

Tailoring copper (II) methacrylate-containing copolymers and its use as electrode modifier agent in electroanalytical applications

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ABSTRACT: This work focuses on the synthesis of a new class of copolymer materials consisting of traditional vinyl monomers (essentially, vinyl acetate, ethyl acrylate, and methyl methacrylate) and copper (II) methacrylate (Cu(II)MA) intended to be used as surface modification agents in electrochemical quantifications of organic and inorganic analytes. Voltammetry assays showed that when deposited on glassy-carbon electrode (GCE), Cu(II)MA-based copolymers are very promising materials to be applied in electrochemical determinations, exhibiting high analytical signal in the oxidation and reduction peaks during quantification of potassium hexacyanoferrate (III) in comparison to a bare GCE, contributing to increase the effective electrode area. When employed for the determination of ascorbic acid, PVAcCu(II)MA/GCE exhibited performance similar to that of the bare GCE. Polymers characterizations showed that glass transition temperature of the Cu(II)MA-based materials increased in approximately 10–20°C, as consequence of the copper present in molecular structure of the copolymer chains (bidentate bridging coordination mode). Energy-dispersive X-ray spectroscopy measurements of Cu(II)MA monomer and Cu(II)MA-based copolymers showed strong characteristic peaks $K\alpha$ and $K\beta$ at 8.04 and 8.90 keV, respectively, with an average amount of copper of 99%. The performance of the Cu(II)MA-based copolymers modified electrodes is strongly dependent on the amount of copper into the copolymer chains and consequently on the monomers conversion. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43202.

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INTRODUCTION

Metal-containing monomers (MCMs) were defined as metallic complexes normally presenting specific ligands, which undergo free-radical polymerization.¹ The MCMs have been first synthesized with the idea of obtaining an electrostatic interaction or even a covalent bond (σ or π) between metal and ligand. The type of bond is extremely important for the properties of polymers derived from MCMs, acting on the stability and behavior of the final material.²

Depending on the metallic complex, MCMs can successfully originate several homopolymers, copolymers, and cross-linked materials with the aid of reticulating agents. In both cases, the observed reaction behavior in the synthesis of homopolymers and copolymers is characterized by an inhibitory effect caused by the insertion of the metal in the polymeric chains, which is responsible for decreasing the reaction rate and conversion of the system, requiring long reaction time.³ To overcome these

undesirable effects, it is frequently necessary to increase the concentration of the initiator of polymerization.⁴ In spite of that, it is worth to keep in mind that an excess of initiator concentration may lead to polymers with low average molar masses.^{5,6}

Polymers based on these monomers have many advantages, such as, the protection of metal center by the organic polymer (allowing the metal to maintain its valence and complex geometry even during the polymerization reaction) and the homogeneous distribution of the metals in the polymeric chain.¹ Because of these interesting properties, MCMs have been applied in different applications such as molecularly imprinted polymer,^{7,8} catalysis,^{9–12} and quasicrystals.¹³ Many types of metals are used for MCMs such as palladium, titanium, iron, copper, cadmium, chromium, and many others.²

For copper-containing monomers, the most common ligands are carboxylates molecules, as for example, acrylates and methacrylates. In this polymer field, it is very important to highlight

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the studies performed by the group of Professor Pomogailo focusing on the spectroscopic and the thermal features of copper acrylate homopolymers.^{14,15} These pioneering studies initiated developments about the application of polymer based on copper carboxylates.

Uflyand *et al.*¹⁶ have modified the copper acrylate with 2,2'-bipyridyl or 1,10-phenanthroline. Sequentially, these MCMs have been grafted in the polymeric chain of polyfluoroethylene. The final materials have shown to be useful as additive in plastic lubricant applications due to its good tribotechnical properties. Modified copper acrylate polymers with both the 2,2'-bipyridyl and the 1,10-phenanthroline exhibited a further signal increase due to a reduction of Cu^{2+} to Cu^0 followed by a modification in the structure of polyfluoroethylene that promoted an interaction of these polymers on the metal surface. Another important example of the application of copper-containing monomers is the production of molecularly imprinted polymers.

Dam *et al.*¹⁷ have obtained a polymer based on the copper methacrylate and the reticulating agent, glycol dimethacrylate. This material showed a good absorption of ions Cu^{2+} , when compared to Ni^{2+} and Cd^{2+} . At pH 6, the adsorption of Cu^{2+} was determined to be around 6 times higher than Ni^{2+} and 10 times higher than Cd^{2+} . The adsorption was enhanced with the increment of pH for these three ions because of the dissociation of carboxylic groups.

