



Poly(*N*-octadecylaniline) Synthesis and Its Electrochemical Parametric Characterizations

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ABSTRACT

N-Substituted polyaniline (poly(*N*-octadecylaniline)) was prepared through *N*-alkylation reaction, by introducing octadecyl chains into a highly stable "leucoemeraldine base" (LEB) form of polyaniline nanostructure synthesized via a new chemical polymerization method. The polymer was characterized by FTIR, ¹H NMR and UV-Vis spectroscopy techniques. Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC) methods were carried out to investigate thermal behaviour of the obtained poly (*N*-octadecylaniline). Thermal analysis showed two endothermic transitions at 41°C and 60°C during the heating and two exothermic transitions at 20°C and 43°C during the cooling stages. Scanning electron microscopy (SEM) study revealed a significant morphology change by grafting of octadecyl chains onto the polyaniline backbone. The electrical conductivity of poly(*N*-octadecylaniline) that was doped with dodecylbenzene sulphonic acid (DBSA) was 8×10^{-4} S.cm⁻¹ and the investigation of cyclic voltammograms (CV) showed that the electroactivity of this polymer is acceptable. The obtained polymer was completely soluble in non-polar organic solvents such as xylene and *n*-hexane. A thin flexible film of the synthesized poly(*N*-octadecylaniline) was prepared by casting from *n*-hexane solution and the electroactivity property of the obtained film was investigated by CV method.

Key Words:

conducting polymer;
polyaniline;
poly(*N*-octadecylaniline);
electroactivity;
solubility.

INTRODUCTION

Among those known organic conducting polymers, polyaniline (PANI) has attracted much attention due to its low cost, environmental stability [1,2], adequate level of electrical conductivity [3-6] and wide range of commercial and technological applications such as secondary batteries [7], electromagnetic interference shielding [8], solar cells [9], bio/chemical sensors [10], corrosion protection [11], organic light emitting diodes

(OLEDs) [12] and electrorheological (ER) materials [13-15].

Electrorheological fluids are currently regarded as smart/intelligent materials, because their structural and rheological properties can be systematically tuned by controlling their electric field strengths. Three different types of basic PANI, i.e., fully reduced leucoemeraldine (LEB), half oxidized emeraldine (EB), and fully oxidized pernigraniline (PAB)

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are known. Polyaniline can be transformed to a conducting material from its insulating state through several doping techniques, i.e., (1) chemical doping by charge transfer groups, (2) electrochemical doping, (3) acid-base chemistry, (4) photodoping and (5) doping by charge injection at a metal/semiconducting polymer interface.

When treated with dopants, the electric conductivities of PANI salt vary reversibly from 10^{-10} S.cm⁻¹ to $\sim 10^3$ S.cm⁻¹ depending on the types and the contents of dopants and many computational approaches have attempted to comprehend the relationship between the structure of a single PANI molecule and its electrical properties. The chemical change in the molecular structure of PANI affects its microscopic structure, electrical properties and the doping techniques which influence the potential applications of PANI [16-18].

The commercial applications of polyaniline, like most conductive polymers, are limited due to their insolubility and infusibility. Lack of solubility of PANI may be resulted from the stiffness of its main chain and the existence of a strongly conjugated π electron system. Therefore, in order to increase the solubility and induce fusibility of the stiff chain of this polymer, a large number of methods have been studied, such as polymerizing a derivative of aniline with solubilizing property. The substituents used to increase the solubility can range from ring-alkyl [19] or alkoxy [20] and *N*-alkyl [21] groups to sulphonic acid [22] groups.

Also, copolymerization of aniline with ring or *N*-substituted anilines leads to polymers which have conductivity like PANI and solubility of substituted anilines [23,24]. An approach to obtain the soluble polyaniline was reported by Yue et al. [25] and Kohlman et al. [26]. They synthesized the sulphonic acid ring-substituted PANI (SPAN) by a reaction of emeraldine base (EM) with fuming sulphuric acid, which is soluble in water only after conversion to its salt form.

Another approach towards soluble polyaniline is incorporation of flexible polymers into the PANI structure by *N*-substitution method. Wang et al. [27] synthesized poly (ethylene glycol)-grafted polyaniline with enhanced solubility in common organic solvents and water.

In our previous study, we were able to improve the solubility of polystyrene-*g*-polyaniline (PS-*g*-PANI) copolymers in common organic solvents by increasing the degree of *N*-grafting [28]. The post-processing technique, emulsion polymerization and preparation of composites or blends are the other methodologies that have been developed to improve the solubility of PANI [29-32]. One other useful and common method to synthesize the modified polyaniline is the incorporation of flexible alkyl chains into monomer or polymer backbone [33].

By introducing various alkyl halides into the emeraldine or leucoemeraldine base forms of polyaniline, Zhao and co-workers [34] synthesized *N*-alkylated polyaniline through *N*-alkylation method. The obtained polymers showed remarkable improved solubility in common organic solvents such as THF, CHCl₃ and CH₂Cl₂, but there was no report of their solubility in non-polar solvents.

There are so many reports regarding PANI having alkyl chain up to 12 carbons (dodecyl), few works are known for PANI with an alkyl chain above 12 carbons. Levon and co-workers synthesized *N*-octadecyl substituted polyaniline by using *N*-alkylation method via NaH in DMSO on the leucoemeraldine base form of polyaniline [35]. In this case, the obtained polymer was soluble in THF, dioxane, toluene and hexane and had a melting point at 144°C and still there is no report on the electroactivity and conductivity of the obtained polymer in their study.

Finally, Falcou and co-workers have used another method to provide poly(*N*-octadecylaniline) [36]. First, the octadecyl chain was incorporated into the aniline monomer, and the monomer was polymerized in a mixture of hexane, water and THF. The resulted polymer exhibited characteristics such as solubility in THF and presence of a melting transition at 37°C. Also, the prepared poly(*N*-octadecylaniline) was a semiconductor material with conductivity in the range of 10^{-4} to 10^{-6} S.cm⁻¹.

The main emphasis in our study, compared to studies reported earlier, is to prepare fully soluble PANI in common non-polar solvents in order to have appropriate conductivity and electroactivity required for applications as conducting polymers. Also, we describe a new chemical polymerization method for synthesis of nanostructure polyaniline. Using this

method and reduction of the polyaniline nanostructures lead to unique characteristics including its fully reduction and high stability against auto-oxidation in a long period of time. Also in comparison to all existing reduced forms of polyaniline, the present form can be suitable for performing various *N*-substituted reactions on polyaniline backbone, because of having more number of N-H groups. The results of thermal behaviour are explained on comparative basis of studies reported earlier. The effect of large alkyl chains on the structure, conductivity, electroactivity, crystallinity, morphology and solubility of the obtained PANI are investigated in this study.

