Bioengineering Functional Copolymers. XI. Copper(II)-Poly(N-vinyl-2-pyrrolidone-co-N-isopropylacrylamide) Macrocomplexes

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ABSTRACT: A series of poly(N-vinyl-2-pyrrolidone-co-N-isopropylacrylamide)s, poly(VP-co-NIPA) copolymers with different compositions were prepared by radical copolymerization of VP and NIPA in N,N'-dimethylformamide at 65°C using 2,2'-azobisisobutyronitrile as initiator. Cu(II)-copolymer macrocomplexes were prepared by complexation of the copolymers with copper sulfate in aqueous solution at 40°C. The structure and composition of the copolymers, and the formation of coordinated Cu(II)-complexes between amide VP units and Cu^{2+} ions, were studied by FTIR spectroscopy, DSC and TGA-DTG in addition to electrical conductivity. Studies on the relationship between composition and thermal behavior showed that the values of T_g and T_d of the copolymers and their coordinated macrocomplexes increased with increasing VP content. The copolymers predominantly show amorphous structure while their Cu(II)-macrocomplexes show the presence of a crystalline phase. The conductive properties of the synthesized Cu(II)-poly(VP-co-NIPA) complexes are also discussed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 903–909, 2008

Key words: radical polymerization; metal-polymer complexes; thermal properties; bioengineering; conducting polymers

INTRODUCTION

Polymeric metal complexes are finding applications in several different fields of chemistry, such as catalysis, metal separations, biochemistry, medicine, and environmental chemistry.[1] Several hydrophilic polymers incorporating functional chelating ligands suitable for complexation with metal ions have been prepared and investigated for homogeneous complexation reactions. Hydrophilic noncrosslinked functional polymers that are able to complex metal ions have been termed polychelatogens. Polychelatogens characteristicly have two attributes: a polymer backbone which usually provides solubility and stability; and the presence of functional groups capable of metal complexation. Different approaches have been examined for preparation of polychelatogens including the introduction of metal-complexing groups into the polymers backbone, and preparation of copolymers with pendant functionality.[2] It is well known that copper forms metal complexes with amino-, pyridine-, and imidazole-containing polymers through coordination of the nitrogen atom and copper ion.[3–5] These N-containing Cu-macrocomplexes were used in ion conductors,[6,7] biomolecules separation,[8,9] and gas separation membranes.[10]

Metal macrocomplexes often show a specific catalytic activity[11,12] based on the nature of the ligand and complexed metal and are often compared to metal enzymes; indeed they are considered to be analogues of synthetic enzymes. Complexation of polymeric ligands with metal ions and ligand substitution reactions of polymer-metal complexes are used to separate metal ions and/or small molecules form contacting solutions.[2] Complexation of metal ions in solution is an important process in several fields, for example, design of ligands as therapeutic reagents for the treatment of metal intoxication,[13,14] design of antibiotics that owe their antibiotic action to specific metal complexation,[15] design pf complexes to act as imaging agents,[16] and in the design of functional groups for chelating ion-exchange materials[17] and catalysts.[18,19]

Some specific research has shown the usefulness of polychelates include complexes between poly(acrylic acid) and divalent, trivalent, and tetravalent metal ions and the stability constants for complex-formation determined.[20–22] The crystalline behavior and temperature-dependent electrical conductivity[23] of the Cu, Ni, and Cd polychelates formed with

poly(maleic acid-*alt*-acrylic acid) at different pH values were determined by X-ray diffraction spectroscopy.[17,24] Other polychelates have been prepared and studied including a terpolymer of ethyl methacrylate, *N*-phenylmaleimide, and itaconic acid, poly (EMA-*co*-PhMI-*co*-IA) complexed with Cu^{2+}, Co^{2+}, and Ni^{2+} ions.[25] Complexation of the terpolymer occurred through coordination of carboxylic groups of itaconic acid units with the added metal ions.[26] Poly(maleic anhydride-*alt*-methyl vinyl ether)/Fe^{2+} complexes were synthesized by reaction of the alternating copolymer with salts of divalent iron ($FeCl_2$, $FeBr_2$ or $FeSO_4.7H_2O$), which showed more prolonged action in chemotherapy than previously known Fe-containing compounds.[27]

