

Synthesis, Characterization, and Ion Exchange Voltammetry Study on 2-Acrylamido-2-methylpropane Sulphonic Acid and *N*-(hydroxymethyl) Acrylamide-Based Copolymer

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ABSTRACT: A random copolymer of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and *N*-hydroxymethyl acrylamide (NHMA) was prepared by solution polymerization using ceric ammonium nitrate as an initiator. A grade of poly(AMPS)-*co*-poly(NHMA) (PAMPS-*co*-PNHMA) random copolymer was synthesized with AMPS and NHMA. The homopolymerization of AMPS and NHMA was also carried out by the same way as that of random copolymer. PAMPS-*co*-PNHMA and homopolymers of AMPS and

NHMA were characterized by FTIR, rheology, FT-NMR, scanning electron microscope, thermal analysis, and X-ray diffractometry. Cyclic voltammetry is used to explain the ion exchange properties of PAMPS-*co*-PNHMA and its possible application in the trace analysis. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 929–935, 2012

Key words: random copolymer; rheology; ion exchange voltammetry; modified electrodes; thionine

INTRODUCTION

Modified polymers can be obtained by copolymerization of monomers with different functional groups. The range of properties of polymeric materials is continuously being extended by the use of linear and crosslinked copolymers.¹ Copolymerization modulates both the intermolecular and intramolecular forces exercised between like and unlike polymer segments.² Usually, random copolymers are synthesized by the reaction of an initiator system in the presence of two or more different monomers.

2-Acrylamido-2-methyl-propane sulfonic acid (AMPS) is an anionic monomer with high solubility (150 g/100 mL of water at 25°C), because it contains a hydrophilic sulfonic acid (–SO₃H) functional group in its molecular structure.³ AMPS has often been used as the monomer of polymerization to improve the performance of synthetic resins.⁴ Polymers derived from AMPS were found to be highly useful. Its high swelling capacity was used in mak-

ing ionic hydrogel,^{5,6} in the synthesis of offset ink, in cosmetics, etc.

Several AMPS-based copolymers have been studied extensively with various other monomers such as acrylamide^{7–10} and isodecyl methacrylate.¹¹ The graft copolymers based on AMPS and various polysaccharides like xanthan gum¹² and starch¹³ have been studied for their metal ion sorption capacity, swelling behavior, etc. *N*-hydroxymethyl acrylamide (NHMA) is one of the hydrophilic monomers. It is reported that the lower critical solution temperature of thermo-sensitive hydrogel may rise close to physiologic temperature by introducing a proportion of NHMA.^{14,15} Moreover, NHMA can bind with some dyes, for example, an affinity dye Cibacron Blue F3GA, which contains Cl. Therefore, ligands having interaction abilities with biological molecules may be incorporated more easily into the hydrogel network.¹⁶

Ion exchange voltammetry technique has been developed recently.^{17,18} It is based on the concept of chemically modified electrodes, in which the modifier is an ion exchange material. The analytical technique takes advantage of the accumulation capabilities of the polymer coating to enhance concentrations of electroactive ionic species at the electrode surface.¹⁹ Several ion exchange materials are used for that purpose, including a wide range of organic polymers (both polyanionic^{17,18} and polycationic ionomers^{20,21}), charged conducting polymers,²² clays,^{23–25} zeolites,²⁶ and silica-based organic–inorganic hybrids.^{27,28} However, still, there is search for ionomers with high-ion

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exchange capacities and perm-selective properties or with improved mass/charge transport properties and, more importantly, with good mechanical stability at the electrode surface.^{17–28}

In this work, a new random copolymer of AMPS and NHMA is prepared by solution copolymerization technique using ceric ammonium nitrate (CAN) as an initiator with AMPS and NHMA (abbreviated as PAMPS-*co*-PNHMA). The homopolymers and PAMPS-*co*-PNHMA are characterized by various characterization methods. The applicability of PAMPS-*co*-PNHMA for the ion exchange voltammetry and possible exploitation in trace analysis is demonstrated.