EXPERIMENTAL

Materials

Sodium hydride (NaH), toluene, octadecyl bromide, ammonium persulphate (APS), methanol, sulphuric acid, hydrochloric acid, acetone, phenylhydrazine, dodecylbenzene sulphonic acid (DBSA), acetonitrile, xylene, *n*-hexane, ether and ammonia were purchased from Merck and they were used as received. Aniline purchased from Merck was distilled twice under a reduced pressure before use. Dimethylsulphoxide (DMSO) purchased from Merck was totally dried and then distilled under a reduced pressure. Tetrahydrofuran (THF) (Merck) was dried and distilled under argon atmosphere.

Synthesis

Emeraldine Base Polyaniline (PANI-EB)

Emeraldine salt polyaniline (PANI-ES) was synthesized by a new chemical polymerization method. Distilled aniline (0.064 mol) was dissolved in toluene (200 mL) as an organic solvent. APS (0.016 mol) was dissolved in 200 mL of HCl 1 M. The organic phase was transferred to a two-necked flask, equipped with a dropping funnel and an argon inlet, and the aqueous phase was added dropwise into the organic solution during 7 h at room temperature (in general, the two solutions are carefully transferred to a beaker, generating an interface between the two layers [37]).

The polymerization reaction was continued for another 18 h, under argon atmosphere without

stirring. The aqueous phase was collected and filtrated. The filtrate was washed with water and methanol and it was followed by washing with acetone. The collected dark green polyaniline salt was then converted into its base form by stirring in ammonia solution 3 wt% for 2 h. This de-doped polyaniline was filtered and washed several times with water. The resulted dark-blue powder was dried under a reduced pressure.

Leucoemeraldine Base Polyaniline (PANI-LEB)

In order to prepare a fully reduced polyaniline, 3.8 mL (0.038 mol) of phenylhydrazine was added to 0.6 g of the obtained emeraldine base form of polyaniline in a flask equipped with a magnetic stirrer, at room temperature. The reaction mixture was stirred for 1 h, and then 300 mL of ether was added which was stirred again for less than 5 min. The resulted gray-white polymer was filtered and dried under vacuum.

*Synthesis of Poly(*N*-octadecylaniline)*

Sodium hydride (0.25 g, 0.01 mol) was added to 34 mL of DMSO in a three-neck round-bottom flask that was dried and kept under argon atmosphere throughout all reactions. The mixture was heated to 60°C and stirred until NaH was completely dissolved in DMSO. Leucoemeraldine base nanostructure (0.45 g) was added to sodium methylsulphanyl carbanion solution. The mixture was stirred at 60°C for 4 h and then it was cooled to 40°C. The solution of octadecyl bromide (13.5 g) in 20 mL of THF was added to the reaction mixture and it was stirred under argon atmosphere at 40°C for 18 h. The solution was cooled, and then poured into 100 mL of methanol to precipitate poly(*N*-octadecylaniline). The polymer was washed with a large amount of acetone to remove the unreacted alkyl bromide. The dark-blue precipitate was dried under vacuum for 48 h.

Characterization

The FTIR spectra (Shimadzu FTIR 8600s, Japan) were recorded to identify the chemical structure of obtained polymers. Samples of emeraldine base polyaniline (PANI-EB), leucoemeraldine base polyaniline (PANI-LEB) and poly(*N*-octadecylaniline) were prepared in disc forms using spectroscopic grade KBr powder. A differential scanning

calorimeter, NETZSCH (Selb/Germany) DSC 200 F₃, was used to determine the thermal transition temperatures under nitrogen in the range of 20-200°C and 200-(-30°C) for the first heating and cooling cycle and -30-350°C for the second heating stage at a rate of 10°C/min.

Thermal stability of obtained poly(*N*-octadecylaniline) was studied by thermal gravimetric analysis (TGA) using Parkin Elmer, Pyrise Diamond, USA, TG/DTG. Proton nuclear magnetic resonance (¹H NMR) spectrum of the poly(*N*-octadecylaniline) was measured in deuterated chloroform (CDCl₃) using a (¹H NMR, Bruker 500, USA) spectrometer. SEM micrographs of obtained polymers were studied by Stereoscan S360 Oxford, UK. X-ray diffraction measurement (XRD Model D500 Ziemence) of poly(*N*-octadecylaniline) was carried out at room temperature. UV-Vis spectra of synthesized samples were measured in DMSO and xylene as solvents using a Shimadzu UV-1601 PC (Japan) in wavelength range of 300-1100 nm.

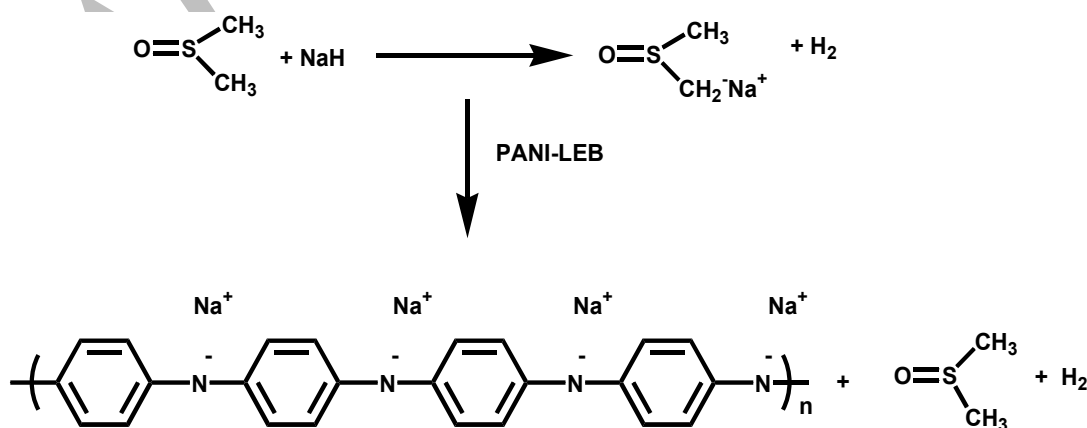
The four probe method (Rizpardazan Model LEO 440i, Iran) was used to measure the conductivity of DBSA-doped poly(*N*-octadecylaniline) sample at room temperature. Cyclic voltammograms (CVs) were recorded by AUTO-LAB model 4.9006 Metrohm, Switzerland.

