



Conducting polyaniline nanorods doped with aromatic carboxyl chain end functionalized polystyrene[☆]



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ARTICLE INFO

Article history:

Received 2 April 2015

Received in revised form 2 July 2015

Accepted 19 July 2015

Available online 15 August 2015

Keywords:

Polyaniline nanorods and nanosheets

Polymeric dopants

Aromatic carboxyl chain end functionalized polystyrene

Carbon nanorods and nanosheets

ABSTRACT

The preparation of new conducting polyaniline (PANI) derivatives with different nanostructures is described. PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrene derivatives of different number average molecular weights between 18×10^3 and 3×10^3 g/mol were prepared to determine the effect of the structure and number average molecular weights of the aromatic carboxyl chain end functionalized polystyrene dopant on the morphology of the resultant doped polyaniline derivatives. The aromatic carboxyl chain end functionalized polystyrene derivatives of different number average molecular weights were prepared by atom transfer radical polymerization (ATRP) methods using α -bromo-*p*-toluic acid as the aromatic carboxyl functionalized initiator. The chemical oxidative polymerization of aniline with ammonium persulphate as oxidant in the presence of aromatic carboxyl chain end functionalized polystyrenes as the dopants affords PANI derivatives as nanorods and nanosheets. The use of polymeric acids as dopants in the chemical oxidative polymerization of aniline leads to improved morphological control, eliminates dopant volatility, retains the electrical conductivity and promotes the processibility of the final polymeric carboxylic acid doped polyaniline derivatives. Also, the chemical oxidative polymerization of aniline with ammonium persulphate as oxidant in the presence of α -bromo-*p*-toluic acid as the dopant affords doped PANI derivatives as hollow microspheres. Furthermore, heating of the PANI nanorods doped with aromatic carboxyl chain end functionalized polystyrene under nitrogen atmosphere above 800 °C affords carbon nanorods and nanosheets. The aromatic carboxyl chain end functionalized polystyrenes and the different PANI derivatives were characterized by size exclusion chromatography, ¹H NMR and ¹³C NMR spectrometry, FTIR spectroscopy, UV–Vis spectroscopy, non-aqueous titrations, scanning electron microscopy, thermogravimetric analyses, transmission electron microscopy, X-ray diffraction and electrical conductivity measurements.

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1. Introduction

Polyaniline (PANI) is a unique, conducting engineering polymer used extensively in industry because of its high conductivity, excellent environmental stability, low synthesis cost, ease of production and the unique chemical and physical properties controlled by the redox state [1–5]. In general, conducting polyaniline is insoluble in common organic solvents and the poor processibility of PANI limits its applications in thin film devices, batteries and solar cells. Thus, current academic and industrial research is

focused on different methods to increase the processibility of PANI while maintaining well-defined morphology and high electrical conductivity [1–5]. PANI with well-defined micro- and nanomorphology, such as nanofibres, nanotubes and hollow microspheres, has potential applications for use as chemical sensors [6,7], organic optoelectronic displays [8,9], drug delivery systems [10], ionomers in fuel cells [11] and nanodevices in the nanotechnology industry [12–14]. The most efficient method for the preparation of polyaniline involves the chemical oxidative polymerization of aniline using different inorganic compounds as oxidants in the presence of inorganic and organic acids as dopants [15–29]. In addition, the morphology of each PANI derivative is dependent on the nature of the chemical oxidant and the dopant used in the chemical oxidative polymerization process for the preparation of a specific PANI derivative [15–29]. A plethora of PANI derivatives with different micro- and nanostructures are obtained for PANI derivatives

[☆] Poster presentation: World Polymer Congress, IUPAC, MACRO 2012, Virginia Tech, Blacksburg, Virginia, USA, 24–29 June 2012.

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doped with different inorganic acids such as HCl, H₂SO₄, H₃PO₄ and H₂MoO₄, inorganic salts, sulfonated C₆₀ and carboxylated and sulfonated carbon nanotubes [15–29]. Furthermore, PANI derivatives doped with different aliphatic and aromatic sulphonic acids affords conducting PANI derivatives with nanostructures [30–41]. In addition, PANI derivatives doped with simple aliphatic and aromatic carboxylic acids, hydroxyl acids and amino acids affords the preparation of a wide variety of PANI morphological structures ranging from microspheres and microplatelets to nanofibres and nanotubes [42–55]. Moreover, an efficient method for the preparation of a series of polyaniline derivatives with nanofibre, nanotube, nanowire and nanosphere morphology has been developed by the chemical oxidative polymerization of aniline via an emulsion polymerization process in the presence of an organic carboxylic acid as dopant and surfactant [55]. However, the incorporation of small inorganic acids and simple sulphonic and carboxylic acids dopants into the polymer matrix of the conducting PANI derivative results in the loss of dopant from the matrix at high processing temperature which ultimately leads to the loss of electrical conductivity and change in the morphology of the PANI derivative [42–55]. Thus, the use of polymeric acids as dopants in the chemical oxidative polymerization of aniline leads to improved morphological control, eliminates dopant volatility, retains the electrical conductivity and promotes the processibility of the final doped PANI derivative. A series of PANI derivatives doped with polymeric acids have been reported in the literature [56–77]. Polyaniline doped with sulfonated polyanions such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and poly(4-styrenesulfonic acid) has been prepared by the chemical oxidative polymerization of aniline to afford polyanilines composites as nanospheres and nanoplates with excellent electrical conductivity [56–70]. Furthermore, carboxylated functionalized polymers such as polyacrylic acid and poly(methylvinylether-alt-maleic acid) have been employed as polymeric dopants in the chemical oxidative polymerization of aniline to afford well defined conducting doped PANI derivatives with controlled nanomorphology [71–77]. In addition, polymeric dopants with well-defined number average molecular weight and narrow molecular weight distribution significantly improve the processibility and electrical conductivity of polymer acid-doped polyaniline derivatives [58,59]. To our knowledge, the preparation of polyaniline doped with aromatic carboxyl chain end functionalized polymers has not been reported in the literature. The current study focuses on the preparation of new conducting polyaniline derivatives doped with aromatic carboxyl chain end functionalized polymers of different number average molecular weights by the chemical oxidative polymerization of aniline via an emulsion polymerization process. The aromatic carboxyl chain end functionalized polystyrene derivatives of different number average molecular weights were prepared by atom transfer radical polymerization (ATRP) methods using α -bromo-*p*-toluic acid as the aromatic carboxyl functionalized initiator. A series of new conducting PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrene derivatives of different number average molecular weights between 18×10^3 and 3×10^3 g/mol were prepared to determine the effect of the structure and number average molecular weights of the aromatic carboxyl chain end functionalized polystyrene dopant on the morphology of the resultant doped polyaniline derivatives. The chemical oxidation polymerization of aniline using ammonium persulfate as oxidant in the presence of the different aromatic carboxyl chain end functionalized polymers as dopants afforded doped PANI derivatives as nanorods and nanosheets. The use of polymeric acids as dopants in the chemical oxidative polymerization of aniline leads to improved morphological control, eliminates dopant volatility, retains the electrical conductivity and promotes the processibility of the final polymeric carboxylic acid doped polyaniline derivatives. Also, the

chemical oxidative polymerization of aniline with ammonium persulfate as oxidant in the presence of α -bromo-*p*-toluic acid as the dopant affords doped PANI derivatives as hollow microspheres. Furthermore, heating of the PANI nanorods doped with aromatic carboxyl functionalized polystyrene under nitrogen atmosphere above 800 °C affords carbon nanorods and nanosheets.

