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Chemical modification of polysulfone: anionic synthesis of dipyridyl functionalized polysulfone

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Abstract

A new method for the synthesis of dipyridyl functionalized polysulfone is described. The functionalization process involves the formation of lithiated polysulfone from polysulfone (**1**) and subsequent reaction with 2,2′-vinylidenedipyridine (**2**) in tetrahydrofuran at −78°C under argon atmosphere. The dipyridyl functionalized polysulfone (**3**) was evaluated for the chelation of trace heavy metal ions such as copper and nickel in aqueous medium. The dipyridyl functionalized polysulfone shows better complexing affinity for nickel ions at specific concentrations of test solutions. Quaternization reactions of dipyridyl functionalized polysulfone with dimethyl sulfate in the presence of perchloric acid quantitatively affords the corresponding polymeric pyridinium perchlorate derivative (**4**). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polysulfone; Dipyridyl functionalized polysulfone; Quaternization

1. Introduction

Polysulfone is an engineering thermoplastic widely used as precursor material for the fabrication of membranes for applications in the area of liquid and gas separations [1–14]. Commercial applications include carbon dioxide stripping from natural gas streams and the production of high purity nitrogen from air. In addition, polysulfones are used as ion exchange membranes in electromembrane processes, such as electrodialysis, and polymer electrolyte membrane electrolysis [5–8]. The chemical and physical characteristics of polysulfone such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance makes polysulfone the material of choice for use as membrane substrates [1–14] However, the hydrophobic nature of polysulfone inhibits its application as polymeric substrates in membrane separation technology and chelation of heavy metals in hydrophilic environments. Thus, the synthesis and applications of new, reactive functionalized polymers has been the focus of industrial and academic research to meet the increased industrial need for hydrophilic polysulfones.

Several reviews on the chemical modification of polysulfone by different mechanisms for the introduction of functional groups onto the polysulfone backbone have been reported [1–16]. Anionic polymerization methodology provides the most efficient route to the synthesis of polymers with controlled molecular weight, molecular weight distribution, chain-end and in-chain functionality and morphology [17–19]. The general method for the introduction of functional groups onto the polysulfone backbone by anionic methods involves the formation of the lithiated polysulfone precursor followed by the addition of an appropriate electrophile to afford the corresponding functionalized polysulfone derivative. For example, the quantitative lithiation of polysulfone or the corresponding brominated polysulfone precursor and subsequent addition of methyl iodide produced the methyl substituted polysulfone [1–2] Guiver and coworkers [2] reported on the formation of carboxylated polysulfone by the direct lithiation of polysulfone followed by quenching the lithiated intermediate with carbon dioxide to afford carboxylated polysulfones in quantitative yields. Recently, a quantitative and regiospecific method for the synthesis of primary amine functionalized polysulfones via novel azide intermediates has been developed [4–5]. The process involves the regioselective lithiation of polysulfone and the lithiated intermediates converted quantitatively to azides by treatment with tosyl azide. The azide functionalized polysulfone was subsequently reduced to the primary amine derivative with sodium borohydride. Kerres and coworkers [8] reported a new process for the sulfonation of polysulfones by reacting lithiated polysulfone with sulfur dioxide followed by

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oxidation of the resulting polymeric sulfinate intermediate. Membranes made from the sulfonated polysulfone show good conductivity, permselectivity and hydrolytic stability in acid and water at elevated temperature.

The synthesis of functionalized polymers containing metal-ion chelating ligands for the selective and quantitative chelation of heavy metals has been extensively applied in the metallurgy and environmental and water purification fields [1–16]. Kan and coworkers [9] prepared functionalized polysulfone by immobilizing metal-ion chelating ligands such as 8-hydroxyquinoline, 1-(2-pyridylazo)-2-naphthol and 4-(2-pyridylazo)resorcinol onto the polysulfone backbone by diazo coupling with primary amine functionalized polysulfone precursor. The 8-hydroxyquinoline modified polysulfone showed the greatest chelating efficiency to heavy metal ions as well as greater chemical stability to alkaline environments. Also, the polymers functionalized with quaternary ammonium and pyridinium functionalities are effective for chelating heavy metals as well as for the removal of viruses from water by filtration [15–16].