RESULTS AND DISCUSSION

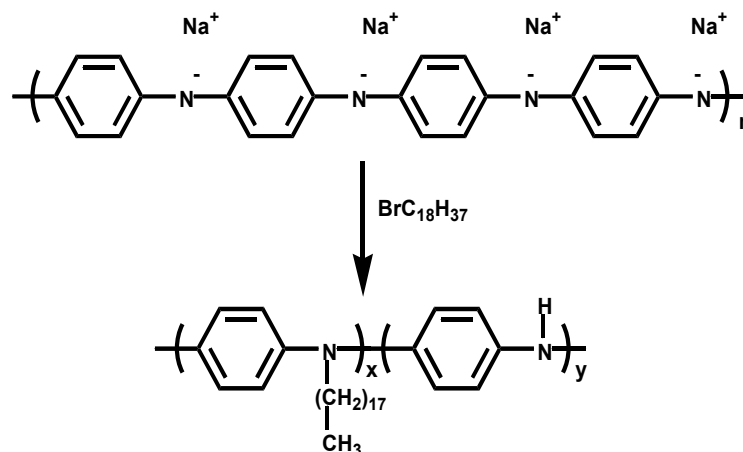
There are two principal methods for the synthesis of

PANI. The first one is the direct oxidation of aniline by chemical oxidants and the second way is through electro-oxidation on an inert electrode. In chemical synthesis, PANI-ES can be easily obtained as dark green powder by polymerization of aniline in aqueous media using oxidizing agents such as ammonium persulphate, potassium iodate, hydrogen peroxide, potassium dichromate, etc. Several other methods such as emulsion polymerization, dispersion polymerization and interfacial polymerization are also available for the polymerization of aniline via chemical route. The anodic oxidation of aniline is generally carried out on an inert electrode material which is usually platinum. However, other electrode materials such as iron, copper, zinc, lead, etc. have also been used.

For many conceivable applications, deposition of the polymer as a thin film or thick coating is desirable which can be easily achieved using electrochemical polymerization. Many derivatives of polyaniline were also synthesized by polymerization of ring- or nitrogen-substituted aniline monomers and by copolymerization [38-40]. In this study, polyaniline was synthesized by a new chemical polymerization method, using ammonium persulphate as an oxidant, toluene as an organic solvent and HCl 1 M. The technique employed is different from the interfacial method of synthesis of PANI reported in the literature where the two immiscible solutions are carefully transferred to a beaker to generate an interface between them. Here, we transferred the organic phase into a flask and the aqueous phase was added



Scheme I. Synthesis of the methylsulphinyl carbanion solution.



Scheme II. Preparation of poly(*N*-octadecylaniline).

dropwise into the organic solution under argon atmosphere during 7 h without stirring.

The produced dark-green salt was neutralized by an ammonia solution in order to prepare an emeraldine base (EB). The reduced form of polyaniline, leucoemeraldine base (LEB), was prepared by treating the obtained emeraldine base (EB) with phenylhydrazine. The introduction of alkyl side chains into the leucoemeraldine base backbone was carried out by deprotonation of NH groups of highly stable leucoemeraldine base nanostructures and subsequent treatment with alkyl halide under argon atmosphere. The solution of methylsulphinyl carbanion in DMSO, formed from the reaction of sodium hydride with dry DMSO was used to abstract proton from the amine nitrogen of leucoemeraldine base chains as shown in Scheme I.

Obtained polyanion was reacted with a solution of octadecyl bromide in THF to prepare poly(*N*-octadecylaniline), as shown in Scheme II.

FTIR Spectroscopy of Synthesized Polymers

FTIR spectra of all synthesized polymers in their neutral state are presented in Figure 1. These results are in agreement with the spectra reported by Hwang et al. [33], Brozova et al. [41] and Choi et al. [42]. The spectrum of PANI-EB (spectrum a in Figure 1) shows the N-H stretching with hydrogen bonding at 3377 cm^{-1} and the phenyl C-H stretching at 3230 cm^{-1} . Stretching bands of the quinoid and benzenoid rings of the polymer are observed at 1581 cm^{-1} and

1498 cm^{-1} , respectively. The stretching mode of the imine group (C=N) has been appeared at 1296 cm^{-1} .

The absorption peak at 1155 cm^{-1} is a characteristic of the electronic-like absorption of the N=Q=N vibration (where Q denotes out-of-plane bending vibration of the *para*-substituted benzene ring). The spectrum of the leucoemeraldine base polyaniline (PANI-LEB) is almost similar to the spectrum of the emeraldine base polyaniline (PANI-EB), but there are some differences between them as shown as spectrum b in Figure 1. In the spectra of fully reduced polyaniline, the absorption bands at 1581 cm^{-1} (quinoid ring stretching) and 1155 cm^{-1} (N=Q=N vibration) are disappeared, but, the intensities of bands at 1504 cm^{-1} (C=C stretching of benzenoid rings) and 3382 cm^{-1} (N-H stretching vibration) are increased (Figure 2).

In the spectrum of poly(*N*-octadecylaniline) as shown as spectrum c in Figure 1, two new absorption bands have emerged. The aliphatic C-H stretching vibrations of the alkyl groups in *N*-substituted polymer are observed at 2852 and 2920 cm^{-1} . Also the absorption band at 823 cm^{-1} due to the out-of-plane bending vibration of the *para*-substituted ring of the polymer, together with the absence of its split into two peaks at 823 and 870 cm^{-1} , indicates that no ring substitution occurred in the alkylation reaction. The presence of the absorption peak at 1249 cm^{-1} attributed to the aliphatic C-N stretching, suggests that the alkyl substituents are linked to the nitrogens of polyaniline chain.