This article discusses the synthesis and characterization of a series copper macrocomplexes with poly (*N*-vinyl-2-pyrrolidone-*co*-*N*-isopropylacrylamide)s [poly(VP-*co*-NIPA)s] copolymers, which were prepared by radical copolymerization in *N*,*N*′-dimthylformamide (DMF) at 65°C with 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The copolymers were prepared from a wide range of the monomer feed ratios. Especial attention was directed to the study of the Cu(II)-macrocomplex composition-properties (thermal behavior and conductivity) relationships, and to the evaluation of the conductive behavior of the synthesized Cu(II)-poly(VP-*co*-NIPA) complexes.

EXPERIMENTAL

Materials

VP monomer (Aldrich) was purified by distillation under moderate vacuum. NIPA monomer (Aldrich) was purified before use by distillation under vacuum and recrystallization from diethyl ether: bp (91.5 ± 0.5)°C/2 mm, m.p. 61.8°C (by DSC); ^{1}H-NMR spectra (CHCl$_3$-d_1), ppm: 1H NH 7.75, 1H CH = multiplet 6.19–6.26, 2H CH$_2$ = two doublets at 6.11–6.16 and 5.45–5.48, 1H CH (isopropyl group) 4.16 and 6H CH$_3$ (isopropyl group) 1.12. 2,2′-Azobisisobutyronitrile (AIBN) (Fluka) was twice recrystallized from methanol: m.p. 102.5°C.

Copolymerization procedure

A series of copolymerizations of VP with NIPA were carried out under nitrogen atmosphere in DMF at 65°C with AIBN as the radical initiator at constant total concentration of monomers.

Random copolymers of VP with NIPA, poly(VP-*co*-NIPA)s, were synthesized by radical-initiated copolymerization of different molar ratio's of the comonomers with AIBN as the initiator in DMF at 65°C under nitrogen atmosphere. Monomer feed molar ratios varied from 80 : 20 [VP] : [NIPA] to 20 : 80 [VP] : [NIPA]. Homopolymers of VP, and NIPA, poly (VP) and poly(NIPA), were also synthesized under similar conditions. Reaction conditions: $[M]_{total}$ = 1.66 mol/L, [AIBN] = 4.55 × 10^{-3} mol/L and monomer ratios of [VP]/[NIPA] = 0.25–4.0.

The VP-NIPA copolymers were isolated from the reaction mixtures by precipitation into diethyl ether. Each copolymer was dissolved in 1,4-dioxane and reprecipited by addition to diethyl ether, then washed with several portions of benzene and diethyl ether, and dried under vacuum at 40°C.

Preparation of complexes

In a typical example of the synthesis of Cu(II)-poly (VP-*co*-NIPA) macrocomplexes an aqueous solution of the copolymer was added to a 0.05M aqueous solution of $CuCl_2 \cdot H_2O$ then stirred vigorously for 45 min at 25°C. The solid polymeric Cu(II)-complex precipitated instantaneously and was filtered. Excess copper ions in the complex were removed by washing with deionized water. Then the solid powder was dried under vacuum at 50°C for 48 h. A molar ratio of copolymer (VP-unit) : $CuCl_2$ = 1 : 1 was used in all synthesis. The complexes were characterized by FTIR spectroscopy, DSC and TGA analyses, as well as by measurement of electrical conductivity.

Characterization

The molecular weights (M_n and M_w) and the dispersity index (M_w/M_n) of the copolymers were determined by Gel-Permeation Chromatography using a Shimpack 804 column with THF as a mobile phase-eluent at flow rate of 1.0 mL/min at 35°C. Polystyrene standards were used for molecular weight calibration. The intrinsic viscosities ($[\eta]_{in}$) of the copolymers were determined in dioxane at (25 ± 0.1)°C in the concentration range of 0.1–1.0 g/dL using an Ubbelohde viscometer. Copolymer compositions were determined by FTIR and ^{1}H-NMR spectroscopy using integration of analytical bands 3070 cm^{-1} for NIPA unit and 1495 cm^{-1} for VP unit, respectively, for quantitative analysis.

