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Synthesis, characterization and cyclic voltammetric study of copper(II) and nickel(II) polymer chelates

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ABSTRACT

Graft copolymers based on dextran (Dx) and 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) were synthesized by free radical initiated solution polymerization technique using ceric ammonium nitrate as initiator. These graft copolymers were used to prepare Cu(II) and Ni(II) chelates by reactions with Cu(II) and Ni(II) metal ions respectively. Graft copolymer and metal chelates were characterized by elemental analysis, intrinsic viscosity, FT-IR, scanning electron microscopy (SEM), atomic force microscopy (AFM), thermogravimetric analysis (TGA) and powder X-ray diffraction (XRD). Elemental analysis, intrinsic viscosity and FT-IR studies revealed the incorporation of metal ions to form metal chelates. SEM studies showed the change in morphology due to metal incorporation. From AFM studies it was observed that there was increase in Root mean square (RMS) roughness values in case of metal complexes. Metal chelates were observed to be thermally more stable than graft copolymer from TGA. UV–vis spectroscopy study revealed increase in absorbance values and cyclic voltammetric (CV) studies showed more than tenfold increase in redox current due to formation of Cu(II) and Ni(II) metal chelates. The binding constants of each complex determined by using UV–visible spectroscopy revealed that Cu(II) has more binding ability than Ni(II).

1. Introduction

Grafting is one of the most effective methods for modifying structure and properties of natural polymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides. Synthesis of grafted polymers essentially involves free radical mechanism (Buwalda, Dijkstra, & Feijen, 2012). There is growing interest in metal-containing polymer systems as they constitute a broad class of easily processable materials with unique and valuable properties (Pfister & Fraser, 2006). Polymer systems with metal centres may find use as artificial enzymes, imaging agents, macromolecular catalysts, probes, sensors, and stimuli-responsive materials (Kaliyappan, Swaminathan, & Kannan, 1996). Many biomedical applications are found by the incorporation of metal ions into polymers; which can enhance bioavailability, circulation time, solubility, decrease toxicity, and serve as a platform for multifunctional systems incorporating drug loading, targeting, imaging, and degradation capabilities (Bachelder, Beaudette, Broaders, Dashe, & Freíchet, 2008; Bajgai et al., 2009).

Dextran (Dx) $(C_6H_{10}O_5)_n$ is the generic term for a family of neutral water soluble polysaccharides consisting (95%) of α-(1 → 6) linked D-glucose main chain with varying branches, and 5% branches arising from α-(1 → 2), α-(1 → 3), and α-(1 → 4) glycosidic linkages. In our present work the choice of dextran as the backbone polysaccharide for grafting relies on several aspects. Firstly, dextran of various molecular weights is commercially available. Secondly, the degree of branching of dextran can be as low as 0.5%, making it ideal molecular model for scientific studies. Further, dextran possesses high water solubility, stability under mild acid and basic conditions, and it contains a large number of hydroxyl groups for conjugation (Raynaud et al., 2008). It has common solubility in water and dipolar aprotic solvents. It is biocompatible and biodegradable and can lead to biopolymer derivatives with balanced hydrophobic/hydrophilic character (Krishnamoorthi, Mal, & Singh, 2007; Kutsevol, Guenet, Melnik,

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Sarazin, & Rochas, 2006). Dextran has been successfully used in the medical and biomedical fields for more than four decades. Dextran graft copolymers are also used in stabilizing nanoparticles and simultaneously find their application in removal or degradation of environmental pollutants (Rastogi, Ganesan, & Krishnamoorthi, 2012a). 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) is a relatively strong acid that has a wide variety of applications including foam stabilizers, packaging films, photographic materials, water absorbents, ion-exchange voltammetry and in electrocatalysis (Adhikary & Krishnamoorthi, 2012; Rastogi, Ganesan, & Krishnamoorthi, 2012b; Rastogi, Krishnamoorthi, & Ganesan, 2012; Rastogi, Ganesan, & Krishnamoorthi, 2014). Copolymers of AMPS with ethylene dimethacrylate have been used to make contact lenses and poly (AMPS-graft-styrene) gives self-reinforced hydrogels (Durmaz & Okay, 2000; Qiao, Hamaya, & Okada, 2005; Rosa, Bordado, & Casquilho, 2003; Song, Zhang, Ma, Wang, & Yang, 2007; Zhang & Easteal, 2003). Copolymers of itaconic acid (IA) with (AMPS) have been prepared by free radical polymerization in N,N-dimethylformamide at 70 °C. Cu(II) and Ni(II) metal chelates of these copolymers were also prepared (Coskun, Soykan, & Delibas, 2006; Miguel, Catalina, & Peinado, 2008; Nanjundan, Selvamalar, & Jayakumar, 2004; Soykan, Coskun, & Kirbag, 2007).

The present article reports the grafting of dextran with poly 2-acrylamido-2-methyl-1-propane sulphonic acid (PAMPS). Their metal chelates with Cu(II) and Ni(II) [(Dx-g-PAMPS)-Cu(II) and (Dx-g-PAMPS)-Ni(II)] have not been reported so far. The graft copolymer (Dx-g-PAMPS), its Cu(II) and Ni(II) chelates have been characterized by elemental analysis, FT-IR, scanning electron microscopy, thermogravimetric analysis and powder X-ray diffraction studies. The UV–vis spectroscopy and cyclic voltammetric studies were carried out to understand the efficient formation of copper and nickel polymer chelates (Ilanchelian & Ramaraj, 2011).

2. Experimental

2.1. Materials

Dextran (Average M_W = 482,000 Da) was purchased from Sigma–Aldrich chemicals USA and 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) was purchased from Sigma–Aldrich chemicals, Germany. Ceric ammonium nitrate (CAN) was purchased from Lobacheime, Mumbai. Acetone, Hydroquinone, Cu(II)$SO_4 \cdot 5H_2O$ and Ni(II)$Cl_2 \cdot 6H_2O$ were purchased from E. Merck, Mumbai, India.

2.2. Synthesis of polymer metal chelates

The synthesis of graft copolymers (Dx-g-PAMPS1 to Dx-g-PAMPS4) based on dextran and PAMPS was done by free radical polymerization technique in aqueous medium using Ce(IV)/HNO_3 induced solution polymerization technique. The details of synthetic procedure have been given elsewhere (Azmeera, Adhikary, & Krishnamoorthi, 2012). Dx-g-PAMPS3 has been observed as best grade with highest intrinsic viscosity of 15.3 dl/g. Thus Cu(II) and Ni(II) polymeric metal chelates have been prepared using Dx-g-PAMPS3 and the procedure is as follows: 1 g of synthesized graft copolymer (Dx-g-PAMPS3) and 10 mL of 0.5 wt% of metal salt solution ($CuSO_4 \cdot 5H_2O$ and $NiCl_6 \cdot 6H_2O$) were dissolved in 20 mL of water and stirred for 24 h at room temperature. The coloured polymer metal complex was precipitated with acetone, and dried under vacuum at 50 °C (Coskun et al., 2006).