In this study, the novel synthesis of dipyridyl functionalized polysulfone by quantitative lithiation of polysulfone followed by the reaction with 2,2′-vinylidenedipyridine is described. The functionalized polymer has been evaluated for its efficiency in chelation of trace amounts of heavy metal ions from aqueous solution. In addition, the dipyridyl functionalized polysulfone undergoes quaternization reactions with dimethyl sulfate in the presence of perchloric acid to form the corresponding dipyridinium perchlorate polysulfone derivative.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF) (Aldrich Chemical Company) was carefully purified as described previously [20]. *n*-Butyl lithium (Aldrich Chemical Company) was used as received. Polysulfone (**1**) was synthesized by the condensation polymerization of bisphenol A and bis(4-fluorophenyl)-sulfone according to the procedure of Matyjaszewski and coworkers [21], with modifications.

2.2. Characterization

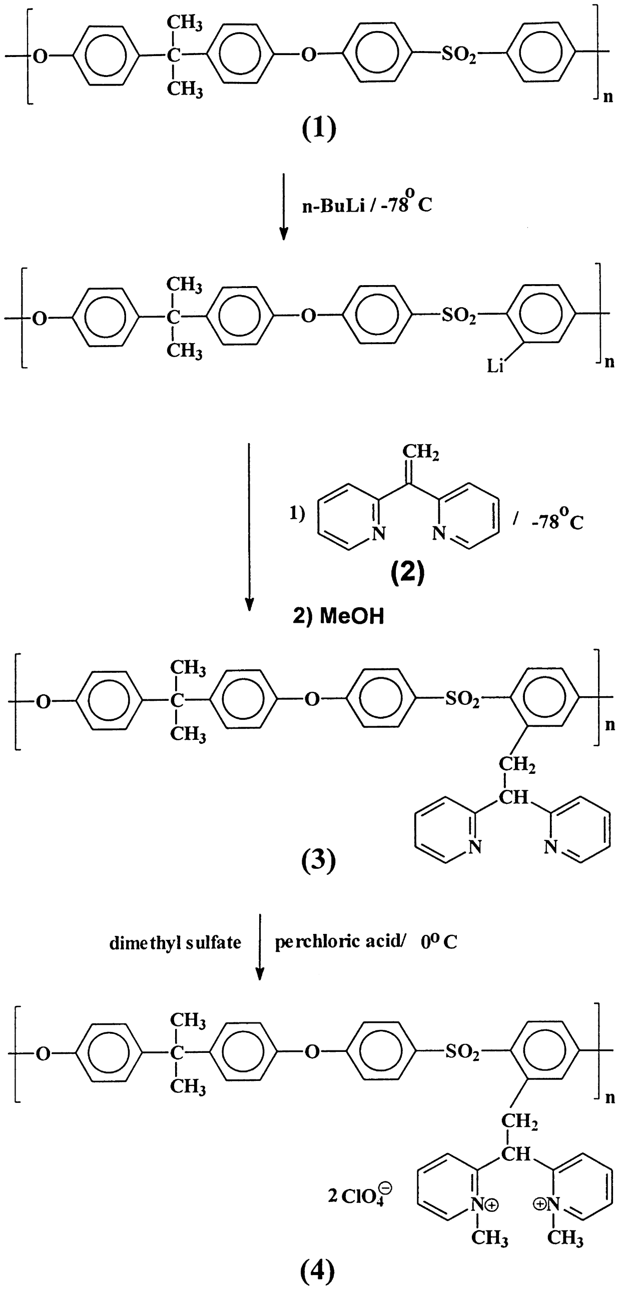
Size exclusion chromatographic analysis of polymers was utilized for the determination of the molecular weights and molecular weight distributions of polymers and was performed at a flow rate of 1 ml/min in THF at 30°C using a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5 m, 500 Å pore size, 1–15 K MW range, $300 \times 7.8\ \mathrm{mm}^2$) in series with Refractive Index and Dual Angle Laser Light Scattering Detectors, after calibration with standard polystyrene samples (Aldrich Chemical Company), where applicable. ^{1}H NMR ($CDCl_3$ or d_6-DMSO) spectra were recorded on a Bruker 300 MHz spectrometer. Thin layer chromatographic analysis were performed on silica gel plate (Merck, Silica Gel 60 F 254). Infrared spectra were recorded on a Perkin–Elmer 883 Infrared Spectrophotometer. Atomic Absorption Spectrophotometric analysis was performed on a Varian AA: Series 1275 Spectrophotometer equipped with CRA-90 carbon rod atomizer and Cu (3.5 mA) and Ni (3.5 mA) lamps.