Fourier transform infrared (FTIR) spectra of the copolymers (KBr pellet) were recorded using a FTIR Nicolet 510 spectrometer in the 4000–400 cm^{-1} range, where 30 scans were taken at 4 cm^{-1} resolution. ^{1}H{^{13}C} NMR (DEPT-135) spectra were recorded on a JEOL 6X-400 (400 MHz) spectrometer with CHCl$_3$-d_1 as the solvent at 27°C. The compositions of the copolymers synthesized using various monomer feed ratios were determined by known FTIR[28,29] and NMR methods[29,30] and were achieved by comparing the absorbance values of NH (amide) and CH$_2$ (VP ring) bands and the integrals of the
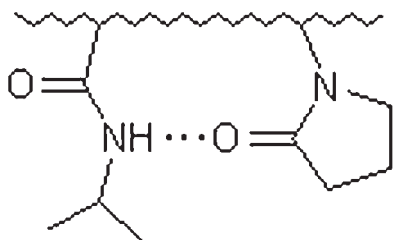
Scheme 1 Schematic representation of H-bonded linkage in copolymer structure.

CH_3 and NH regions in FTIR and ^{1}H-NMR spectra of NIPA and VP units, respectively.

Differential scanning calorimetry (DSC) and differential (DTG) and gravimetrical (TGA) thermal analyses of copolymers were performed on a DuPont TA 2000 calorimeter and Setaram Labsys TG-DTA 12 Thermal Analyzer, respectively, under nitrogen atmosphere at a heating rate of 10°C/min. Before conducting these analyses, all the polymer samples (10 mg) were thermotreated at 110°C for 30 min to remove their prior thermal history, followed cooling to 20°C.

Electrical conductivity (σ) of macrocomplexes was determined by a known method[13] by using a HP 740B standard voltage and a Keithley 6512 electrometer. The samples in the form of pellets were sandwiched between two stainless steel electrodes of 1 × 0.4 × 0.1 cm^3 area. Temperature was controlled using a Chromel-Alumel thermocouple. Polymer samples allowed to equilibrate for 20 min at (25 ± 0.1)°C. The values of voltage and current used were changed from 10 to 350 mV and from 5 to 120 mA, respectively. The values of σ (in 1/Ω.cm) for the studied polymer systems were calculated from plots of voltage (mV) versus current (mA).

RESULTS AND DISCUSSION

Synthesis of copolymers

The copolymers of VP with NIPA, poly(VP-co-NIPA) with different compositions were synthesized by radical-initiated copolymerization of different molar ratio's of the comonomers with AIBN as the initiator in DMF at 65°C under nitrogen atmosphere.

Poly(NIPA-co-VP) synthesized from equimolar (1 : 1) ratios of starting monomers has the following average characteristics: the number-average molecular weight M_n 10,200 g/mol, the weight-average molecular weight M_w 13,600 g/mol and the polydispersity index 1.33 (by GPC); the monomer unit ratio, m_1 (VP) : m_2 (NIPA) = 51.3 : 48.7 (by ^{1}H-NMR); [η]$_{in}$ 0.24 dL/g in 1,4-dioxane at (25 ± 0.1)°C; glass-transition temperature T_g 147.9°C, ΔH 0.29 J/g (by DSC) and decomposition temperature T_d 375°C (by TGA).

^{1}H-NMR spectra (in CHCl$_3$-d_1 at 27°C), ppm: (5 and 6) 6H, CH$_3$ (in NIPA isopropyl group) 1.13, (1) 2H, CH$_2$ (backbone in NIPA unit),(2) 1H, CH (backbone in NIPA unit) and 2H, CH$_2$ (backbone in VP unit) 1.25–2.12, (10) 2H, CH$_2$ (VP ring) 2.35, (11) 2H, CH$_2$ (VP ring) 3.21, (9) 2H, CH$_2$ (VP ring) 3.41, (4 and 8) 1H, CH (in NIPA side-chain and VP backbone) 3.62–4.15, (3) 1H NH (in NIPA amide group) 6.09–7.28 (broad signal).