EXPERIMENTAL

Materials

AMPS and NHMA are procured from Aldrich Chemicals (St. Louis, MO). CAN is obtained from Merck (India). Acetone is supplied by S.D. Fine Chemicals (Mumbai, India). Thionine is obtained from HIMEDIA-Mumbai, India. All the above chemicals were used without further purification.

Synthesis of copolymer PAMPS-*co*-PNHMA

Polymerization is carried in a reactor equipped with a stirrer, a dropping funnel, and a gas inlet tube. The monomers AMPS (0.0241 mol) and NHMA (0.0048 mol) are dissolved in water. Although stirring, U-type nitrogen is bubbled into the monomer solution for 30 min, and the solution is heated to 50°C, after which CAN solution is added in a drop wise manner into the monomer solution. The polymerization is continued at 50°C for 5 h. Then, the reaction mixture becomes a clear viscous solution. After cooling to room temperature, the copolymer is isolated by precipitation with acetone. Finally, the copolymer (PAMPS-*co*-PNHMA) is dried in an oven at 50°C to constant weight and pulverized. The homopolymers of APMS and NHMA (PAMPS and PNHMA, respectively) are synthesized by the same technique as that of copolymer. The H⁺ content of the polymers (0.1%) is determined by the titration with 0.1N NaOH solution using phenolphthalein indicator.

CHARACTERIZATION

IR spectroscopy

A Varian 3100 FTIR (excalibur series, USA) spectrophotometer is used to record the IR spectra within the range of 4000–400 cm⁻¹. The IR spectra of PAMPS, PAMPS-*co*-PNHMA, and PNHMA are recorded in the solid state with a KBr pellet method.

NMR analysis

The FT-NMR analysis of PAMPS-*co*-PNHMA is performed with JEOL AL300 FTNMR spectrometer. The spectra are recorded in the range of 0–8 ppm, and the solvent used is D₂O.

Rheological measurements

The rheological measurements of aqueous solutions of the random copolymer are carried out with Brookfield programmable rheometer DV-III ultra (Mumbai, India). The measurement is carried at room temperature (25°C ± 0.1°C) with CP-52 spindle.

Scanning electron microscopy

The surface morphology of homopolymers and copolymers examined by scanning electron microscopy (SEM), XL 20, Philips, operating at 10 kV (Cambridge Scanning Co., Cambridge, UK) was used for the study.

Thermal analysis

The differential scanning calorimetry (DSC) analysis of the homopolymer and copolymer is carried out with a METTLER DSC 4000 instrument (Germany). DSC analysis of the samples is performed up to a temperature of 380°C, starting at 40°C, in an atmosphere of nitrogen. The heating rate is uniform in all cases (10°C/min).

X-ray diffractometry

PAMPS, PNHMA, and PAMPS-*co*-PNHMA are subjected to X-ray diffractometry (XRD) analysis. An ID 3000 SEIFERT, Germany, and XL-20 X-ray generator (Phillips, Holland) are used.

Electrochemical studies

Polymer-modified electrodes (abbreviated as Pt/respective polymer) are prepared by coating 10 µL of 0.5% respective polymer solution on 0.03-cm² area of a Pt electrode and air dried. Cyclic voltammetry (CV) was performed with one-compartment three electrode system (Pt or polymer modified Pt as working, Pt wire as counter, and Ag/AgCl as reference electrodes) using CHI electrochemical work station (CH Instruments, TX) under nitrogen atmosphere and at room temperature (25°C). Solutions are prepared with triply distilled water.

RESULTS AND DISCUSSION

Synthesis of the copolymers

The polymer codes and feed compositions are given in Table I. The resultant random copolymer

TABLE I
Synthesis Details of PAMPS, PNHMA, and PAMPS-co-PNHMA

S.N.	Sample	AMPS (mol)	NHMA (mol)	CAN (mg)	Yield (%)	Solubility (in water)	H ⁺ content (mol/g)	% Increase in current
I	PAMPS	0.0241	Nil	15	95	Soluble	1.89	Nil
II	PNHMA	Nil	0.0240	20	75	Insoluble	Nil	Nil
III	PAMPS-co-PNHMA	0.0241	0.0048	15	70	Partially soluble	1.26	360

Yield (%) = $W_p / (W_1 + W_2)$, where W_p is the weight of copolymer, W_1 the weight of AMPS, and W_2 the weight of NHMA.

