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Oligomeric synthesis and density functional theory of leucoemeraldine base form of polyaniline

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ABSTRACT

Oligomeric synthesis of phenyl-end-capped oligoaniline (4PANI LB) has been carried out through a weak oxidizing agent, $CuCl_2$, using chemical oxidative polymerization protocol. The sample was characterized by mass spectrometry, UV–vis, IR, and CHN elemental analysis. The experimental results are counter-checked with the aid of Quantum mechanical calculations such as density functional theory (DFT). DFT at B3LYP/6–31 G (d) level of theory was used for the geometric and electronic properties simulations which also confirm the existence of 4PANI LB. Excellent correlation is observed between the experiment and theory, particularly in the UV–vis spectra which conclude the formation of tetramer (fully reduced form) 4PANI LB ($C_{24}H_{20.06}N_{4.07}$). Electronic properties such as Ionization Potential (I.P), Electron Affinities (E.A), the coefficient of highest occupied molecular orbital (HOMO), the coefficient of lowest unoccupied molecular orbital (LUMO) of 4PANI LB were evaluated at the above-mentioned level of theory.

1. Introduction

Conducting polymers (CPs) have recently received considerable attention due to their wide range of applications in solar cells, lightweight batteries, sensors, actuators, corrosion protection, light emitting diodes, surgical instruments, and mercury removal from waste water etc [1–3]. CPs such as polypyrrole (PPy), polythiophene (PT), polyaniline (PANI), polyacetylene (PA) and redox polymers such as poly(*o*-phenylenediamine) (POPD) and Poly (*o*-aminophenol) [4] have extensively been explored both experimentally and theoretically after the discovery of PA by Shirakawa et al. in 1975 [5]. Among CPs, PANI is of great interest mainly due to its ease of synthesis, easy doping de-doping ability, environmentally friendly and of low-cost monomer [6]. PANI exists in four different fundamental oxidation states; leucoemeraldine base (PANI LB), emeraldine base (PANI EB), pernigraniline base (PANI PNB), and the conducting emeraldine salt form (PANI ES). The interconversion of all these states of PANI is shown in Scheme 1 [7]. Neutral PANIs have the general formula $[(\text{-B-NH-B-NH-})_y(\text{-B-N = Q = N-})_{1-y}]_x$, where B and Q represent benzenoid and quinoid units, respectively. In this formula, y is the oxidation number and can be varied from 1, 0.5, and 0 while moving from completely reduced (PANI LB) to semi-oxidized (PANI EB) and fully oxidized (PANI PNB) respectively.

Conventional methods such as oxidative polymerization, usually give high yields for the bulk synthesis of PANI and its oligomers, where aniline (ANI) monomer are oxidized into PANI in few hours under strong acidic medium/solution [8]. A number of synthetic techniques are reported regarding the oligomeric state of PANI for a wide range of applications [9,10].

The oxidized oligomeric states (highly reactive oligomers) of phenyl-capped di-aniline and tetra-aniline are also reported through simple chemical polymerization method, further, their polaronic and bipolaronic nature were confirmed by EPR, IR and XPS [11]. In this connection a similar study from Zotti and co-workers is also reported, where a linear relation between 1/n (n = 1, 2, 4) and optical band gap of phenyl-N-capped aniline oligomers is found [12].

An interesting report in the synthetic roots of aniline oligomers was proposed by Wei and co-workers [13] who synthesized aniline oligomers from three amine segments up to eight units, without using any external oxidizing agent. Aniline trimers (high oxidation state) cause oxidation of ANI monomers.

Synthesis of ANI oligomers in the presence of a catalyst and the acidic reaction medium is also one of the prominent methods of chemical synthesis [14] including oxidative and inverse emulsion

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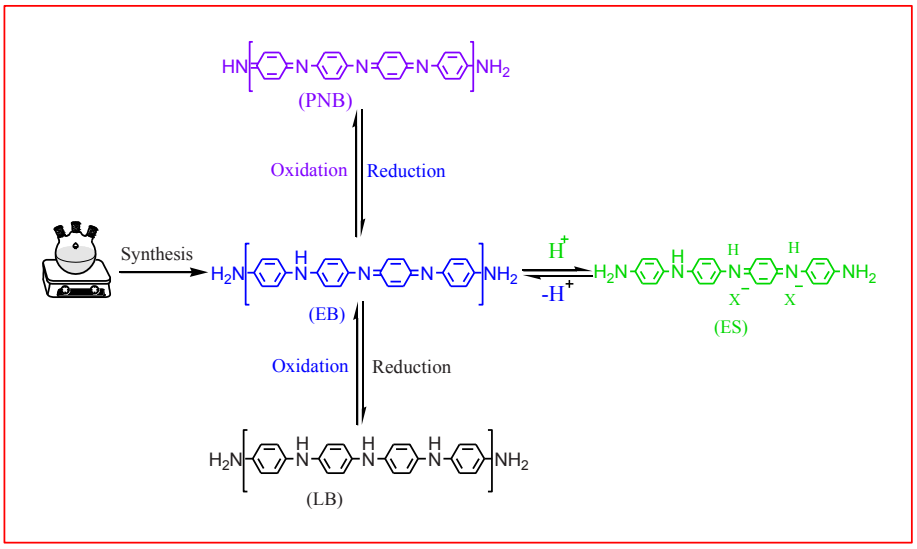