Some characteristics of the homopolymers and copolymers prepared from starting monomer mixtures with molar ratios of VP:NIPA = 80 : 20 and 20 : 80 for this study follow: Poly(VP) : [η]$_{in}$ 0.061 dL/g in 1,4-dioxane at (25 ± 0.1)°C and T_g 172.7°C (by DSC). ^{1}H-NMR spectra (in CHCl$_3$-d_1), ppm: 1H CH backbone 3.95–4.11, 2H CH$_2$ (N-CH$_2$ ring) doublet centered at 3.45, 2H CH$_2$ (CO—CH$_2$ ring) doublet at 2.43–2.59, 2H CH$_2$ (C—CH$_2$—C ring) doublet centered at 2.27 and 2H CH$_2$ backbone around 1.64–1.94. Poly(NIPA): [η]$_{in}$ 0.012 dL/g in dioxane at 25°C and T_g 143.5°C (by DSC). ^{1}H-NMR spectra (in CHCl$_3$-d_1), ppm: 1H NH broad peak with centered at 6.44, 1H CH (isopropyl group) 4.24, 1H CH back-
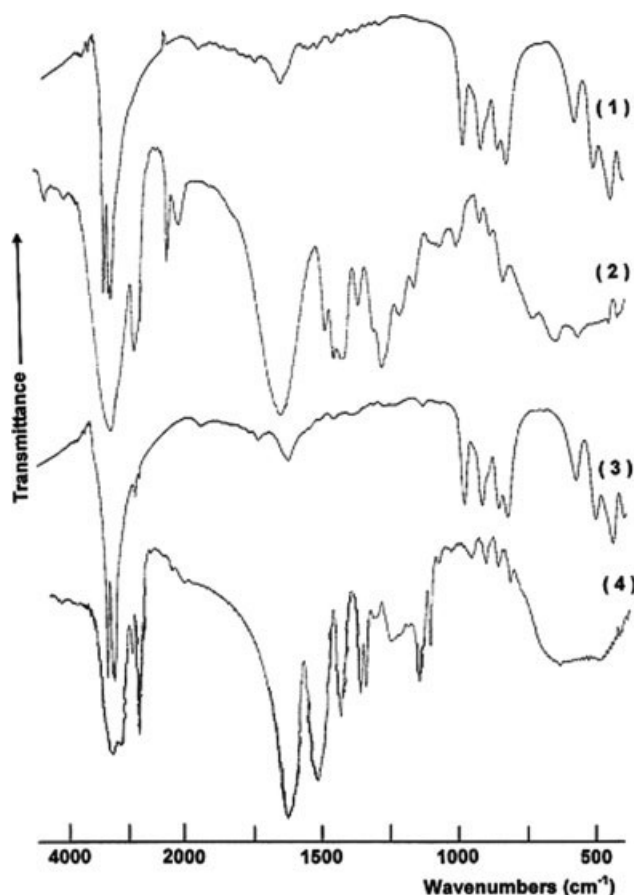
Figure 1 FTIR spectra of Cu(II)-macrocomplexes: (1) Cu(II)-poly(VP), (2) poly(VP), (3) Cu(II)-poly(NIPA), and (4) poly(NIPA).
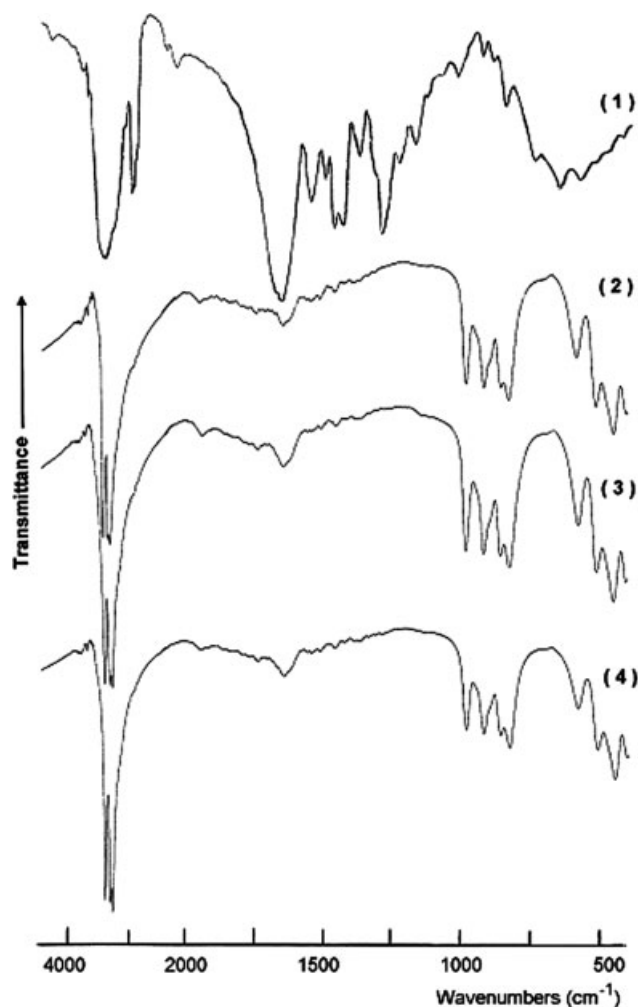
Figure 2 FTIR spectra of Cu(II)-macrocomplexes: (1) poly (VP-*co*-VP), (2) Cu(II)-poly(VP-*co*-NIPA)-I, (3) Cu(II)-poly (VP-*co*-NIPA)-II, and (4) Cu(II)-poly(VP-*co*-NIPA)-III.

