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Synthesis of conductive poly (3-aminobenzoic acid) nanostructures with different shapes in acidic ionic liquids medium

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ABSTRACT

A series of acidic ionic liquid (ILs) based on imidazole and pyridine were synthesized and fully characterized by using FTIR, ^{1}H and ^{13}C NMR techniques. The acidic ILs applied as solvent and dopant for polymerization of 3-aminobenzoic acid (3ABA) by using of ammonium persulfate as an initiator. The synthesized P3ABAs-acidic ILs were characterized by FTIR, XRD, SEM, UV-Visible and TG-DTG analysis. The electrical conductivity of P3ABAs samples was measured by four probe method. The P3ABA-[PyCAA][HSO_4] (0.30 S/cm) exhibited a higher electrical conductivity than that of the P3ABA-[HPy]HSO_4] (0.28 S/cm), P3ABA-[IMBS][Cl] (0.22 S/cm) and bare P3ABA (0.20 S/cm). Based on the SEM micrographs, the acidic ILs changed the morphology of the P3ABA from being completely granular. The XRD patterns of the P3ABAs-acidic ILs samples displayed a more crystalline nature than that of bare P3ABA. The solubility and viscosity of P3ABAs-acidic ILs in polar organic solvents were greater than in bare P3ABA. Moreover, absorption (UV-vis) properties of the synthesized P3ABAs in the presence and absence of acidic ILs were examined. Based on TG-DTG curves, the thermal stability of the P3ABAs-acidic ILs was improved relative to bare P3ABA. The results showed that acidic ILs species form soft templates which assembled 3ABA molecules into specific nanostructures.

1. Introduction

Conducting polymers (CPs) such as polypyrrole, polythiophene, poly (3,4-ethylenedioxythiophene), polyfuran and polyaniline (PANI) have been widely studied to understand advanced technologies in different areas such as biosensors, catalysts, photovoltaic cells and others [1–3]. Among them, PANI and its derivatives have attracted great attention due to easy synthesis, electrical conductivity, cheap, and environmental stability [4]. PANI derivatives have the same chemical structure to PANI with different pendant functional groups at ortho, meta and para positions corresponding to the amine group of PANI. Compared with PANI, PANI derivatives have shown good solubility in common organic solvents but with poor conductivity [5]. PANI and its derivatives synthesized by the oxidation polymerization of the corresponding monomers with ammonium persulfate (APS) in the acidic aqueous medium display the morphology of highly agglomerated spherical particles with wide size distribution [6]. Rivas and coworkers were synthesized poly(2-) and (3-aminobenzoic acids) and their copolymers with aniline by chemical oxidation polymerization in HCl and NaOH medium. They were carried out polymerization in an acid medium in the presence of metal ions, such as Cu(II), Ni(II), and Co(II) [7]. They reported that the electrical conductivity, no important changes with the incorporation of the metal ion. The electrical conductivity values were close to 10^{-8}–10^{-10} Scm^{-1}, which was similar to the base form of the copolymer (10^{-10} Scm^{-1}) [7]. On the other hand, different synthetic methods have been developed in order to obtain PANI and its derivatives with different morphology for instance; Jang et al. introduced PANI nanorods synthesized by using of ferric chloride. They expressed that the experimental parameters such as oxidant, stirring, and temperature could play important role in the synthesis of PANI nanorods [8]. Neelgund et al. studied a facile method for the synthesis of PANI nanospheres by using ammonium persulfate without any protonic acid [9]. Han et al. presented poly(*o*-phenylenediamine) (PoPD) hollow spheres by a simple solution route using APS as the oxidizing agent with changing the oxidizing agent of APS to chloroauric acid ($HAuCl_4$) [10]. Samanta et al. synthesized PoPDA from the *o*-phenylenediamine monomer in various organic solvent medium such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethyl formamide (DMF) and methanol using APS as a radical initiator [11]. Zhang et al. prepared poly(*m*-phenylenediamine) (PmPD) nanospheres and nanorods through chemical oxidation polymerization of *m*-phenylenediamine monomers using APS as an oxidant at room temperature. They suggested that the pH value showed a critical role in controlling the morphology of the nanostructures [12]. Lakouraj et al. introduced poly(*p*-phenylenediamine) (PpPD) nanorods

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through emulsion polymerization using sodium dodecyl sulfate (SDS) as an anionic emulsifier and APS as an oxidant [13].

