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Purification and characterisation of poly(2-methoxyaniline-5-sulfonic acid)

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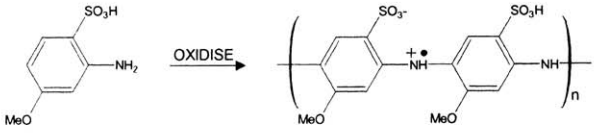
Abstract

The chemical oxidative synthesis of water soluble sulfonated polyaniline, poly (2-methoxy aniline-5-sulfonic acid) (PMAS) has been shown to result in an impure mixture of polymeric isomers. A tangential cross flow dialysis system has been developed to rapidly and efficiently separate high molecular weight polymer from low molecular weight oligomers, and results compared to conventional tubing dialysis. Characterisation of the purified polymer fractions has been made using UV-vis spectroscopy, gel permeation chromatography, cyclic voltammetry, conductivity measurement and thermal analysis. Results indicate that while the conventional dialysis tubing is not able to separate the mixture of high and low molecular weight materials efficiently, the cross flow dialysis is able to separate them more rapidly and efficiently. Purified high molecular weight PMAS exhibited enhanced electrical conductivity and significant property changes with respect to tubing dialysed PMAS. The pure PMAS, which is the high molecular weight species (Mw 10157 Da) obtained from the cross flow dialysis, has a twofold higher conductivity than the impure PMAS dialysed by the conventional method.

Keywords: conducting polymer, water-soluble, self-doping.

1. Introduction

Functionalized polyaniline has been the area of interest due to its unique electrochemical properties, water solubility, improved processability and potential industrial applications. Sulfonated polyaniline (SPAN) was the first reported water-soluble conducting derivative of polyaniline [1]. Substitution of methoxy groups onto the aniline ring has improved the properties of SPAN [2]. Poly (2-methoxy aniline 5-sulfonic acid), PMAS, has been synthesised by chemical polymerization of 2-methoxyaniline-5-sulfonic acid (MAS) under basic conditions (pyridine) [2] and by electrochemical oxidation of MAS using NH_4OH solution as electrolyte [3,4]. Post-synthesis purification of the polymer and optimization of different reaction variables during polymerization to produce the pure high molecular weight of PMAS has been a major synthetic challenge.



MAS PMAS

In this work, PMAS has been produced by chemical polymerization of MAS in NH_4OH solution using ammonium per sulfate as oxidant. This process leads to a mixture of high molecular weight (HMWt) polymer *ca.* 10KDa and low molecular weight (LMWt) oligomers, less than 2.5KDa which are typical products of both chemical and electrochemical synthesis methods. Due to similar solubility properties of these two fractions it has proven difficult to separate the oligomers from the polymer at the gram scale via conventional dialysis or chromatographic techniques such as GPC. In this work, we have developed an effective procedure for the separation and purification of these fractions using a tangential cross flow dialysis membrane system. Characterisation of these purified fractions with respect to conventionally dialysed PMAS has been made by GPC, UV-vis, cyclic voltammetry (CV) and electrical conductivity testing.

2. Experimental

2.1 Materials

MAS was provided by Mitsubishi Rayon, Japan and purified by acid base crystallization before polymerization. All reagents used were of analytical grade and all solutions were prepared in Milli-Q water (18 MΩ cm).

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2.2 Monomer Purification

20g of the crude MAS was dissolved in 200 ml water by adding 28% ammonia solution dropwise. After filtering, solution pH was dropped to less than 1 by adding concentrated HCl. The precipitate was filtered and washed by 200 ml of a 70:30 mixture of methanol/water and dried in oven 50°C for 24 h with a yield of 60% w/w.

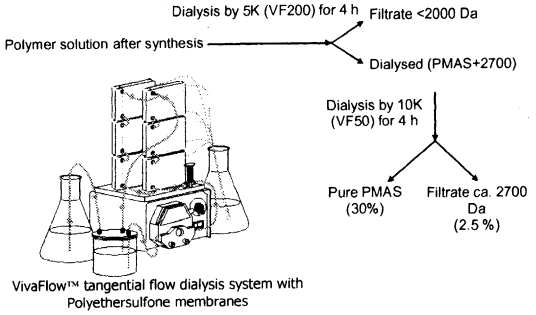
2.3 PMAS synthesis

PMAS was chemically synthesised by reacting a 50 mL 0.5M $MAS_{(aq)}$ monomer and 0.5M $NH_4OH_{(aq)}$ with a 25 mL 1.25 M $(NH_4)_2S_2O_{8(aq)}$ was added drop wise over 30 min at 16-18 °C for 4hr while. The solution was then left overnight to complete the reaction, and then dialysed.

