FTIR, Raman and NMR spectroscopic and DFT theoretical studies on poly(N-vinylimidazole)

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HIGHLIGHTS

- Synthesis and spectroscopic analysis of poly(N-vinylimidazole) [poly(NVIM)].
- The FTIR and FT-Raman spectra of poly(NVIM) were recorded.
- The vibrational frequencies were calculated by DFT method and discussed.
- The TGA–DTA analyses reveals that poly(NVIM) is thermally stable up to 489 °C.
- HOMO–LUMO energies were calculated.

GRAPHICAL ABSTRACT
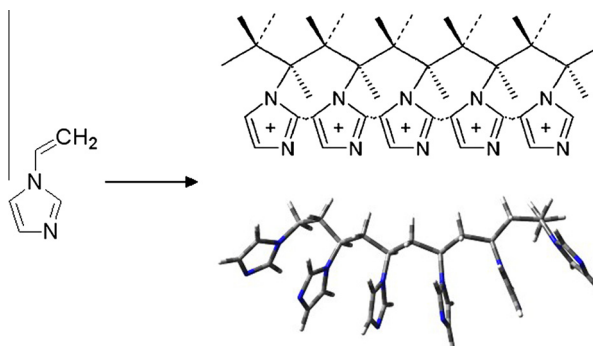
ABSTRACT

In this study where the FTIR, Raman, ^{1}H NMR and ^{13}C NMR spectra of poly(N-vinylimidazole) which can be abbreviated as poly(NVIM) are first reported, a comparison of the experimental and theoretical vibrational spectral data of monomer NVIM and water-soluble poly(NVIM) has been given; such a comparison over the vibrational modes and associated spectral data calculated at B3LYP/6-31+G(d) level of theory for NVIM and its stable dimer forms provided significant contributions for getting a reliable interpretation of the observed vibrational spectra of poly(NVIM). The obtained results revealed that the change from NVIM to poly(NVIM) should be characterized by the disappearance of the CH$_2$═CH bonds of the vinyl group and the appearance of the aliphatic C─H and CH$_2$ bonds. Besides this, the thermal properties of poly(NVIM) were elucidated by thermogravimetric analyses such as TGA, DTA and DSC, while some electronic structure parameters of the most stable dimers of NVIM were investigated through the structure calculations performed by using B3LYP method and 6-31+G(d) basis set within the density functional theory (DFT) methodology.

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Introduction

The polymerization reactions involving N-vinylimidazole (NVIM) and its derivatives have stimulated great interest due to the wide possibilities of the preparation of new materials, including the synthetic analogs of biologic active polymers with imidazole fragments in the macromolecules. It is known that macromolecules containing imidazole groups play an important role in α-chymotrypsin catalyses [1]. Investigations concerning synthetic polymeric enzyme models containing pendent imidazole groups have been reported [2]. The roles of imidazole groups in polymers, such as metal-ion complexation, counter ion binding

and dye binding, have been extensively studied [3,4]. Furthermore, the conformational behavior of poly(N-vinylimidazole) [poly (NVIM)] has been described in terms of nature of the solvent, quaternizing group, ionic strength and counter ion type [4,5]. Poly(NVIM) can be considered as a good polymeric model for investigations about interactions with neutral salts, complexing metal ions and dye molecules. Spectrophotometrically, conducto-metric and viscometric investigation of poly(NVIM)-metal ion complex formation has been reported by Pekel et al. [6,7]. From the conductometric and viscometric curves, it was found that four imidazole units were coordinated with one metal ion in the complex systems. The synthesis, characterization and electrical properties of iodinated poly(NVIM) has been reported by Özyalçın and Küçükyavuz [8]. It was shown that more stable charge transfer complexes can be formed even in non-conjugated polymers. Addition of an electron-withdrawing substituent gives the more positive character to the structure so that the interaction between polymer and dopant anion becomes stronger.

The copolymerization of NVIM with different donor–acceptor monomers, such as styrene, 4-aminostyrene, vinyl acetate, N-vinyl-2-pyrrolidone, maleic anhydride, methyl acrylate, acrylonitrile, methyl methacrylate, dialkyl fumarates, ethyl acrylate and the determination of the monomer reactivity ratios have been also reported [9–15]. It was shown that these imidazole-containing copolymers obtained from a wide range of monomer feeds had different compositions, which vary from random to alternating structures.

A large number of quantum mechanical studies have been devoted to study the structural and electronic properties of conducting oligomers and polymers derived from thiophene and pyrrole [16–20]. These investigations have been extremely useful not only to rationalize the experimental observations but also to develop the comprehensive design of new conducting materials by using the knowledge provided by such calculations. In the last decade some theoretical studies have been devoted to study oligo-anilines and/or PAn using *ab initio* and/or density functional theory (DFT) methods [20]. To the best our knowledge, there have been no reports in the literature about the DFT study on water-soluble poly(NVIM).