Ionic liquids (ILs) are organic molten salts composed of organic cations and inorganic or organic anions [14]. ILs have received significant attention in chemical synthesis, polymerization, and catalysis due to unique properties such as extremely low vapor pressure, low melting temperature, non-flammability, and excellent solvating power for organic and inorganic compounds [14]. They are considered as a green alternative to volatile and toxic solvents. ILs play a quite important role in polymer nanostructures synthesis as well [15]. ILs applied as a solvent or additive in chemical oxidative polymerization of aniline (ANI) [6,14,16–18]. According to previous publications, ILs can greatly enhance the physical properties of polymers [14,16–18].

The literatures review showed that no studies on the use of acidic ILs for synthesis of poly (3-aminobenzoic acid) (P3ABA) nanostructure with various shapes have been reported to date. Thus, the aims of this research were: I) to expose the effects of 4-(1-imidazolium) butanesulfonic chloride [IMBS][Cl], pyridinium carboxylic acid sulfate [PyCAA][HSO_4] and pyridinium hydrogen sulfate [HPy][HSO_4] as reaction medium on the morphological characteristics of P3ABA, and II) to characterize the physicochemical properties and electrical conductivity of the various P3ABA products obtained using [IMBS][Cl], [PyCAA][HSO_4] and [HPy][HSO_4] as reaction medium in P3ABA polymerization. The morphology of P3ABAs was investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The chemical structure, thermal stability and electrical conductivity of P3ABAs were studied by spectroscopic methods (FT-IR, and UV-Vis), thermogravimetric analysis (TG/DTG) and four probe technique, respectively. The solubility behavior and inherent viscosity of P3ABAs with and without added ILs were studied.

2. Materials and methods

2.1. Materials

1, 4-butane sultone (purity >99%), imidazole (purity >99%), pyridine, chloroacetic acid, acetone, acetonitrile, methanol, ethanol, chloric acid, sulfuric acid, nitric acid, calcium hydride, *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAC), 1,4-dioxane (DOX), acrylonitrile (ACN), ammonium persulfate (APS) and 3-aminobenzoic acid (3ABA) were purchased from Merck Company.

2.2. Characterization

^{1}H and ^{13}C NMR spectra were taken in DMSO d_6 and D_2O solution using a Bruker Avance DRX-400 spectrometer (Bruker, Ettlingen, Germany). Fourier transform infrared (FT-IR) spectra of the samples were recorded using a Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany). The synthesized samples were dissolved in NMP in order to record the ultraviolet visible (UV-Vis) spectra by the Cecil 5000 UV-Vis (UK) spectrophotometer. Surface morphology and crystallinity of synthesized samples were examined by using scanning electron microscope (SEM) (Hitachi S4160, Tokyo, Japan) and X-ray diffraction (XRD) (Shibuya-ku, Japan) at room temperature on a Riga kuD/Max-2550 powder diffractometer with a scanning rate of 5°/min, respectively. Elemental analysis was carried out on an ECS 4010 CHNSO analyzer (Costech-Italy). Thermal stability of synthesized samples was investigated by thermogravimetric analysis (TG-DTG) (Netzsch, Selb, Germany) from 25 to 600 °C at a heating rate of 10 °C/min under an air atmosphere. Melting point was measured with a Barnstead Electro thermal 9100 apparatus (UK). The inherent viscosity of the synthesized polymers was determined for the solutions of 0.5 g/dL in DMSO at constant temperature of 25 °C by using an Ubbelohde viscometer. The electrical conductivity of the polymers was measured by a standard four-probe method (Azar Electrode, Tabriz, Iran) under laboratory conditions.

2.3. Synthesis of acidic ionic liquids (ILs)

2.3.1. Synthesis of 4-(1-imidazolium) butanesulfonic chloride [IMBS][Cl]

4-(1-imidazolium) butanesulfonate [IMBS] was synthesized according to our *previous* work (Scheme 1(a)) [19]. Imidazole (1.36 g) and 1, 4-butanesultone (0.26 g) were mixed in anhydrous acetonitrile (10 mL) and stirred at 80 °C for 24 h. The resulting white precipitate washed with ethanol and diethyl ether to remove any unreacted starting materials and dried in vacuum oven. Yield: 90% and m.p: 193 °C. For preparation of acidic [IMBS], 0.5 g [IMBS] was dissolved in deionized water under stirring, and then a stoichiometric amount of HCl was added. The solution was slowly heated up to 80 °C and stirred for 4 h. Then, water was evaporated and [IMBS][Cl] was washed repeatedly with diethyl ether to remove nonionic residues and dried in vacuum. The product was formed quantitatively as a hydrophilic light yellow viscous liquid.