Table 1
Intrinsic viscosity and elemental analysis of graft copolymer and its metal chelates.

Graft copolymer and metal chelates	Intrinsic viscosity (dl/g)	Elemental analysis		
		Carbon %	Hydrogen %	Nitrogen %
Dx-g-PAMPS3	15.3	37.1	6.5	5.1
(Dx-g-PAMPS3)-Cu(II)	10.1	29.23	5.87	4.05
(Dx-g-PAMPS3)-Ni(II)	11.9	28	6.22	3.75

3. Characterization

3.1. Elemental analysis

Elemental analysis of the graft copolymer (Dx-g-PAMPS3) and its polymeric metal chelates were performed under helium atmosphere by using CHN analyzer CE-440 Elemental analyzer, Mexico.

3.2. Intrinsic viscosity measurement

Intrinsic viscosity measurements of the aqueous solution of graft copolymer and its polymeric metal chelates were carried out with the help of Ubbelohde viscometer (CS/S: 0.00386) 25 ± 0.1 °C. Intrinsic viscosities of all these samples were determined from the point of intersection of two extrapolated (to zero concentration) plots of inherent viscosity versus concentration (η_{inh} vs. C) and reduced viscosity versus concentration (η_{red} vs. C). The standard method used to evaluate intrinsic viscosity has been reported earlier (Krishnamoorthi et al., 2007). The intrinsic viscosities of graft copolymer and its polymeric metal chelates have been reported in Table 1.

3.3. FTIR spectroscopy

Thermo Nicolet FT-IR spectrophotometer (Model JASCO FT-IR-5300) was used to record the IR spectra within the range of 4000–400 cm^{-1}. The IR spectra of graft copolymer Dx-g-PAMPS3, (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) were recorded in solid state using KBr pellet method.

3.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images of powdered graft copolymer Dx-g-PAMPS3 and its polymeric metal chelates (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) were taken by HRSEM SUPRA 40, ZEISS (Germany).

3.5. Atomic force microscopy (AFM)

AFM imaging had been carried out on NT-MDT Model Solver NEXT. All calculations and image processing were carried out by a software NOVA Px 3.1.0 Rev 3880 provided by the manufacturer. The images were recorded in a semi contact mode using a non-contact silicon cantilever (NSG10-DLC). Sample films, for AFM observations, were prepared from the graft copolymer and its polymeric metal chelates by dissolving 10 mg polymer sample in 100 μL water to form clear solution and 20 μL of this solution is deposited on a neat glass slide (1 cm × 1 cm) allowing it to dry in air. The films were air dried followed by vacuum dry for 24 h before AFM observation. The reported roughness was determined from the root-mean-square (RMS) values of 20 μm × 20 μm scan areas of the respective materials.

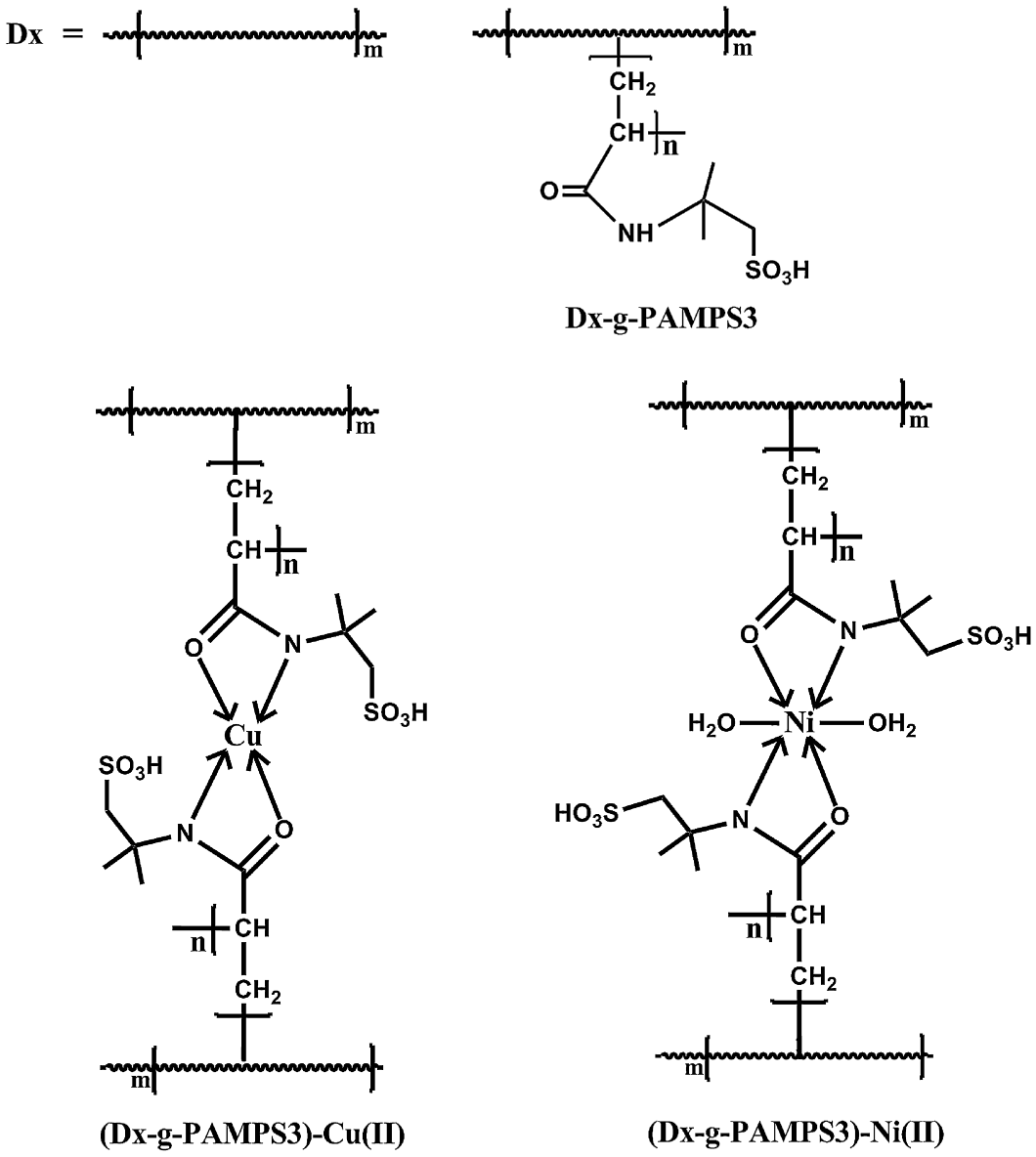

Fig. 1. Structure of graft copolymer (Dx-g-PAMPS3) and its polymeric metal chelates.