bone 2.32, 2H CH_2 backbone 1.86–2.07 and 6H CH_3 (isopropyl group) 1.38. *Poly(VP-co-NIPA)-I*: monomer unit ratio $m_1 : m_2 = 74.7 : 25.3$, $[\eta]_{in}$ 0.26 dL/g in 1,4-dioxane at 25°C, $M_n = 10,500$ g/mol and T_g 223°C (by DSC). *Poly(VP-co-NIPA)-III*: monomer unit ratio $m_1 : m_2 = 30.1 : 69.9$, $[\eta]_{in}$ 0.28 dL/g in 1,4-dioxane at 25°C, $M_n = 11,700$ g/mol and T_g 226°C (by DSC).

These homo- and copolymers with different compositions were also characterized by FTIR and ^{1}H $\{^{13}C\}$NMR spectroscopy. It was previously demonstrated that hydrogen-bonding between the amide and carbonyl groups of monomers and monomer units (Scheme 1) played an important role in the formation of the copolymers reaching the alternating diads.[29]

Poly(VP-*co*-NIPA)s show pH- and temperature sensitive behavior in aqueous solutions, which are advantageous for various bioengineering applications. Low critical solution temperature of these copolymers strongly depends on the VP unit contents, and

increases from 29.8 to 44.6°C with increasing VP content in copolymers.[29]