Scheme 1. Synthesis of PANI and its different oxidation states.

polymerization. Oxidative polymerization of ANI oligomers is extensively investigated [15] using ammonium persulfate (APS) as an oxidizing agent in the presence of hydrochloric acid. Different oxidizing agents and supporting electrolytes (medium) are reported for the chemical oxidative polymerization [10,16] such as KIO_3, $FeCl_3$ (oxidizing agent) and HCl, $CHCl_3$ (reaction medium). Chemical synthetic protocol generally involves: (a) rapid mixing [17] in which reaction kinetics are modified in such a way to use all reactants during the initial stage of synthesis; (b) dilute polymerization [18] where the formation of agglomerates is hindered by reducing the concentration of both the oxidant and monomer; (c) interfacial polymerization [19] where the reactants are separated into immiscible aqueous and organic phases, and the polymerization reaction proceeds between the interfaces of two phases; and (d) avoiding mechanical agitation [20] where the reaction is carried out at high temperature, responsible for the growth process and hinders the formation of granular morphology. Besides synthesis, the crystalline arrangement of both PANI and its different oligomers are determined through simply subjecting a mixture of p-amino diphenylamine (ANI dimer) and ANI, followed by fractionation [21].

The conductivity of conducting polymer system is related to molecular size. The electronic cloud is delocalized in the long conjugated system resulting high conductivity; however, increasing the molecular size beyond a certain level may cause distortion of the molecular chain symmetry which adversely leads to the decrease in conductivity. High level of conductivity is obtained with a tetramer of PANI [6,22–25]. Most of the applications of PANI are reported for the tetramer system such as PANI (4LEB) was as cathode material [26]. Similarly, partial oxidation of 4 PANI LB leads to the formation of EB-PANI which on 50% doping show the highest conductivity and has many industrial applications. The molecular size, level of doping, oxidation level and percentage of crystallinity play a significant role to achieve high conductivity which is easily possible with tetramer PANI system [25,27–29].

The relatively weak photo-induced absorption capacity of 4PANI (EB, LEB, and PNB) makes it an appropriate medium for erasable optical information and in non-linear optics [26,30–32].

Udeh et al. [33] have presented various synthetic routes and strategies for the synthesis and modification of tetra (aniline)s oligomers in their review article. A theoretical investigation has been shown to support the experimental data regarding the synthesis of tetra (aniline)s, tri and di-block structures. The usefulness of aniline oligomers and their possible applications in various technological fields have been highlighted.

PANI can be converted from almost insulating leucoemeraldine form (LB) to highly conducting emeraldine salt form (ES) which enables it to be used in digital memory devices [26]. Applications of short and medium size ANI oligomers for the protection of steel corrosion were recently reported by Grgur and co-workers [10,16]. The oligomers were electrochemically coated on mild steel electrode for the study corrosion protection mechanism. They found a slight change in the structure of ANI oligomers during this process of corrosion. The use of para-toluenesulfonic acid (p-TSA) as a soft template and dopant for the synthesis of ANI oligomers have been reported in the literature [34]. APS was used as an oxidizing agent via *in situ* self-assembly method. They reported the effect of p-TSA and ANI molar ratio on the thermal stability and magnetization values of the oligomers. Ding et al. [26] have used, $FeCl_3$, cerium sulfate, and high concentration of $CuCl_2$ to control the diameter of PANI nanofibers. Ozkazanc et al. [35] have used ammonium persulfate as an oxidizing agent in addition to $CuCl_2$ as a dopant. PANI has been synthesized/polymerized in different states extensively in the presence of strong oxidizing agents at favorable condition by various groups as we discussed (*vide supra*) [36–40], However very less is known about the synthesis of PANI oligomers using weak oxidizing agents.

In this paper we report on the oligomerization of phenyl-end-capped oligoaniline (4PANI LB) from ANI under a nitrogen atmosphere, using $CuCl_2$, as a weak oxidizing agent in the presence of p-TSA. The study of these small oligomers is important because these oligomers have different characteristics properties especially from that of infinite chains. Sometimes the bulkiness of a polymer decreases its valuable traits such as conductivity, crystallinity, stability and solubility [41–43] etc. A cost effective chemical method for the synthesis of different oligomers is presented. The experimental data is validated and correlated the data with theoretical findings.

2. Experimental

2.1. Materials

ANI monomer (Analytical grade) was purchased (Sigma-Aldrich) and distilled twice at reduced pressure prior to use. p-TSA