3.6. Thermal analysis

The thermo gravimetric analysis (TGA) of graft copolymer Dx-g-PAMPS3 and its polymeric metal chelates were carried out with a TGA-DTA, METTER-TOLEDO (Germany) instrument. Analysis of the Dx-g-PAMPS3 and (Dx-g-PAMPS3)-Cu(II) samples were performed from 50 °C up to a temperature of 600 °C and in the case of (Dx-g-PAMPS3)-Ni(II) sample it was up to a temperature of 800 °C in nitrogen atmosphere (Bao, Ma, & Li, 2011; Maia, Carvalho, Coelho, Simões, & Gil, 2011). The heating rate was uniform in all cases at 10 °C per min.

3.7. X-ray diffractometry

X-ray diffractometric studies of the graft copolymer Dx-g-PAMPS3 and its polymeric metal chelates were done by an 18-KW Cu-rotating anode RIGAKU (TOKYO, JAPAN) X-ray powder diffractometer. The contact angle of the peaks was in the range 14–40°.

3.8. UV–visible spectroscopy

UV–visible spectrophotometric measurements were carried out by 2802 PC UV–vis absorption spectrophotometer (Unico-USA). The 5 wt% solutions of graft copolymer Dx-g-PAMPS3 and its metal chelates were prepared by dissolving them separately in distilled water at 25 °C, for 30 min.

3.9. Cyclic voltammetric studies

Cyclic voltammetric study of graft copolymer Dx-g-PAMPS3 and its metal chelates was done using 0.1 M Na_2SO_4 as supporting electrolyte and CHI-660C (CH Instruments, USA). The supporting electrolyte solutions were deoxygenated by bubbling high purity N_2 for 20–30 min. prior to each electrochemical experiment at room temperature (25 °C). Solutions were prepared with triply distilled water.

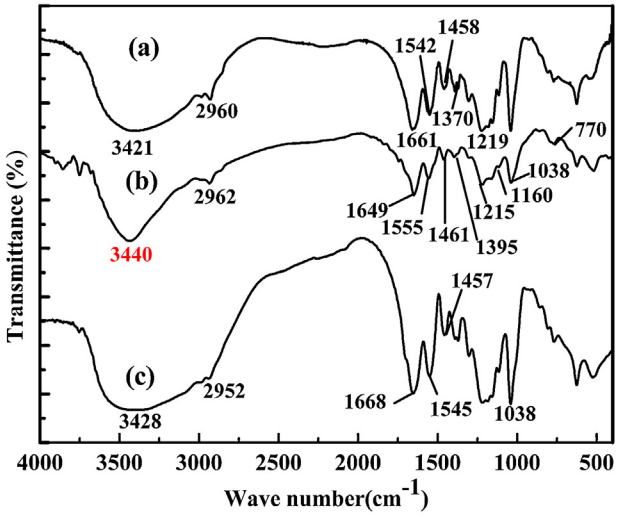

Fig. 2. FTIR spectra of (a) (Dx-g-PAMPS3)-Ni(II), (b) Dx-g-PAMPS3, (c) (Dx-g-PAMPS3)-Cu(II).

4. Results and discussion

4.1. Synthesis of polymer metal chelates

The synthesis of four grades of graft copolymers were done by solution polymerization technique. Dx-g-PAMPS3 was observed to have highest intrinsic viscosity. Thus polymeric metal chelates based on Dx-g-PAMPS3 were synthesized. PAMPS present in Dx-g-PAMPS3 contained amide functionality and it would act as bidentate chelating ligand containing nitrogen and oxygen donor centres of —NH and C=O groups respectively. It was believed that Cu(II) and Ni(II) polymeric metal chelates possessed square planner and octahedral structures respectively. These linkages are shown in Fig. 1.

4.2. Elemental analysis

The results of elemental analysis of the graft copolymer Dx-g-PAMPS3, (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) are shown in Table 1. In case of (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II), percentages of carbon, hydrogen and nitrogen decreased as Cu(II) and Ni(II) metals were included in the calculation of percentages. It supported the fact of metal ions incorporation into the graft copolymer.

4.3. Intrinsic viscosity measurement

As the concentration of AMPS was optimized in graft copolymer Dx-g-PAMPS3, it showed higher intrinsic viscosity than other graft copolymers in the series (Dx-g-PAMPS1–Dx-g-PAMPS4) (Azmeera et al., 2012). It was also observed that the intrinsic viscosities of the polymeric metal chelates of Cu(II) and Ni(II) decreased. It confirmed the metal ions incorporation into the graft copolymer Dx-g-PAMPS3. The calculated binding constant (K_{bin}) values as observed in Section 4.9, showed that the binding ability of Cu(II) was more than that of Ni(II). This implied that Cu(II) was incorporated more into Dx-g-PAMPS3 than Ni(II). Due to more binding ability of Cu(II), the extent of PAMPS chain straightening reduced. So, the intrinsic viscosity which is proportional to the chain linearity in case of (Dx-g-PAMPS3)-Cu(II), was found to be relatively lower than (Dx-g-PAMPS3)-Ni(II). The intrinsic viscosity values of graft copolymer and its polymeric metal chelates are reported in Table 1.

