



In situ preparation and properties of sulfonic and phosphonic acid substituted polyphosphazene/polyaniline composites



Ferda Hacivelioglu*, Nazmiye Kılıç, Elif Büşra Çelebi, Serkan Yeşilot

Gebze Technical University, Department of Chemistry, Turkey

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ABSTRACT

The first examples of polyaniline/polyphosphazene conducting composites with different ratios of the sulfonic or phosphonic acid functional polyphosphazenes and aniline were prepared in water via chemical oxidation of aniline with ammoniumperoxydisulfate by using in situ polymerization method. The novel conducting composites have been characterized by standard spectroscopic techniques; ^1H and ^{31}P NMR, FT-IR, and UV–vis spectroscopy. SEM and XRPD technics were used to investigate the surface and film properties and conductivity of the resulting polymer composites were investigated by four-point probe. Thermal behaviours and redox properties were also investigated by DSC, TGA and CV measurement.

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1. Introduction

Intrinsically conducting polymer plastics (ICPs) have attracted attention since the discovery of doped polyacetylene (PA) in 1977 [1]. However, PA was not environmentally stable and only a few example; polythiophene (PT), polypyrrole (PPy) and polyaniline (PANI) were stable enough to be incorporated in practical applications [2]. Among the others (PT, PPy) in this series of conducting polymers, PANI has more advantages and attracted attention due to its low cost, good environmental stability [3], adequate level of electrical conductivity [4], and a wide range of commercial and technological applications [5–10]. Moreover, PANI is thermally stable and can be easily synthesized chemically and electrochemically via oxidative polymerization in various organic solvents and/or in aqueous media [11]. However, similar to other π -conjugated polymers, the application range of PANI, is limited due to its insolubility and infusibility [12,13] which may come from its strongly conjugated π -electron system, inter chain hydrogen bonding and charge delocalization effects [14]. There are several methods to improve processability of PANI, covalent substitution such as ring substitution [15–17], N-alkylation [18] and protonation

with functionalized protonic acids such as dodecylbenzene sulfonic acid [19], sulfosalicylic acid [20], camphorsulfonic acid [21], phosphoric acid esters [22,23] or phosphonic acids [24] merit mention [25]. In addition, conducting polymers can be doped with sulfonic or phosphonic acid substituted insulating polymer matrices for preparation of electrically conducting composites while the acid substituted part protonating the PANI backbone and the main chain of the polymer matrix ensure solubility thus processability of the composite [26,27].

The design of materials that bear acid substituted polyaryloxyphosphazenes have attracted attention due to the close proton conductivity to the perfluorosulfonic acid (PFSA) membranes, lower fuel crossover, higher thermal stability and high resistivity against to chemical oxidation [28–30]. Polyphosphazenes are inorganic polymers comprised of a backbone of alternating P and N atoms with two side groups linked to each phosphorus atom. Although the structure of these polymers are written as a sequence of alternating single and double bonds, in fact the bonding is not of the classical $p\pi - p\pi$ type as in classical conjugated polymers. Hence, classical long-range electron delocalization phenomena are not found in polyphosphazenes and they are good insulators rather than semi-conducting or conducting polymers [31]. The most attractive properties of the polyphosphazenes are the stability of the inorganic chain to oxidation, reduction, and photochemical, or thermal bond cleavage, provided appropriate selection of side groups are attached to phosphorus atom [32]. These properties and

* Corresponding author. Gebze Technical University, Department of Chemistry, P.O. Box: 141, 41400, Gebze, Kocaeli, Turkey.

E-mail address: ferda@gtu.edu.tr (F. Hacivelioglu).

the synthetic versatility, ease of preparation via nucleophilic replacement reactions with alkoxides, aryloxides, amines or combination of different organic or organometallic reagents, make polyphosphazenes as attractive alternatives for a wide range of technological applications [33].

There are several examples of sulfonic and phosphonic acid substituted organic polymer PANI composites in the literature to enhance the solvent induced solubility and thus processability of PANI [26,27]. However, sulfonic or phosphonic acid substituted polyaryloxyphosphazenes never examined as dopant for PANI up to date. The reason for this absence is most probably that preparation of fully phosphonic acid substituted polyaryloxyphosphazene was not possible few years ago and low phosphonic acid substituted polyaryloxyphosphazenes was not soluble in water or organic solvents [30]. We recently showed that fully phosphonic acid substituted water soluble polyaryloxyphosphazene can be prepared easily which can be a good candidate as a doping agent for PANI. On the other hand, sulfonic acid substituted polyaryloxyphosphazenes can be prepared via post sulfonation with SO_3 in chlorinated organic solvents [34]. Thus, we achieved 95% sulfonation of polybis(3-methylphenoxy)phosphazene by using fuming sulfuric acid ($\text{H}_2\text{SO}_4:3\text{SO}_3$, or 65% free SO_3) in dichloroethane which was very soluble in water after sulfonation. Therefore, we have thought that it is possible to introduce at least two times higher acid functionality on each repeating unit of polyphosphazene, which means it is possible to decrease the ratio of the insulating polymer matrix while doubling the dopant ratio for conducting part or one of the acid substituted group doping the PANI while the remaining one ensure solubility in the aqueous media. Thus, one can use these two highly acid containing polymers to test the hypothesis, i.e. are these acid bearing insulating polyaryloxyphosphazenes useful matrices to produce conducting, soluble and thus processable PANI composites.