(PAMPS-co-PNHMA) yield and H⁺ content are 70% and 1.26 mol/g, respectively. The partial solubility (in water) of copolymer indicates that the PNHMA has been incorporated to the PAMPS chains. The hydrophobic content (PNHMA) in the copolymer (PAMPS-co-PNHMA) is limited to their solubility in water. When the hydrophobic PNHMA is part of the copolymers, their contribution to solubility may not be negative to the extent as one would expect from their

structure. This is because polymers are long molecules and generally have flexibility to fold themselves in a manner that allows their hydrophobic area to be folded away from the water, much the way amphiphiles aggregate to form a hydrophobic core. This arrangement allows the hydrophilic PAMPS to stay in contact with water. This partial solubility helps to adhere the polymer at the modified electrode even in the presence of solution for long time.

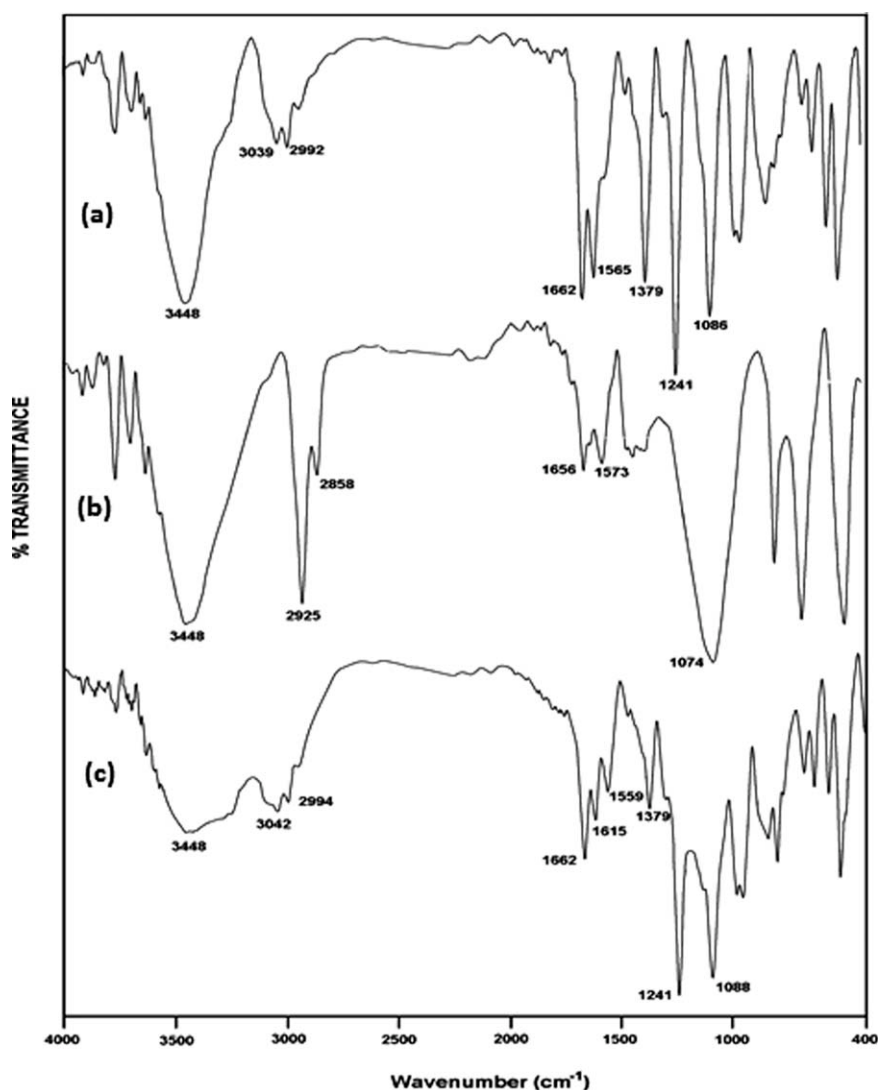


Figure 1 IR spectra of (a) PAMPS, (b) PNHMA, and (c) PAMPS-co-PNHMA.