2.3. The synthesis of 2,2′-vinylidenedipyridine (2)

2,2′-Vinylidenedipyridine was synthesized according to the procedure outlined by Eckhard and Summers [22], with modifications. Dimethyl sulfoxide (Aldrich Chemical Company) was purified under an argon atmosphere by distillation from calcium hydride. Under an argon atmosphere, sodium hydride (1.3 g, 0.054 mol, Aldrich Chemical Company) was added to freshly distilled dimethyl sulfoxide (50 ml). The reaction was heated to 65–70°C. A yellow–green colour was observed with the evolution of gases (hydrogen gas). The reaction mixture was allowed to stir for 90 min at 68°C. The reaction flask was cooled in an ice bath, followed by the addition of methyltriphenylphosphonium bromide (19.3 g, 0,054 mol, Aldrich Chemical Company) in dimethyl sulfoxide (100 ml). Immediately after the addition, a green–yellow colour was observed in the reaction flask. The reaction mixture allowed to stir at 25°C for 25 min. Upon the addition of di-2-pyridyl ketone (10 g, 0.054 mol, Aldrich Chemical Company) in dimethyl sulfoxide (100 ml), the reaction mixture immediately turned dark red and eventually brown–red in colour with an increase in temperature to 45°C. The brown–red mixture was allowed to stir at 60°C for 45 min. Excess dimethyl sulfoxide was removed by vacuum distillation at 98°C. The residue was dissolved in 10% hydrochloric acid and repeatedly extracted with chloroform to remove triphenylphosphine oxide. The aqueous layer was made alkaline and then extracted with chloroform. The red–brown chloroform solution was washed with water and dried with magnesium sulfate. The chloroform solution was concentrated on a rotary evaporator to afford a brown oil. The brown oil was purified by silica gel column chromatography with acetonitrile as mobile phase to afford 4.26 g (41%) of pure 2,2′-vinylidenedipyridine. ^{1}H NMR ($CDCl_3$): d 6.05 [s, 2H, CH_2]; 6.97–7.70 [m, 6H, aromatic H]; 8.50–8.60 ppm [d, 2H, aromatic H]. TLC (Silica Gel $60F_{254}$, Merck): R_f (acetonitrile) = 0.35. IR (oil): 1634 cm^{-1} (C=N).

2.4. The synthesis of dipyridyl functionalized polysulfone (3)

In a typical procedure, under an argon atmosphere, polysulfone (1 g, 0.0023 mol, $M_n = 4.1 \times 10^3$ g/mol; $M_w/M_n = 1.52$) was transferred into a clean, dry 250 ml round bottomed flask. Freshly distilled THF (40 ml) was added to the flask to dissolve the polymer. The reaction mixture



Scheme 1. Synthesis of dipyridyl functionalized polysulfone (**3**) and pyridinium perchlorate functionalized polysulfone (**4**).

was cooled to −78°C using an acetone–liquid nitrogen bath. Lithiation of polysulfone was effected by the addition of *n*-butyllithium (2.2 ml of 1.6 M solution in hexane, Aldrich Chemical Company) to the reaction mixture. The reaction mixture was stirred for 2 h at −78°C to effect complete metalation.

