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Preparation and characterization of chemically synthesized poly(N-methylaniline)

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A B S T R A C T

Poly(N-methylaniline) (PNMA), a electrically conductive derivative of polyaniline was synthesized by chemical polymerization of N-methylaniline (NmANI) using ammoniumpersulfate (APS) as an oxidizing agent and studied by electrical conductivity measurement, UV–vis and FTIR spectroscopy. The observed electrical conductivity was found to have a dependence on some synthesis parameters. The oxidant/monomer molar ratio ~1 and p-toluenesulfonic acid (PTSA)/monomer molar ratio ~4 showed higher values of electrical conductivity for the polymer. The d.c. conductivities of PTSA doped poly(N-methylaniline) have been measured in the temperature range 298–373 K. The conductivity of the samples has been observed to show an increasing trend with increasing temperature. However, on increasing temperature from 298 K to 373 K, the conductivity rise was found to be more for the samples having lower dopant/monomer ratio. The observed d.c. conductivity data was described by Mott's three-dimensional variable range hopping (VRH) model.

1. Introduction

During the last decade, conducting polymers have raised great interest in the world of research due to their various physical, chemical properties and numerous possible applications [1]. The conducting polymers such as polypyrrole, polythiophene, poly(p-phenylene) and polyaniline have commonly been used in scientific and industrial studies and in various applications as rechargeable batteries [2,3], sensors [4–7], diodes, in transistors and microelectronic devices [8]. Among the conducting polymers, polyanilines are considered to be one of the most promising class of organic conducting polymers due to their easy doping/dedoping, good environmental stability, and ease of preparation [9]. A number of papers are available reporting the synthesis of polyaniline using different dopants and its characterization [9–13]. However a major problem related to its successful utilization lies in its poor mechanical properties and processability due to its insoluble nature in common organic solvents. Incorporation of polar functional groups or long and flexible alkyl chains in the polymer backbone is a common technique to prepare polyaniline type polymers, which are soluble in water and/or organic solvents. For example, substituted polyanilines like polytoluidines, polyanisidines, poly(N-methylanilines) and poly(N-ethylanilines) are more soluble in common organic solvents than the unsubstituted polyaniline but exihibit the low conductivity. The conductivity of these polyaniline derivatives can be enhanced by doping them with different protonic acids, which make them conductive as well as soluble in organic solvents [14,15].

During the last 10 years, there have been quite a few reports on N-alkyl substituted polyanilines [16,17] and in particular on poly(N-methylaniline) PNMA [18–20]. Poly(N-methylaniline) is considered to exist in three redox states, namely the fully reduced leucoemeraldine (LE) form, the only conducting emeraldine form (E) and the fully oxidized pernigraniline (PN) form [21]. The molecular structures of three different forms of PNMA are shown in Fig. 1 [22,23]. PNMA, a substituted polyaniline is known to possess better stability to oxidation than polyaniline [24]. Investigating new preparation methods and optimum conditions to obtain polymer is important because it can improve its properties or its synthesis can become time saving and cheaper, which may give rise to its fortuitous new application. In the present work, we report the chemical polymerization of N-methylaniline doped with p-toluenesulfonic acid (PTSA), its characterization by spectroscopic and conductivity measurements.

2. Experimental

N-methylaniline (NmANI) (AR, 99.5%) monomer was purchased from alfa aesar. Ammoniumpersulfate (APS) (Merck), N,N-dimethylformamide (DMF) (alfa aesar), 1-methyl-2-pyrrolidone (NMP) (Merck) and p-toluenesulfonic acid (PTSA) (alfa aesar) were used as received. All the solutions were prepared in de-ionized water having resistivity of ~18 MΩ. The monomer N-methylaniline