In this study, we present density functional calculation of the geometrical and vibrational properties of the ground state of water-soluble poly(NVIM) and its dimeric forms. The theoretical data (molecular parameters, FTIR and Raman spectra) are compared to the results of the experimental studies performed in the solid state. Natural bond orbitals (NBO) charges were performed at the same level of theory. Most stable dimeric forms were analyzed according to their hydrogen bonding energy and geometric characterization. Besides, ^{1}H NMR and ^{13}C NMR spectra of poly (NVIM) have been recorded and discussed. Thermal properties of poly(NVIM) were investigated by using TGA, DTA and DSC.

Computational

All of the DFT based calculations reported for NVIM, poly(NVIM) and its possible stable dimers were carried out on a personal computer by using the Gaussian03 suite of programs [21]. The input geometrical parameters used in these calculations were obtained from the energy minimization calculations carried out by using the molecular mechanics (MM) method with "universal force field (UFF)" [22]. The main calculations were performed using standard techniques with B3LYP functional [23,24] and 6-31+G(d) basis set [25]. Vibrational frequencies have been checked for the optimized structures to confirm that the true energetic minima had been found. Theoretical vibrational spectrum of the most stable dimer conformer has been interpreted by means of the internal coordi-

nate analysis implemented in the Gaussian03. A Monte-Carlo method of calculating the molecular volumes of the previously optimized structures requested by using the additional keyword "volume", which was based on 0.001 e/bohr^3 density envelope.

Experimental

Reagents

NVIM monomer (Merck) was distilled before use. It had the following characteristics: NVIM, bp 192–194 °C, $n_D^{20} = 1.5290$, $d_4^{20} = 1.038$. Azobisisobutyronitrile (AIBN) initiator (Acros) was twice recrystallized from methanol: mp 102.5 °C. The solvents (1,4-dioxane, methanol, diethyl ether, and n-hexane) used as polymerization medium and for purification of homopolymers by precipitation and washing, were all analytical grade reagents. They were purified using standard methods and were distilled before use.

Apparatus

FTIR spectra of the NVIM and poly(NVIM) were obtained using a Bruker Optics IFS 66/S Model spectrophotometer in the 4000–550 cm^{-1} range. The resolution of the spectrometer was 2 cm^{-1}, and the samples were examined by ATR apparatus. Raman spectrum of the poly(NVIM) was obtained using a Bruker FRA 106/S FT-Raman Module. ^{1}H NMR spectra were recorded using a Bruker Avance DPX400 (400 MHz) spectrometer with DMSO-d$_6$ as a solvent at 25 °C. DSC, DTA and thermogravimetric analyses (TGA) of NVIM and poly(NVIM) were performed using a Shimadzu DSC-60 calorimeter and Shimadzu TG-DTA 60/60H Thermal Analyzer, respectively, in a nitrogen atmosphere at a heating rate of 10 °C/min. The CHNS-932 Model LECO Elemental Analyzer was used for the determination of C, H and N contents in the poly(NVIM) synthesized. Intrinsic viscosity of the poly(NVIM) was determined in DMSO at 25 °C in the concentration range 0.1–1.0 g/dL using an Ubbelohde viscometer. Molecular weights of poly(NVIM) was determined by Gel-Permeation Chromatography using Polymer Laboratories PL-GPC 220 THF as a mobile phase-eluent.

Preparation of poly(N-vinylimidazole) [poly(NVIM)]

Free radical polymerization of NVIM was carried out in 1,4-dioxane at 65 °C for 24 h with AIBN as the initiator. Monomer, AIBN and 1,4-dioxane were added to a three-necked flask that was equipped with a stirrer, condenser and thermometer. The flask was placed in a glycerin bath. Poly(NVIM) were isolated from the reaction mixture by precipitation with methanol and purified by two reprecipitation procedures from diethyl ether to n-hexane. Purified poly(NVIM) was dried at 40 °C for 24 h under vacuum. Obtained poly(NVIM) have the following characteristics: $[\eta]_{in}$ 0.40 dL/g in DMSO at 25 °C, $\overline{M}_v$ = 64,000 g/mol.

^{1}H NMR and ^{13}C NMR results of NVIM and poly(NVIM)

^{1}H NMR spectra of NVIM (DMSO-d$_6$, 27 °C), δ: (1) 4.86 (2H, doublet from CH$_2$ of vinyl group), (2) 5.50 (1H, doublet from CH of vinyl group), (3, 4, 5) 7.96–7.02 (3H, CH groups of imidazole ring).

^{1}H NMR spectra of poly(NVIM) (DMSO-d$_6$, 27 °C), δ: (1) 2.00 (2H, singlet from CH$_2$ backbone), (2) 2.50–3.32 (1H, singlet from CH backbone for the syndiotactic triads, s), (2) 2.90–3.15 (1H, singlet from CH backbone for the heterotactic triads, h), (2) 3.32 (1H, singlet from CH backbone for the isotactic triads, i), (3, 4, 5) 7.48–6.52 (3H, CH groups of imidazole ring).

^{13}C NMR spectra of poly(NVIM) (DMSO-d$_6$, 27 °C), δ: (1) 101.24 (1C, singlet from CH$_2$ of vinyl group), (2) 116.56 (1C, singlet from