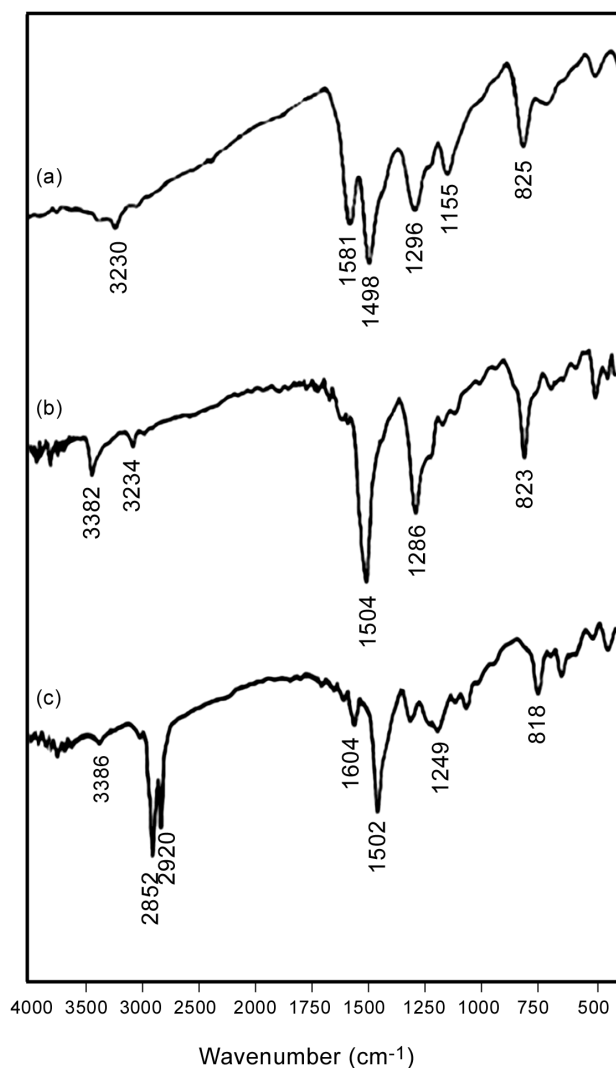


Figure 1. FTIR Spectra of (a) PANI-EB, (b) PANI-LEB, and (c) PANI-18 carbons.

The stability of obtained fully reduced leuco-emeraldine base nanostructures was investigated by FTIR method. The FTIR spectra show the stability of the leucoemeraldine base maintained for one month (Figure 2). After one month the leucoemeraldine base underwent auto-oxidation to change to an emeraldine form. Figure 2 illustrates the oxidation steps of leucoemeraldine base through its FTIR spectra. The experimental stability evaluation of leucoemeraldine base versus auto-oxidation during one month is presented here for the first time.

¹H NMR Spectroscopy

¹H NMR spectrum of poly(*N*-octadecylaniline) in

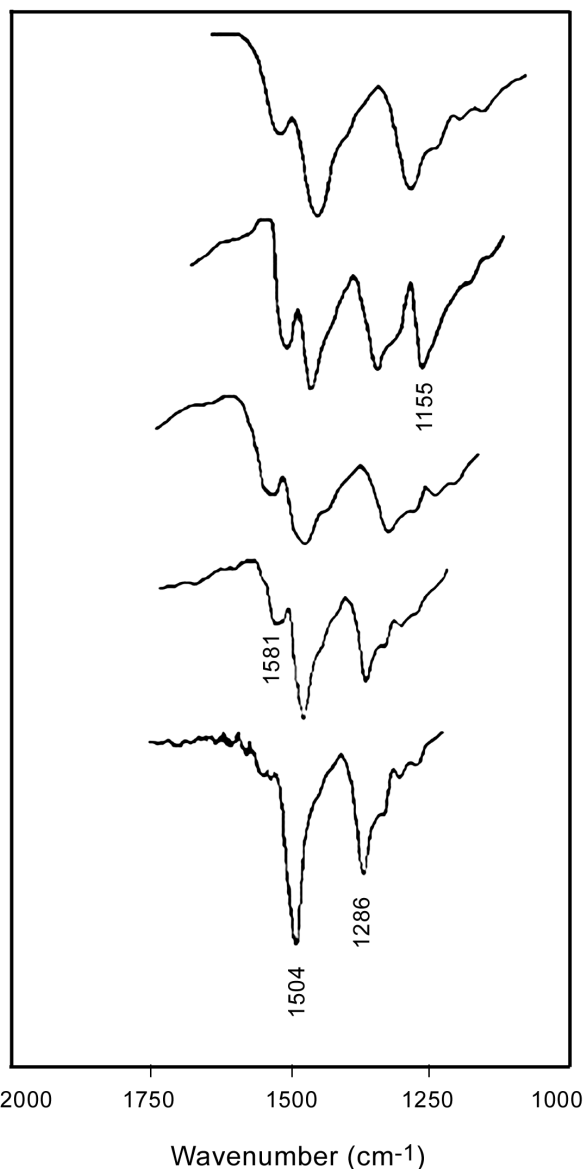


Figure 2. FTIR Spectra of a fully reduced polyaniline (PANI-LEB) and its gradual transformation through the oxidation step.

CDCl_3 is shown in Figure 3. The peaks of hydrogen atoms of phenyl ring have appeared in the range of 6.64-6.94 ppm (6.64, 6.78 and 6.94 ppm). The peaks for inner methylene hydrogens are located at 1.24 and 1.64 ppm. The peak at 3.58 ppm is characteristic of H atoms of CH_2 connected to N atom. Also, the peak of terminal methyl hydrogens is evident at 0.86 ppm [43,44].

Thermal Analysis

In order to investigate the effect of long aliphatic side

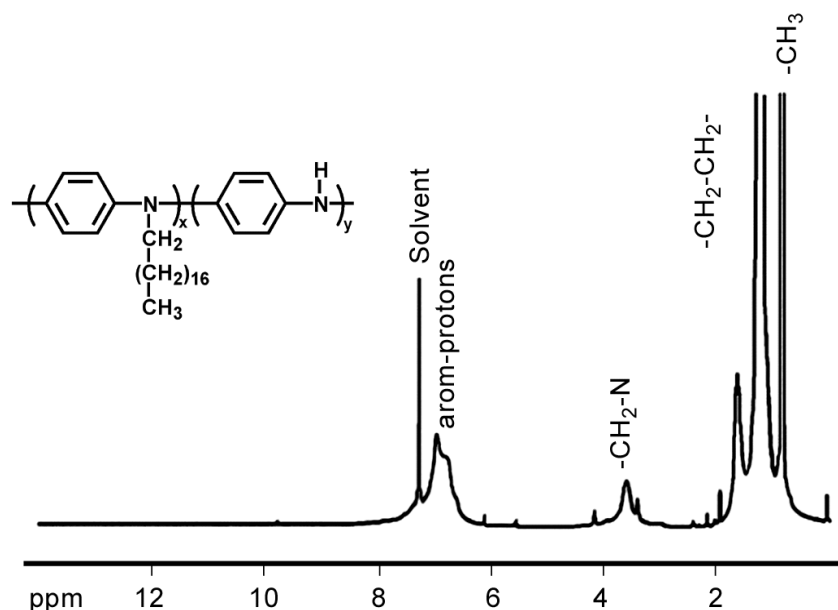


Figure 3. ^1H NMR Spectrum of poly(*N*-octadecylaniline).

chains on thermal properties of the rigid polyaniline backbone, the heating and cooling processes were carried out by differential scanning calorimetry (DSC) at the heating/cooling rate of $10^\circ\text{C}/\text{min}$ in the range of $20\text{--}200^\circ\text{C}$ and $200\text{--}(-30)^\circ\text{C}$ for the first heating and cooling stages under N_2 flowing, respectively. The second heating stage was carried out within the range of $-30\text{--}350^\circ\text{C}$ under N_2 flow at the heating rate of $10^\circ\text{C}/\text{min}$.