2. Experimental

2.1. Chemicals and solvents

All chemicals and solvents were purchased from the Sigma-Aldrich Chemical Company, South Africa, unless otherwise stated. α -Bromo-*p*-toluic acid (ABTA), copper (I) bromide (CuBr), 2,2'-bipyridyl (bpy), diphenylether (DPE), tetrahydrofuran (THF), methanol, aniline, ammonium persulfate (APS), benzoic acid (BA), propanoic acid (PA) and hydrochloric acid were used as received. Styrene was purified by stirring over calcium hydride for 24 h, followed by vacuum distillation and drying over molecular sieve before use [78].

2.2. Synthesis of aromatic carboxyl chain end functionalized polystyrene derivatives by ATRP methods: PSCOOH

The synthesis of a series of aromatic carboxyl chain end functionalized polystyrene derivatives of different number average molecular weights was effected by the α -bromo-*p*-toluic acid initiated atom transfer radical polymerization (ATRP) of styrene in solution by varying the initial monomer to initiator ratio in each reaction [78]. In a typical procedure, under dry argon atmosphere, copper (I) bromide (0.0431 g, 0.0003 mol), 2,2'-bipyridyl (0.141 g, 0.0009 mol) and dry diphenylether (1.5 mL) were added to Schenk flask, with stirring. Freshly distilled styrene (0.99 g, 0.9 mL) and α -bromo-*p*-toluic acid (0.065 g, 0.0003 mol) were added successively and the resultant heterogeneous mixture was degassed by three freeze–pump–thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 110 °C for 12 h, with stirring. Upon cooling and addition of THF (5 mL), the blue green solution was purified by passage through a short silica gel column to remove catalyst and ligand impurities. The polymer solution was concentrated in vacuo and precipitated into methanol to afford the functionalized polymer in the carboxylate form. The aromatic carboxyl chain end functionalized polystyrene was isolated by precipitation several times from THF solution into methanol containing 1% aqueous hydrochloric acid, filtered and vacuum dried at 30 °C to afford 0.89 g of aromatic carboxyl chain end functionalized polystyrene, PSCOOH/3000, as a white solid: M_n (SEC) = 3×10^3 g/mol; M_n (titration) = 3.1×10^3 g/mol; M_w/M_n = 1.14. Similarly, aromatic carboxyl chain end functionalized polystyrene derivatives of different number average molecular weights between $M_n = 18 \times 10^3$ and 7×10^3 g/mol were prepared, where PSCOOH/18000, PSCOOH/14000 and PSCOOH/7000 = aromatic carboxyl chain end functionalized polystyrene with $M_n = 18 \times 10^3$, 14×10^3 and 7×10^3 g/mol, respectively. The resultant aromatic carboxyl chain end functionalized polystyrenes were characterized by SEC, NMR, FTIR and non-aqueous titration measurements and is consistent with the data reported in the literature [78].

2.3. Synthesis of conducting polyaniline doped with polymeric and simple carboxylic acids

2.3.1. Polyaniline doped with aromatic carboxyl chain end functionalized polystyrenes: PANI-PSCOOH

The synthesis of polyaniline doped with aromatic carboxyl chain end functionalized polystyrene was effected by the general

procedure outlined by Liu, with modifications [55]. In a typical procedure, the polyaniline derivative (PANI-PSCOOH/3000) doped with the aromatic carboxyl chain end functionalized polystyrene with $M_n = 3 \times 10^3$ g/mol (PSCOOH/3000) was prepared as follows: aniline (1.212 g, 0.013 mol) in cold distilled water (100 mL) in a 250 mL Erlenmeyer flask was cooled in an ice bath. The resultant cold aqueous aniline solution was poured into a 500 mL Erlenmeyer flask containing a cold solution of PSCOOH/3000 (0.1215 g) in distilled water (100 mL) at 0 °C. The mixture was rapidly stirred with a magnetic stirrer bar for 30 min to form an emulsion at 0 °C. An aqueous solution of cold ammonium persulfate (2.9685 g, 0.013 mol) in distilled water (100 mL) was added slowly to the resultant emulsion at 0 °C, with stirring. After complete addition of the ammonium persulfate, the mixture was allowed to stand for additional 12 h, without stirring. The colour of the reaction mixture changed with time from orange to dark brown. After 12 h, the resultant black solution was filtered and washed with distilled water to afford 2.21 g of polyaniline doped with the aromatic carboxyl chain end functionalized polystyrene with $M_n = 3 \times 10^3$ g/mol (PANI-PSCOOH/3000) as a black solid. Similarly, different polyaniline derivatives doped with the aromatic carboxyl chain end functionalized polystyrene with $M_n = 7 \times 10^3$ g/mol (PANI-PSCOOH/7000), $M_n = 14 \times 10^3$ g/mol (PANI-PSCOOH/14000) and $M_n = 18 \times 10^3$ g/mol (PANI-PSCOOH/18000) were prepared by the chemical oxidative polymerization of aniline using ammonium persulfate as oxidant in water at constant [aniline]:[oxidant]=1 and aniline:dopant=10 (w/w) for all polymerization reactions in the presence of the respective polymeric carboxylic acids as dopant.

2.3.2. Polyaniline doped with α -bromo-*p*-toluic acid: PANI-ABTA

The synthesis of doped polyaniline (PANI-ABTA) using α -bromo-*p*-toluic acid (ABTA) as the carboxylic acid dopant was effected according to the procedure outlined by Zhang and Wan [42], with modifications. In the typical procedure, aniline (1.218 g, 0.013 mol) in distilled water (100 mL) in a 250 mL Erlenmeyer flask was cooled in an ice bath. The resultant cold aqueous aniline solution was poured into a 500 mL Erlenmeyer flask containing a cold solution of α -bromo-*p*-toluic acid (1.398 g, 0.0065 mol) in distilled water (100 mL) at 0 °C. The mixture was rapidly stirred with a magnetic stirrer bar for 30 min at 0 °C. An aqueous solution of cold ammonium persulfate (2.9851 g, 0.013 mol) in distilled water (100 mL) was added slowly to the resultant reaction mixture at 0 °C, with stirring. After complete addition of the ammonium persulfate, the mixture was allowed to stand for additional 12 h, without stirring. The colour of the reaction mixture changed with time from orange to dark brown. After 12 h, the resultant black solution was filtered and washed with distilled water to afford 2.21 g of polyaniline doped with α -bromo-*p*-toluic acid (PANI-ABTA) as a black solid.

2.4. Preparation of carbon nanorods and nanosheets

In a typical procedure, under nitrogen atmosphere, a 0.1 g sample of the polyaniline derivative doped with the aromatic carboxyl chain end functionalized polystyrene (PANI-PSCOOH/3000) was heated in a TGA chamber at a rate of 10 °C/min from room temperature to 800 °C. At completion of the heating cycle, the morphology of the resultant black residue was evaluated by transmission electron microscopy.

