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Synthesis, optical and morphological properties of novel pyrazole-based oligoamide film

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ABSTRACT

The aim of this study is to prepare novel pyrazole-based oligoamide (oligo-pyrazole) film and to investigate its optical properties. The oligo-pyrazole was obtained by reacting pyrazole-3,4-dicarbonyl dichloride and 2,3-diaminopyridine in a single step reaction. The synthesized oligo-pyrazole was characterized by ^{1}H, ^{13}C NMR, FT-IR, Elemental Analysis and Gel Permeation Chromatography (GPC). The novel oligo-pyrazole film was prepared using synthesized oligo-pyrazole with 94 μm thickness. The optical properties of the prepared film such as absorbance, transmittance and optical band gap were determined by UV–vis spectroscopy. The E_g value of the oligo-pyrazole film was found to be 1856 eV. The surface morphology of the sample was investigated by an Atomic force microscopy (AFM) tool. It was found that average roughness of the film was 15.55 nm with the homogeneous grain distribution on the surfaces. The oligo-pyrazole film may be a good device in optoelectronic applications due to optical and morphological properties.

1. Introduction

The conjugated polymers (CPs) are one of the most important issues of the polymer chemistry. In particular, the CPs have extensive workspace because of optic, optoelectronic and photonic properties [1,2]. The CPs have potential applications due to their excellent optoelectronic properties. Some known applications are solar cells, charge storage devices, organic field-effect transistors, biosensors, light emitting diodes (LEDs), electrochromic panels and photovoltaic panels [3–5]. In recent years, the CPs having polyamide structures have continued to grow too significant due to thin film transistors and industrial applications [6–9]. Polyamides (PAs) are quite significant one class of the conjugated polymers. PAs are used in many application fields in terms of organic light emitting diodes, organic photovoltaics and optoelectronic technology properties [10–13]. Some applications of PAs can be listed as known; medicine, automotive, electronic devices, agriculture *etc.* [14–19]. Furthermore, pyrazole-based PAs have advantages in many application fields such as optics and optoelectronic technology [20,21]. The PA based films had advantages in terms of technological applications such as mechanical flexibility, high sensitivity and resistive switching [22–24]. Moreover, PA based films were used for semiconductor devices and superconducting devices because of their optic and optoelectronic properties. In addition, PAs were also used in the fields of desalination, production of pure water, beverages, wastewater treatment *etc.* [25–27]. Additionally, PAs were used in separation technologies in terms of the separation of proteins [28,29].

In this study, we synthesized novel pyrazole-based oligoamide, to prepare its film and investigated the optical properties such as absorbance and transmittance. AFM was used for the two- or three-dimensional surface imaging, average roughness measurements, height distribution graph and determination of the surface characterization parameters.

2. Experimental

2.1. Starting materials

All chemicals and solvents were received from Sigma-Aldrich and Merck companies. The purchased materials were used without purification. The infrared spectra were recorded on a Perkin Elmer Precisely Spectrum one spectrometer using pressed disc in the range of 4.000–450 cm^{-1}. Elemental analyses were performed on Thermo Scientific Flash 2000. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DRX-400 high performance digital FT-NMR spectrometer. Molecular weight and PDI of the oligo-pyrazole was determined by gel permeation chromatography (GPC) using Agilent 1100 Series, equipped with refractive index detector. Both Ethyl 4-(cholorocarbonyl)-1,5-diphenyl-1*H*-pyrazole-3-carboxylate (**1a**) (mp 173 °C)

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and its derivatives 1,5-diphenyl-1*H*-pyrazole-3,4-dicarboxylic acid (**1b**) (mp 224–225 °C) and 1,5-diphenyl-1*H*-pyrazole-3,4-dicarbonyl chloride (**1c**) (mp 86–89 °C) as our starting compounds were synthesized via related literature [30,31]. The optical measurements of the oligo-pyrazole film were carried out with a Shimadzu model UV-1800 Spectrophotometer in the wavelength range of 1100–190 nm at room temperature. The Ambios-Scope atomic force microscope was used to get information about the surface topography of the micro structured oligo-pyrazole film [32].