DSC thermogram of the poly(*N*-octadecylaniline) (Figure 4) shows two sharp endothermic peaks at 41°C and 60°C in the first heating stage. It seems that the appeared peak at 41°C may be due to melting of

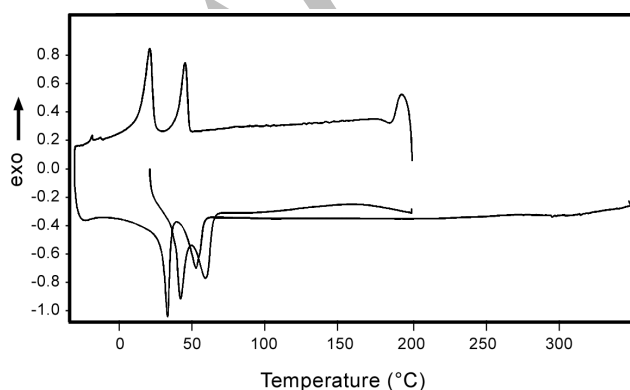


Figure 4. DSC Thermograms of PANI-18 carbons at the rate of $10^\circ\text{C}/\text{min}$.

high degree grafted octadecyl groups and the other one at 60°C can be due to melting process of the low degree grafted octadecyl groups. These two endothermic peaks have appeared in the second heating stage, as well. In the cooling stage, two exothermic peaks have appeared at 43°C and 20°C which can be attributed to the presence of a crystalline structure caused by the side-chain crystallization.

However, in research works on *N*-substituted polyanilines which have been reported, e.g., in Levon's work [35], the two endothermic peaks which appeared in the first heating stage were eliminated in the second heating and finally emerged as one peak. Also there was only one exothermic peak at 6°C due to the side chain crystallization in the cooling stage [35]. Most previous reports on *N*-substituted polyanilines [33-35,45] did not show any peak of melting transition of PANI backbone or melting points which may have been located at higher temperatures.

The thermal stability of poly(*N*-octadecylaniline) was evaluated using TG and DTG analyses at the heating rate of $10^\circ\text{C}/\text{min}$ in the range of $30\text{--}600^\circ\text{C}$ under N_2 flow as shown in Figure 5.

Curve a in Figure 5 represents the thermogram of the poly(*N*-octadecylaniline). This polymer exhibits a four-stage decomposition pattern. In the first stage,

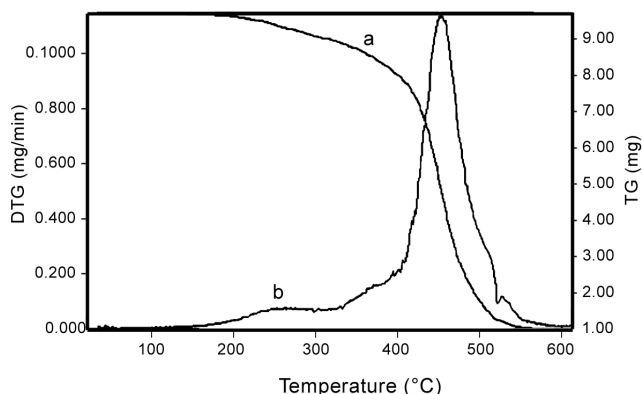


Figure 5. TG and DTG curves of poly(*N*-octadecylaniline).

starting at about 150°C, the slow weight loss is due to the loss of trapped water or solvents in the polymer. The second stage of weight loss observed from 220°C to 350°C is attributed to the loss of oligomers. While, the third stage loss from 350°C to 450°C is a result of the elimination of alkyl side groups. The sharp degradation stage owing to the great part of weight loss at about 600°C is related to the complete degradation of the polymer. As shown in curve b in Figure 5, the poly(*N*-octadecylaniline) exhibits a DTG curve having two peaks at about 250°C and 450°C due to oligomers and polymer degradation, respectively [46].

Solubility

Solubility tests performed for undoped state of poly(*N*-octadecylaniline) are reported in Table 1. This polymer is insoluble in strong polar solvents such as DMSO and NMP. However, non-polar organic solvents such as xylene and *n*-hexane are very good solvents for *N*-substituted PANI. This can be attributed to the lowering polarity and stiffness of the polymer chains by incorporation of the octadecyl side chains. Also, the flexible thin films of the synthesized poly(*N*-octadecylaniline) can be prepared by casting from *n*-hexane solution.

Table 1. The solubility of poly(*N*-octadecylaniline) in various solvents.

Acetone	acetonitrile	DMSO	NMP	THF	CHCl ₃	Xylene	<i>n</i> -hexane
Insoluble	insoluble	insoluble	Partially soluble	Mainly soluble	Mainly soluble	Totally soluble	Totally soluble

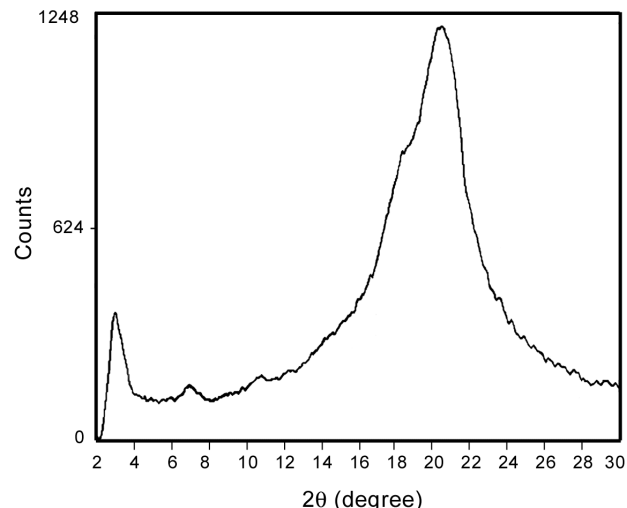


Figure 6. X-Ray diffraction pattern of poly(*N*-octadecylaniline).

X-Ray Diffraction Measurement

The X-ray diffraction (XRD) diagram of poly(*N*-octadecylaniline) is shown in Figure 6. The introduction of long alkyl groups on nitrogen atoms of the PANI had considerable effect on the diffraction pattern. Two strong and sharp diffraction peaks were observed at small angles in the meridian direction of $2\theta = 3.14^\circ$ (28.16 Å) and at large angles of $2\theta = 20.61^\circ$ (4.31 Å) in the equator direction corresponding to the interlayer and inter-side chain distances, respectively [43,47]. This may suggest the crystallization tendency of long aliphatic side chains which contain 18 carbon atoms each.