2.5. Characterization

The characterization of the research products were conducted at the University of South Africa, unless otherwise stated. The number average molecular weights and molecular weight distributions

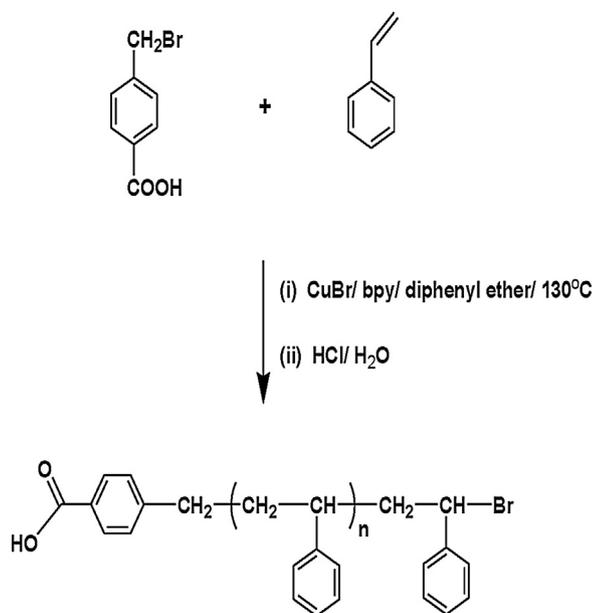
of each polymers was evaluated by size exclusion chromatographic analyses using a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5 μ m, 500 Å pore size, 1–15 K MW range, 300 mm \times 7.8 mm) in series with a refractive index and a Precision dual angle laser light scattering detector. THF was used as eluent at a flow rate of 1 mL/min at 30 °C. The SEC system and the Precision dual angle light scattering detector were calibrated with polystyrene standards ($dn/dc = 0.186$ mL/g) and the chromatograms were analyzed using a Varian Star Discovery 5.5 software package. ^1H NMR (CDCl_3) and ^{13}C NMR (CDCl_3) spectra were recorded on a Varian Gemini 300 spectrometer with CDCl_3 solvent at ambient temperature. Infrared spectra were recorded on a Digilab FTS-7000 FTIR spectrometer equipped with infra-red hyperspectral imaging capabilities or a Bruker Platinum ATR Vertex 70 FTIR spectrometer in the range from 4000 to 400 cm^{-1} . UV–Visible spectra of the different doped PANI derivatives in DMF were recorded with a CECIL CE 9500 UV–Visible spectrometer. Samples of 0.1 g of the doped PANI derivative in DMF (10 mL) were prepared for UV–Vis spectroscopic analyses. The concentrations of the aromatic carboxyl chain ends of the polystyrene samples were determined by non-aqueous titrations with sodium hydroxide as a base. A 0.1 g sample of a specific polymer derivative was dispersed in toluene and titrated with standardized methanolic sodium hydroxide using phenolphthalein as indicator [78]. Thin layer chromatographic analyses were performed on silica gel plates (Merck, Silica Gel 60F, 254). The characterization of the research samples was conducted with the following instrumentation at the Council for Scientific and Industrial Research (CSIR) in Pretoria, South Africa: (a) the morphology of each doped PANI derivative in the powder form was observed using the Scanning Electron Microscope 7500F instrument; (b) the structure of the carbon nanorods was confirmed by transmission electron microscopy using a Thermo Scientific JEM-2100 HR-TEM instrument fitted with a tungsten element and operating at an accelerator voltage of 200 000 kV. Sample preparation for TEM analyses involves the sonication of the black sample in ethanol for 3 min. The drop of the resultant sample was placed onto a copper grid which was coated with carbon prior to TEM analyses; (c) the thermal analysis data for each doped PANI derivative in the powder form was analyzed using TA Instruments TGA Q500 instrument. The samples were analyzed at a heating rate of 10 °C/min from room temperature to 800 °C; (d) powder XRD patterns of the different doped PANI derivatives were recorded on a Panalytical Expert Pro Instrument; and (e) the electrical conductivity of compressed pellets (diameter = 8 mm, thickness = 0.2 mm) of different doped PANI derivatives were measured by a standard four point probe method at room temperature using a Keithley 42000 semiconductor characterization system.

3. Results and discussion

3.1. Synthesis of aromatic carboxyl chain end functionalized polystyrenes: PSCOOH

The general synthesis pathway for the α -bromo-*p*-toluic acid initiated atom transfer radical polymerization (ATRP) of styrene in the presence of copper (I) bromide as the catalyst and 2,2'-bipyridyl as the ligand in diethyl ether at 130 °C was effected according to Summers et al. [78] and is outlined in Scheme 1.

The polymerization proceeded via a controlled free radical process to afford quantitative yields of the corresponding aromatic carboxyl chain end functionalized polystyrene derivatives with predictable number average molecular weights ($M_n = 18 \times 10^3$ and 3×10^3 g/mol) and narrow molecular weight distributions ($M_w/M_n = 1.14$ – 1.32). α -Bromo-*p*-toluic acid was employed as the



Scheme 1. Synthesis pathway for the preparation of aromatic carboxyl chain end functionalized polystyrenes.

Table 1
Characterization of the aromatic carboxyl chain end functionalized polystyrenes^a

Polymer	$M_{n,th}^b$	$M_{n,SEC}^b$	$M_{n,titration}^b$	M_w/M_n
PSCOOH/18000	18000	18×10^3	18.32×10^3	1.31
PSCOOH/14000	14000	14×10^3	14.24×10^3	1.32
PSCOOH/7000	7000	7×10^3	7.12×10^3	1.16
PSCOOH/3000	3000	3×10^3	3.1×10^3	1.14

^a α -Bromo-p-toluic acid initiated atom transfer radical polymerization (ATRP) of styrene in the presence of copper (I) bromide/2,2'-bipyridyl at the initial molar ratio of [CuBr]₀:[α -bromo-p-toluic acid]₀:[2,2'-bipyridyl]₀ = 1:1:3. The results of the quantitative formation of aromatic carboxyl chain end functionalized polystyrenes in solution are outlined in Table 1.

^b Number average molecular weight in g/mol.

aromatic carboxyl functionalized initiator in the ATRP of styrene in solution in the presence of copper (I) bromide/2,2'-bipyridyl at the initial molar ratio of [CuBr]₀:[α -bromo-p-toluic acid]₀:[2,2'-bipyridyl]₀ = 1:1:3. The results of the quantitative formation of aromatic carboxyl chain end functionalized polystyrenes in solution are outlined in Table 1.

For example, the size exclusion chromatogram of aromatic carboxyl chain end functionalized polystyrene derivative PSCOOH/3000 shows a monomodal molecular weight distribution (Fig. 1) with $M_n = 3 \times 10^3$ g/mol and $M_w/M_n = 1.14$.

The ¹H NMR spectrum of PSCOOH/3000 show a multiplet at $\delta = 6.8$ –7.8 ppm, due to the resonances of the aromatic protons of the benzene rings of the polystyrene backbone and the characteristic peaks between 2.4 and 4.1 ppm, due to resonances of the protons of the CH₂ and CH groups of the polymer backbone [78]. The ¹³C NMR spectrum of PSCOOH/3000 shows a resonance at 172.3 ppm, which indicates the incorporation of the aromatic carboxyl group into the polymer chain [78]. The FTIR spectrum of PSCOOH/3000 exhibits a strong absorption band at 1689.19 cm⁻¹, due to the presence of carbonyl group and is consistent with the incorporation of aromatic carboxyl functional group at the polymer chain end [78]. In addition, the $M_n = 3.1 \times 10^3$ g/mol value, obtained from non-aqueous titration measurements of PSCOOH/3000 with standardized potassium hydroxide, is in good agreement with the theoretical M_n and SEC measurements, indicating the quantitative incorporation of the carboxylic acid group into the polymer chain end.

