Synthesis and characterization of electroactive novel poly-2-cyanoaniline

UMESH S WAWARE^{1,*}, MOHD RASHID^{2,*}, AFIDAH A RAHIM³ and S S UMARE⁴

¹Department of Mechanical and Industrial Engineering, Qatar University, 2713 Doha, Qatar

²Department of Chemistry, Aligarh Muslim University, Aligarh 202 001, India

³School of Chemical Science, Universiti Sains Malaysia, Pinang, Malaysia

⁴Department of Chemistry, Visvesvaraya National Institute of Technology, Nagpur 440 011, India

MS received 29 July 2013; revised 2 December 2013

Abstract. Uniform needle-like structures of poly-2-cyanoaniline are formed without the use of any template by electrochemical oxidative polymerization method on copper electrode in acidic medium. The structural characterizations are performed by FT-IR, UV-Visible spectroscopy and X-ray diffraction studies. The morphology of the polymer is demonstrated by scanning electron microscopy (SEM). The framework of the needle-like structure, which is seen at low and high magnifications appeared as nanorods of 50–80 nm diameter and of length up to a few micrometres to form a scaffold of interconnected nanorods. Thermogravimetric analysis (TGA) indicates that poly-2-cyanoaniline is thermally more stable than polyaniline. The conductivity of pressed pellet of the as-synthesized polymer measured at room temperature of 25 °C by four-probe measurement method was found to be 9.1824×10^{-5} S/cm. The polymer is easily dispersed in some organic solvents and shows high solubility.

Keywords. Poly-2-cyanoaniline; nanorods; conducting polymer.

1. Introduction

The conducting property of organic polymers was discovered co-incidentally for the first time by three polymer chemists, Shirakawa *et al* (1977). Among the conducting polymers, polyaniline and its derivatives still remains the most extensively studied conjugated-smart polymer and possesses acid–base doping/dedoping reversible unique chemistry as reported in the literature. Polyaniline and its derivatives have been studied most extensively for its highly becoming acid–base chemistry and its potential applications as conducting polymers as reported by Virji *et al* (2004, 2006). Huang *et al* (2003), Huang and Kaner (2006) and Zhang *et al* (2004) have reported that the nanostructured polyaniline was prepared by using chemical oxidative, electrochemical and physical methods. Conventionally, polyaniline and its derivatives can be synthesized by chemical oxidative polymerization of aniline, using an oxidant and a strong mineral acid as a dopant, as reported by Huang *et al* (1986). Addition of surfactant during the synthesis decides the structural morphology of the polymer Liu *et al* (2003) or addition of polyelectrolytes (Liu *et al* 1991) to the chemical polymerization bath is another way

to obtain polyaniline nanostructures. Microtubes, fibres or rod-like structures can be formed depending on the nature of the dopant and surfactant used (Langer *et al* 2001; Qiu *et al* 2001; Wei *et al* 2002, 2003). Electrochemical polymerization (Liang *et al* 2002; Liu *et al* 2003) and such physical methods, as electrospinning, reported by MacDiarmid *et al* (2001), and mechanical stretching (He *et al* 2001) can also produce conducting polymers nanofibres without templates. The only limitation electrochemical synthesis is that it is very sensitive and it deposits a very small quantity of polymer film on the electrode surface. Here we report the synthesis of novel poly-2-cyanoaniline by electrochemical potentiodynamic method without using any template.

2. Experimental

2.1 Materials

Analytical grade 2-cyanoaniline (99%) from Aldrich was used as received. Ammonium persulphate was of analytical grade. NMP, DMF, DMSO, propanol and toluene used were of spectroscopic grade. Hydrochloric acid (37.5%, Aldrich, UK) was used without further purification. Acetone was purchased from System^R Chem AR, used as received. Double-distilled water was used to prepare the 0.2 M solution of 2-cyanoaniline.