The use of polymeric films for chemical modification of electrode surface represents a very important stage in the electroanalytical determination of chemicals compounds. The concept of chemically modified electrodes (CMEs) has been widely discussed by Murray *et al.*¹⁸ in an interesting review article, which focus on the main aspects that influence the electrode performance after the deposition of chemical reagents on its surface. According to the authors, important phenomena (such as adsorptive and coating effects, selectivity of electrochemical reactions) that may take place during the electroanalysis may be appropriately controlled through proper selection of the chemical nature of the reagent attached on the electrode surface.

Other studies focusing on the films performance showed that an increase in analytical signal, electrochemical window, and selectivity may be frequently observed.^{18–20} In this scenario, the use of MCM-based polymers to form chemically modified electrodes for analytes detection/determination may be very attractive.

Although the importance of the MCMs as precursor of polymeric materials, it should be recognized that few studies in the open literature regarding the applications of these materials have been effectively performed. And if one specifically considers the production of copolymers of vinyl monomers and MCMs, there are no studies published in the open literature concerning the synthesis and characterization, which reveals that both the applications and the properties of these materials are largely unexplored.

Based on this observation, this work first aimed to evaluate a new class of copolymers consisting of traditional vinyl monomers (such as vinyl acetate, ethyl acrylate, or methyl methacry-

late) and copper (II) methacrylate for a better understanding of the thermal and structural properties. The second goal of this work was to evaluate the potential use of these copolymeric materials as surface modification agents in chemically modified electrodes in order to enhance the current signal (analytical signal) for voltammetric determination of potassium hexacyanoferrate (III) and ascorbic acid as model analytes.

EXPERIMENTAL

Materials

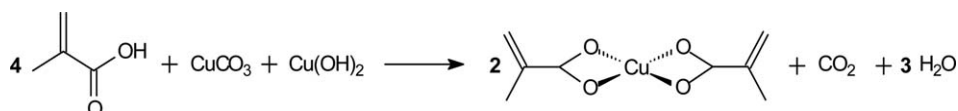
Synthesis of Copper (II) Methacrylate [Cu(II)MA] Monomer. The reagents used for the synthesis of Cu(II)MA were methacrylic acid (MAA) with purity of 99%, provided by VETEC Química Fina Ltda (Rio de Janeiro, Brazil). Basic copper (II) carbonate [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$] with purity of 99.9% and dichloromethane with purity of 99% were provided by Dinâmica Química Contemporânea Ltda (Diadema, Brazil). All chemicals were used as received, without further purification.

Synthesis of Copolymers Based on Vinyl Monomers and Copper (II) Methacrylate. The comonomers used for the copolymers syntheses were vinyl acetate (VAc) with purity of 99% and methyl methacrylate (MMA) with purity of 99.5%, supplied by VETEC Química Fina Ltda (Rio de Janeiro, Brazil). Ethyl acrylate (EA) with purity of 99.5% was provided by Sigma-Aldrich Brasil Ltda (São Paulo, Brazil). Benzoyl peroxide (BPO), LUPEROX 78, used as initiator of the polymerization reactions, was kindly donated by Arkema Química Ltda, São Paulo, Brazil with a minimum purity of 75%, containing water as stabilizer with a mass fraction 25% and 5 wt % active oxygen. Ethanol with purity of 95%, used as continuous phase of reaction, was provided by VETEC Química Fina Ltda. All chemicals were used as received, without additional purification.

Voltammetric Studies with the Polymeric Films. Tetrahydrofuran, HPLC grade with 99.5% purity, was provided by J.T. Baker[®] (São Paulo, Brazil) and used as solvent for dispersion of polymeric films. Ultrapure water (resistivity $>18.2 \text{ M}\Omega\text{-cm}$) was used as solvent for the remaining solutions. Solutions of supporting electrolyte were prepared with potassium chloride (KCl) with purity of 99.9%, provided by Dinâmica Química Contemporânea Ltda (Diadema, Brazil), and sulfuric acid (H_2SO_4) with purity of 99.9%, provided by Quemis Indústria Química do Brasil Ltda (Joinville, Brazil). The analyzed compounds were potassium hexacyanoferrate (III) with purity of 99.9%, supplied by Fluka (São Paulo, Brazil) and ascorbic acid with purity of 99.99% were provided by Sigma-Aldrich Brasil Ltda (São Paulo, Brazil). All chemicals were used as received, without further purification.

Experimental Methodology

Synthesis of Copper (II) Methacrylate Monomer. The copper (II) methacrylate was synthesized based on the experimental method described by Dam *et al.*,¹⁷ and slightly modified in this work. Initially, 29.5 mmol of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (6.51 g) was added to 80 mL of dichloromethane under magnetic stirring. In the sequence, 117.9 mmol of methacrylic acid (10.15 g) was added to the previous solution. The reaction was kept for 2 days with continuous stirring at room temperature. After this,



Scheme 1. Kinetic mechanism for the formation reaction of copper (II) methacrylate.

the product of the reaction was filtered and dried to eliminate reagents (basic copper (II) carbonate and methacrylic acid) unreacted. A blue solid was formed at the end of the procedure. Scheme 1 shows the kinetic mechanism of the formation reaction of the Cu(II)MA.