2,2′-Vinylidenedipyridine (1.03 g, 0.0023 mol) in THF (20 ml) was then added to the viscous deep red lithiated polymer via a cannula, whereupon the reaction mixture turned deep orange–brown in colour. The reaction mixture was allowed to stir at −78°C for 4 h. The colour and the viscosity of the reaction mixture remained unchanged. Upon quenching the reaction mixture with methanol, a homogenous orange solution was obtained. The mixture was concentrated on a rotary evaporator and the dipyridyl functionalized polysulfone was precipitated in excess methanol, filtered off and vacuum dried at 120°C. ^{1}H NMR ($CDCl_3$): δ 3.78–3.91 [broad m, 2H, CH_2]; 4.68–4.85 [broad m, 1H, CH]; 6.43–8.62 ppm [d, 2H, aromatic H]. IR (film): 1634 cm^{-1} (C=N).

2.5. Quaternization of dipyridyl functionalized polysulfone

In a typical procedure, dimethyl sulphate (5 ml) was added to a solution of dipyridyl functionalized polysulfone (0.15 g) in THF (1.5 ml). The reaction mixture turned from light brown to a yellow–white cloudy mixture. The reaction mixture was stirred at room temperature for 5 min. Upon the addition of concentrated perchloric acid (5 ml), a white solid was formed. The mixture was added into excess ethyl acetate and the precipitate was filtered off and vacuum dried at 120°C to form the corresponding dipyridinium perchlorate functionalized polysulfone (**4**).

^{1}H NMR ($CDCl_3$): δ 3.60–3.81 [broad m, 2H, CH_2]; 4.15 [s, 6H, $2\times CH_3$]; 4.78–5.10 [broad m, 1H, CH]; 6.19–8.79 ppm [m, aromatic H's].

2.6. Evaluation of chelation efficiency of dipyridyl functionalized polysulfone: Adsorption of metal ions to polymers

In a typical procedure, copper (II) ion solutions in water with concentrations ranging between 5 and 20 mmol at room temperature were prepared. A column (Tygon tubing; 4 mm i.d. 50 mm in length) packed with finely ground dipyridyl functionalized polysulfone (100 mg) was prepared and coupled to a peristaltic pump (Gilson Minipulse 2). An aliquot of the Cu (II) solution (30 ml) was passed through the column at a flow rate of 0.2 ml per minute and the column effluent was collected to measure the non-retained fraction. After each aliquot of the test solution was passed through the column, the column was flushed at a flow rate of 0.2 ml per minute successively with distilled water (30 ml), 1% hydrochloric acid (30 ml) and deionized water. Atomic absorption spectroscopic measurements were performed to determine the concentration of heavy metal ions in the non-retained effluent as well as the acid eluent and compared to the concentration of metal ions in the feed. Similar reactions were conducted for the analysis of nickel (II) ions.

3. Results and discussion

3.1. Synthesis of 2,2′-vinylidenedipyridine (**2**)

The reaction of lithiated polysulfone with the 2,2′-vinylidenedipyridine was utilized to effect the incorporation of