2.2. Synthesis of oligo(2-aminopyridine-3yl)-5-phenyl-1H-pyrazole-3,4-dicarboxyamide (oligo-pyrazole) (2)

1,5-diphenyl-1*H*-pyrazole-3,4-dicarbonylchloride (0.364 g, 1 mmol) was dissolved in anhydrous tetrahydrofuran (10 ml). 2,3-diaminopyridine (0.218 g, 2 mmol) was added to the reaction pot and the mixture was refluxed for 24 h under an atmosphere of argon gas with low pressure. It was cooled to at room temperature. The solvent was evaporated. The precipitated product was washed with diethyl ether. Then, it was filtered and dried. Yield: 94%. IR (ν, cm^{-1}): 3442, 3314 (N−H, amide), 3064, 3028 (Aromatic −CH), 2921 (Aliphatic −CH), 1718 (C═O, acyl), 1664 (C═O, amide), 1596-1580 (C═N), 1511-1447 (Aromatic C═C), 1315 (C−N) Anal. calc. for $C_{93}H_{67}N_{23}O_8$: C 68.33, H 4.13, N 19.71; found: C 68.56, H 4.35, N 19.79. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 10.4–9.8 (−NH, amide), 7.4–7.0 (m, aromatic-H), 5.0, 4.9 (−NH, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.1, 164.7, 161.2, 160.2 (-C═O), 152.5 (C_3), 139.0 (C_5), 138.6, 137.2, 136.5, 135.1, 131.3, 132.0, 130.7, 130.3, 129.6, 129.6, 128.2, 127.8, 126.1, 126.1, 123.3, 122.7, 122.3, 112.5 (C_4). *Mn* = 1637 g/mol, *Mw* = 2103 g/mol, (polydispersity index, PDI, 1.21).

2.3. Preparation of film the synthesized oligo-pyrazole

The oligo-pyrazole molecule was added to 1 ml DMF until the solubilized. The solution of the oligo-pyrazole was stirred at room temperature for 1 h. Any insoluble oligo-pyrazole was removed by filtrating with filter paper. The glass surface was first cleaned with a piranha solution (sulfuric acid and hydrogen peroxide). Then, it was rinsed with water. The solution of oligo-pyrazole was added dropwise to coat the film on the glass and left to dry automatically. 94 µm coated oligo-pyrazole film was obtained. The thickness value of film was measured using a micrometer (sensitivity = 0.001 mm) shown in Fig. 1.

3. Results and discussion

3.1. Synthesis and characterization

Conjugated polyamides and oligoamides are extremely significant target in the polymer structures for polymer and organic chemists due to industrial applications such as automobile, electronic and packing [33–35]. Therefore, the novel pyrazole-based oligoamide was designed and synthesized. Firstly, 1,5-diphenyl-1*H*-pyrazole-3,4-dicarboxylic acid was synthesized from hydrolysis of the prepared pyrazole-3-carboxylic acid according to literature [30,31]. The monomeric starting material, 1,5-diphenyl-1*H*-pyrazole-3,4-dicarbonylchloride was obtained by reaction pyrazole-3,4-dicarboxylic acid and sufficiently thionyl chloride. All the synthesized compounds were confirmed by spectroscopic methods which are agreement with our previous findings [36]. Afterwards, for preparation the novel pyrazole-based oligoamide were performed the one step procedure in Scheme 1. The olygo (2-aminopyridine-3yl)-5-phenyl-1H-pyrazole-3,4-dicarboxyamide (**2**) (oligo-pyrazole) was synthesized from the reaction of the pyrazole-3,4-dicarbonylchloride and 2,3-diaminopyridine in tetrahydrofuran as solvent under an atmosphere of argon gas (Scheme 1).