2.4 Dialysis procedure

In order to purify the polymer and remove the residual monomer, oxidant and oligomers, two different membrane systems were used:

1. Cellulose dialysis tubing with 12KDa molecular weight cut off (MWCO), Sigma. Dialysis was performed against Milli-Q water 3 times over 2 hours and finally 24 hours. The dialysed solution (inside the tubing) was evaporated under fume hood for later analysis.
2. VivaFlow™ 50 and 200 polyethersulfone (PES) membranes with 5 and 10KDa MWCO by Sartorius Group. Prior to purification the polymerization solution was diluted by 3 times with Milli-Q water and dialysed by flowing through two 5KDa MWCO VivaFlow™ 200 membranes in series at 400 mL/min for 4 hours. The retained polymer was then flowed through two 10KDa MWCO VivaFlow™ 50 membranes in series over 4 hours by a Masterflex peristaltic pump (model 7518-00), Scheme 1.



Scheme 1 Tangential flow dialysis system.

The dialysed solution from the 10KDa membrane (pure polymer) was concentrated further and dried under fume Hood. The filtrate solution of 10KDa membrane (brown coloured fraction) was concentrated using the 5K membrane and evaporated. During this concentration phase of the brown fraction, a filtrate solution (pink coloured fraction) was isolated and also concentrated. The retained polymer and oligomer solids were dried in vacuum oven at 50 °C before being used for characterisation.

2.5 Characterisation

Molecular weight was determined using a Waters GPC system with Millenium software using Waters Ultrahydrogel 125 and 250 columns in series held at 35°C in a column oven with a mobile phase consisting of 20% v/v methanol and 80% v/v aqueous solution of 0.2M $NaNO_3$ and 0.01M disodium hydrogen phosphate buffer (pH 9) at a 0.8mL/min flow rate. Chromatograms were recorded using a photodiode array detector, Waters 996 PDA. All molecular weight calibrations were determined via relative calibration against polystyrene sulfonate standards, Polymer Laboratories. Throughout the text the peak molecular weight, M_p, has been quoted for clarity. Full characterisation of each fraction can be found in Table 1. UV-vis spectra were recorded by a Shimadzu UV-1601 UV-vis spectrophotometer. Thermogravimetry was carried out using a DTA/TGA SETARAM 92B thermoanalyzer. Temperature was increased from 50 °C to 450 °C at a heating rate of 10 °C per minute under nitrogen atmosphere. Cyclic voltammetry (CV) of 0.5 mg/ml PMAS solution was carried out in a three electrode cell using a glassy carbon working electrode with a platinum mesh and Ag/AgCl (3M NaCl) auxiliary and reference electrode, respectively. CV's were recorded using a Bioanalytical Systems (BAS) CV-27 voltammograph, interfaced with ADInstruments/4e (ADI/4e) MacLab analogue/digital converter to a computer. The potential was swept between –0.2 and +0.9 V, using a sweep rate of 50 mV/s. Conductivity measurements were performed on dried films of 10μm thickness (obtained by air evaporative casting using a glass slide substrate) on a JANDEL resistivity system (model RM2) using linear four-point probe.

3. Results and Discussion

In order to establish a comparison between the new and conventional dialysis system approaches the molecular weight distribution of the dialysed polymer solutions were obtained by GPC analysis. The chromatogram obtained for the polymer solution dialysed using dialysis tubing showed two peaks (figure 1). The fist peak at retention time of *ca.* 15 minutes was attributed to HMWt polymer (8-9 KDa) exhibiting two absorption maxima at *ca.* 470 and 700nm (z-axis) which are the typical π-π* and polaron transitions compact coil conformation form of PMAS in the GPC buffer at pH 9 [6]. The second peak at 17 minutes attributed to LMWt oligomers (2-3 K Da) is significantly different in that no second peak at *ca.* 700 nm, namely the polaron band, was observed. The 12 KDa MWCO dialysis tubing successfully removed the residual monomer, oxidant and pink coloured fraction containing oligomers less than *ca.* 1KDa, but was unable to eliminate the 2-3 K Da fraction.

GPC analysis indicated that cross flow membrane removed the LMWt fraction effectively after 8 hours (Figure 2). Using the procedure described above, the

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