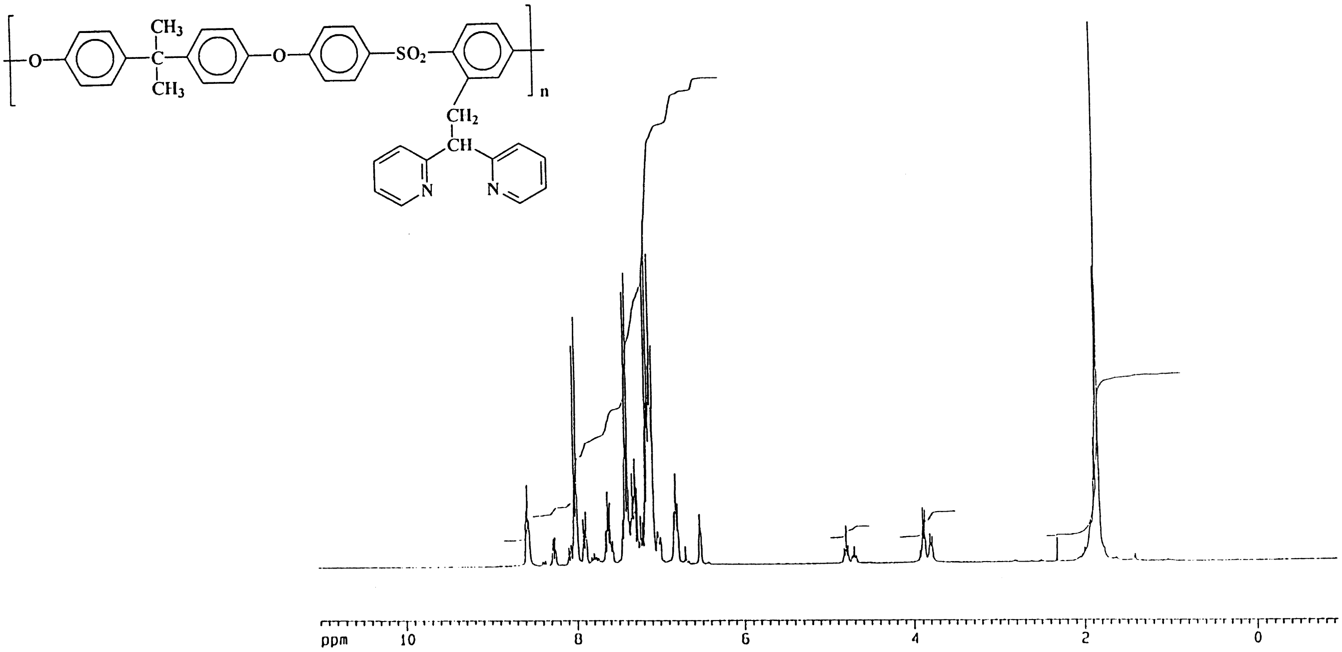


Fig. 1. ^{1}H NMR ($CDCl_3$) spectrum of dipyridyl functionalized polysulfone (**3**).

dipyridyl units onto the polysulfone backbone. A 41% yield of 2,2′-vinylidenedipyridine was obtained by the classical Wittig reaction of di-2-pyridyl ketone with the ylide, an intermediate which was generated from the reaction of sodium hydride and methyltriphenylphosphonium bromide in dimethyl sulfoxide. The ^{1}H NMR spectrum of 2,2′-vinylidenedipyridine shows a singlet at $\delta = 6.05$ which is attributed to the resonance of alkene protons, as well as a multiplet between $\delta = 6.05$ and 8.60 due to the chemical shifts of the aromatic protons of the pyridyl rings. The structure of the 2,2′-vinylidenedipyridine was also confirmed by IR spectral data by the presence of a strong C=N absorption frequency of the pyridyl groups at 1634 cm^{-1}.