UV-Vis Absorption Spectroscopy

UV-Vis absorption spectra of unsubstituted polyaniline in neutral state in DMSO and poly(*N*-octadecylaniline) in neutral state and DBSA-doped states in xylene are presented in Figures 7, 8 and 9, respectively. The electronic spectrum of neutral form of the polymers is composed of two absorption bands at about 300 and 600 nm. The band with a maximum

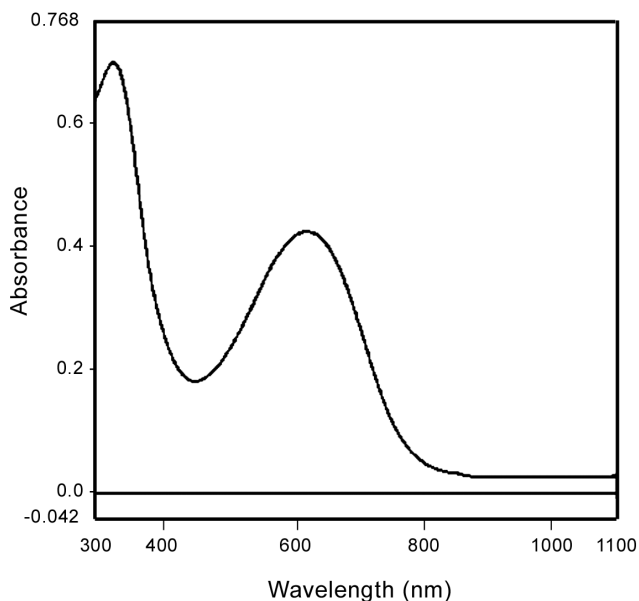


Figure 7. UV-Visible absorption spectrum of undoped unsubstituted polyaniline in DMSO.

at 300 nm is assigned to the $\pi \rightarrow \pi^*$ transition of benzenoid rings of the polymer and the band around 600 nm is due to the absorption of the unit containing quinoid rings [48,49].

The electronic spectroscopy of the unsubstituted polyaniline shows that two transitions have approximately the same intensity, while in the case of the poly(*N*-octadecylaniline), the intensity of the

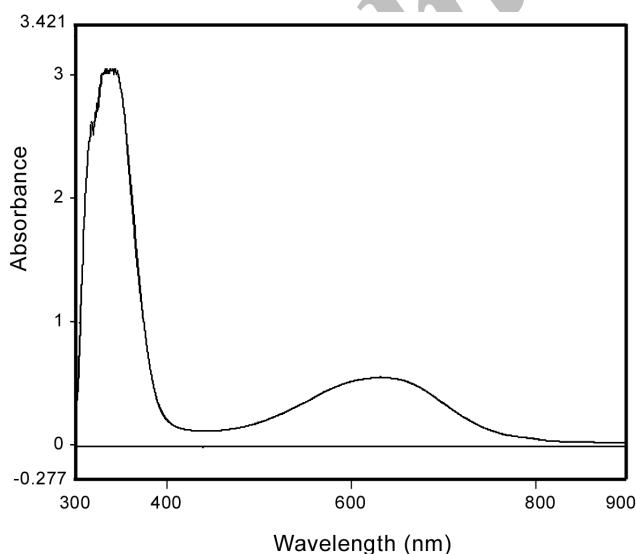


Figure 8. UV-Visible absorption spectrum of undoped solution of poly(*N*-octadecylaniline) in xylene solvent.

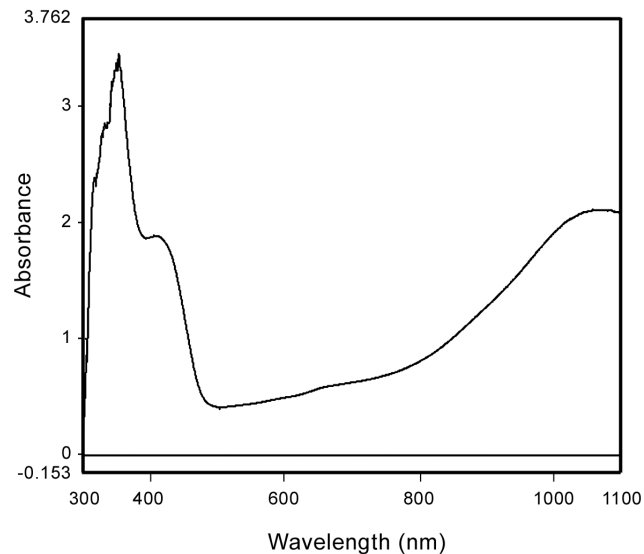


Figure 9. UV-Visible absorption spectrum of DBSA-doped state of poly(*N*-octadecylaniline).

transition at 600 nm is lower in comparison with the transition at 300 nm, due to the weak conjugation induced by a modification carried out on the nitrogen atoms of the polyaniline [50,51]. In fact, there is an agreement with the information obtained from FTIR and UV-Vis spectra.

The intensity of the electronic transitions due to quinoid rings is much smaller than the transitions due to the benzenoid units. Doping of poly(*N*-octadecylaniline) with DBSA does not alter the position of the peak at about 300 nm which is due to the *p*-phenylenediamine units, but a new band is observed at 420 nm associated with the presence of the radical cations on the polymer chains [Figure 9]. The band at about 600 nm has completely disappeared and it has been replaced by a new band at 1050 nm which is due to the formation of the polarons (radical cations) [52].

As it can be seen, the position of polaron band at 1000-1100 nm has appeared at lower energy for DBSA-doped poly(*N*-octadecylaniline) in comparison with unsubstituted PANI. Thus, the reduction of the extent of conjugation through *N*-grafting on polyaniline may be a reason for decreasing the conductivity of the copolymer. The steric effect of octadecyl chains substituent might be increased due to the torsional angle between the adjacent phenyl rings thus disturbing the overlapping of the orbital of π -electrons of phenyl and that of the lone pairs of

nitrogen, resulting in lowering of the degree of conjugation.

Electrical Conductivity

Electrical conductivities of DBSA-doped poly(*N*-substituted aniline) and unsubstituted PANI were determined by four-probe technique at room temperature. Conductors generally show ohmic behaviour wherein the voltage across the material varies linearly with the current and the I-V plot has a constant slope which is attributed to the resistance of a material. This means that the current density linearly increases with the applied electric field.