^{1}H NMR (DMSO-d_6): δ (ppm) 1.54 (m, 2H), 1.89 (m, 2H), 2.63 (d, 2H), 4.20 (t, 2H), 7.66 (t, 1H), 7.75 (t, 1H), 9.09 (t, 1H), 14.05 (s, 1H). ^{13}CNMR (DMSO-d_6): 22.16, 26.54, 47.97, 48.89, 120.36, 122.50, 135.90 [19].

2.3.2. Synthesis of pyridinium hydrogen sulfate [HPy][HSO_4]

Pyridinium hydrogen sulfate [HPy][HSO_4] was synthesis according to Tao et al. procedure (Scheme 1(b)) [20]. In a typical preparation procedure, pyridine (10 g) was placed in a two-necked flask, immersed in a water bath. H_2SO_4 (12.38 g) solution in water was added slowly over a period of 1 h while stirring and cooling to maintain the temperature at 0–5 °C. The mixture was stirred for 5 h to complete the reaction. Water was removed in vacuum at 95 °C to give the product as a colorless liquid. Yield: 90%. ^{1}H NMR (DMSO-d_6): δ (ppm) 8.12 (d, 2H), 8.64 (t, 1H), 8.93 (d, 2H); ^{13}C NMR (DMSO-d_6): δ 61.27, 128.12, 146.75, 146.65, 167.97 [20].

2.3.3. Synthesis of pyridinium carboxylic acid sulfate [PyCAA][HSO_4]

Pyridine (9.8 g) and chloroacetic acid (3.85 g) were charged in a round bottom flask, and the mixture was allowed to stirring for 24 h at 95 °C. Light brown precipitation was formed, which was then washed with ether, and dried to obtain the solid light brown powder. For obtained acidic ILs, light brown precipitation was solved in acetonitrile and then, a stoichiometric amount (6.19 g) of conc. H_2SO_4 *was added dropwise* to solution and the mixture was stirred at 0 °C for 4 h. The precipitate was obtained with add *excess* of ethyl acetate to above solution. Finally precipitate washed with ethyl acetate/ether to remove the unreacted material and dried under high vacuum at 80 °C for 24 h ((Scheme 1(c)). ^{1}H NMR (DMSO-d_6): δ (ppm) 5.66 (d, 2H), 8.22 (t, 2H), 8.68 (t, 1H), 9.16 (d, 2H); 10.68 (s, 1H), ^{13}C NMR (DMSO-d_6): δ 128.79, 142.98, 148.21. FTIR (KBr): 3450 (OH), 2821 (aliphatic C—H), 1736 (C═O), 1650 and 1560 cm^{-1} (C═C).

2.4. Synthesis of poly(3-aminobenzoic acid) in acidic ionic liquids (P3ABA/acidic ILs)

Poly (3-aminobenzoic acid) (P3ABA) has been synthesized by the chemical oxidation of 3ABA in the presence and absence of different acidic ILs with APS as an oxidant ((Scheme 1(d)). The molar ratios of 3ABA to acidic ILs ([IMBS][Cl], [PyCAA][HSO_4] and [HPy][HSO_4]) in the polymerization medium were 3:1, 1:1, and 1:3. In a typical procedure 3ABA (7 mmol) was dissolved in 50 mL of distilled water on the magnetic stirrer and then 7 mmol of the ionic liquids (([IMBS][Cl], [PyCAA][HSO_4] and/or [HPy][HSO_4]) was added to this solution. Polymerization was started by the addition of 20 mL APS solution (0.32 M) during 30 min under stirrer at room temperature. The reaction mixture was kept under continuous agitation using a magnetic stirrer for 24 h. The red precipitated polymer was collected and washed with deionized water and methanol and dried in a vacuum oven for 24 h at 60 °C (yield 70%).