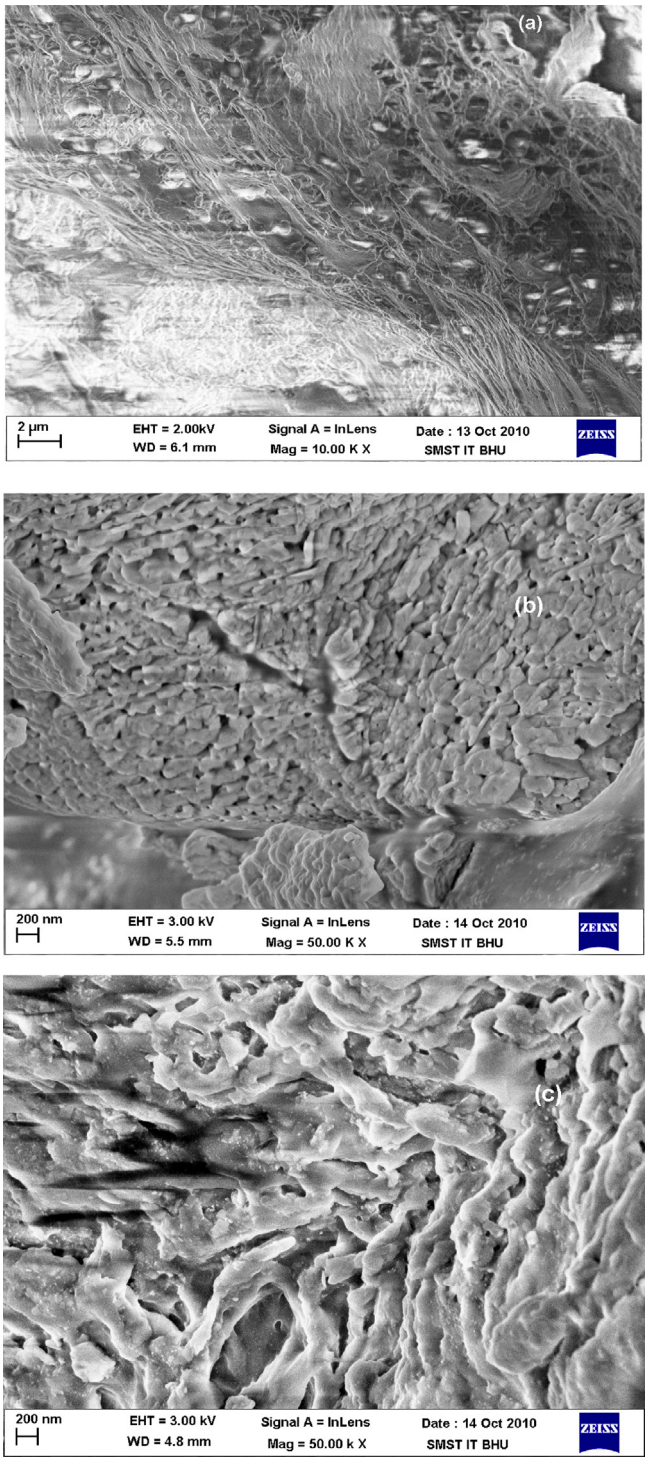

Fig. 3. SEM of (a) Dx-g-PAMPS 3, (b) (Dx-g-PAMPS3)-Cu(II), (c) (Dx-g-PAMPS3)-Ni(II).

4.4. FTIR spectroscopy

An attempt has been made to understand the mode of coordination of the metal ion with the ligand system. The shift and presence of certain bands in the spectrum of polymer metal chelates gives an idea about the nature of coordination. According to chemical structure of the polymer and polymeric metal chelates, coordination is expected to exist between the amide linkages and metal ions. FT-IR spectra of Dx-g-AMPS3 and its metal chelate complexes were recorded. Fig. 2 shows the FT-IR

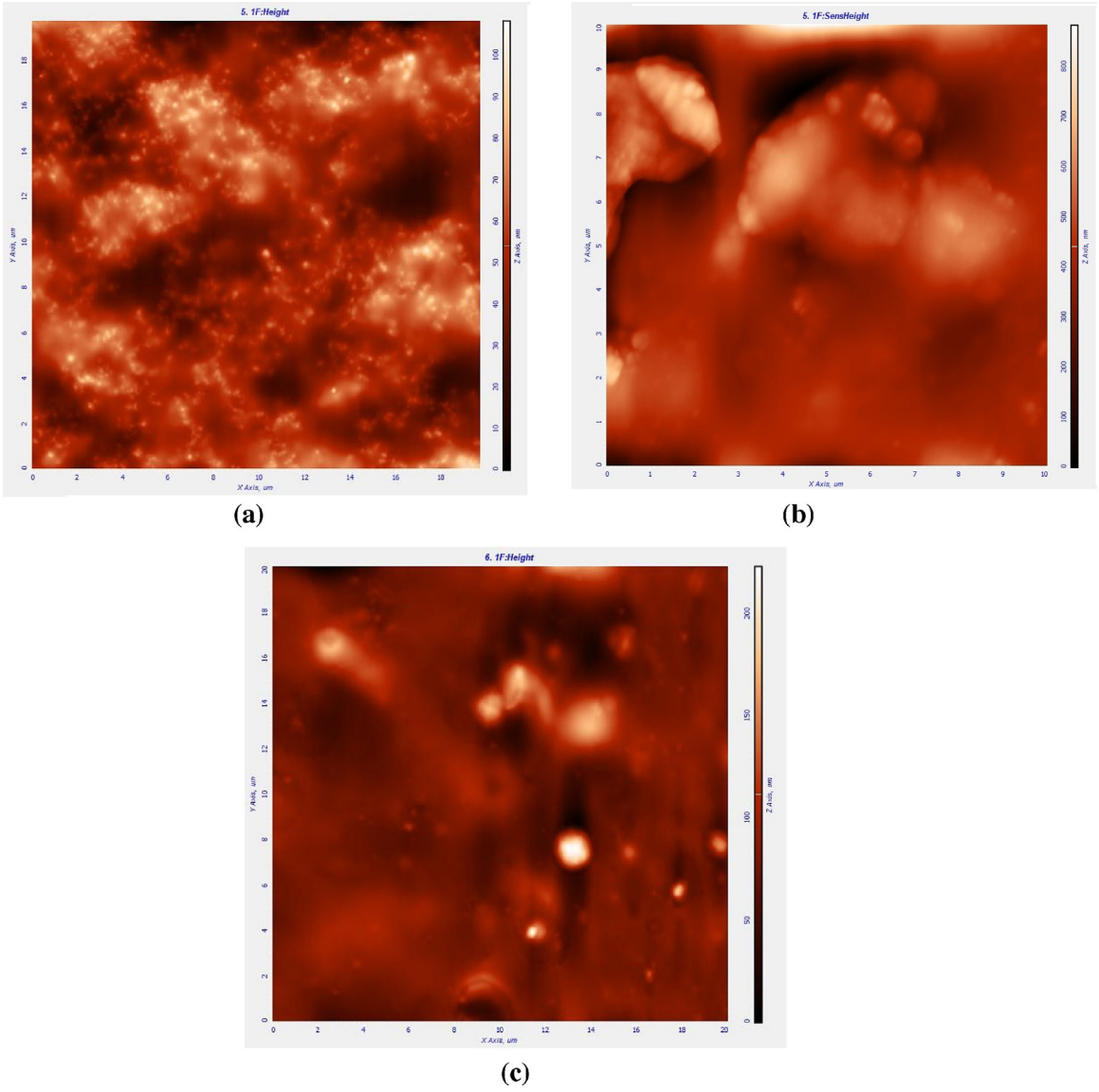

Fig. 4. AFM of (a) Dx-g-PAMPS3, (b) (Dx-g-PAMPS3)-Cu(II), (c) (Dx-g-PAMPS3)-Ni(II).