Hence, we prepared three different compositions of PANI/poly[bis(4-phosphonicacid)phenoxy]phosphazene (PPAP) and PANI/poly[bis(3-methylbenzenesulfonicacid-1-oxy)]phosphazene (PSAP) using in situ polymerization via chemical oxidation method where the PANI stoichiometric ratio changing from 0.5 to 1.5 against the constant amount (1eq.) of the insulating polymer. The structural characterization of new composites were determined by standard spectroscopic techniques. Thermal, morphologic, redox and conductivity properties of the composites were investigated and compared to the PANI.

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (trimer) was obtained from Aldrich (98%) purified by vacuum sublimation before the ring opening polymerization and only 60% of the material allowed to be sublimed. The deuterated solvents (CDCl_3 , D_2O and DMSO-d_6) for NMR spectroscopy and the following chemicals were obtained from Merck: NaH (60% suspension in mineral oil), ethanol, HCl (37%), tetrahydrofuran (THF). All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

2.2. Equipment

UV–Vis spectra of PANI, PSAP, PPAP and the composites 1a–c&2a–c were recorded on an Oceanoptics MAYA 2000^{PRO} in the range of 220–1100 nm in 200 ppm water solutions whereas the saturated NMP solution of PANI filtered through a 0.45 μm filter measured in the same range. FT-IR spectra were recorded on a Bruker Alpha-P in ATR in the range of 400–4000 cm^{-1} . ^1H and ^{31}P

NMR spectra were recorded in CDCl_3 , DMSO-D_6 and D_2O solutions on a Varian 500 MHz spectrometer. Thermal properties of the compounds were investigated on Mettler Toledo TGA/SDTA 851 thermogravimetric analyser (TGA) and differential scanning calorimeter DSC 821^e (DSC) equipped with Mettler Toledo Star^e software at a heating rate of 10 $^\circ\text{C min}^{-1}$ under spectroscopic grade argon flow (50 mL min^{-1}) between 25 and 700 $^\circ\text{C}$ for TGA and –40 to 140 $^\circ\text{C}$ for DSC, respectively. Freshly dried polymer samples were used for DSC analysis and the second heating DSC results were used to calculate glass transition temperatures.

The ion exchange capacities (IEC) and thus acid substitution degree of samples were determined by volumetric titration [30]. A known amount of freshly dried sample was immersed and stirred in 30 mL of 0.10 N NaOH/1.0 M NaCl mixed aqueous solution (1/4 by volume) for 12 h at room temperature and 15 mL of 0.10 N HCl solutions was added. Then the excess amount of HCl was back titrated with 0.025 N NaOH aqueous solutions via automatic titrator. The IEC value (mmol/g) of the sample is calculated using the Eq. (1);

$$\text{IEC} = 0.025(V_{\text{NaOH}} - V_{\text{B}})/W_{\text{dry}} \quad (1)$$

where V_{NaOH} is volume of 0.025 N NaOH aqueous solutions for the volumetric titration, V_{B} is volume of the NaOH aqueous solution for blank titration, and W_{dry} is the dry weight of the sample.

Redox properties of composites have been investigated by CV measurements on an Ivium XR^e electrochemical analyser with three electrode electrochemical cell (Pt wire counter electrode, glassy carbon working electrode and Ag/Ag^+ reference electrode) between 0.2 and 1.0 V with a scan rate of 50 mV/s against Ag/Ag^+ (1 M KCl) reference electrode in aqueous media.

The conductivity properties of a 1 cm diameter pressed pellets of composites 1a–c&2a–c and PANI were investigated by standard four point probe in-line method on Keithley 2400 SMU equipped with Jandel cylindrical probe and multiheight stand system at room temperature and the conductivity is calculated from the equation Eq (2);

$$\sigma_{\text{dc}} = 1/(R*4.532*\ell) \quad (2)$$

where σ_{dc} is the DC conductivity, R is the sheet resistance, 4.532 is the correction factor and ℓ is the thickness of the pellet (cm). The given values is an average of ten readings from the centre of four pellets of same composite. The XRPD analysis of the sample is carried out using a fully automated Rigaku Smartlab X-ray diffractometer and recorded in the 2θ range of 2° – 40° using CuK_α radiation ($\lambda = 1.5059 \text{ \AA}$). The SEM images of composites were taken in a Philips XL 30 SFEG operated at 10 kV.

2.3. Synthesis

Poly(dichlorophosphazene) (PDCP) was prepared by ring opening polymerization of hexachlorocyclotriphosphazatriene at 250 $^\circ\text{C}$ in a sealed evacuated tube [33]. Polybis(4-oxy-phenylphosphonic acid)phosphazene (PPAP) and polybis(3-methylbenzenesulfonic acid-1-oxy)phosphazene (PSAP) were prepared according to literature procedures [30] and [34] respectively.

2.3.1. Synthesis of polyaniline

Polyaniline (PANI) was synthesized according to literature procedure with little modifications [35]. Freshly distilled aniline (0.93 g, 10 mmol) was dissolved in 10 ml 0.2 M HCl and this solution was stirred for 15 min in an ice bath. Ammonium persulfate (2.28 g, 10 mmol) was dissolved in 15 ml water and added slowly to the aniline solution at same temperature. The reaction mixture was

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