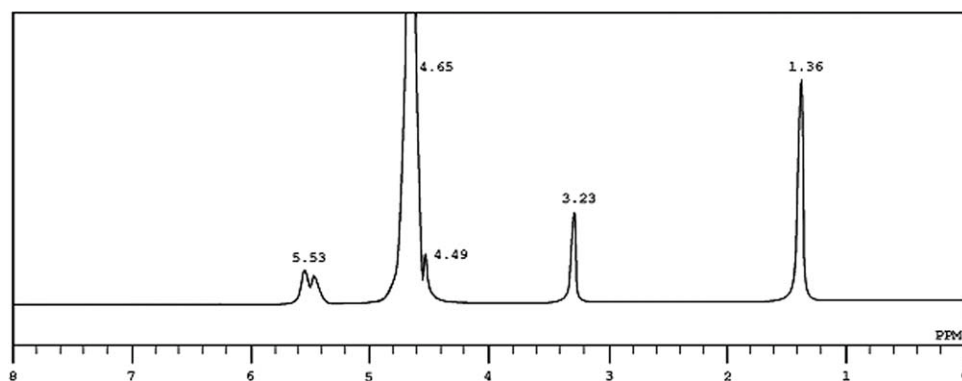


Figure 2 NMR spectrum of PAMPS-co-PNHMA.

IR spectroscopy

The FTIR spectra of PAMPS, PNHMA, and PAMPS-co-PNHMA are shown in Figure 1. In PAMPS, PNHMA, and PAMPS-co-PNHMA, the peak present around 3448 cm^{-1} is due to the stretching frequency of —OH groups. PAMPS shows the following structural peaks at 1379 and 1241 cm^{-1} (S=O), at 1662 and 1565 cm^{-1} (amide I and amide II bands), at 3039 cm^{-1} (N—H stretching), and at 2992 cm^{-1} (—CH_3). PNHMA shows the following structural peaks at 1656 and 1573 cm^{-1} (amide I and amide II bands), at 2925 cm^{-1} (N—H stretching), and at 1074 cm^{-1} (C—O stretch primary —OH). PAMPS-co-PNHMA shows absorption bands at 1379 and 1241 cm^{-1} (S=O), at 1662 and $1615/1559\text{ cm}^{-1}$ (amide I and amide II bands), at 3042 cm^{-1} (N—H stretching), and at 1088 cm^{-1} (C—O stretch primary —OH). The presence of all the peaks due to PAMPS and PNHMA that is present in PAMPS-co-PNHMA proves the copolymerization.

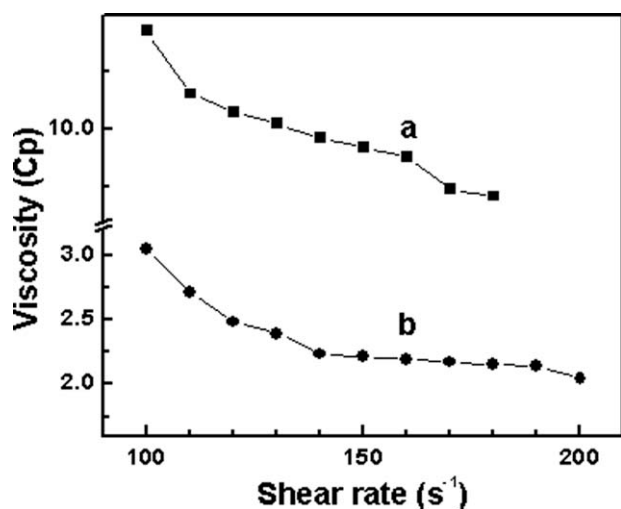


Figure 3 Viscosity versus shear rate curves of (a) PAMPS and (b) PAMPS-co-PNHMA.

