



# Preparation of PANI coated polymer microspheres and their use as Michael acceptor for direct immobilization of amines and amino acids



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## ABSTRACT

A new and convenient protocol is presented for creating thick Emeraldine Green layers on crosslinked PS–DVB microspheres. This was performed by persulfate oxidation of anilinium salt of sulfonated linear poly (styrene) brushes tethered to the cross-linked poly (styrene–divinyl benzene) (PS–DVB) micro spheres. The carrier polymer was prepared by surface initiated ATRP of styrene from PS–DVB micro beads (210–420  $\mu\text{m}$ ) and followed sulfonation by Vink process. Sulfonic acid groups (4.2 and 4.8  $\text{mmol g}^{-1}$ ) on the surface brushes were then neutralized with aniline. Oxidation of the anilinium salts so formed on the microspheres proceeded solely on the polymer microbeads to give thick PANI layers. The red-brown Pernigriline generated by further oxidation of the PANI layer was demonstrated to act as an efficient Michael acceptor in covalent immobilization of amines, amino acids and polyamines in good to excellent yields (i.e. 1.7  $\text{mmol g}^{-1}$ ) as inferred from FT-IR spectra and wet chemical analyses.

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## 1. Introduction

Polyaniline (PANI) is one of the most important and oldest members of inherently conducting polymers. Its tunable electrical conductivity [1], excellent stability to air oxidation [2], and simplicity of its preparation from cheap materials make it a promising candidate for preparing light-weight batteries [3], electrochromic devices [4], sensors [5], and electro-luminescent devices [6].

Traditional method of aniline polymerization involves oxidation of anilinium salts with the oxidants such as, potassium or ammonium persulfates,  $\text{FeCl}_3$  and  $\text{MnO}_2$  in aqueous solutions [7]. This method yields insoluble PANI, so called “Emeraldine Green” consisting of nearly equal number of benzenoid and quinoid rings connected. A great deal of work has been devoted to enhance solubility and conductivity of PANI [8–11]. Interestingly, polymerization of aniline in the presence of polyacids such as, poly (4-styrene sulfonic acid) [12] and polyacrylic acid [13] has been reported to give doped and soluble PANIs. This can be ascribed to template the effect of the polyacids.

Catalytic air oxidation of aniline without acid has been demonstrated to give high molecular weight and soluble PANI in Emeraldine base form [14]. Recently the Kitani group developed electro-polymerization process yielding microspherical PANI in the presence of DNA as the template [15]. Zhang et al. described preparation of urchin-like PANI microspheres without using a template [16]. Microspherical PANI has been considered as a potential candidate as sensor materials due to its relatively easy modification especially by Michael addition via quinonimine

moieties of its Pernigriline form [17,18]. Having considerable reactivity for Michael addition, fully oxidized form of PANI, pernigriline was considered as good candidate for immobilizing appropriate reagents and catalyst carriers.

Taking these into consideration, in the present work we have studied polymerization of anilinium salt formed on sulfonic acid functional linear poly (styrene) brushes tethered to the cross-linked poly(styrene–divinyl benzene) (PS–DVB) micro spheres.

PANI encapsulated submicron particles have been described as promising materials as electrorheological fluid components [19]. Choi et al. reported direct precipitation of PANI on PMMA microspheres (2–9  $\mu\text{m}$ ) by oxidation of anilinium hydrochloride in aqueous solution [20]. Although PANI surfaces so obtained are rough, dispersions of the microspheres were demonstrated to show electrorheological (ER) fluid behaviors due to polarizability of the surfaces under electrical field. Interestingly electrorheological response was found to be proportional to core size, but not the thickness of the particles. In a similar study Liu et al. described PANI encapsulated polystyrene particles in 1.2  $\mu\text{m}$  sizes [21]. They observed similar electrorheological behavior under 0.3–2.0 kV/mm of electric field. Our PANI coating process described in this work is completely different from those reported so far. First of all, aniline was fixed on the microspheres via salt formation with surfaces bound sulfonic acid groups. Secondly 210–420  $\mu\text{m}$  sizes of PS–DVB microbeads were chosen as starting beads, instead of few micron sizes particles in PANI encapsulations.