Structural peculiarities

The macrocomplexes easily precipitate from aqueous solutions of the copolymer/$CuCl_2$ mixtures with given compositions. The structure of the macrocomplexes synthesized in this study was confirmed by FTIR spectroscopy by comparative analysis of the spectra of the homopolymers, copolymers, and Cu(II)-copolymer complexes. The results are illustrated in Figures 1 and 2. Figure 1 presents the spectra of poly(VP) and poly(NIPA) and their Cu(II)-complexes. The FTIR data shows that the most significant changes are observed in the region of carbonyl groups, which are directly involved in complex formation with Cu(II) ions. The considerable decrease in intensity of C=O bands observed in the spectra of Cu(II)-polymer complexes when compared with their Cu-free analogs indicate the formation of physically crosslinked and intermolecular complexed ligands with a rigid structure. This fact is also con-
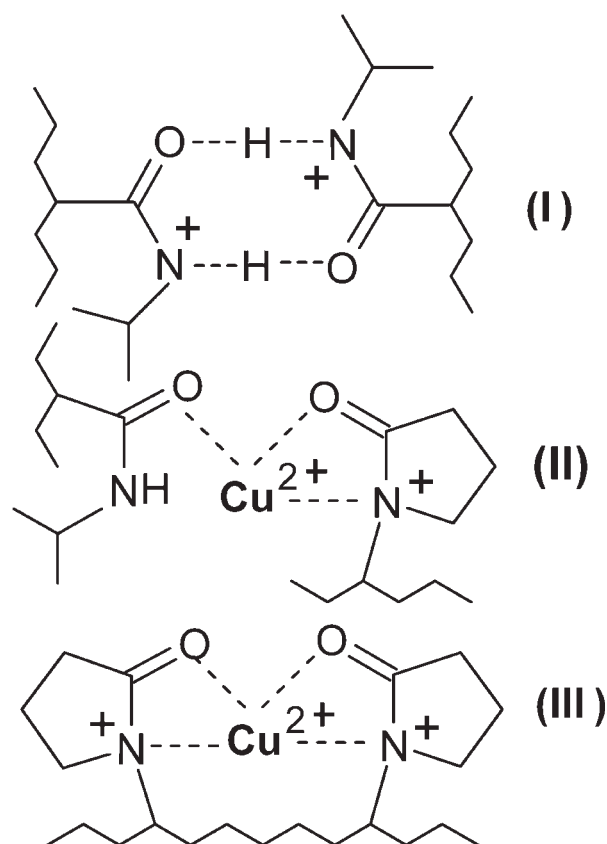
Scheme 2 Schematic representation of poly(VP-*co*-NIPA)/Cu-macrocomplex structures. (I): Hydrogen bonding complex between NIPA/NIPA linkages, (II): Coordinated Cu-complex between NIPA/VP linkages, (III): Coordinated Cu-complex between VP/VP linkages.

TABLE I
Thermal Behavior of Homo- and Copolymers of VP and NIPA and Their Cu(II) Macrocomplexes

(Co)polymers and their macrocomplexes	VP-unit in polymer (mol %)	$T_g{}^a$ (°C)	$T_m{}^a$ (°C)	$T_d{}^b$ (°C)	TGA analysis		
					Loss weight (%) at (°C)		
					200	300	400
Poly(VP)	100	172.7	–	394	0.0	1.2	25.0
Cu(II)-poly(VP)	63.6		228.2	260	0.0	14.5	14.9
Poly(NIPA)	0.00	143.5	–	350	7.3	15.5	37.6
Cu(II)-poly(NIPA)	0.00		236.9	275	0.0	13.0	16.5
Poly(VP-co-MA)-I (80:20)	74.7	159.8	–	387	0.9	1.7	52.0
Cu(II)-poly(VP-co-NIPA)-I	52.2		226.0	257	1.3	16.3	17.2
Poly(VP-co-MA)-II (50:50)	51.3	147.9	–	375	1.0	1.5	29.0
Cu(II)-poly(VP-co-NIPA)-II	39.4		235.3	266	0.0	10.0	10.2
Poly(VP-co-MA)-III (20:80)	30.1	156.9	–	361	1.6	2.1	27.0
Cu(II)-poly(VP-co-NIPA)-III	26.1		223.0	265	0.0	8.5	9.6

[a] Obtained values from DSC analysis.
[b] The maximum values of decomposition temperature in DTG curves.

firmed by the observed insolubility of Cu(II)-polymer complexes in organic solvents and water.