spectra of (Dx-g-PAMPS3)-Ni(II) (a), Dx-g-PAMPS3 (b) and (Dx-g-PAMPS3)-Cu(II) (c). All three FT-IR spectra exhibited similar qualitative absorption signal for corresponding —NH, —CH, amide-I and amide-II, S═O, S—O—C groups. However, variations in the positions and intensity of —NH and —OH bands between Dx-g-PAMPS3 and its polymeric metal chelates were clearly observed. In case of Dx-g-PAMPS3 a broad stretching frequency signal at 3440 cm^{-1} due to–NH stretching frequency was observed. After incorporation of Cu(II) and Ni(II), broadening of this peak considerably increased due to additional —OH stretching frequency from the water molecules coordinated to the Ni(II) and Cu(II) complexes.

The amide carbonyl stretching frequency of Dx-g-PAMPS3 (1649 cm^{-1}) shifted to higher frequency of 1661 and 1668 cm^{-1} in case of (Dx-g-PAMS3)-Ni(II) and (Dx-g-PAMPS3)-Cu(II), respectively. In polymer metal complex, the lone pair present on nitrogen is involved in metal complex formation so the conjugation is restricted and hence carbon-oxygen double bond character increases. Thus the stretching frequency of carbonyl group increases. The —NH bending frequency reduced to lower values 1542 and 1545 cm^{-1} in case of (Dx-g-PAMS3)-Ni(II) and (Dx-g-PAMPS3)-Cu(II) respectively. The NH bending frequency decreases in metal complexes in comparison to pure graft copolymer. The lone pair on nitrogen is involved in complex formation so the bond angle is reduced. This leads to lower bending frequency. From the above characteristics bands shifts it is evident that there is complex formation by the coordination of the amide nitrogen and oxygen to the Ni(II) and Cu(II) ions (Coskun et al., 2006; Song et al., 2007).

4.5. Scanning electron microscopy

Fig. 3(a)–(c) shows the SEM micrographs of Dx-g-PAMPS3, (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) respectively. Fig. 3(a) of Dx-g-PAMPS3 micrograph shows that the surface morphology is in fibrillar form. Fig. 3(b) of (Dx-g-PAMPS3)-Cu(II) micrograph reveals its flattened pebbles like structure. Fig. 3(c) of (Dx-g-PAMPS3)-Ni(II) has a partially haematic exudates structure. A difference in surface morphology between graft copolymer and metal complexes is clearly evident from the figures. Thus SEM study is an evidence for Cu(II) and Ni(II) implantation in the graft copolymer.

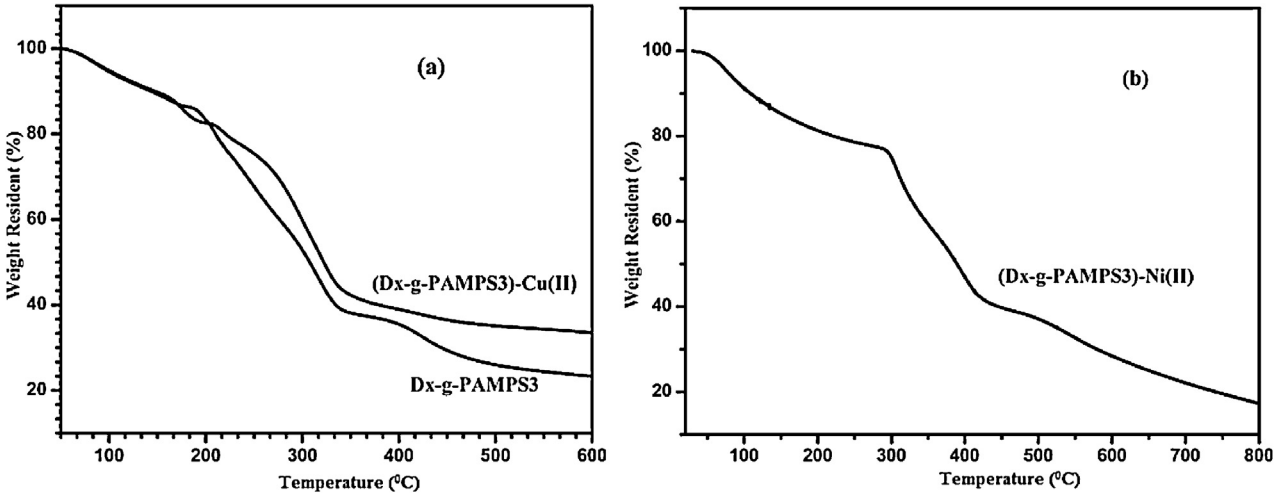

Fig. 5. TGA of (a) Dx-g-PAMPS3, (Dx-g-PAMPS3)-Cu(II), (b) (Dx-g-PAMPS3)-Ni(II).

4.6. Atomic force microscopy (AFM)

Fig. 4(a)–(c) are the AFM images showing the roughness of Dx-g-PAMPS3, (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) respectively. Fig. 4(a) of Dx-g- PAMPS3 shows the spherical domains which are clearly observed in the film. The Root mean square roughness (RMS) is found to be 13.815 nm and average roughness is 11.082 nm. Fig. 4(b) of (Dx-g-PAMPS3)-Cu(II) reveals that it has very small granules like surface. Root mean square roughness (RMS) is found to be 77.432 nm and average roughness is 105.505 nm. Fig. 4(c) of (Dx-g-PAMPS3)-Ni(II) reveals that the Root mean square roughness is 20.266 nm and average roughness is 13.236 nm. Thus extent of Cu(II) incorporation in graft copolymer is higher than Ni(II).