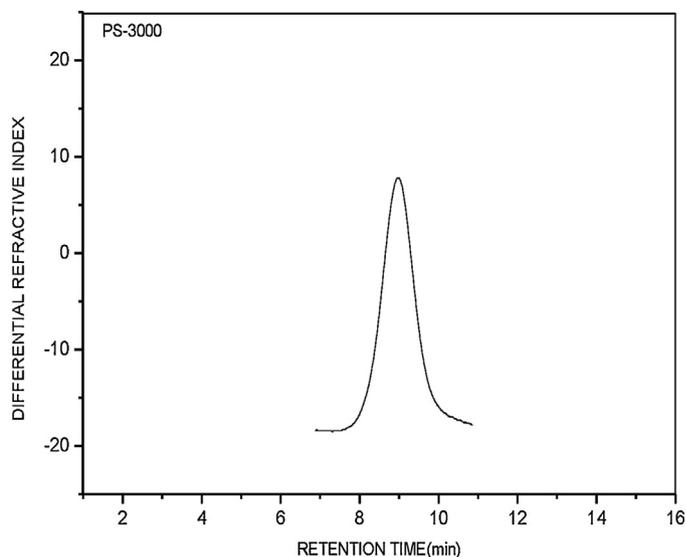


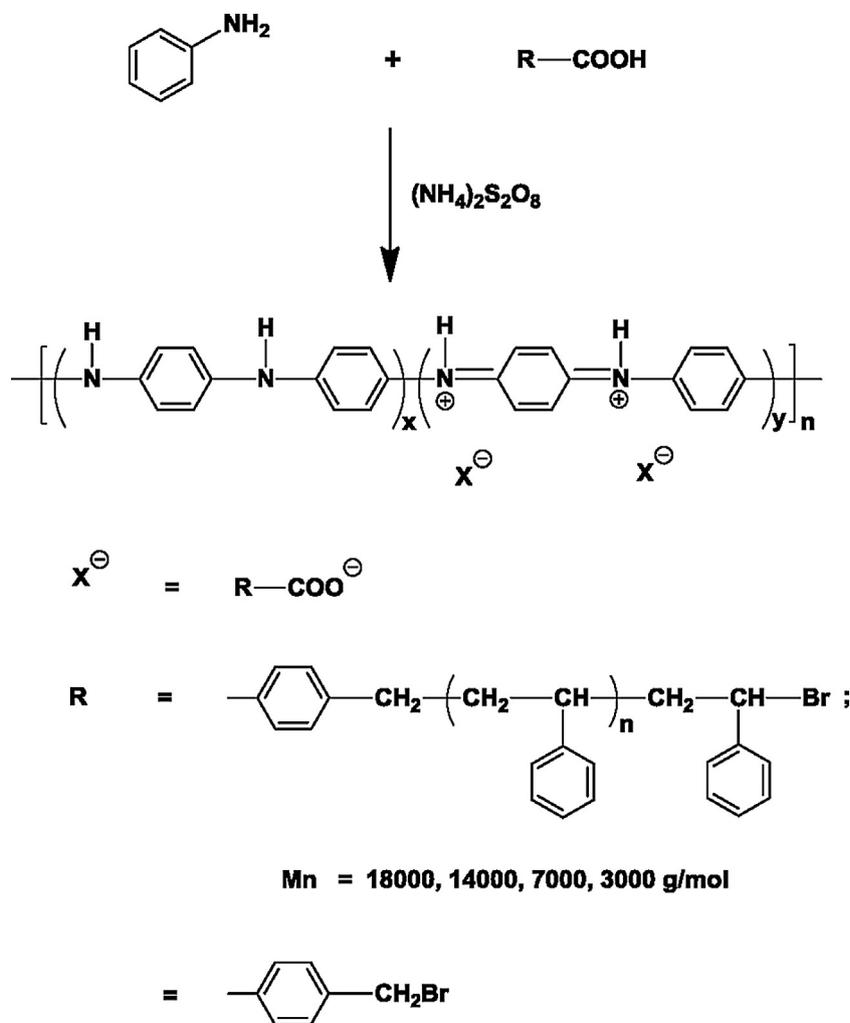
Fig. 1. Size exclusion chromatogram of aromatic carboxyl chain end functionalized polystyrene, PSCOOH, $M_n = 3 \times 10^3$ g/mol; $M_w/M_n = 1.14$.

3.2. The synthesis of polyaniline doped with aromatic carboxyl chain end functionalized polystyrenes: PANI-PSCOOH

In the current study, a series of polyanilines doped with aromatic carboxyl chain end functionalized polystyrenes of different number average molecular weights (PANI/PSCOOH) were prepared by the chemical oxidative polymerization of aniline in the presence of ammonium persulfate as oxidant, as outlined in Scheme 2.

For the preparation of the different PANI/PSCOOH derivatives, the molar ratio of [aniline]:[oxidant] = 1 and the aniline:polymeric carboxylic acid dopant ratio = 10 (w/w) were employed for chemical oxidative polymerization of aniline in the presence of the different polymeric dopants. In each reaction, the resultant polymer sample, which precipitated from water, was filtered and vacuum dried at 60 °C to afford the specific PANI/PSCOOH derivative as a black powder. The preparation of the different PANI/PSCOOH derivatives proceeded via an emulsion polymerization process where the polymeric acids were used as the surfactant in the emulsion polymerization process as well as the dopant of the resultant conducting polymer. The aromatic carboxylic chain end functionalized polystyrenes display dopant–surfactant characteristics because of the hydrophilic carboxylic group and the hydrophobic polymer backbone, thus the formation of micelles in aqueous solution. In addition, the aromatic carboxylic functionalized polystyrenes are carboxylic acids which reacts with aniline to form the aniline/dopant salt in the reaction mixture. Due to the excess of aniline in the reaction mixture, the dopant/aniline salt, the dopant micelles and the free aniline coexist during the polymerization process.

To evaluate the effect of the structure of the dopant on the chemical oxidative polymerization of aniline, the characterization data of representative samples, polyaniline doped with aromatic carboxyl chain end functionalized polystyrene with $M_n = 18 \times 10^3$ g/mol (PANI-PSCOOH/18000) and $M_n = 3 \times 10^3$ g/mol (PANI-PSCOOH/3000) are discussed in detail and compared with the other doped polyaniline samples, where applicable. The morphology of each doped PANI derivative (PANI-PSCOOH) was evaluated by scanning electron microscopy. Results show that the structure and number average molecular weight of the aromatic carboxyl chain end functionalized polystyrene used as the dopant in the chemical oxidative polymerization of aniline affects the morphology of the resultant PANI sample [58,59]. The SEM images of the



Scheme 2. Synthesis pathway for the preparation of PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrenes by the chemical oxidative polymerization of aniline.

PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrenes of different number average molecular weights (PSCOOH) are shown in Fig. 2.

The PANI-PSCOOH derivatives doped with PSCOOH of different M_n values are observed as nanorods with the average nanorod width between 83 and 118 nm and the length of the nanorods ranging from 400 to 1000 nm. In addition, the PANI nanorods undergo a self-assembly process to form PANI nanoplates or nanosheets. Thus, the size or number average molecular weight of aromatic carboxyl chain end functionalized polystyrene dopants employed in the synthesis of polyaniline by chemical oxidative polymerization methods affects the size and shape of the resultant doped PANI nanorods. The size and shape of the doped PANI nanorods, PANI/PSCOOH increases with increase in the M_n of the PSCOOH derivative. The PANI-PSCOOH/18000 sample is observed as long and thin nanorods (Fig. 2a), with an average nanorod length of 500 nm, whereas the PANI-PSCOOH/3000 derivative is observed as shorter and thicker nanorods (Fig. 2d). Fig. 3 shows the UV-Visible spectra of the different PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrenes with $M_n = 18 \times 10^3$, 14×10^3 , 7×10^3 and 3×10^3 g/mol.