NMR analysis

The copolymerization of PAMPS and PNHMA is confirmed by NMR spectroscopy. In Figure 2, the resonances at 1.36 and 3.23 ppm are attributed to the protons of two —CH_3 and $\text{—CH}_2\text{—}$ groups, respectively, of PAMPS molecule. The resonance at 4.49 ppm is due to the proton of $\text{—CH}_2\text{—}$ group of PNHMA molecule. Two broad peaks near 5.53 attributed to the proton of —NH group of PAMPS and PNHMA molecules. The results prove that PAMPS and PNHMA are found in the product. The ethylenic protons peaks are absent showing the removal of monomers in the copolymer.

Rheology

The rheological studies of aqueous solution of PAMPS and PAMPS-co-PNHMA are carried out at concentrations of $0.5\text{ wt } \%$. The shear viscosity and shear rate on two axes are plotted. Figure 3 illustrates the shear viscosity versus shear rate curves of PAMPS and PAMPS-co-PNHMA in aqueous solution. In both the cases, the shear viscosity decreases with the increase in shear rate, and the samples show shear-thinning non-Newtonian behavior (pseudo-plastic). The viscosity of PAMPS solution is more than PAMPS-co-PNHMA solution at all shear rates. This is due to the repulsion of two negatively charged groups (—SO_3^-) on adjacent carbon atoms, which lead to chains straightening and hence higher shear viscosity. The disturbances in order of the —SO_3^- groups by PNHMA chains and also the decrease of —SO_3^- groups in PAMPS-co-PNHMA are the other reasons for this difference in viscosity.

Scanning electron microscopy

Figure 4(a–c) shows scanning electron micrographs of PAMPS, PNHMA, and PAMPS-co-PNHMA, respectively. There is drastic change in morphology of homopolymers and copolymer. The surface

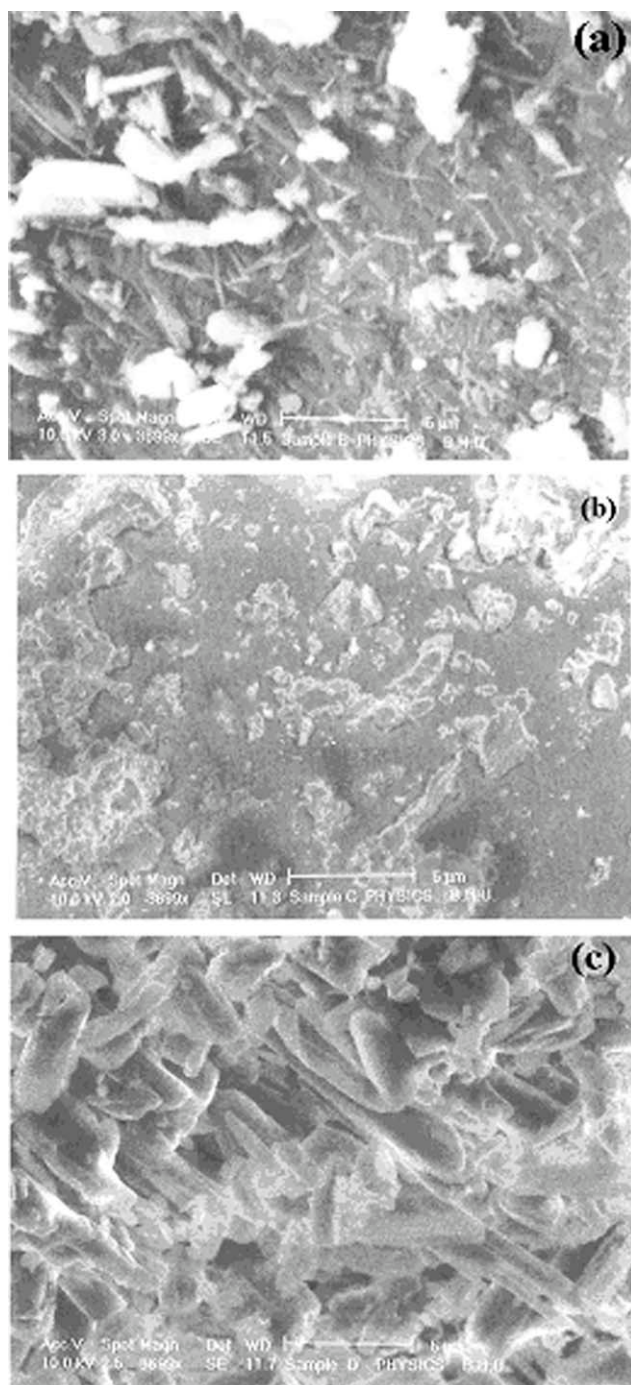


Figure 4 Scanning electron micrographs of (a) PAMPS, (b) PNHMA, and (c) PAMPS-co-PNHMA.