*Authors for correspondence (uswaware@gmail.com; rashidchem@gmail.com)

2.2 Electrochemical procedure

The potentiodynamic polarization was carried out by using potentiostat/galvanostat/ZRA (Gamry, Reference 600). The cylindrical electrochemical cell was used with three conventional electrodes cell assembly: counter electrode-platinum wire; reference electrode-saturated calomel electrode; copper plate was used as a working electrode, with dimension 2.5×2.5 cm. The exposed area of the working electrode was 1 cm^2 and the rest of the electrode being covered with araldite epoxy. Potentiodynamic study was carried out at the 0.1 M molar concentration of 2-cyanoaniline in 1 M HCl as an electrolyte. Polarization was carried out in the range of -0.3 – 0.3 V from a cathodic to an anodic potential in oxygen-free nitrogen atmosphere at 25°C . The polymer deposited electrochemically on the copper electrode surface was carefully peeled off for further characterization by UV–Vis and FT–IR techniques.

2.3 FT–IR and UV–Visible spectroscopy

The structure of the polymer was determined by FT–IR spectroscopy system 2000 (Perkin–Elmer, USA). The electrochemically synthesized polymer was peeled off from the copper plate and collected as an orange-coloured powder; it was purified by washing with water and subsequently with acetone until the extract became colourless. The scanning resolution of FT–IR was 4 cm^{-1} . The absorption spectrum of the sample solution (in DMSO) in the region of 255 – 555 cm^{-1} was obtained using a UV–Vis spectrophotometer (V-500, JASCO, Japan). The solubility of the poly-2-cyanoaniline in the salt form was confirmed by dissolving 10 mg of polymer powder in propanol, NMP and toluene, and the DMF of the polymer

powder was taken in 100 mL of the solvent and dispersed thoroughly.

2.4 X-rays diffraction study (XRD)

The wide-angle X-ray diffraction (WAXRD) spectrum was recorded on a PW-7000 (Phillips, Holland) automatic X-ray diffractometer using $\text{CuK}\alpha$ radiation of wavelength $1.54 \text{ \AA}$ to an accuracy of ± 0.010 .

2.5 Scanning electron spectroscopy (SEM)

The scanning electron microscopy (SEM) equipped with an Oxford INCA 400 energy dispersive X-ray (EDX) using a Leo Supra 50 VP field emission microanalysis system (Bucks, UK) was used to elucidate the morphology of the poly-2-cyanoaniline. The SEM micrograph of homopolymer sample was recorded at different magnifications.

2.6 Thermogravimetry analysis (TGA)

Thermal analysis of the polymer sample was conducted using an Auto Hi-Res Q500 thermogravimetric analyser in a dry nitrogen atmosphere, with a heating rate of $10^\circ\text{C}/\text{min}$ and using platinum pans. The temperature range was from 30 to 800°C .

3. Results and discussion

3.1 FT–IR-spectroscopy

The FT–IR spectrum of the as-synthesized polymer is shown in figure 1, the characteristic bands at 1613 and

Figure 1. Infrared spectrum of as-synthesized poly-2-cyanoaniline prepared by electrochemical deposition on copper electrode.

1528 cm^{-1} are mainly attributed to the quinoid and benzenoid in the rings, respectively, in poly-2-cyanoaniline. The peak at 1455 cm^{-1} is attributed to C–N stretching of nitrile group attached to the benzene ring. The bands at 1120 and 762 cm^{-1} can be attributed to the in-plane and out-of-plane C–H bending vibration modes, respectively. The 1331 cm^{-1} band may be assigned to C–C stretching mode of the quinoid ring. The adsorption peak at 1306 cm^{-1} corresponds to the C–N stretching mode of the leucoemeraldine component. The peak at 1136 cm^{-1} is due to the C–H in-plane bending mode of pernigraniline and the vibration at 1265 cm^{-1} is related to the C–N group (Cao *et al* 1989; Palle *et al* 2002). The band close to 1600 cm^{-1} is assigned to the quinoid C=C stretching mode of the polymer chain and a band near 1500 cm^{-1} is assigned mainly to the benzenoid C–C ring stretching vibration mode (Phillips *et al* 1989). The relative peak intensity of quinoid rings is larger than that of benzenoid rings, indicating the pernigraniline form prevailed in the poly-2-cyanoaniline chain. A broadband at 3270–3467 cm^{-1} is assigned to the N–H stretching vibrations of $-\text{C}_6\text{H}_4\text{NHC}_6\text{H}_4$ group. In the region of 1015–1175 cm^{-1} , aromatic CH in-plane bending modes are usually observed. For polyaniline, a strong band that characteristically appears at 1150 cm^{-1} , which has been explained as an electronic band or a vibrational band of nitrogen quinone, is missing in this case.

