD-PPD copolymer showed emission characteristics. The emission spectra appeared at λ = 460 and 490 nm. The dc and ac electrical conductivities and dielectrical properties at different temperature and frequencies are investigated. The dominant conduction mechanism for ac conductivity in SMBD-PPD copolymer is found to be quantum mechanical tunneling.

1. Introduction

Conducting polymers are a very important class of materials because of their unique chemical, optical and electrical properties leading to a wide range of technological applications. Nowadays, the most commonly used conducting polymers include polyaniline (PANI) [1,2], polypyrrole (PPy) [3], poly [3,4-ethylenedioxythiophene] (PEDOT) [4,5] and poly[*p*-phenylenevinylene] (PPV) [6]. In general, conducting polymers can be synthesized either chemically (by addition or condensation) or electrochemically (which is done by oxidation of relevant monomer in solution in most cases) [7]. Conducting polymers, as unique class of π-conjugated materials have been extensively studied because of their wide potential applications such as super capacitors [8], biosensors [9], polymer solar cells [10], laser [11] and polymer light emitting diodes (PLEDs) [12].

Conducting polymers which containing S–N linkage, are of interests due to their superior electrical conduction [13]. It is, Also, reported that amino compounds, both aliphatic and aromatic when treated with thionyl chloride gave N–Sulphinyl compounds containing −N═S═O group [14]. Many researches have used Michael addition method in synthesis of this class of polymers. The optical, electrical and thermal behaviors of the conducting polymers have been studied by many authors [16–27]. Conducting polymers exhibit a direct band gap, which allowed absorption or emission at the band edge [15]. It has been shown that the delocalized electron along polymer chain, giving rise to the formation of valence and conduction bands [16]. Depending on the polymer species, semiconducting polymers can exhibit strong fluorescence, which can be described in terms of orbital molecular

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theory. The most widely examples of fluorescent semiconducting polymers include polyfluorene [17], poly (*p*-phenylenevinylene) [18], poly (*p*-phenylene) [19] and polythionphene [20]. The tunable optical properties made semiconducting polymers as a fascinating class of materials that have been widely demonstrated as active materials for range of optoelectronic devices, including organic light emitting devices, biological sensors and laser [11,21–23]. Thermogravemetric analysis for polymers containing S–N linkage such as poly (bis-*p*-phenylenediaminesulphoxide) and poly (bis-2,6-diaminopyridinessulphoxide) indicated that the polymers were fairly stable than other conducting polymers up to 200 °C with activation energy in range of 10–50 kcal mole [24,25]. Diab et al. [26,27] reported that conducting polymers containing S–N linkage are found to have an increased conductivity, possibly due to the participation of lone pairs of electrons on nitrogen and sulpher atoms with σ bond of macro chain.

Due to the variation of properties of conducting polymers and significant contributions in several fields, it is interesting to study this type of polymers. This study aimed to design, synthesize and characterize a new conducting polymer that possesses good conducting behavior and good absorption of visible light in presence of photoluminescence phenomena. This makes the synthesized polymer promising in many advanced applications such as chemical and biosensors, polymer solar cells and light emitting diodes.

2. Experimental

2.1. Materials

m-Phenylenediamine and *p*-phenylenediamine (Aldrich chemical Co., Inc.) are purified by dissolving in hot water and ethanol, respectively. The solutions are left to cool, the pure materials then being collected by filtration forming light brown crystals with melting points 64 and 142 °C, respectively.

Thionyl chloride ($SOCl_2$, Aldrich chemical Co., Inc.) is freshly distilled before use. All other chemicals and solvents are purified by standard procedures.

2.2. Preparation of N,N′-bissulphinyl-m-benzenediamine (SMBD)

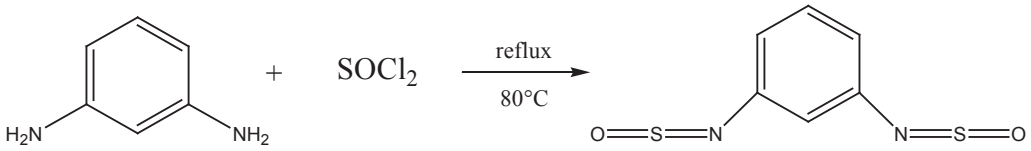
Recrystallized *m*-phenylenediamine (0.1 mol) is placed in 250 ml round bottomed flask fitted with a dropping funnel containing thionyl chloride (0.3 mol) and a thermometer. The flask is kept in an ice-bath and $SOCl_2$ is added dropwise to *m*-phenylenediamine such that the reaction temperature is kept below 0 °C. The flask is taken out of the ice bath and allowed to attain room temperature. Then, the reaction mixture is refluxed for ≈6–8 h at 80 °C. Unreacted $SOCl_2$ is removed by distillation under reduced pressure. The residual of $SOCl_2$ is removed by addition of dry benzene and distilling off when a dark brown needle crystals of N,N′-bissulphinyl-*m*-benzenediamine (SMBD) are formed. The chemical reaction for synthesis of SMBD is shown in Scheme 1.

2.3. Preparation of copolymer N,N′-bissulphinyl-m-benzenediamine-p-phenylenediamine (SMBD-PPD)

Copolymer N,N′-bissulphinyl-*m*-benzenediamine-*p*-phenylenediamine (SMBD-PPD) is prepared by using Michael addition mechanism of *m*-phenylenediamine with N,N′-bissulphinyl-*m*-benzenediamine. N,N′-bissulphinyl-*m*-benzenediamine is dissolved in DMF in round-bottomed flask and warmed with stirring in atmosphere when a dark brown solution is obtained. Equimolecular amounts of *p*-phenylenediamine solution in DMF is added to N,N′-bissulphinyl-*m*-benzenediamine solution with stirring. The reaction mass is allowed to reflux for ≈48 h at 180–200 °C by using few drops of pyridine. A viscous brown mass is formed. It is cooled to room temperature and poured in ice water to obtain dark brown precipitate. It is then filtered, washed thoroughly with water, and dried. The polymerization reaction of SMBD-PPD copolymer is presented in Scheme 2.

2.4. Chemical and physical measurements

The FTIR spectra are recorded as KBr disks using FT-IR spectrophotometer Jasco 4100 spectrophotometer in the spectral range 4000–400 cm^{-1}. The ^1H NMR spectrum is obtained with Bruker 400 MHz spectrometer with DMSO-d_6 as the solvent and TMS as an internal reference. Thermogravimetric analysis (TGA) is performed using a TGA-50H detector under flowing N_2 (20 mL/min) on platinum crucible with a heating rate of 10 °C/min from ambient temperature to 800 °C. Photoluminescence spectra are recorded on Fluorimeter spectrophotometer (Model 6285, for Excitation and Emission spectra, 200–700 nm). The excitation light wavelength is 365 nm. The absorbance spectra are measured at room temperature in the wavelength range 200–900 nm using a double-beam Jasco spectrophotometer Model V-630 UV/Vis. SMBD-PPD copolymer is dissolved in methanol and ethanol for optical measurements. The shape of samples which used for dc and ac electrical measurements are pellets of thickness about 1 mm and surface area of about 25 mm^2. Silver paste is used as ohmic contacts. Samples are sandwiched between two copper electrodes during measurements. The dc



Scheme 1. Synthesis of N,N′-bis-sulphinyl-m-phenylenediamine SMBD.