4.7. Thermal analysis

Fig. 5 shows the thermal stabilities of graft copolymer and its polymeric metal chelates, which were investigated by thermogravimetric analysis (TGA). Dx-g-PAMPS3 and its Cu(II) and Ni(II) complexes underwent three stages of decomposition. In TGA curve of Dx-g-PAMPS3 [Fig. 5(a)], decomposition in the range of 50–250 °C was due to water evolving. The second decomposition at 250 °C was assigned to the decomposition of sulphonic acid groups. The decomposition at 300 °C was due to degradation of main chain. Finally, combustion of the degraded products began at 350 °C. In the case of (Dx-g-PAMPS3)-Cu(II) Fig. 5(a), the first stage decomposition was at 175 °C due to the release of water molecules, second decomposition in the range of 220–275 °C was due to removal of the coordinated water molecules and decomposition of sulphonic acid groups. Third degradation which was due to combustion of the degraded products began at 355 °C. In case of Ni(II) chelate [Fig. 5(b)], the first stage decomposition was in the range of 62–290 °C and was about 10% due to the removal of the water molecules and decomposition of sulphonic acid groups. The second stage decomposition temperature in the range of 295–440 °C was attributed to degradation of main chain. Third degradation due to combustion of the degraded products began at 450 °C (Coskun et al., 2006). Thus grafted polymeric metal chelates exhibited high thermal stability.

4.8. X-ray diffractometry (XRD)

Representative X-ray diffraction of Dx-g-PAMPS3 and its polymeric metal chelates (Dx-g-PAMPS3)-Ni(II) and (Dx-g-PAMPS3)-Cu(II) are given in Fig. 6(a)–(c) respectively. The XRD analysis of Dx-g-PAMPS3 showed amorphous, whereas (Dx-g-PAMPS3)-Ni(II) and (Dx-g-PAMPS3)-Cu(II) showed crystalline behaviour. The percentages of crystallinity shown by (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) were 60.89% and 40.06% respectively. Thus the presence of crystalline peaks in (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II), proves the incorporation of Ni(II) and Cu(II) metal ions in the graft copolymer (Nanjundan et al., 2004).

4.9. UV–visible spectroscopy

Incremental addition of Dx-g-PAMPS3 to aqueous solution of Cu(II) ion is shown in Fig. 7(i). Dx-g-PAMPS3 alone did not show any absorbance in the range 600–1000 nm (curve not shown). However, Cu(II) in water showed a broad peak centred at 809 nm due to the $CuSO_4{\cdot}5H_2O$ species. When Dx-g-PAMS3 was added incrementally, slow increase in the absorbance of the broad band (inset of Fig. 1) with a slight blue shift (809–800 nm) was observed, which was due to the formation of (Dx-g-PAMPS3)-Cu(II) complex. The formation of such (Dx-g-PAMPS3)-Cu(II) complex will be useful in electroanalytical studies and also in catalysis. Similarly, Ni(II) in water showed band around 395 nm and a broad band in the region

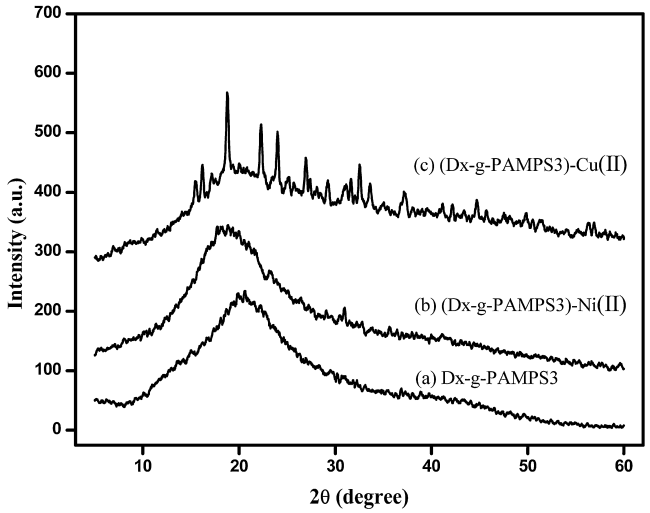

Fig. 6. XRD of (a) Dx-g-PAMPS3, (b) (Dx-g-PAMPS3)-Ni(II), (c) (Dx-g-PAMPS3)-Cu(II).

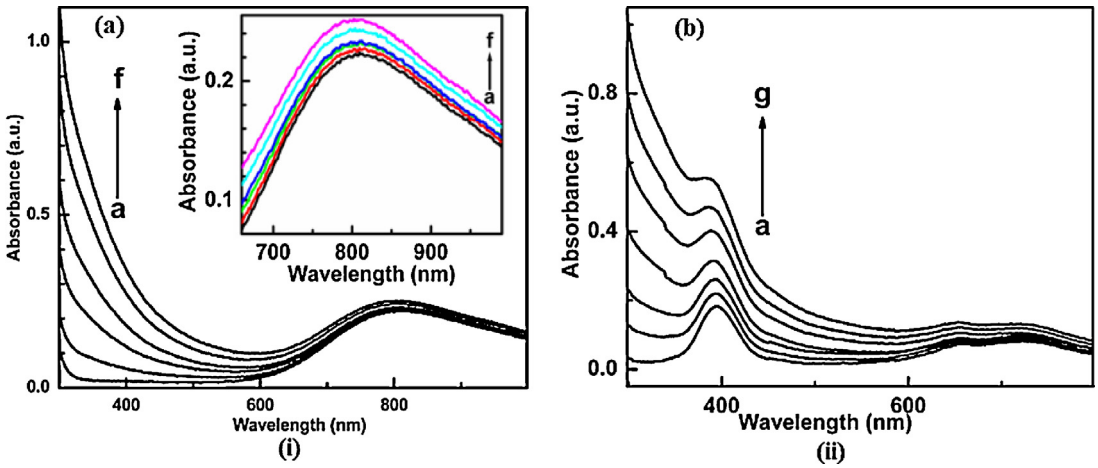

Fig. 7. (i) UV–vis spectra of pure $CuSO_4{\cdot}5H_2O$ (0.018 M) (a) and after addition of 0.008, 0.025, 0.042, 0.058 and 0.075 wt% aqueous Dx-g-PAMPS3 solution (b–f). (ii) UV–vis spectra of pure $NiCl_2{\cdot}6H_2O$ (0.026 M) (a) and after addition of 0.008, 0.016, 0.033, 0.050, 0.067 and 0.083 wt% aqueous polymer solution (b–g).