morphology of PAMPS and PNHMA shows fibrillar structures, but, in the case of copolymer cylindrical sphere, shaped structure is obtained. This indicates that PAMPS-co-PNHMA contains no homopolymers of AMPS and NHMA.

Thermal analysis

The melting behavior of (a) PNHMA, (b) PAMPA, and (c) PAMPS-co-PNHMA is investigated by means

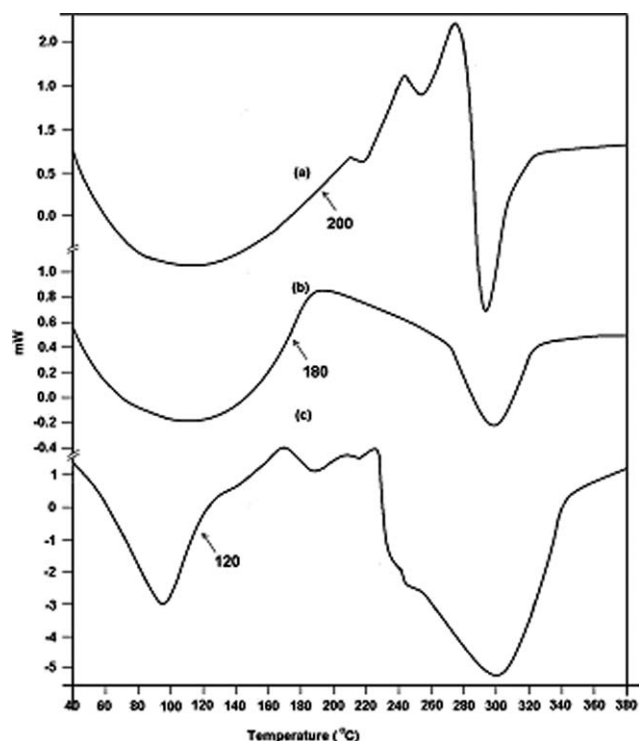


Figure 5 DSC curves of (a) PNHMA, (b) PAMPS, and (c) PAMPS-co-PNHMA.

of differential scanning calorimetry (Fig. 5). It can be seen that the melting temperature peak of the PAMPS-co-PNHMA copolymer is broad compared to homopolymers of PAMPS and PNHMA. The glass transition temperature of PNHMA and PAMPS is 200°C and 180°C, respectively. In case of the copolymer (PAMPS-co-PNHMA), the T_g reduces to 120°C. This may be attributed to the disturbances in order of the PNHMA and PAMPS chains, which leads to decrease of crystallinity and hence T_g .

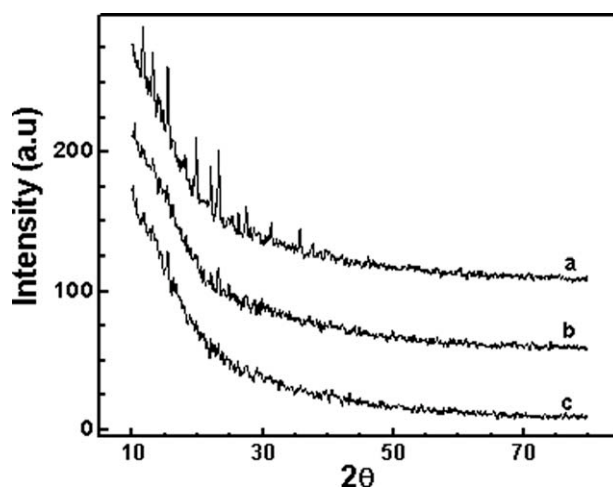


Figure 6 X-ray diffraction patterns of (a) PNHMA, (b) PAMPS, and (c) PAMPS-co-PNHMA.