3.2. Functionalization of polysulfone with 2,2′-vinylidenedipyridine

The reaction of living polymeric carbanions with 2,2′-vinylidenedipyridine provides an efficient functionalization method for the synthesis of pyridyl functionalized polymers [23]. The functionalization of polysulfone (**1**) with (**2**) involves two steps: (a) the regiospecific lithiation of polysulfone with *n*-butyl lithium at low temperature; and (b) the reaction of lithiated polysulfone with (**2**) at low temperature. Initial results of the reaction of lithiated polysulfone with stoichiometric amounts of (**2**) in dry THF at 0°C produced low yields of functionalized polysulfone, with concomitant formation of crosslinked material. At 0°C, precipitation of the lithiated polysulfone is observed, possibly due to aggregation of lithiated species and intermolecular rearrangement reactions [1–2]. The most efficient functionalization reaction was effected by the treatment of lithiated polysulfone with stoichiometric amounts of (**2**) in THF at −78°C to afford the corresponding dipyridyl functionalized polysulfone (**3**) with degree of functionalization of 45%, as determined by nuclear magnetic resonance spectroscopy (Scheme 1). The presence of the lithiated polysulfone carbanions was manifested by the initial formation of a green–brown colour and then formation of a red–brown homogenous, viscous solution. Upon the addition of (**2**), the colour of the reaction mixture immediately changed to brown orange. Upon quenching the reaction mixture with methanol, the functionalized polysulfone was precipitated in methanol, filtered off and vacuum dried. The ^{1}H NMR spectrum (Fig. 1) for dipyridyl functionalized polysulfone (**3**) exhibits resonances at $\delta = 3.78$ and 4.65 due to the presence of CH_2 and CH proton resonances of the functionalizing agent, respectively, indicating the incorporation of the functionalizing agent onto the polysulfone backbone. Furthermore, the resonances between $\delta = 6.3$ and 6.7 and 7.4–7.8 and 8.1–8.4 are attributed to the aromatic proton resonances of the pyridyl groups. These resonances are absent in the proton NMR spectrum of unfunctionalized polysulfone (**1**). FTIR analysis shows the presence of an absorption band at 1634 cm^{-1}, which is characteristic of the C=N stretching mode of the pyridine group [22]. This absorption band is absent in the FTIR spectrum of unfunctionalized polysulfone (**1**).

3.3. Quaternization of dipyridyl functionalized polysulfone (3): synthesis of pyridinium perchlorate functionalized polysulfone (4)

The dipyridyl functionalized polysulfone (**3**) was subjected to process of quaternization by the reaction of dimethyl sulfate in the presence of perchloric acid