The UV-Vis spectra of the different doped PANI derivatives displays three distinct absorption bands located between 290 and 800 nm. For example, the UV-Vis spectrum of the PANI-PSCOOH/3000 sample shows a strong absorption band at 375 nm which is attributed to the π - π^* transitions within the phenyl rings

of the polyaniline backbone [44,74,75]. The observed weak absorption band at 572 nm, due to the exciton transition from a higher energy occupied benzenoid moiety to a lower energy unoccupied quinoid moiety along the PANI backbone, indicates incomplete or low degree of doping [44,74,75]. Furthermore, the band at 293 nm is due to the excitation of nitrogen in the benzenoid segments of PANI doped with polymeric acids, which indicates the extent of the doping effect of the carboxylic acids [44,74,75]. The FTIR spectrum (Fig. 4) of PANI-PSCOOH/3000, whereby PANI is doped with aromatic carboxyl chain end functionalized polystyrene with $M_n = 3 \times 10^3$ g/mol shows the characteristic bands of the emeraldine salt form of PANI.

The strong broad absorption band at 3225 cm^{-1} is assigned to the N-H stretching vibrations of the hydrogen bonded N-H groups of the PANI backbone [42–44,79]. The absorption band at 1568 cm^{-1} is assigned to the characteristic stretching vibrations of the C=C groups of the quinoid rings, whereas the absorption band at 1495 cm^{-1} corresponds to the C=C stretching modes of the benzenoid rings along the PANI backbone [42–44,79]. The absorption bands at 1289 and 1149 cm^{-1} are assigned to the C-N and C=N stretching vibrations of the aromatic amine groups of the PANI derivative [42–44,79]. The absorption bands at 970 and 858 cm^{-1} are attributed to the aromatic C-H in-plane and out-of-plane bending vibrations for the 1,4 disubstituted phenyl rings [42–44,79]. In addition to the characteristic PANI bands, the weak absorption band at 1610 cm^{-1} is attributed to the stretching vibration

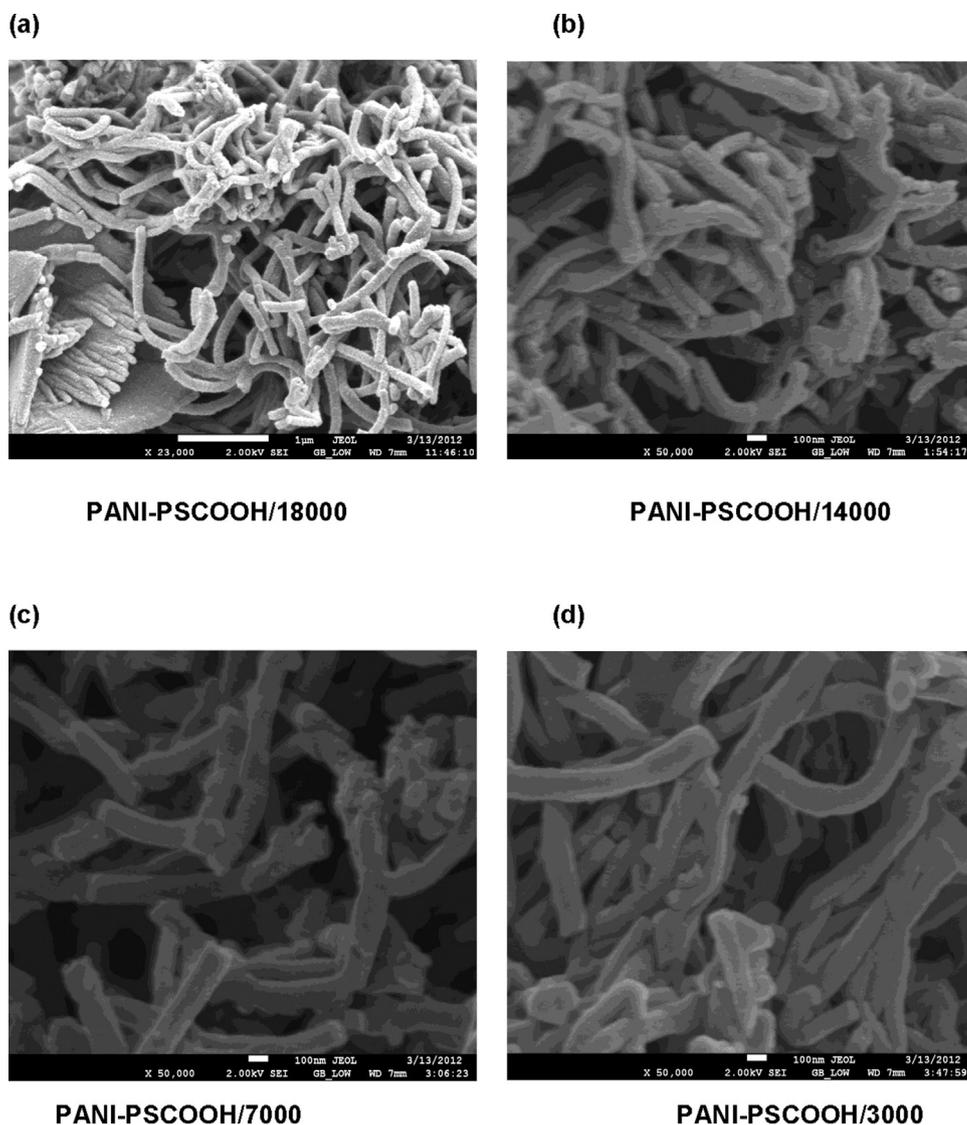


Fig. 2. SEM images of the PANI nanorods doped with aromatic carboxyl chain end functionalized polystyrenes with different number average molecular weights: (a) PANI-PSCOOH/18000, $M_n = 18 \times 10^3$ g/mol; (b) PANI-PSCOOH/14000, $M_n = 14 \times 10^3$ g/mol; (c) PANI-PSCOOH/7000, $M_n = 7 \times 10^3$ g/mol; (d) PANI-PSCOOH/3000, $M_n = 3 \times 10^3$ g/mol.

modes of the C=O group of the carboxylate group of the polymeric dopant and indicates the incomplete doping or low degree of dopant in the final product and confirms that the aromatic carboxyl functionalized polystyrene is incorporated within the PANI nanorods [80]. The thermal stability of each polyaniline sample was determined by TGA analysis. For example, the TGA curves of the different PANI doped with aromatic carboxylic chain end functionalized polystyrene derivatives with M_n between 18×10^3 g/mol (PANI-PSCOOH/18000) is shown in Fig. 5.

The TGA curve of PANI-PSCOOH/18000 nanorods depicts a characteristic three step degradation pattern or a three step weight loss process: (a) a weight loss of 5% below 100°C , due to the loss of residual moisture or solvent from the sample, followed by (b) a gradual weight loss of 30% at $168\text{--}400^\circ\text{C}$, due to the de-doping and decomposition of the polymeric dopant at the onset temperature of 168°C and (c) the weight loss of 15% at $410\text{--}700^\circ\text{C}$, due to decomposition of PANI chain [58,59]. In addition, as the size of the polymer dopant increases, the nanorod decomposition temperature slightly increases [58,59]. Fig. 6 shows the X-ray scattering patterns of the different PANI nanorods doped with

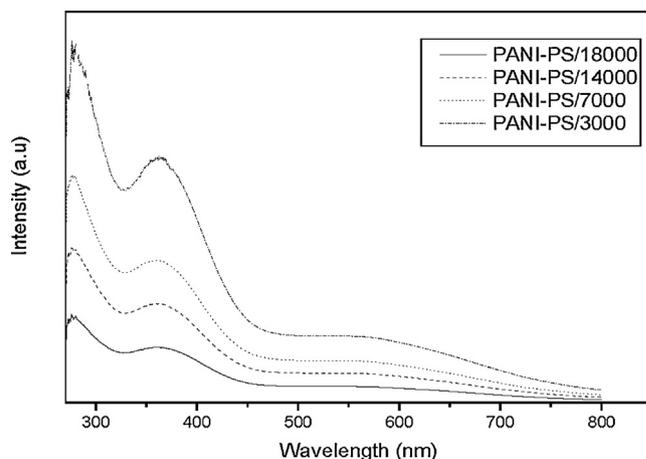


Fig. 3. UV-Vis spectra of the PANI nanorods doped with aromatic carboxyl chain end functionalized polystyrene of different number average molecular weights.