When the EB is doped by a protonic acid, protonation occurs at the imine nitrogen sites to yield poly-semiquinone in which polarons delocalize along the chain. The measured conductivity for DBSA-doped unsubstituted PANI is 0.5 S.cm^{-1} , while in the case of DBSA-doped poly(*N*-octadecylaniline) the obtained conductivity is $8 \times 10^{-4} \text{ S.cm}^{-1}$. The lower conductivity of the poly(*N*-octadecylaniline) is assigned to the additional ring twisting along with the polymer backbone due to the increased steric hindrance and decreased conjugation caused by the long alkyl chains. This leads to the reduced movement of charge carriers and finally weakens the conductivity of the polymer.

In other words the reduction in conductivity can be explained by the volumetric "diluting effect" of the grafted octadecyl chains. The intermolecular steric effect introduced by the bulky octadecyl side chains has diluting effect on the PANI chains and thus contributes to the reduction in conductivity of the poly(*N*-octadecylaniline) sample. The *N*-substituted octadecyl chains can also alter the conformation of the PANI chains. The bulky side chains can introduce non-planar conformations which in turn can cause a decrease in the effective conjugation length of the PANI backbone. In this way, the bulky side chain destabilizes the polysemiquinone radical cation which gives rise to higher redox potentials. Similar phenomenon is reported in the literature for the substituted PANI derivatives [27]. Compared to another reported results [36], the conductivity of the synthesized poly(*N*-octadecylaniline) in its doped state has been proved to be higher.

Cyclic Voltammetry

Major interest in this work was the synthesis of a typical PANI, soluble in nonpolar organic solvents, maintaining the conductivity of its modified polymer prototype. Electrochemical experiments were carried out in a typical three-electrode cell. A glass carbon (GC) with an area of 0.07 cm^2 was used as a working electrode. A platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The DBSA-doped poly(*N*-octadecylaniline) film was prepared by casting on GC electrode.

Cyclic voltammetry curves of this substituted polymer recorded at different scan rates between -0.1 V and 0.9 V versus saturated calomel electrode (SCE) in 1 M sulphuric acid (H_2SO_4) confirmed the electroactivity of this polymer. As shown in Figure 10, at a high scan rate, the polymer shows only one oxidation peak and one reduction peak corresponding to the E_{Pa} and E_{Pc} values. This can be attributed to the decrease in electroactivity of the obtained polymer having high degree of alkyl substitution that provides the resistance of this polymer to oxidation. Cyclic voltammetry data of DBSA-doped poly(*N*-octadecylaniline) is shown in Table 2.

In order to increase the conductivity of this modified polymer, we have electropolymerized aniline on the poly(*N*-octadecylaniline) film deposited on the electrode surface. As shown in Figure 11, the cyclic voltammogram shows two

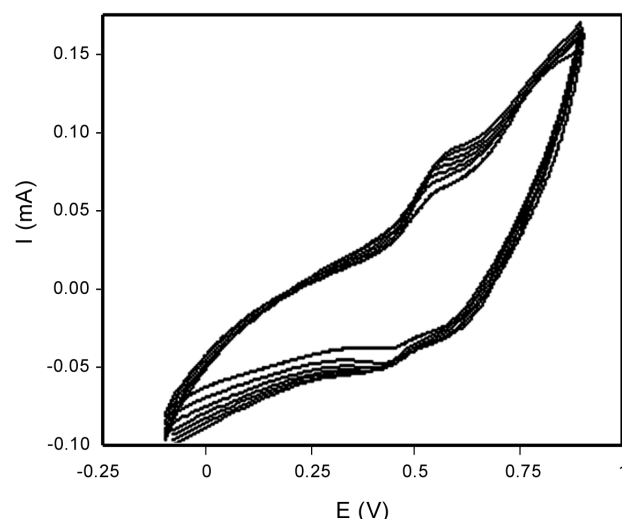
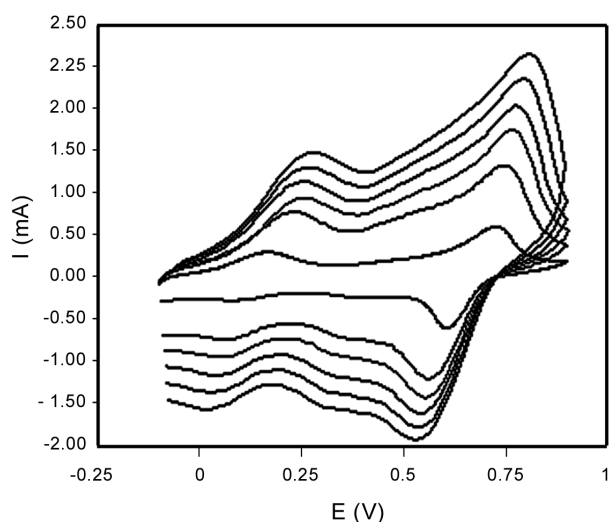


Figure 10. Cyclic voltammetry curves of DBSA-doped solution of poly(*N*-octadecylaniline).

Table 2. Cyclic voltammometry data of DBSA-doped poly(*N*-octadecylaniline).

scan rate	$I_{(Pa)}$ (mA)	$V_{(Pa)}$ (V)	$I_{(Pc)}$ (mA)	$V_{(Pc)}$ (V)
25	0.063	0.517	-0.0455	0.477
50	0.068	0.525	-0.0459	0.460
100	0.072	0.534	-0.0500	0.443
125	0.077	0.542	-0.0504	0.426
150	0.082	0.551	-0.0509	0.409
175	0.087	0.559	-0.0527	0.392
200	0.090	0.568	-0.0536	0.375

$I_{(Pa)}$: current of the anodic peak; $V_{(Pa)}$: potential of the anodic peak; $I_{(Pc)}$: current of the cathodic peak; $V_{(Pc)}$: potential of the cathodic peak.

**Figure 11.** Cyclic voltammometry curves of DBSA-doped film of poly(aniline-co-*N*-octadecylaniline).

oxidation peaks and two reduction peaks similar to unsubstituted polyaniline. This is due to the addition of aniline in the modified polymer composition. The peaks are ascribed to polaronic and bipolaronic transitions for the first and second peaks, respectively [53,54]. Table 3 shows the current and potential quantities for electropolymerization of aniline on the modified poly(*N*-octadecylaniline) electrode.