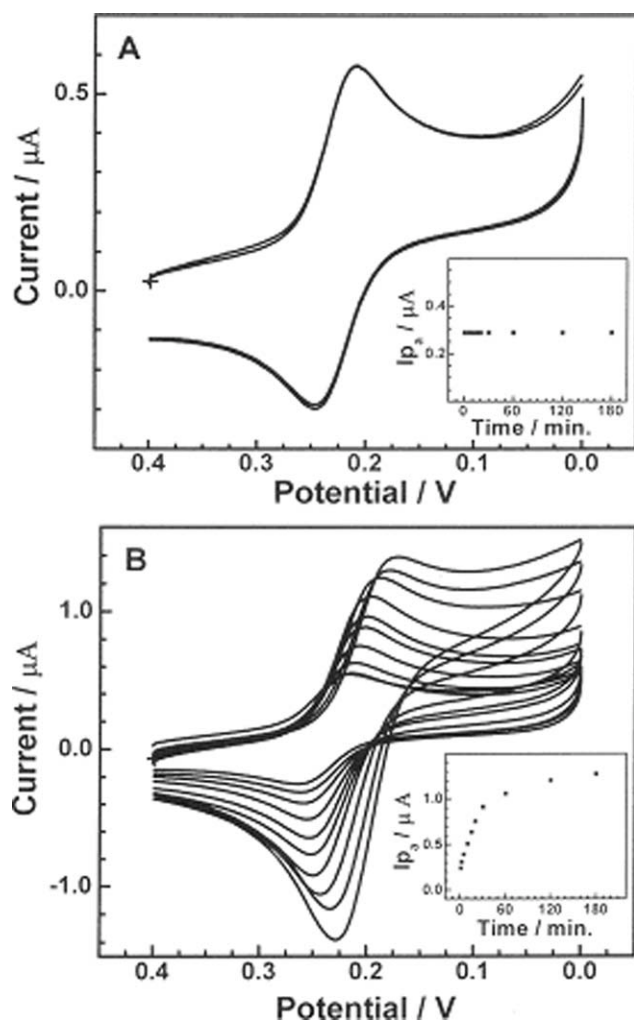


Figure 7 CV of (A) Pt and (B) Pt/PAMPS-*co*-PNHMA in 0.01 mM TH⁺ and 0.01N H₂SO₄ at different time intervals (1, 2, 5, 10, 15, 20, 30, 60, 120, and 180 min). + Sign indicates the starting point of the scan. Inserts show the plot of oxidation peak current against time for the respective electrodes.

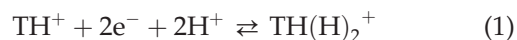
X-ray diffractometry

The X-ray diffraction patterns of PNHMA, PAMPS, and PAMPS-*co*-PNHMA at room temperature from $2\theta = 10^\circ$ – 80° are shown in Figure 6. XRD analysis shows that PNHMA exhibits a small degree of crystallinity in the range from 10.8° to 28° in contrast to that of PAMPS and PAMPS-*co*-PNHMA, which show no crystallinity. From this study, it can be concluded that the homopolymer (PNHMA) is absent in the copolymer.

Ion-exchange voltammetry

To test the applicability of PAMPS-*co*-PNHMA for the ion exchange voltammetry, thionine (TH⁺) is used as an electroactive probe. TH⁺ is a phenothiazine dye with well-defined electrochemical properties.^{29,30} Figure 7 shows the CV curves of Pt and Pt/

PAMPS-*co*-PNHMA dipped in 0.1 mM TH⁺ and 0.01N H₂SO₄ with different time intervals. Both electrodes exhibit the typical redox behavior attributed to TH⁺ redox system^{27,28} as shown in eq. (1).



where TH(H)₂⁺ is the reduced form of TH⁺.