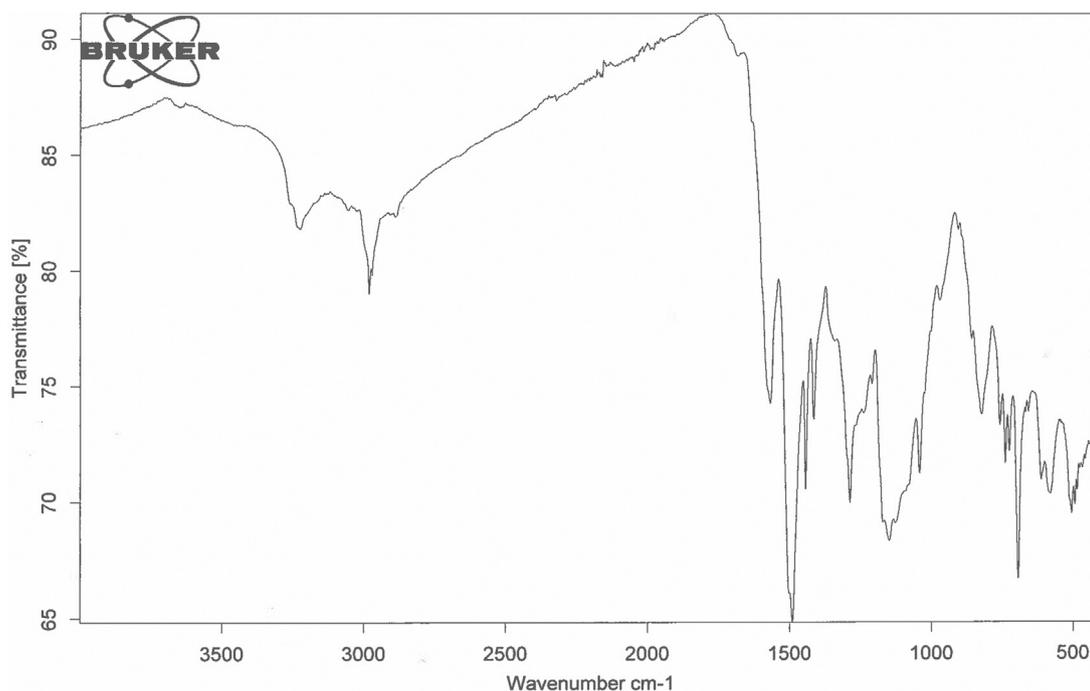


Fig. 4. The FTIR spectrum of the PANI nanorod doped with aromatic carboxyl chain end functionalized polystyrene with $M_n = 3 \times 10^3$ g/mol.

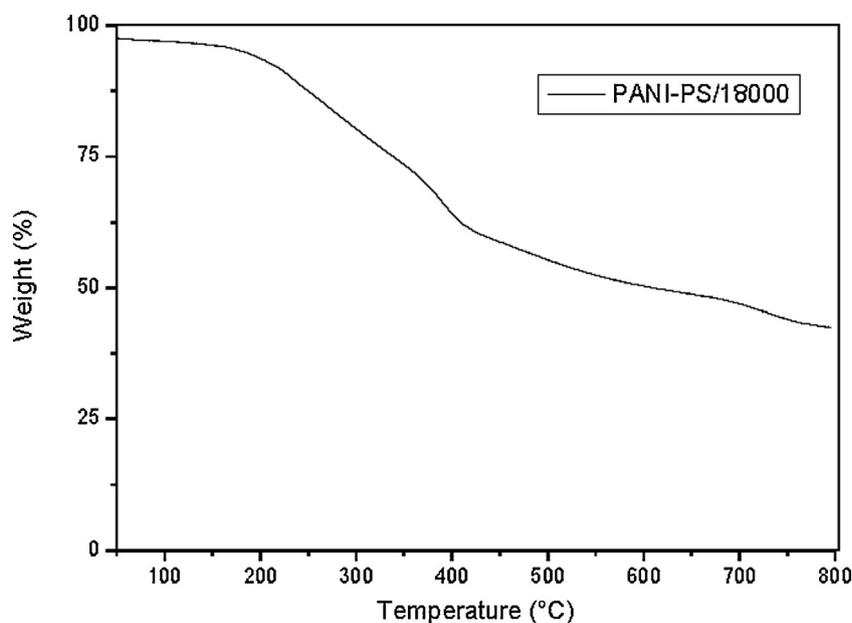


Fig. 5. TGA curve of PANI nanorods doped with aromatic carboxyl chain end functionalized polystyrene of number average molecular weights of $M_n = 18 \times 10^3$ g/mol (PANI-PSCOOH/18000).

aromatic carboxyl chain end functionalized polystyrenes with different number average molecular weights.

The X-ray scattering pattern of the PANI-PSCOOH/18000 nanorod shows that the sample is crystalline in character. The sharp peak at $2\theta = 6.47^\circ$ corresponds to the periodicity distance between dopant and the N atom on the backbone of the adjacent polyaniline chain. The intensity of the peak at $2\theta = 6.47^\circ$ increases with decreasing molecular weight of the polymeric dopant, indicating an increase in the level of crystallinity of the PANI nanorod with decreasing number average molecular weight of the amorphous aromatic carboxyl chain end functionalized polystyrene dopant [58,59]. The broad peaks between

$2\theta = 18\text{--}28^\circ$ are attributed to the orientation of the repeat unit of the polyaniline chain and the periodicity parallel and perpendicular to the polyaniline backbone, respectively. The half width of the peak at $2\theta = 26^\circ$, which is assigned as periodicity perpendicular to the polyaniline chain, increases with decreasing M_n of the aromatic carboxyl chain end functionalized polystyrene dopant, with the highest M_n reducing the orientation of the periodicity perpendicular to the polymer chain. The room temperature electrical conductivity data for a series of PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrene of different number average molecular weights is depicted in Table 2.

