Materials Chemistry and Physics xxx (2016) 1–10

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Ionic liquid – Assisted emulsion polymerization of aniline in organic medium

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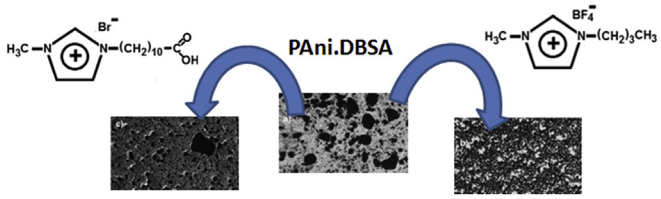
HIGHLIGHTS

- Imidazolium-based ionic liquids as soft templates for polyaniline synthesis.
- PAni with higher conductivity and different morphologies was achieved in the presence of IL.
- Good IL/aniline salt interaction resulted in confinement inside PAni particles.
- IL confinement confirmed by TGA and XPS analyses.
- Excellent dispersability of PAni. DBSA prepared with ionic liquids, in epoxy matrix.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form
4 May 2016
Accepted 9 May 2016
Available online xxx

Keywords:
Composite materials
Polymers
Chemical synthesis
Electrical characterization
Electrical conductivity
Thermogravimetric analysis

ABSTRACT

Polyaniline doped with dodecylbenzene sulfonic acid (PAni.DBSA) with different conductivities and morphologies was prepared by inverted emulsion polymerization, in toluene using ammonium peroxydisulfate as the oxidizing agent, in the presence of two different imidazolium – based ionic liquids, such as, 1-methyl-3-butyl imidazolium tetrafluorate (bmim.BF_4) and 1-(11-carboxyundecyl)-3-methylimidazolium bromide (mimC_{10}COOH.Br). The influence of ionic liquid on the morphology and particle size of formed PAni.DBSA samples was investigated by field emission - scanning electron microscopy (FEG-SEM) and dynamic light scattering (DLS) measurements. Ultraviolet–visible measurements were also employed to confirm the structure of the conducting polymer. PAni.DBSA samples were also characterized by thermogravimetric analysis, cyclic voltammetry and X-ray photoelectron spectroscopy (XPS). PAni.DBSA samples prepared in the presence of ionic liquids have shown improved dispersability in epoxy resin as indicated by optical micrograph.

1. Introduction

Ionic liquids have recently appeared as very promising compounds for applications in several fields of material science due to

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http://dx.doi.org/10.1016/j.matchemphys.2016.05.028
0254-0584/

their unique characteristics provided by their peculiar structure consisted by a bulky organic cation and an organic or inorganic anion [1]. Such structures, which can be easily tuned by changing both cations and anions, are responsible for their melting point, usually lower than 100 °C, and also for their ionic conductivity, low vapor pressure and relatively high thermal stability. Several papers and reviews highlight the success of ionic liquids as solvents for several organic synthesis and polymerization process [2,3], as catalysts for several organic reactions [4] as media for the synthesis of inorganic particles [5,6],, as curing agent for epoxy resin [7–10], as plasticizer for several polymer systems [11] as a medium for electrochemical synthesis [12], etc.

Polyaniline (PAni) has been considered one of the most popular and versatile conducting polymers due to its chemical and environmental stability, high electronic conductivity (which depends on the oxidation state and protonation degree), easy synthesis and low cost [13]. However its low solubility and poor processability limit its applications. Several approaches have been reported in the literature to improve its processability and dispersability in aqueous and organic media. The use of surfactants, also denoted as "soft template", has been considered as an interesting strategy for tuning the PAni morphology and improving its processability [14]. Following similar approach, ionic liquids also play an important role in the morphology [15–17], electrochemical properties [18] and dielectric properties of PAni. In fact, ionic liquids have been successfully employed as a solvent or additive for the electropolymerization [19–22], photo-induced polymerization [23] and chemical oxidative polymerization [15–17,24–26], as well as enzymatic polymerization of aniline [27]. The chemical polymerization of aniline in aqueous medium using 2-hydroxyethyl ammonium formate as the solvent resulted in organo-soluble PAni [24]. The interfacial polymerization of aniline in a water/IL system resulted in Pani nanoparticles with 30–80 nm and conductivity of about 7×10^{-2} S/cm, by using 1-butyl-3-methyl-imidazolium hexafluorophosphate ($bmimPF_6$) and hydrochloride acid (HCl)/ammonium persulphate (APS) as the dopant/oxidant system [15]. Similar approach was employed by Haldorai et al. [26] for the synthesis of poly(aniline-co-*p*-phenylene diamine) assisted by microwave radiation, obtaining nanorod structures. All these examples employ ILs as solvent. Recently, Pahovnik et al. investigated the effect of imidazolium- [16,17], pyridinium [17] and quaternary ammonium- based ILs [17] as additive instead of solvent on the polymerization features of aniline in aqueous medium, using HCl/APS as the protonating/oxidizing system and observed that the type of IL and the aniline/IL molar ratio affect the final PAni morphology, although the conductivity values stayed in the range of 0.15–0.60 S/cm [17].