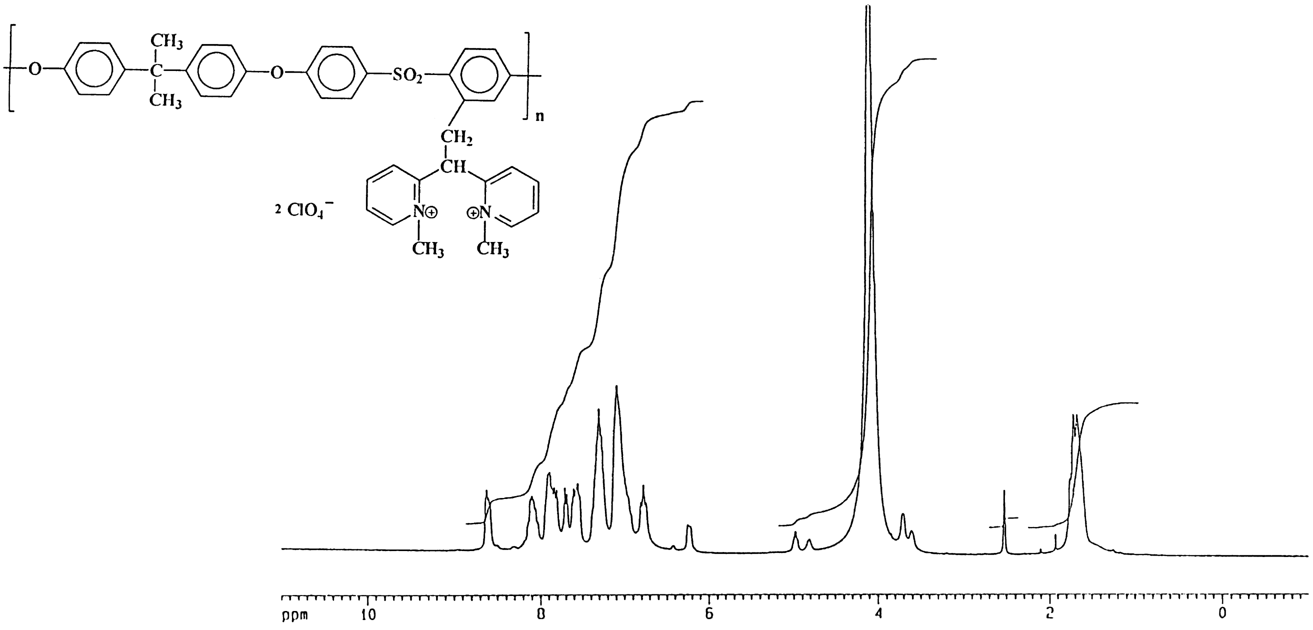


Fig. 2. ^{1}H NMR (d_6-DMSO) spectrum of pyridinium perchlorate functionalized polysulfone (**4**).

(Scheme 1). The pyridinium perchlorate functionalized polysulfone (**4**) was precipitated in ethyl acetate, filtered off and vacuum dried. The ^{1}H NMR (d_6-DMSO) spectrum of (**4**) exhibits a strong, broad resonance at $\delta = 4.15$, which corresponds to the presence of the *N*-methyl protons of the *N*-methyl pyridinium groups (Fig. 2). The success of the quaternization reaction confirms the presence of the dipyridyl groups on the polysulfone backbone.

3.4. Chelation of heavy metals by polysulfone (1) and dipyridyl functionalized polysulfone (3)

Finely ground powders of polysulfone (**1**) and dipyridyl functionalized polysulfone (**3**) were packed into columns and analysed for their ability to complex with heavy metal ions. The concentration of separate copper and nickel ion solutions ranged between 5 and 20 mmol in distilled water. In the analysis using unfunctionalized polysulfone (**1**) as substrate, complete recovery of the metal ions, after passage through the column, was observed. With the functionalized polysulfone (**3**) as substrate, the heavy metal ions were retained due to complexing with the pendant dipyridyl groups on the polysulfone backbone. The metal ions were flushed from the column with an acidic solution and subjected to Atomic Absorption Spectroscopic measurements. Fig. 3 shows the chelating behaviour of dipyridyl functionalized polysulfone (**3**) when treated with different standard concentrations of solutions of copper and nickel ions, respectively. Results show that the uptake of heavy metal ions increases with increase in the concentration of the standard solutions. In addition, the dipyridyl functionalized polysulfone (**3**) shows better complexing affinity for nickel ions at low concentrations of test solutions. However, higher chelation efficiency for copper ions is observed at higher concentrations.

4. Conclusion

The functionalization reaction of lithiated polysulfone with 2,2′-vinylidenedipyridine produces the corresponding dipyridyl functionalized polysulfone, with the degree of functionalization of 45%. The dipyridyl functionalized polysulfone powder shows good chelating efficiency to heavy metal ions such as copper and nickel. The quantitative quaternization reaction is effected by the addition of

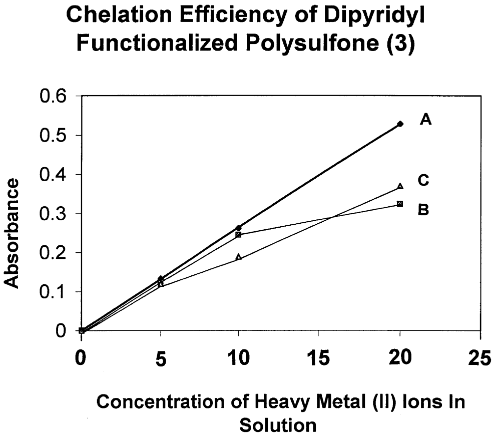


Fig. 3. Plot of absorbance vs concentration for the trace metal analysis of heavy metal (II) ions in aqueous solution for: (A) unfunctionalized polysulfone (**1**); (B) Chelation of copper (II) ions by dipyridyl functionalized polysulfone (**3**); and (C) Chelation of nickel (II) ions by dipyridyl functionalized polysulfone (**3**).

dimethyl sulfate to dipyridyl functionalized polysulfone precursor in the presence of perchloric acid to afford the corresponding polymeric pyridinium salt derivative.

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