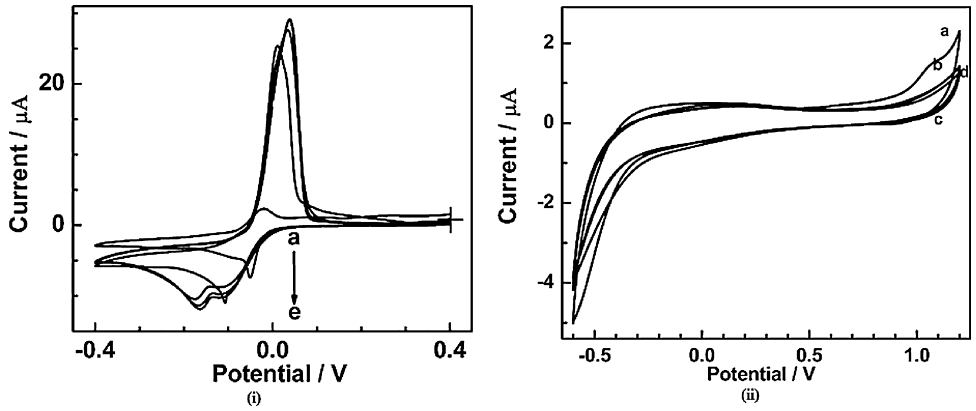

Fig. 8. (i) Cyclic voltammetry of pure $CuSO_4{\cdot}5H_2O$ (0.5 mM) (a) and after addition of 0.01, 0.02, 0.03 and 0.05 wt% aqueous polymer solution (b–e) in 0.1 M Na_2SO_4 at 20 mV/s. (ii) Cyclic voltammetry of pure $NiSO_4{\cdot}6H_2O$ (0.5 mM) (a) and after addition of 0.01, 0.02 and 0.05 wt% aqueous polymer solution (b–d) in 0.1 M Na_2SO_4 at 20 mV/s.

600–800 nm as shown in Fig. 7(ii). On the addition of Dx-g-PAMPS3 to the Ni(II) solution, there was a small increase in the absorbance at 395 nm with a slight blue shift (395–382 nm), which was similar to the observation with Cu(II) ions. This result indicates the formation of (Dx-g-PAMPS3)-Ni(II), which could find useful application in catalysis. The binding constants of Cu(II) and Ni(II) chelates with Dx-g-PAMPS3 were calculated using the following Equation (Ilanchelian & Ramaraj, 2011).

$$\frac{1}{\Delta A} = \frac{1}{\varepsilon_1 - \varepsilon_0}[C_0] + \frac{1}{\varepsilon_1 - \varepsilon_0}[C_0]K_{bin} \times \frac{1}{\text{Dx-g-PAMPS3}} \quad (1)$$

where, ΔA is the difference in absorption intensities of Cu(II) and Ni(II) in the absence and presence of Dx-g-PAMPS3 ($\Delta A = (A_0 - A)$). A_0 is the absorption intensity of Cu(II) and Ni(II) in the absence of Dx-g-PAMPS3. A is the absorption intensity of Cu(II) and Ni(II) at a given concentration of Dx-g-PAMPS3. ε_1 and ε_0 are molar extinction coefficients of Cu(II) and Ni(II) and Dx-g-PAMPS3, respectively. $[C_0]$ is initial concentration of Cu(II) and Ni(II). K_{bin} is the binding constant. Further the binding constants of Cu(II) and Ni(II) metal ions with Dx-g-PAMPS3 are calculated using Eq. (1) and the values are tabulated in Table 2.

Table 2
Binding constants of UV–visible spectra of (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II).

UV–visible spectra	K_{bin} ($dm^3\ mol^{-1}$)
(Dx-g-PAMPS3)-Cu(II)	9.33528
(Dx-g-PAMPS3)-Ni(II)	0.63

4.10. Cyclic voltammetric studies

Electrochemical oxidation and reduction of Cu(II) ions with Na_2SO_4 as supporting electrolyte is shown in Fig. 8(i). In the absence of Dx-g-PAMPS3, it shows a pair of redox peaks ($E_{1/2} = -40$ mV, $\Delta E_p = 30$ mV) which is attributed to the Cu(II)/Cu^0 redox couple. It shows 2.5 μA redox current (0.5 mM of Cu(II)) and when the polymer is added incrementally, the redox current increases and levelled off at 29.1 μA at 0.05 wt% of Dx-g-PAMPS3. Thus the addition of Dx-g-PAMPS3 increases the current more than ten times. This large increase in current is due to the formation of (Dx-g-PAMPS3)-Cu(II) complex which prevent the adsorption of Cu^0 metal on the electrode surface. Similarly, the ΔE_p values increased to 150 mV which indicates the slow diffusion of (Dx-g-PAMPS3)-Cu(II) complex and slow redox kinetics. Very similar results are observed with Ni(II) on addition of Dx-g-PAMPS3 and are shown in Fig. 8(ii). The large increase in current can be effectively utilized for electro catalytic applications.

5. Conclusions

Graft copolymers based on Dextran (Dx) and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) had been prepared by free radical polymerization in water at 50 °C. Cu(II) and Ni(II) chelates

of the graft copolymer were prepared and characterized. The FT-IR and UV–visible measurements confirmed the formations of complexes between the graft copolymer and the metal cations. The binding constant calculated from UV–visible absorption spectra showed that the formation of (Dx-g-PAMPS3)-Cu(II) was more than (Dx-g-PAMPS3)-Ni(II). Due to more binding ability of Cu(II), the intrinsic viscosity of (Dx-g-PAMPS3)-Cu(II) was found to be lower. SEM studies which showed morphology variation of Dx-g-PAMPS3, (Dx-g-PAMPS3)-Cu(II) and (Dx-g-PAMPS3)-Ni(II) also supported complex formation. The AFM studies revealed that Root mean square roughness (RMS) and average roughness of (Dx-g-PAMPS3)-Cu(II) was more than (Dx-g-PAMPS3)-Ni(II). The TGA studies concluded that complexes were thermally more stable than Dx-g-AMPS3, over the whole investigated temperature range. (Dx-g-PAMPS3)-Cu(II) were found to be thermally more stable than (Dx-g-PAMPS3). The amorphous nature of graft copolymer and crystalline nature of polymeric metal chelates were confirmed by X-ray diffraction analysis. Cyclic voltametric studies had shown large increase in current with metal chelates which would lead to effective electro catalytic applications.

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References

Adhikary, P., & Krishnamoorthi, S. (2012). Synthesis, characterization, and application of amylopectin-graft-poly(AM-co-AMPS). *Journal of Applied Polymer Science*, *126*, E312–E317.

Azmeera, V., Adhikary, P., & Krishnamoorthi, S. (2012). Synthesis and characterization of graft copolymer of dextran and 2-acrylamido-2-methylpropane sulphonic acid. *International Journal of Carbohydrate Chemistry*, 1–7.