Similar changes were observed in the spectra of Cu(II)-poly(VP-co-NIPA)s (Fig. 2). It is known that when macromolecules change from a linear structure to a crosslinked form, as a consequence of formation of metal-ligand complexes, the intensities of the main stretching (preferably) and bending bands are significantly decreased and are accompanied by decreased motion of the macromolecular chain, and therefore, vibrations of the backbone and neighboring side-chain bonds joining around cupper ions. These results allow us to propose the following probable structures in the form of Cu(II)-polymer ligands through Cu-monomer units complexation, preferably via VP linkage (structures II and III), as well as through H-bonding in the case of NIPA units (Structure I), which are represented in Scheme 2.

Thermal behavior

The thermal behavior of the homo- and copolymers and their Cu(II)-macrocomplexes were studied by TGA-DTG and DSC techniques at a heating rate of 10°C/min under a nitrogen atmosphere. The results obtained in these analyses are summarized in Table I. Characteristic TGA-DTG curves and fragments of DSC scans of the Cu(II)-poly(VP-co-NIPA) are illustrated in Figure 3. Cu-free homo- and copolymers exhibited a typical glass-transition behavior, which is a characteristic for the amorphous physical state of polymers. By contract, Cu(II)-macrocomplexes also exhibit a melt-transition that indicated the semicrystalline structure of these complexes. Similar semicrys-
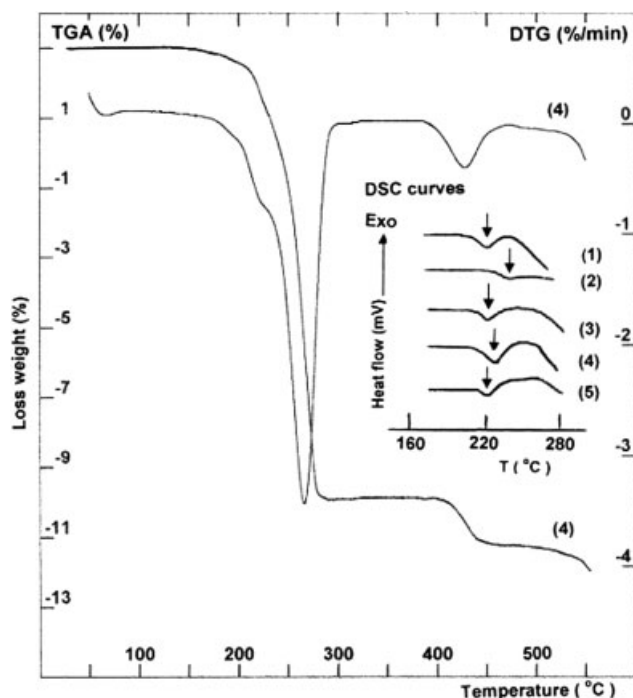
Figure 3 TGA-DTG (4) and DSC (1–5) curves of Cu(II)-macrocomplexes: (1) Cu(II)-poly(VP), (2) Cu(II)-poly (NIPA), (3) Cu(II)-poly(VP-co-NIPA)-I, (4) Cu(II)-poly(VP-co-NIPA)-II, and (5) Cu(II)-poly(VP-co-NIPA)-III.

TABLE II
Electrical Conductivity (σ) of Cu(II)-Poly(VP-co-NIPA)s with Different Compositins