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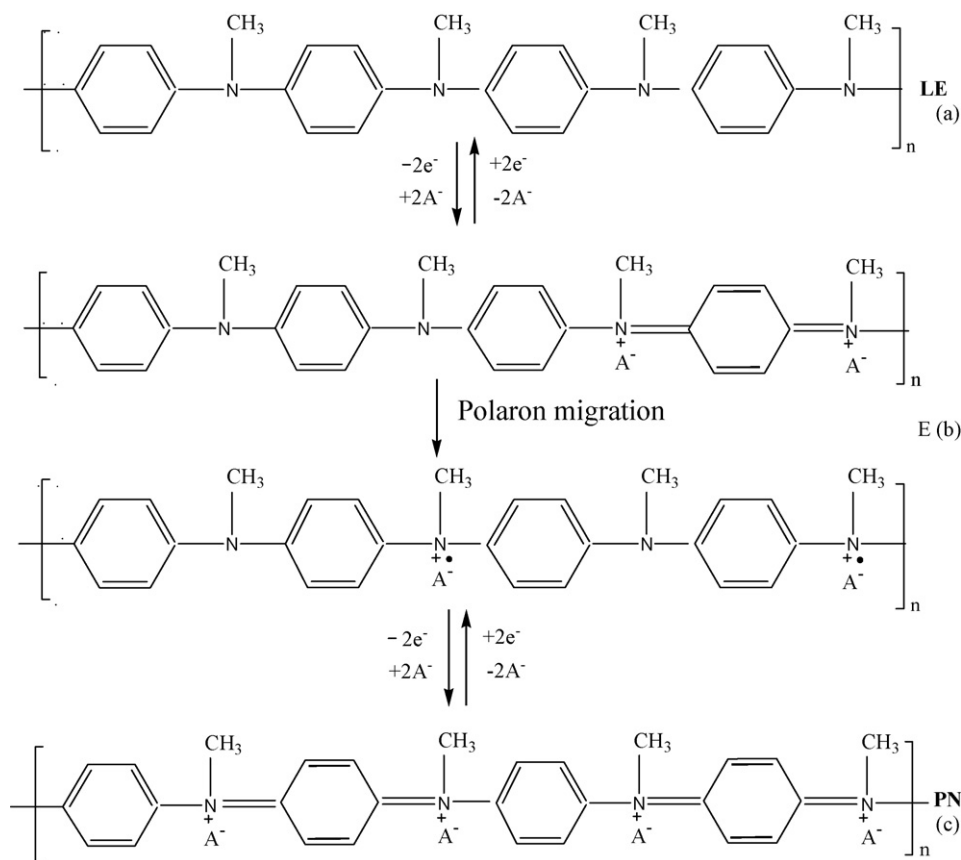
Fig. 1. The scheme shows the structure of different forms of PNMA, (a) leucoemeraldine (LE), (b) emeraldine (E) and (c) pernigraniline (PN). (A⁻ represents the counter anion.)

(0.005 mol) was dissolved in DMF (3 ml) and cooled down to 0–5 °C. It was then slowly added to 50 ml aqueous solution of PTSA (0.02 mol). The polymerization was initiated by the drop wise addition of the precooled oxidant solution containing 0.005 mol of APS dissolved in 50 ml of water. Precooled reactants at 0–5 °C were used, as the reactions involved are exothermic in nature. The polymerization was allowed to proceed in the open ambient for 5 h with continuous stirring. Dark green colored precipitate of the polymer was isolated by filtration, washed with de-ionized water and finally dried at about 45 °C in an oven for 24 h. In order to observe the conductivity of non-conducting PNMA, the obtained powder was treated with ammonia solution for 5 h [25].

UV–vis absorption spectra of the polymer solution in NMP were recorded using UV-240 Shimadzu spectrophotometer in the wavelength range of 200–1000 nm. The FTIR spectra of the polymers were taken using a Perkin-Elmer Spectrum 2000 spectrophotometer between 400 cm⁻¹ and 4000 cm⁻¹, for which, the samples were prepared in the pellet form using spectroscopic grade KBr powder. Conductivity measurements were performed by standard four-point technique. Dry powdered samples were made into pellets of ~10 mm diameter using a steel die in a hydraulic press. For conductivity measurements, Keithley source meter (model 2400) and Keithley electrometer (model 6514) were used for sourcing current and measuring voltage, respectively. Temperature dependent electrical conductivity of polymer samples was measured by passing a constant current from the source meter and measuring the voltage using electrometer at different temperatures.

The conductivity (σ) was calculated using the relation [26]

$$\sigma = \frac{\ln 2}{\pi d} \left(\frac{I}{V} \right) \tag{1}$$

where d is the thickness of the pellet.

3. Results and discussion

The conductivity and yield of poly(N-methylaniline) as a function of oxidant to monomer molar ratio is represented in Fig. 2.

The conductivity of the polymer increases as the ratio increases and becomes maximum for oxidant to monomer ratio of unity and start decreasing as the ratio is further increased beyond unity. Thus at optimum molar ratio of unity, the conductivity is maximum. It is reported in the literature that excess of oxidizing agent causes shorter conjugation length which decreases the electrical conductivity [27]. At low concentration of oxidant, an under oxidation of monomer takes place which produces polymer in an oxidation state lower than that of the emeraldine state. The yield of the polymer obtained after synthesis is also dependent on the oxidant to monomer molar ratio. As shown in Fig. 2, the yield increases at
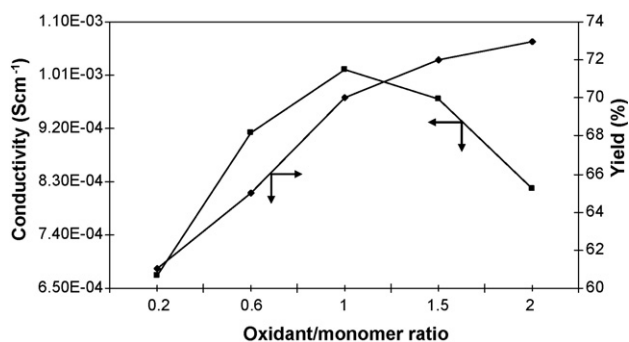

Fig. 2. Dependence of electrical conductivity and yield on the oxidant to monomer ratio.