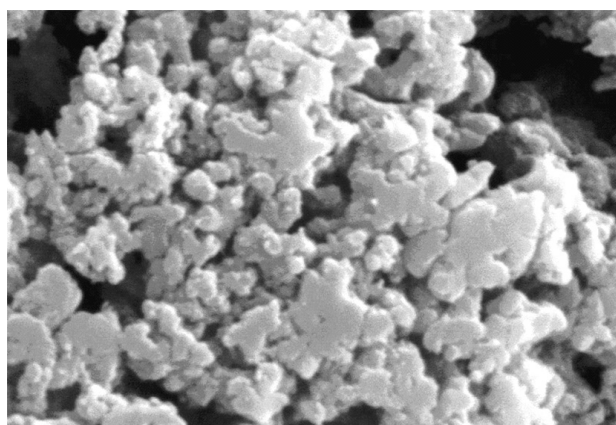
Morphology

Figures 12a and 12b show SEM micrographs of unsubstituted polyaniline nanostructures and poly(*N*-octadecylaniline), respectively. Unsubstituted polyaniline nanostructures show the diameter of approximately 200 nm (Figure 12a). High resolution image of untreated polymer (leucoemeraldine form

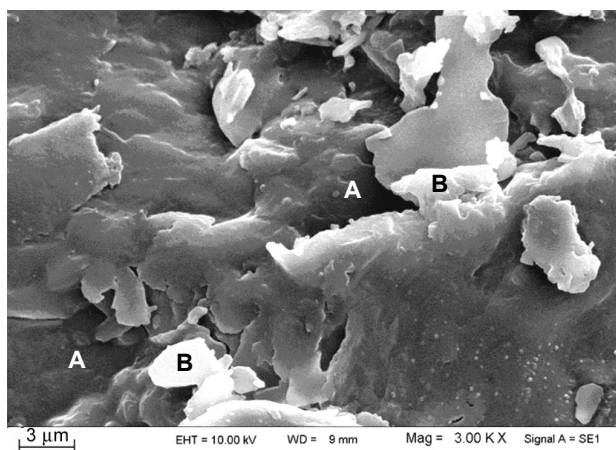
Table 3. Electropolymerization of aniline on the modified electrode by poly(*N*-octadecylaniline).

scan rate	$I_{(Pa)1}$ (mA)	$I_{(Pa)2}$ (mA)	$V_{(Pa)1}$ (V)	$V_{(Pa)2}$ (V)	$I_{(Pc)2}$ (mA)	$I_{(Pc)1}$ (mA)	$V_{(Pc)2}$ (V)	$V_{(Pc)1}$ (V)
25	0.333	0.666	0.161	0.741	-0.566	-0.330	0.590	0.081
50	0.834	1.362	0.232	0.759	-1.182	-0.751	0.555	0.063
100	1.000	1.752	0.260	0.777	-1.466	-0.983	0.554	0.054
125	1.233	2.083	0.268	0.795	-1.549	-1.224	0.537	0.045
150	1.362	2.167	0.286	0.822	-1.834	-1.433	0.535	0.027
175	1.502	2.388	0.295	0.840	-1.933	-1.583	0.527	0.018

$I_{(Pa)1}$: current of the first anodic peak; $I_{(Pa)2}$: current of the second anodic peak; $V_{(Pa)1}$: potential of the first anodic peak; $V_{(Pa)2}$: potential of the second anodic peak; $I_{(Pc)1}$: current of the first cathodic peak; $I_{(Pc)2}$: current of the second cathodic peak; $V_{(Pc)1}$: potential of the first cathodic peak; $V_{(Pc)2}$: potential of the second cathodic peak.



(a)



(b)

Figure 12. (a) The morphology of unsubstituted leucoemeraldine form of PANI nanostructures and (b) The morphology of poly(*N*-octadecylaniline).

of polyaniline) is an indication of globular structure with droplets whereas it has a cauliflower-like structure in this case.

Grafting of octadecyl chain onto the leucoemeraldine backbone leads to a significant change in the morphology and formation of two distinct phases: A (unsubstituted leucoemeraldine polyaniline) and B (poly(*N*-octadecylaniline) phases, as a result of SEM phase image (Figure 12b). The distinguished phase contrasted in the Figure 12b confirms thermodynamically the partial miscibility of species B (octadecyl chains) into polymer backbone A (unsubstituted leucoemeraldine polyaniline) and the appearance of endothermic DSC peaks at about 33°C and 53°C is another proof. It is thought that

due to the increasing of the composition of graft species B (octadecyl chains) which imposes a boosted viscosity onto polymer matrix, a phase inversion occurs which appears in DSC thermogram as an alleviated single endothermic peak. This depends on two main parameters according to the original Paul and Barlow equation as follows [55].

$$\frac{V_I}{V_{II}} \times \frac{\eta_{II}}{\eta_I} = X$$

If $X > 1$, Phase I is continuous

If $X = 1$, Dual phase continuity or phase inversion

If $X < 1$, Phase II is continuous

CONCLUSION

Polyaniline nanostructures were synthesized by a new chemical polymerization method and resulted to a fully reduced leucoemeraldine base which was very stable against auto-oxidation for about one month. Subsequent incorporation of octadecyl chains into leucoemeraldine form of polyaniline (PANI-LEB) backbone was carried out by treatment of (PANI-LEB) nanostructures with the solution of methylsulphanyl carbanion in DMSO and led to the formation of negatively charged nitrogens, and gave rise to *N*-alkylation of high stable leucoemeraldine base form of polyaniline nanostructures. The resulted polymer exhibited remarkable solubility in common nonpolar organic solvents such as xylene and *n*-hexane, while it was insoluble in common organic polar solvents such as DMSO and NMP. The structure of the synthesized polymers (PANI-EB, PANI-LEB and poly(*N*-octadecylaniline)) was determined by the FTIR and ¹H NMR spectroscopy techniques. SEM study revealed that there is a significant morphology change in the unsubstituted leucoemeraldine form of polyaniline nanostructures and poly(*N*-octadecylaniline). The UV-Vis absorption spectra of poly(*N*-octadecylaniline) in the DBSA-doped state exhibited the polaronic transition which occurred at longer wavelength ($\lambda > 1000$ nm) in comparison with the unsubstituted PANI ($\lambda \approx 800$ nm). The conductivity measured by four-probe technique was 8×10^{-4} S.cm⁻¹ for DBSA-doped poly(*N*-octadecylaniline). The

cyclic voltammetry curves of poly(*N*-octadecylaniline) in the doped state showed the electroactivity of this polymer. The poly(*N*-octadecylaniline) exhibited interesting thermal properties. The results of TG and DTG analyses showed that thermal stability of the obtained poly(*N*-octadecylaniline) is fairly good. The incorporation of the long side chains led to two endothermic peaks appeared in the first and second heating curves and two exothermic peaks appeared in the cooling thermogram. The introduction of the alkyl substituent into the nitrogen atoms of polyaniline had a considerable effect on the diffraction pattern. The X-ray diffraction measurement of poly(*N*-octadecylaniline) showed that the inter-digitations of side chains were sufficiently well-defined to form a crystalline phase which was confirmed by DSC results. The prepared film can be used as gas sensors among other applications.

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