The number of average molecular weight (*Mn*), average molecular weight (*Mw*) and polydispersity index (PDI) of the synthesized oligo-pyrazole **2** were confirmed by Gel Permeation Chromatography (GPC) using poly (methyl methacrylate). These values of the synthesized oligo-pyrazole were observed 1637, 2103 and 1.21 g/mol^{-1}, respectively. As shown Scheme 1, the synthesized oligo-pyrazole should be trimer structure according to gel permeation chromatography result. The oligo-pyrazole is unsymmetric due to synthesized monomer structure. The oligo-pyrazole have many aromatic structures such as pyrazole, pyridine and phenol. Also, the low band gap value of film has occurred in terms of its good conjugation structure.

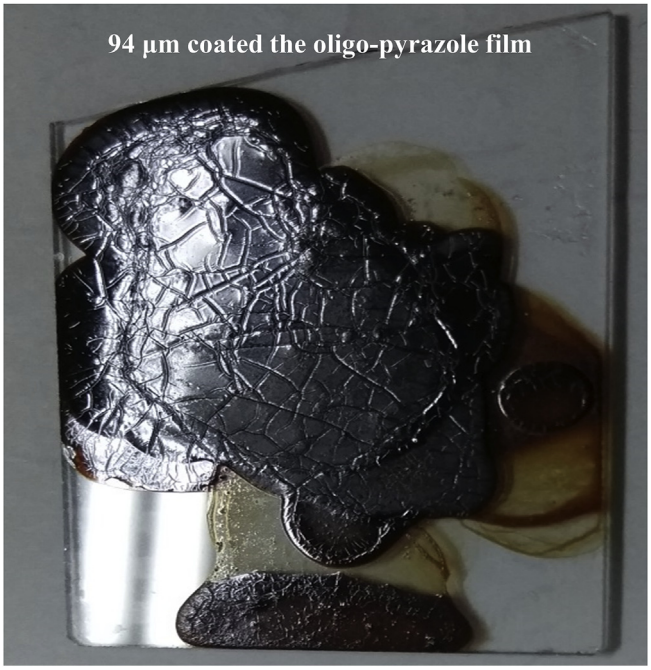

Fig. 1. Image of oligo-pyrazole film.

The structure of oligo-pyrazole **2** was determined by IR, Elemental Analysis, ^{1}H- and ^{13}C- NMR spectra. The FT-IR bands at 3442 and 3314 cm^{-1} observed to the −NH amide groups. The amide (C═O) group stretching was appeared in the region of 1718 and 1664 cm^{-1}. The bands at 3064, 3028 cm^{-1} observed due to the aromatic C−H stretching vibrations. The strong bands at 1596 and 1580 cm^{-1} also appeared due to the C−C stretching in the phenyl rings. In the case of the oligo-pyrazole, the correct structure was established by ^{1}H NMR and ^{13}C NMR spectroscopy in which characteristic the presence of protons of C═NH peaks were observed as one-proton at δ 10.4–9.8 ppm and the protons of the NH peaks for **2** were observed as one-proton singlet at δ 5.0 and 4.9 ppm and also multiplets in the region 7.9 to 7.0 ppm appeared due to the aromatic protons of the oligo-pyrazole (Spectral data of oligo-pyrazole are given in supplementary materials file).

3.2. The optical properties of the synthesized oligo-pyrazole

A graph of absorbance with wavelength was plotted for oligo-pyrazole film in Fig. 2. As seen in the absorbance curve of oligo-pyrazole film, it was observed that the oligo-pyrazole absorbed in every wavelength of light. The sharpest increase in absorbance is the 550–755 nm range. In addition, the absorbance curve of oligo-pyrazole film remained constant at a range of 400–550 nm.

The transmittance graph for oligo-pyrazole film was observed as in Fig. 3. The transmittance value of the oligo-pyrazole film is at most 42%. The transmittance value increased almost constantly with very small increments in the range of 295–601 nm. After 601 nm, it was observed that the transmittance value was clearly increased. Among 641–1100 nm, a sharp increase in the transmittance value was