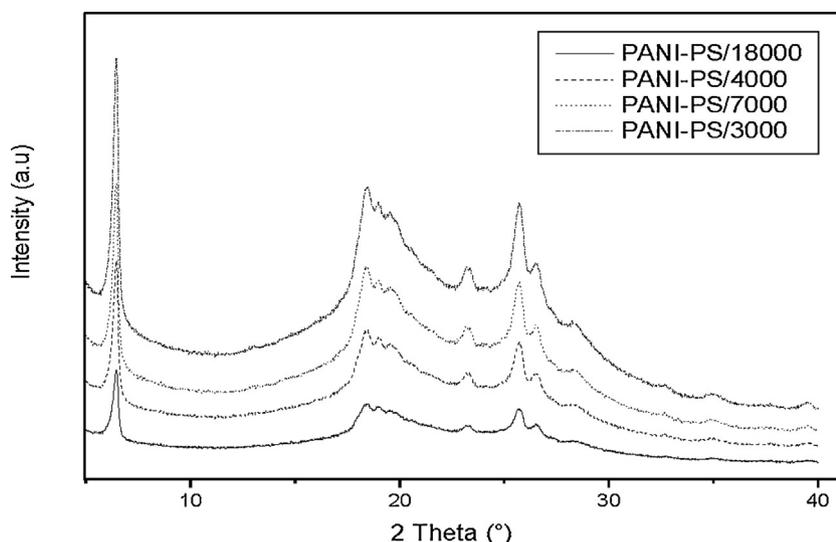


Fig. 6. X-ray diffraction patterns of the PANI nanorods doped with aromatic carboxyl chain end functionalized polystyrenes with different number average molecular weights.

Table 2

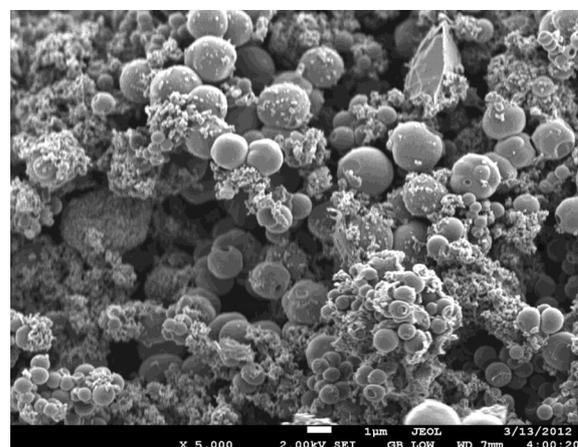
Room temperature electrical conductivity data for different PANI-PSCOOH derivatives.

Polymer	Conductivity ($\text{s/cm} \times 10^{-4}$)
PANI-PSCOOH/18000	5.50
PANI-PSCOOH/14000	4.81
PANI-PSCOOH/7000	2.77
PANI-PSCOOH/3000	2.64

The electrical conductivity at room temperature mainly depends on the morphology, the degree of crystallinity and the degree of doping of the specific doped PANI derivative, whereas the formation of the different morphological structures of the different PANI derivatives is influenced by the structure of the dopant [42,43]. In general, doped PANI derivatives with nanotube and nanofibre morphology usually exhibit higher electrical conductivity than doped PANI derivatives with microsphere morphology [42,43]. Results show that the extent of the room temperature electrical conductivity of the different PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrenes (PANI-PSCOOH) is affected by the morphology and the crystallinity of the resultant PANI derivative. For the different doped PANI/PSCOOH samples, the room temperature electrical conductivity of the PANI nanorods vary between 5.5×10^{-4} and $2.64 \times 10^{-4} \text{ S cm}^{-1}$, which indicates a low degree of doping within the doped PANI nanorods. The conductivity of the different doped PANI/PSCOOH nanorods depends on the dimensions of the specific nanorod as well as the crystallinity of the specific doped PANI sample. The highest electrical conductivity reading of $5.5 \times 10^{-4} \text{ S cm}^{-1}$ is obtained for the PANI-PSCOOH/18000 sample due to the long and thin nanorod morphology as well as the increased crystallinity of the sample [58,59].

3.3. The synthesis of PANI doped α -bromo-*p*-toluic acid: PANI-ABTA

The PANI derivative doped with α -bromo-*p*-toluic acid (PANI-ABTA) was prepared by the chemical oxidative polymerization of aniline using ammonium persulphate as oxidant in water with [aniline]:[oxidant] = 1 and [aniline]:[dopant] = 2. The resultant polymer sample, which precipitated from water, was filtered and vacuum dried at 60°C to afford PANI-ABTA as a black powder. When α -bromo-*p*-toluic acid was used as the dopant, the morphology of



PANI-ABTA

Fig. 7. SEM image of the PANI hollow microsphere doped with α -bromo-*p*-toluic acid (PANI-ABTA).

the resultant PANI-ABTA derivative is observed as hollow microspheres of different diameters as illustrated in Fig. 7, which is different to the morphology of similarly doped polyaniline derivatives, polyaniline-benzoic acid, where the morphology of the latter is observed as nanotubes [42,43].

In addition, the PANI-ABTA sample shows distinct different morphology to the PANI/PSCOOH samples, where the only difference between the aromatic carboxyl chain end functionalized polymer and α -bromo-*p*-toluic acid is the size of the polystyryl chain. The different morphology of each doped PANI derivative is illustrated in the distinctly different TGA degradation pattern observed for the PANI-ABTA sample with hollow microsphere morphology in relation to the PANI/PSCOOH nanorod samples as outlined in Fig. 8.

The degradation pattern for the PANI-ABTA sample with hollow microspheres of different diameters involves a three step weight loss process; (a) a weight loss of 4% below 100°C , due to the loss of residual moisture or solvent from the sample, followed by (b) a rapid and distinct weight loss of 32% between 120 and 167°C , due to the de-doping and decomposition of the simple carboxylic acid dopant and (c) the weight loss of 27% at 175 and 700°C , due to decomposition of the polyaniline chain [42–44]. Results show that the structure of the carboxylic acid dopant affects the

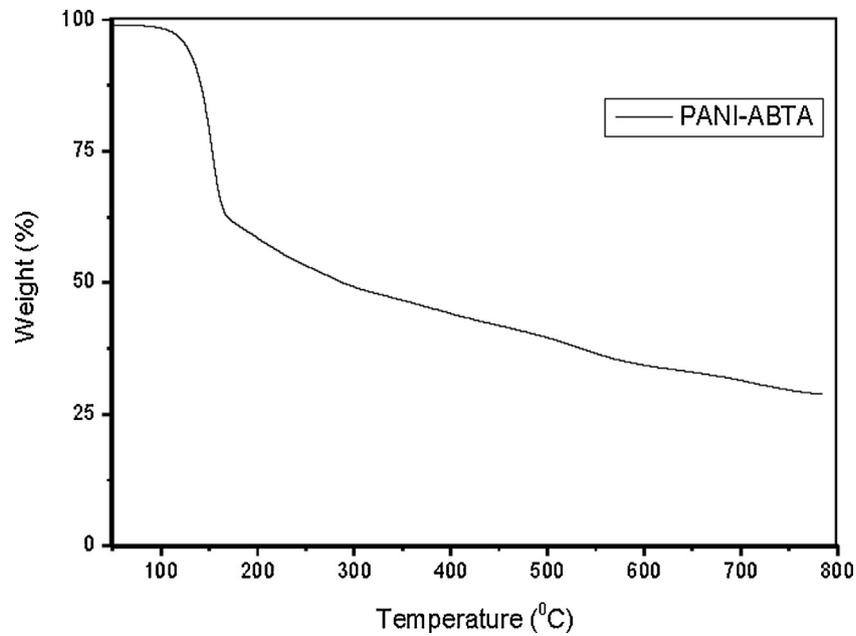


Fig. 8. TGA curve of PANI doped with α -bromo-p-toluic acid (PANI-ABTA).

morphology of the doped PANI derivative and consequently the thermal stability of the doped PANI derivative. The PANI derivative doped with α -bromo-p-toluic acid is thermally less stable than the corresponding nanotubes of PANI doped with benzoic acid and propanoic acid, where the decomposition onset temperature of

each dopant is observed at 228 and 336°C, respectively [42,43]. Furthermore, the XRD plot of the PANI-ABTA microspheres shows distinct sharp peaks at $2\theta=6^\circ$, 13° and 17.5° , indicating high degree of crystallinity for the PANI-ABTA sample with hollow microsphere morphology. In addition, for the doped