Bachelder, E. M., Beaudette, T. T., Broaders, K. E., Dashe, J., & Freíchet, J. M. J. (2008). Acetal-derivatized dextran: An acid-responsive biodegradable material for therapeutic applications. *Journal of the American Chemical Society*, *130*, 10494–10495.

Bajgai, M. P., Parajuli, D. C., Ko, J. A., Kang, H. K., Khil, M. S., & Kim, H. Y. (2009). Synthesis, characterization and aqueous dispersion of dextran-g-poly(1,4-dioxan-2-one) copolymers. *Carbohydrate Polymers*, *78*, 833–840.

Bao, Y., Ma, J., & Li, N. (2011). Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(AA-co-AM-co-AMPS)/MMT superabsorbent hydrogel. *Carbohydrate Polymers*, *84*, 76–82.

Buwalda, S. J., Dijkstra, P. J., & Feijen, J. (2012). Poly(ethylene glycol)-poly(L-lactide) star block copolymer hydrogels crosslinked by metal–ligand coordination. *Journal of Polymer Science Part A: Polymer Chemistry*, *50*, 1783–1791.

Coskun, R., Soykan, C., & Delibas, A. (2006). Study of free-radical copolymerization of itaconic acid/2-acrylamido-2-methyl-1-propanesulfonic acid and their metal chelates. *European Polymer Journal*, *42*, 625–637.

Durmaz, S., & Okay, O. (2000). Acrylamide/2-acrylamido-2-methylpropane sulfonic acid sodium salt-based hydrogels: Synthesis and characterization. *Polymer*, *41*, 3693–3704.

Ilanchelian, M., & Ramaraj, R. (2011). Binding interactions of toluidine blue O with *Escherichia coli* DNA: Formation of bridged structure. *Journal of Fluorescence*, *21*, 1439–1453.

Kaliyappan, T., Swaminathan, C. S., & Kannan, P. (1996). Synthesis and characterization of a new metal chelating polymer and derived Ni(II) and Cu(II) polymer complexes. *Polymer*, *37*, 2865–2869.

Krishnamoorthi, S., Mal, D., & Singh, R. P. (2007). Characterization of graft copolymer based on polyacrylamide and dextran. *Carbohydrate Polymers*, *69*, 371–377.

Kutsevol, N., Guenet, J.-M., Melnik, N., Sarazin, D., & Rochas, C. (2006). Solution properties of dextran-polyacrylamide graft copolymers. *Polymer*, *47*, 2061–2068.

Maia, J., Carvalho, R. A., Coelho, J. F. J., Simões, P. N., & Gil, M. H. (2011). Insight on the periodate oxidation of dextran and its structural vicissitudes. *Polymer*, *52*, 258–265.

Miguel, V. S., Catalina, F., & Peinado, C. (2008). Self-assembly of physically crosslinked micelles of poly (2-acrylamido-2-methyl-1-propane sulphonic acid-co-isodecyl methacrylate)-copper(II) complexes. *European Polymer Journal*, *44*, 1368–1377.

Nanjundan, S., Selvamalar, C. S. J., & Jayakumar, R. (2004). Synthesis and characterization of poly(3-acetyl-4-hydroxyphenyl acrylate) and its Cu(II) and Ni(II) complexes. *European Polymer Journal*, *40*, 2313–2321.

Pfister, A., & Fraser, C. L. (2006). Synthesis and unexpected reactivity of iron tris(bipyridine) complexes with poly(ethyleneglycol) macroligands. *Biomacromolecules*, *7*, 459–468.

Qiao, J., Hamaya, T., & Okada, T. (2005). New highly proton-conducting membrane poly (vinylpyrrolidone) (PVP) modified poly(vinyl alcohol)/2-acrylamido-2-methyl-1-propanesulfonic acid (PVA-PAMPS) for low temperature direct methanol fuel cells (DMFCs). *Polymer*, *46*, 10809–10816.

Rastogi, P. K., Ganesan, V., & Krishnamoorthi, S. (2012a). Ion exchange voltammetry at permselective copolymer modified electrode and its application for the determination of catecholamines. *Journal of Electroanalytical Chemistry*, *676*, 13–19.

Rastogi, P. K., Ganesan, V., & Krishnamoorthi, S. (2012b). Microwave assisted polymer stabilized synthesis of silver nanoparticles and its application in the degradation of environmental pollutants. *Materials Science and Engineering B*, *177*, 456–461.

Rastogi, P. K., Krishnamoorthi, S., & Ganesan, V. (2012). Synthesis, characterization, and ion exchange voltammetry study on 2-acrylamido-2-methylpropane sulphonic acid and N-(hydroxymethyl) acrylamide-based copolymer. *Journal of Applied Polymer Science*, *123*, 929–935.

Rastogi, P. K., Ganesan, V., & Krishnamoorthi, S. (2014). A promising electrochemical sensing platform based on a silver nanoparticles decorated copolymer for sensitive nitrite determination. *Journal of Materials Chemistry A*, *2*, 933–943.

Raynaud, J., Choquenet, B., Marie, E., Dellacherie, E., Nouvel, C., Six, J.-L., et al. (2008). Emulsifying properties of biodegradable polylactide-grafted dextran copolymers. *Biomacromolecules*, *9*, 1014–1021.

Rosa, F., Bordado, J., & Casquilho, M. (2003). Hydrosoluble copolymers of acrylamide-(2-acrylamido-2 methylpropanesulfonic acid). Synthesis and characterization by spectroscopy and viscometry. *Journal of Applied Polymer Science*, *87*, 192–198.

Song, H., Zhang, S.-F., Ma, X.-C., Wang, D.-Z., & Yang, J.-Z. (2007). Synthesis and application of starch-graft-poly(AM-co-AMPS) by using a complex initiation system of CS-APS. *Carbohydrate Polymers*, *69*, 189–195.

Soykan, C., Coskun, R., & Kirbag, S. (2007). Poly(crotonic acid-co-2-acrylamido-2-methyl-1-propanesulfonic acid)–metal complexes with copper(II), cobalt(II), and nickel(II): Synthesis, characterization and antimicrobial activity. *European Polymer Journal*, *43*, 4028–4036.

Zhang, C., & Easteal, A. J. (2003). Study of free-radical copolymerization of *N*-isopropylacrylamide with 2-acrylamido-2-methyl-1-propanesulphonic acid. *Journal of Applied Polymer Science*, *88*, 2563–2569.