3.2 Electronic spectroscopy

The electronic spectrum of as-synthesized poly-2-cyanoaniline is shown in figure 2. Mid-gap state caused by charge transfer can be studied by UV–Vis absorption intensity of the polymeric solutions. The spectrum of sample of polymer solution in DMSO is dominated by two absorption peaks, 260 and 340 nm. These characteristic bands are mainly attributed to $\pi-\pi^*$ and $n-\pi^*$ electronic transitions in benzenoid and quinoid, respectively. The peak observed at 340 nm is attributed to $n-\pi^*$ transition

Figure 2. UV–Visible absorption spectra of poly-2-cyanoaniline dispersed in DMSO.

and the peak at 260 nm is attributed to $\pi-\pi^*$ benzenoid and quinoid units of polyaniline (Cao *et al* 1989; Phillips *et al* 1989), whereas the absorption spectrum obtained in the case of poly-2-cyanoaniline slightly differs from polyaniline. However, there is a notable shift observed in the case of absorption peaks of poly-2-cyanoaniline.

3.3 X-ray diffraction study

In figure 3, XRD patterns are shown for the polymer sample prepared at room temperature 25 °C by electrochemical method. To study the crystalline behaviour of poly-2-cyanoaniline, finely powdered sample is subjected to wide-angle X-ray diffraction analysis at 25 °C. The XRD patterns of as-synthesized polymer show three distinct peaks at $2\theta = 16.5$, 19.1 and 50.5° . The peaks at 20.1 and 25.5° are characteristically assigned for polyaniline and the peak at $2\theta = 6.4^\circ$ is observed for highly ordered polyaniline chain reported by Lunzy and Banka (2000), Jayakannan *et al* (2005), Li *et al* (2006).

3.4 Scanning electron microscopy

The morphology of as-synthesized polymer was studied by field-emission scanning electron microscopy (FE-SEM). In general, the interfacial and facile polymerization yields nanofibres, dendrites, depending on the dopants used in the polymerization (Huang *et al* 2004; Sheng *et al* 2008). Nanofibres are frequently obtained when interfacial polymerization is carried out using inorganic or organic acids as a dopant. The generally granular morphology is obtained by oxidative chemical polymerization of polyaniline route (Avlyanov *et al* 1995). Here we report a scaffold of needle-like structures having nanorods of ~ 50 – 80 nm dimension observed in SEM images (figures 4a–d) by electropolymerization method. The shape and specific morphology of the polymer due to electrochemical deposition on the copper substrate can be attributed to the ionic interaction between Cu and poly-2-cyanoaniline. The average diameter of nanorods of as-synthesized poly-2-cyanoaniline in HCl medium is ~ 50 – 80 nm. At very low concentration of monomer 10^{-3} M, the morphology of electrochemically synthesized was mainly the scaffold of needle. Low-magnification SEM image of poly-2-cyanoaniline nanostructures shown in figure 4(a) reveals that the polymer is composed of mostly needle-like nanostructures with diameters of 50 – 80 nm and length up to 100 – 200 nm. It is clear that these poly-2-cyanoaniline needles are interconnected to form a compact network structure, rather to exist as isolated nanorods or bundles. The magnified SEM image (figure 4b) shows that poly-2-cyanoaniline nanorods are placed on each other randomly with different orientations. In a magnified SEM image (figure 4c–d), it is interesting that these nanorods comprise dendrites and cactus-like appearances on the surface of each nanorods.