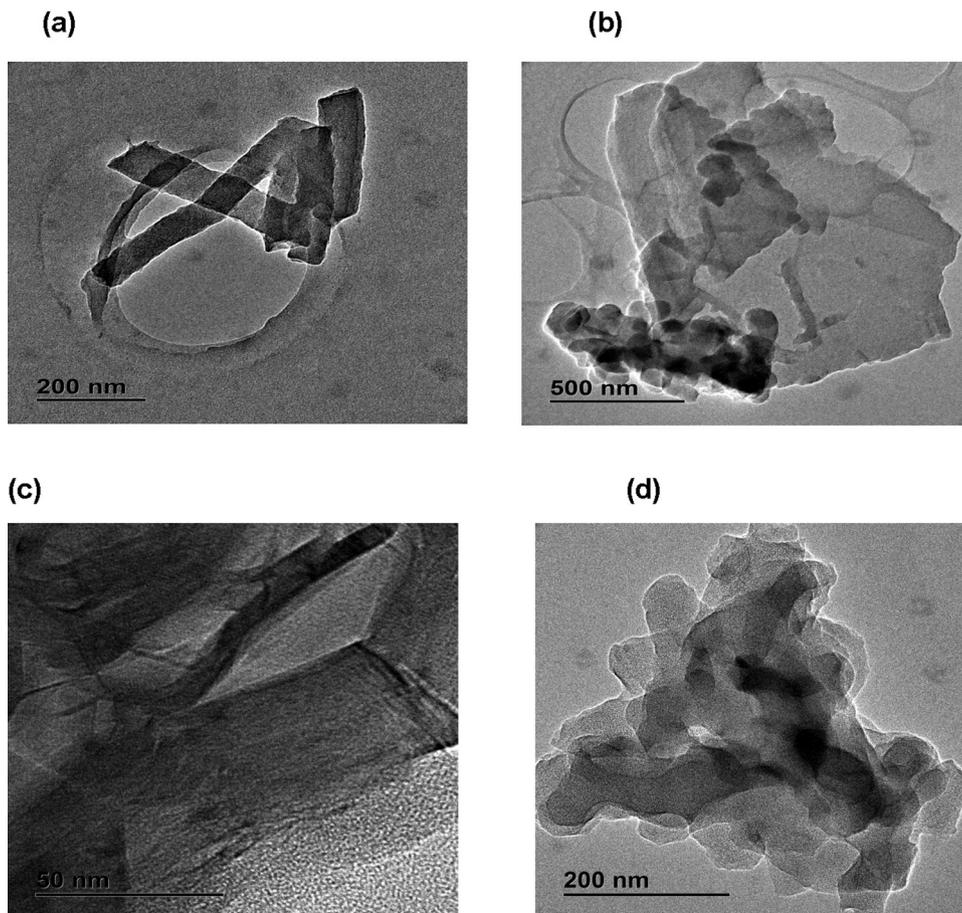


Fig. 9. Representative TEM images of carbon nanorods and nanosheets obtained by the thermal decomposition of the different doped polyaniline derivatives.

PANI derivatives with hollow microsphere morphology (PANI-ABTA), a room temperature electrical conductivity value of $1.65 \times 10^{-4} \text{ S cm}^{-1}$ was obtained [42,43], which is significantly lower than the values of the different doped PANI/PSCOOH derivatives with nanorod and nanosheet morphology.

3.4. Preparation of carbon nanorods and carbon nanosheets

In a typical procedure, a sample of the polyaniline derivative doped with aromatic carboxyl functionalized polystyrene (PANI-PSCOOH/3000) was heated to 800°C under nitrogen atmosphere. At completion of the heating cycle, the morphology of the resultant black residue was evaluated by TEM analyses to confirm the formation of carbon nanorods by the thermal decomposition of polyaniline nanorods. Fig. 9 shows representative TEM images of carbon nanorods and nanosheets obtained by the thermal decomposition of the different doped polyaniline derivatives.

The TEM image of the residue, obtained after thermal decomposition of polyaniline doped with aromatic carboxyl functionalized polystyrene (PANI-PSCOOH/3000), shows the formation of carbon nanorods (Fig. 9a). The sizes of the carbon nanorods obtained from the thermal decomposition of the PANI-PSCOOH/3000 nanorod varies from 260 to 315 nm in length, 80 to 85 nm in width and 204 nm in thickness. Furthermore, the carbon nanorods undergo a self-assembly process to form carbon nanosheets with irregular edges, as illustrated in Fig. 9b for the residue obtained after the decomposition of the PANI-PSCOOH/14000. In addition, the residue obtained after the thermal decomposition of the PANI-PSCOOH/18000 sample (Fig. 9c) is observed as nanosheets of 5 nm in width and 2 nm in thickness. Furthermore, the product obtained from the thermal decomposition of PANI-ABTA hollow microspheres are observed as carbon nanosheets, as illustrated in Fig. 9d.

4. Conclusion

A series of well-defined aromatic carboxyl chain end functionalized polystyrene derivatives with different number average molecular weights ($M_n = 18 \times 10^3 - 3 \times 10^3 \text{ g/mol}$) was prepared by the classic ATRP method via the α -bromo-*p*-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy as the catalyst/ligand system in diphenyl ether at 130°C . A series of PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrenes with different number average molecular weights as well as α -bromo-*p*-toluic acid were prepared by the chemical oxidative polymerization of aniline with ammonium persulfate as oxidant. The chemical oxidative polymerization of aniline with ammonium persulfate as oxidant in the presence of aromatic carboxyl chain end functionalized polystyrene of different number average molecular weights proceeds via an emulsion polymerization reaction. The morphology, size, shape, crystallinity and room temperature electrical conductivity of the doped PANI derivatives are effected by the structure of the polymeric carboxylic acid and the simple carboxylic acid dopants. PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrene are observed as nanorods and nanosheets. The PANI-PSCOOH/18000 sample is observed as long and thin nanorods, whereas the PANI-PSCOOH/3000 derivative is observed as shorter and thicker nanorods. The room temperature electrical conductivity of the different doped PANI derivatives doped with aromatic carboxyl chain end functionalized polystyrenes (PANI-PSCOOH) is affected by the morphology and the crystallinity of the resultant PANI derivative. The highest electrical conductivity reading of $5.5 \times 10^{-4} \text{ S cm}^{-1}$ is obtained for the PANI-PSCOOH/18000 sample due to the long and thin nanorod morphology as well as the increased crystallinity of the sample. The PANI derivative doped with α -bromo-*p*-toluic acid

(PANI-ABTA) is observed as hollow microspheres with an electrical conductivity reading of $1.65 \times 10^{-4} \text{ S cm}^{-1}$. The black residues obtained after the thermal decomposition of the PANI-PSCOOH samples are observed as carbon nanorods and carbon nanosheets.

Acknowledgements

Financial assistance from the National Research Foundation, South Africa, Incentive Funding for Rated Researchers, Grant Number 72397 is gratefully acknowledged. The authors thank Rejoice B. Maseko for conducting preliminary experiments associated with the study and Dr Gerald F. Malgas, National Centre for Nanostructured Materials, CSIR, Pretoria, South Africa for his assistance with the characterization of the research products. Several discussions between G.J.S. and Professor Jaroslav Stejskal, Czech Republic and his research group at conferences on the synthesis and characterization of polyanilines are gratefully acknowledged.

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