On increasing the dipping time, Pt electrodes do not show any change in the redox current [Fig. 6(A)]; however, at Pt/PAMPS-*co*-PNHMA, increase in current with a small potential shift (50 mV in the $E_{[1/2]}$ value) is observed [Fig. 6(B)], which is due to the preconcentration of TH⁺ at Pt/PAMPS-*co*-PNHMA. After certain interval of time (approximately after 2 h), the increase in current levels off [insert of Fig. 6(B)] probably due to the saturation of all exchangeable $-\text{SO}_3^-$ groups at the electrode surface by TH⁺. Pt/PAMPS-*co*-PNHMA electrode showed 360% of increase in oxidation current in comparison with bare Pt electrode due to the preconcentration. The characteristic CV behavior of TH⁺ is retained at Pt/PAMPS-*co*-PNHMA even after transferring to pure supporting electrolyte (0.01N H₂SO₄ alone; Fig. 8). The plot of redox currents (I_{p_a} and I_{p_c}) against the square root of scan rate is linear indicating the diffusion controlled redox processes at the modified electrodes. The possible ion exchange process responsible for the preconcentration of TH⁺ at PAMPS-*co*-PNHMA is shown in eq. (2).

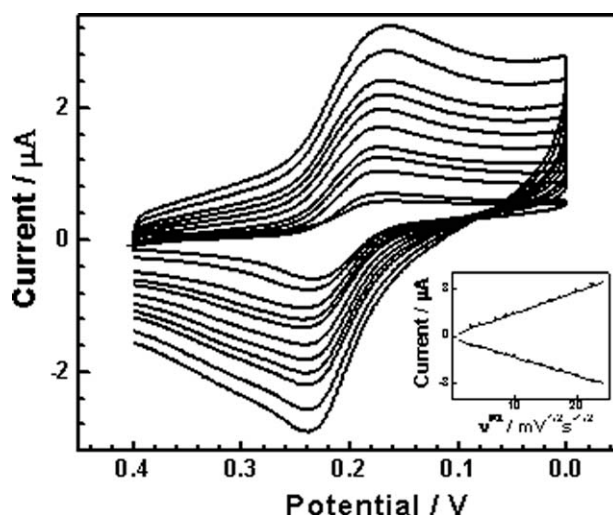
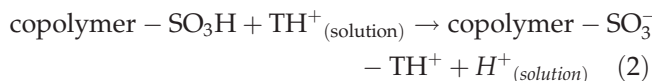


Figure 8 CV of Pt/PAMPS-*co*-PNHMA ion exchanged with TH⁺ at different scan rates (10, 20, 50, 75, 100, 200, 250, 300, 400, and 500 mV s⁻¹). Supporting electrolyte: 0.01N H₂SO₄. + Sign indicates the starting point of the scan. Insert shows the plot of peak currents against square root of scan rate.

Pt/PNHMA did not show any preconcentration capability. Pt/PAMPS shows an initial increase in current. However, after 15–25 min, the current start decreasing due to the slow dissolution of PAMPS into solution. Thus, Pt/PAMPS-*co*-PNHMA is more suitable for ion exchange voltammetry studies because of its improved ion exchange properties and mechanical stability at the electrode surface. This particular property (preconcentration ability) of PAMPS-*co*-PNHMA can be applied to any cationic species for trace level determination, provided the analyte is electroactive (i.e., undergo oxidation and/or reduction; Rastogi et al., in preparation).

CONCLUSIONS

The copolymer of 2-acrylamido-2-methylpropane sulfonic acid (APMS) and *N*-hydroxy methylacrylamide (NHMA) has been successfully synthesized by free radical polymerization using CAN initiator. FTIR spectra and the NMR analysis confirmed the copolymerization of APMS and NHMA. The rheology studies show that the copolymer (PAMPS-*co*-PNHMA) exhibits non-Newtonian behavior (pseudoplastic). SEM analysis demonstrates the drastic change in morphology of PAMPS-*co*-PNHMA, which has cylindrical sphere-shaped structure, whereas the homopolymers show fibrillar structure. The thermal measurements (DSC) confirm that the copolymer has higher T_g than the corresponding homopolymers. X-ray diffraction pattern shows the absence of homopolymer (PNHMA) in the copolymer product PAMPS-*co*-PNHMA. Ion exchange voltammetry at the polymer-modified electrodes demonstrated that the copolymer PAMPS-*co*-PNHMA is more suitable for ion exchange voltammetry studies, which may find applications in trace analysis.

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