Figure 3. X-ray diffraction of poly-2-cyanoaniline synthesized by electrochemical polymerization.

Figure 4. Scanning electron micrograph (SEM) of poly-2-cyanoaniline film deposited on copper plate: (a) $\times 100$ K magnification, scale bar $100\ \mu\text{m}$, (b) $\times 1$ K magnification, scale bar $10\ \mu\text{m}$, (c) $\times 5$ K magnification, scale bar $1\ \mu\text{m}$ and (d) $\times 20$ K magnification, scale bar $200\ \mu\text{m}$.

3.5 Thermal studies

Thermogravimetric study has been shown by TGA curve (figure 5) of as-synthesized polycyanoaniline prepared by electrochemical method at room temperature. The thermo-

gram of the polymer has been recorded from 0 to $800\ ^\circ\text{C}$ at heating rate of $20\ ^\circ\text{min}^{-1}$ purged with nitrogen gas at a flow of $60\ \text{mL/min}$. It clearly shows two major stages of weight loss below $700\ ^\circ\text{C}$. The first weight-loss step at $\sim 100\ ^\circ\text{C}$ corresponds to the loss of water content, which

amounts to 6–7% weight loss. The second weight-loss step starts at $\sim 500^\circ\text{C}$. The decomposition temperature for poly-2-cyanoaniline, $\sim 500^\circ\text{C}$, is difficult to determine accurately due to residual water. TGA curve has shown that poly-2-cyanoaniline is stable up to 500°C . Above this temperature, the polymer begins to decompose. It is evident from the curve that the maximum weight loss occurs at this stage (attributed to the decomposition of the poly-cyanoaniline main chain). The results are similar to those previously reported and confirm that the polyaniline prepared by facile synthesis at 25°C as reported by Sheng *et al* (2008).

Figure 6 shows the derivative of TGA curves, which clearly indicate two endothermic peaks. The first endothermic peak started nearly at 100°C and the centre deepened at 160°C , which corresponds to evaporation of water molecules stuck inside the polymer backbone and it is in agreement with the results obtained in TGA study. The second endothermic peak indicates the endothermic transition temperature starting $\sim 500^\circ\text{C}$ and centred in the region between 600 and 700°C . Thus, the temperature 500°C is referred to as the decomposition temperature of poly-2-cyanoaniline. These results confirm the TGA studies given in figure 5 and similar to the decomposition of polyaniline reported by Jeanine *et al* (1995).

Figure 5. TGA thermogram of as-synthesized poly-2-cyanoaniline using electrochemical method.

Figure 6. DSC determination of transition temperatures of polycyanoaniline.

3.6 Electrical conductivity

Electrical conductivity of the pressed pellet of salt form of the polymer was determined at room temperature by two-probe measurement method by Keithley 617 electrometer to be $9.1824 \times 10^{-5} \text{ S cm}^{-1}$. The electrical conductivity value may be attributed to conjugated π -electrons and the lone pair of electrons available on nitrogen of amine group attached to rings, which is comparable to the electrical conductivity ca. $4.3 \times 10^{-3} \text{ S cm}^{-1}$ reported for the self-assembled polyaniline nanotubes and nanowires synthesized using surfactants reported by Huang and Kaner (2004), Chiou and Epstein (2005), Nan-Rong *et al* (2007). The lower order of the magnitude of the conductivity may be due to the lower level of doping in the polymer.

4. Conclusions

To summarize, SEM study of electrochemically synthesized poly-2-cyanoaniline reveals that the nanostructures are like uniform rods with diameter 50–80 nm and are elongated up to a length of 100 nm. At high magnification, non-uniform outer surfaces are seen on the nanorods. The electrical conductivity measured by two-probe method is found to be $9.1824 \times 10^{-5} \text{ S/cm}$, which is almost equal to the electrical conductivity of polyaniline reported in the literature. The as-synthesized poly-2-cyanoaniline shows thermal stability up to $\sim 550^\circ\text{C}$ and the stability is higher than the polyaniline.