Macrocomplexes	Content of VP-unit (mol %)	Conductivity, σ $(\Omega.cm)^{-1}$
Cu(II)-poly(VP)	63.6	0.97×10^{-10}
Cu(II)-poly(NIPA)	0.0	1.08×10^{-11}
Poly(VP-co-NIPA)	74.7	3.68×10^{-12}
Cu(II)-poly(VP-co-NIPA)-I	52.2	8.12×10^{-10}
Cu(II)-poly(VP-co-NIPA)-II	39.4	6.72×10^{-10}
Cu(II)-poly(VP-co-NIPA)-III	26.1	4.26×10^{-10}
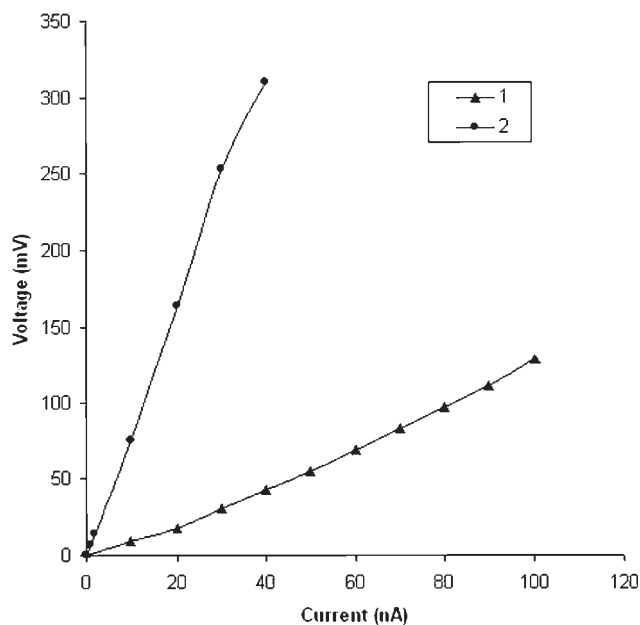
Figure 4 The plots of current (mA) versus voltage (mV) for (1) Cu(II)-poly(VP) and (2) Cu(II)-poly(VP-*co*-NIPA)-I coordinated macrocomplexes. From slope of these plots were calculated the values of conductivity.

talline polychelate structure was observed for the Cu(II)-poly(maleic acid-*alt*-acrylic acid) macrocomplex by using X-ray powder diffraction method.[24]

Monomer unit ratio in the copolymers influenced the thermal behavior of the Cu(II)-macrocomplexes. In the case of Cu(II) complexes of copolymers, (Cu(II)-copolymer-I and Cu(II)-copolymer-III), prepared from monomer feed ratios of VP : NIPA = 80 : 20 and 20 : 80, relatively low values were observed for melting temperature (223 and 226°C, respectively) while the Cu(II) complex of the copolymer (Cu(II)-copolymer-II) prepared from 1 : 1M ratios of monomer feed melted at 235.3°C. This phenomenon can be explained by higher fraction of VP-NIPA diad linkages in copolymer, which are responsible for the formation of a more compact macromolecular structure through complexation of Cu(II) ions predominantly with VP linkages and H-bonding (preferably via NIPA secondary amide groups) as shown in Scheme 2.

Conductivity

The measured values of conductivities of coordinated Cu(II)-macrocomplexes of homo- and copolymers of VP and NIPA at room temperature are summarized in Table II. A typical plot of current (nA) versus voltage (mV) for the Cu(II)-poly(VP) and Cu(II)-poly (VP-*co*-NIPA)-I is illustrated in Figure 4. The values obtained indicate that the copolymers showed a higher tendency to form of Cu(II)-macrocomplexes

than either of the homopolymers. This can be explained by participation of both the VP (preferably) and NIPA linkages in complex formation with the Cu(II) ions. Conductivity of Cu(II)-poly(VP-*co*-NIPA)s depends on the amount of VP units in the copolymer; an increase in the mole fraction of VP in the copolymer is accompanied by an increase in the conductivity of the macrocomplex. Relatively lower conductivity was also shown for the copper free poly(VP-*co*-NIPA) and Cu(II)-poly(NIPA).

CONCLUSIONS

The work presents the synthesis and characterization of Cu(II)-coordinated macro-complexes homopolymers and alternating and random copolymers of VP and NIPA directed at bioengineering applications. Thermal behavior and electrical conductivity of the Cu(II)-macrocomplexes essentially depends on the composition and monomer unit distribution of poly (VP-*co*-NIPA)s. The most compact rigid structure is formed in the Cu(II)-poly(VP-*alt*-NIPA) system, containing alternating VP-NIPA diads. The Cu(II)-macrocomplexes exhibit semicrystalline structure, high thermal behavior and electrical conductivity in contrast to their Cu-free analogues. The macrocomplexes easily precipitate from aqueous solutions. Polymeric ligands showed some pH- and temperature sensitivity. These unique properties may allow application of these copolymer systems for toxic metal separation and bioseparation technology, and other bioengineering processes.

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