In the present work, the base material was prepared starting from (PS–DVB) micro beads (210–420  $\mu\text{m}$ ) in three steps: i) immobilization of bromoacetyl groups, ii) surface initiated ATRP of styrene and iii) sulfonation by sulfuric acid-phosphorous pentoxide mixture.

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The anilinium sulfonate moieties generated on the surface brushes were first oxidized to Emeraldine Green and then to Pernigriline. Michael addition capabilities of the Pernigriline layers were investigated for surface tethering of benzyl mercaptane, triethylene tetramine, glycine and l-alanine. The standard analytical methods, FT-IR and Scanning Electron Microscopy (SEM) techniques were employed for characterization of the materials in each step.

## 2. Experimental

### 2.1. Materials

Aniline (E. Merck), azobis(isobutyronitrile) (AIBN, fluka), styrene (E. Merck) and divinyl benzene (E. Merck) were distilled under vacuum (12–20 mm) before use. Bromoacetyl bromide (E. Merck), mercuric acetate (Aldrich), glacial acetic acid (Aldrich), P<sub>2</sub>O<sub>5</sub> (E. Merck), glycine (E. Merck), l-alanine (E. Merck), benzyl mercaptane (Aldrich), triethylenetetramine (TETA, Aldrich), polyethylene imine (PEI) (25% aqueous solution, Aldrich) and all the other chemicals were used as purchased. The ATRP ligand, H-TETA (1, 1, 4, 7, 10, 10-hexakis [hexyl1, 4, 7, 10- tetraazadecane]) was prepared by reaction of 1-bromohexane with triethylene tetramine as reported before [22].

Cuprous bromide was freshly prepared according to the literature method [23]. PS-DVB microspheres were prepared by copolymerization of styrene with divinyl benzene (with 9/1 M ratio) in aqueous suspension using Gum Arabic as stabilizer, as described before [24]. The bead product was dried, sieved and 210–420 μm size of fraction (the most abundant fraction of the product, 73.4%, upper size fraction was 11.2 and lower fraction was 15.6%) was used as support for surface initiated polymerization of styrene.

### 2.2. Characterizations

FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer. Thermogravimetric Analyses (TGA) were carried out in 50–700 °C temperature range, using Perkin Elmer Pyris 1 in Middle-East Technical University (METU) laboratories, Ankara, The measurements were performed under air atmosphere at a scanning rate of 10 °C/min.

Energy Dispersive X-ray Spectra (EDS) was used to obtain element maps on PANI coated sample surfaces. A JEOL JSM-7600F system was employed for scanning of electrons. These experiments were carried out in Tubitak MAM laboratories.

DC conductivity measurements were carried out using disk-shaped pellets obtained by pressing of 100 mg powder samples with a hydraulic press (ca.10 000 psi). Four-probe technique was employed for measuring resistivity of the samples using 4 channel digitizing oscilloscope from TEKTRONIX TDS 510A. Resistivity values of the yellowish, black and red samples were found to be 148,130.832, 183.744 and 759,587,472 (Ω.mm) respectively.

Optical images of the samples given in Fig. 4 were taken using an ordinary camera with 16 Megapixel resolution.

### 2.3. Incorporation of bromoacetyl groups onto PS-DVB microspheres

Bromoacetyl groups were introduced to PS-DVB microspheres in three steps, i) acetoxy mercuration, ii) chlorine exchange with saturated NaCl solution and iii) followed reaction with bromoacetyl bromide, as described elsewhere [25].