To the best of our knowledge no study was reported in the available literature concerning the use of IL as additive in the inverted emulsion polymerization of aniline. Therefore, the aim of the present work is to investigate the effect of different imidazolium-based ILs added to the reaction medium on the properties of PAni prepared by inverted emulsion polymerization, using toluene medium containing dodecylbenzene sulfonic acid (DBSA), which acts as protonating agent and also as surfactant. The inverted emulsion polymerization, that is, water in oil emulsion, offers some advantages as it gives rise to stable PAni emulsions containing nanoparticles, by using lower amount of protonic acid as the dopant [28]. Moreover, the process should be adapted to the preparation of polymer blends of polyaniline with organic insulating polymers by the "in situ" polymerization, which is an important process for achieving high conductivities. Finally, the use of ionic liquid as an additive for the polymerization is advantageous from the technological point of view because of the low amount of this component employed in the reaction medium. The structures of the ionic liquids chosen for this study are illustrated in Fig. 1. The morphology was characterized by field emission scanning electron microscopy. The particle size was determined by dynamic light scattering and the specific area was evaluated by BET. The electrochemical properties of the synthesized PAni.DBSA were investigated by cyclic voltammetry. The confinement of ILs in the PAni.DBSA particles was suggested by thermogravimetric and XPS analyses. Also the influence of the ILs on the dispersion characteristics of the resulting PAni.DBSA in epoxy resin was evaluated.

2. Experimental

2.1. Materials

Aniline (Ani) (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck, Darmstadt, Germany), dodecylbenzenesulfonic acid (DBSA), (analytical grade, Aldrich), 11-bromo-undecanoic acid (analytical grade, Aldrich), 1-methyl-imidazole (analytical grade, Aldrich), and 1-methyl-3-butyl imidazolium tetrafluoroborate ($bmim.BF_4$) (analytical grade, Aldrich) were used without purification. Diglycidyl ether of bisphenol A (DGEBA) – based epoxy pre polymer (EPON 828) was purchased by Shell Chemicals do Brasil.

2.2. Synthesis of 1-(11-carboxyundecyl)-3-methylimidazolium bromide ($mimC_{10}COOH.Br$)

1.55 g (0.02 mol) of 1-methyl-imidazole was dissolved in 20 mL of toluene. The system was heated at 120 °C under nitrogen atmosphere and 5 g (0.02 mol) of 11-bromo-undecanoic acid was added. After 24 h of heating under stirring, the formed solid product was filtered, washed three times with hexane and dried under reduced pressure. (yield = 75–80%; mp: 137 °C). The structure of this ionic liquid was confirmed by ^1H NMR spectroscopy (200 MHz) in CD_3CD_2OD. δ(relative to TMS in ppm) = 1.32; (m, 13H), 1.58 (m, 2H), 1.89 (m, 2H), 2.24; 2.26; 2.29 (t, 2H), 3.93 (s, 3H), 4.21 (t, 2H), 7.56; 7.62 (d, 2H), 8.93 (s, 1H).

2.3. Synthesis of PAni.DBSA

The inverted emulsion polymerization of aniline was performed according to the literature [29,30]. In a typical procedure, 3.26 g (0.010 mol) of DBSA and 0.93 g (0.010 mol) of aniline were dissolved in 15 mL of toluene under stirring. Then, 0.005 mol of ionic liquid was added to this solution was stirred in a high shear mechanical mixer (IKA – Turrax T25) at 13500 rpm for 20 min. The resulting mixture was transferred to a flask equipped with mechanical stirring and the 5 mL of an aqueous solution containing 0.010 mol of APS were slowly added. The reaction medium was kept at room temperature for 1 h under stirring and left without stirring for 24 h at room temperature. The formed emulsion was destabilized with methanol, filtered and washed with methanol and water and the solid PAni.DBSA was dried under reduced pressure.

2.4. Characterization

The DC conductivity was determined by the four probe method with a Keithley current source Model 6220 for applying the current and a Keithley electrometer Model 6517A for measuring the potential difference. The samples for the DC conductivity measurements were pressed in a disk-shaped form with 1 mm thickness.

The ultraviolet–visible spectra was obtained from a Varian Cary, Model 100 spectrometer, in the range of 250–900 nm, in a quartz cuvette, according to the literature [31]. Toluene solution of around

Please cite this article in press as: L.F. Calheiros, et al., Ionic liquid – Assisted emulsion polymerization of aniline in organic medium, Materials Chemistry and Physics (2016), http://dx.doi.org/10.1016/j.matchemphys.2016.05.028