Acknowledgements

The authors acknowledge the support of Department of Chemistry, AMU, Aligarh, and School of Chemical Science, University Sains Malaysia for providing SEM and XRD facilities. We are also thankful to Qatar University, Doha, Qatar, for funding and supporting the execution of this research.

References

- Avlyanov J K, Josefowicz J Y and MacDiarmid A G 1995 *Synth. Met.* **73** 205
- Cao Y, Smith P and Heeger A 1989 *J. Met.* **32** 263
- Chiou N R and Epstein A 2005 *J. Adv. Mater.* **17** 1679
- He H X, Li C Z and Tao N 2001 *J. Appl. Phys. Lett.* **78** 811
- Huang J X and Kaner R B 2006 *Chem. Commun.* **4** 367
- Huang Jiaxing and Kaner Richard B 2004 *J. Am. Chem. Soc.* **126** 851
- Huang J X, Virji S B, Weiller H and Kaner R B 2003 *J. Am. Chem. Soc.* **125** 314
- Huang W S, Humphrey B D and MacDiarmid A G 1986 *J. Chem. Soc. Faraday Trans.* **82** 2385
- Huang J and Kaner R B 2004 *J. Am. Chem. Soc.* **126** 851

- Jayakannan M, Annu S and Ramalekshmi S 2005 *J. Polym. Sci. Polym. Phys.* **43** 1321
- Jeanine A Conklin, Shu-Chuan Huang, Shiou-Mei Huang, Tianli Wen and Richard B Kaner 1995 *Macromolecules* **28** 6522
- Liu J M and Yang S C 1991 *Chem. Commun.* 1529
- Langer J J, Framski G and Joachimiak R 2001 *Synth. Met.* **121** 1281
- Liu J, Lin Y, Liang L, Voigt J A, Huber D L, Tian Z R, Coker E, Mckenzie B and Mcdermott M J 2003 *J. Chem. Eur. J.* **9** 605
- Liang L, Liu J, Windisch C F, Exarhos G J and Lin Y H 2002 *Angew. Chem. Int. Ed.* **41** 3665
- Li W, Zhu M, Zhang Q and Chen D 2006 *Appl. Phys. Lett.* **89** 103110
- Lunzy W and Banka E 2000 *Macromolecules* **33** 425
- MacDiarmid A G, Jones W E, Norris I D, Gao J, Johnson A T, Pinto N J, Hone J, Han B, Ko F K, Okuzaki H and Llaguno M 2001 *Synth. Met.* **119** 27
- Nan-Rong Chiou, James Lee L and Arthur J Epstein 2007 *Chem. Mater.* **19** 3589
- Palle S R, Sathyanarayana D N and Palaniappan S 2002 *Macromolecules* **35** 4988
- Phillips S D, Yu G and Heeger A 1989 *J. Phys. Rev.* **B39** 10702
- Qiu H J, Wan M X, Matthews B and Dai L M 2001 *Macromolecules* **34** 675
- Shirakawa H, Edwin J, Lois, Macdiarmid A G, Chiang C K and Heeger A 1977 *JCS Chem. Commun.* 578
- Sheng Xu, Du, Cui-Feng Zhou and Yiu Wing Mai 2008 *J. Phys. Chem.* **C112** 19836
- Virji S, Kaner R B and Weiller B H 2006 *J. Phys. Chem.* **B110** 22266
- Virji S, Huang J, Kaner R B and Weiller B H 2004 *Nano Lett.* **4** 491
- Wei Z X, Zhang Z M and Wan M X 2002 *Langmuir* **18** 917
- Wei Z X and Wan M X 2003 *J. Appl. Polym. Sci.* **87** 1297
- Zhang X, Goux W J and Manohar S K 2004 *J. Am. Chem. Soc.* **126** 4502