### 2.4. Determination of the bromine content

The bromide content of the resulting microspheres was determined by gravimetric method, in which 0.42 g of the bromoacetylated polymer was mixed with 10 mL methanolic NaOH solution (5 M) in a 50 mL flask and refluxed for 6 h. The mixture was filtered, washed with distilled

water (10 mL) and neutralized with nitric acid. To the filtrate there was added 15 mL AgNO<sub>3</sub> solution (0.1 M). Silver bromide precipitated was filtered and dried in the dark at 60 °C for 4 h. The weight of AgBr (0.064 g) revealed 0.81 mmol bromine per gram of the polymer.

### 2.5. Surface initiated ATRP of styrene from (PS-DVB) microspheres

To a 100-mL three-necked round-bottom flask equipped with a nitrogen inlet and a reflux condenser, there was added 5.0 g bromoacetylated bead sample and 20 mL toluene. Then 40 mL styrene (0.35 mol), 2.53 g (4.05 mmol) H-TETA and 0.58 g CuBr (4.05 mmol) were added to the reaction mixture under nitrogen atmosphere. The reaction was conducted at 90 °C under continuous stirring of the two samples for 6 and 24 h. The reaction mixture was then cooled, diluted with THF and filtered. To remove copper residues the product was transferred into acetic acid THF mixture (2:1) and shaken on a shaker for 1 h. The mixture was filtered, and washed with THF (40 mL), methanol (40 mL) and ether (30 mL). The products were dried overnight at 60 °C under vacuum.

### 2.6. Sulfonation of the PS brushes

The sulfonation procedure reported by Vink [26] was slightly modified for the sulfonation of polystyrene brushes as reported in our previous paper [27]. 70 mL of H<sub>2</sub>SO<sub>4</sub> (96%) was mixed with 7.1 g P<sub>2</sub>O<sub>5</sub> (0.05 mol) and stirred for 30 min and cooled to 0 °C in an ice-bath. Meanwhile 10 g of bead sample with PS surface brushes was swelled in 60 mL CH<sub>2</sub>Cl<sub>2</sub> for 30 min. The acid mixture was slowly added to this mixture at 0 °C and left to stand for 14 h at room temperature. The acid residues were removed by filtration. The sulfonated beads were added portion wise to 500 mL of ice water while stirring vigorously. The product was collected after filtration and being rinsed several times (5 × 250 mL). The product was stored in wet state, as in the case for the commercial ion exchangers.

### 2.7. Determination of the sulfonic acid contents

Acid content of the resin samples were determined by titration method, in which 0.5 g resin sample was added to 10 mL 1.0 M NaOH solution and shaken for 1 h at room temperature. The mixture was filtered and 2.0 mL of the filtrate was titrated with 0.1 M HCl solution using phenolphthalein as a color indicator. The titer consumptions, 13.6 and 15.8 mL revealed sulfonic acid contents of 4.2 and 4.8 mmol g<sup>-1</sup> for high and low grafted samples respectively.

### 2.8. Polymerization of aniline on the sulfonated microsphere

The aniline polymerization on sulfonated resins was carried out by persulfate oxidation as reported before [28]. Thus, sulfonated resin sample (1.7 g dry weight) was placed in 100 mL volume of flask and 5 mL distilled water was added.

The flask was placed in an ice bath and the solution of 5 mL aniline in 15 mL methanol was then added-portion-wise and the mixture was stirred for 30 min before the filtration, and washed with water (50 mL), methanol (20 mL) and ether (10 mL). The product weighed 2.46 g after drying for 1 h at room temperature. The resin material was then transferred into an aqueous K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution (2.65 g 0.98 mol in 50 mL). The mixture was shaken for 2 h at room temperature and the dark green product was filtered, and washed with water (50 mL), methanol (20 mL) and ether (10 mL). The weight of the dried product was almost the same (2.45 g).

### 2.9. Oxidation of PANI layer to pernigriline

To oxidize the PANI layer 2.0 g of Emeraldine Green coated microbead sample was soaked into aqueous solution of KPS (4.5 g in

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