Synthesis of Cu(II)MA-Containing Copolymers. The experimental set-up employed in the pseudodispersion copolymerization reactions of vinyl monomers (e.g., vinyl acetate—VAc, methyl methacrylate—MMA, and ethyl acrylate—EA) and Cu(II)MA was very similar to the one described by Ferreira *et al.*,²¹ and the reader is referred to this publication for a more detailed description of the protocol of reaction. The polymerizations were performed in a 250 mL, five-necked glass reactor (Quickfit, England), equipped with a hotplate IKA RCT basic (IKA Works, Inc.), connected to an integrated temperature control and a Pt1000 temperature probe (used to kept the reaction temperature constant at the setpoint value); overhead stirrer EUROSTAR POWER control-visc (IKA® Works, Inc., São Paulo, Brazil) linked to a helix-type impeller; and a reflux condenser, coupled to a cold water feed stream.

First, 5 g of Cu(II)MA was dispersed into 90 mL of ethanol under mechanical stirring of 1100 rpm. Then, a mixture containing the 25 g of vinyl comonomer (VAc, EA or MMA) and 1.5 g of benzoyl peroxide (the thermal free radical initiator of polymerization) was added to the reactor system, which was heated to $70 \pm 1^\circ\text{C}$ with constant agitation speed for 9 h. The polymer materials are named as follows: poly(vinyl acetate-*co*-copper (II) methacrylate) as PVAcCu(II)MA; poly(ethyl acrylate-*co*-copper (II) methacrylate) as PEACu(II)MA; and PMMA-Cu(II)MA is reserved to poly(methyl methacrylate-*co*-copper (II) methacrylate).

Voltammetry Studies: Cu(II)MA-Based Copolymers Modified Electrodes. The voltammetric experiments were performed on an AUTOLAB PGSTAT-30 (Ecochemie, Utrecht, Netherlands) potentiostat/galvanostat interfaced with a computer and controlled with the GPES 4.0 software. The system was composed by three electrodes: a reference electrode (Ag/AgCl with $3.0 \text{ mol}\cdot\text{L}^{-1}$ KCl), an auxiliary electrode of platinum, and a working electrode (a glassy-carbon electrode (GCE) with diameter of 3.7 mm or a modified glassy carbon electrode coated with polymeric films). These electrodes were used in a glass cell of 15 mL.

First, the working electrode was polished with a sand paper of 0.10 and 0.05 μm of alumina suspensions to obtain a mirror surface. Then, this electrode was washed with ultrapure water, sonicated for 5 min and then, dried at room temperature. For evaluation of these polymeric films, it was dispersed 1.00 mg of copolymer [PVAcCu(II)MA, PEACu(II)MA, or PMMA-Cu(II)MA] in 1 mL of tetrahydrofuran. This instable dispersion was sonicated for 30 min to obtain a more homogeneous distribution.

Sequentially, it was placed 10 μL of this dispersion on the GCE. After 15 min (drying time), another 10 μL aliquot of dispersion was placed at GCE surface and then the solvent is allowed to evaporate at room temperature for approximately 15 min.

Specifically to evaluate the influence of the copolymer film thickness on the GCE performance, aliquots of the 1.00 mg/mL PVAcCu(II)MA copolymer solution of volumes equivalent to 10, 20, 40, and 60 μL have been applied on the GCE surface, in accordance with the experimental procedure described previously. The relationship between the copolymer film thickness and the copper mass fraction is shown in Figure S2 in Supporting Information.

After drying, this electrode underwent a cyclic voltammetric tests. It was used three analytes to observe the signal response caused by the addition of a copolymer. The first and principal analyte was potassium hexacyanoferrate (III) with a final concentration of $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ and $0.1 \text{ mol}\cdot\text{L}^{-1}$ for the supporting electrolyte KCl. For the ascorbic acid, it was only used the GCE covered by PVAcCu(II)MA. For the ascorbic acid, the final concentration was $10^{-3} \text{ mol}\cdot\text{L}^{-1}$ and $0.1 \text{ mol}\cdot\text{L}^{-1}$ of the supporting electrolyte, KCl.

Material Characterization

The structure of the monomer Cu(II)MA, vinyl homopolymers [poly(vinyl acetate) (PVAc), poly(ethyl acrylate) (PAE), and poly(methyl methacrylate) (PMMA)] and copolymers [PVAc-Cu(II)MA, PEACu(II)MA, and PMMA-Cu(II)MA] were evaluated by mid-infrared spectroscopy (IR) with attenuated total reflectance (ATR) accessory. The measurements were carried out on an FTIR spectrometer FT/IR-4100 (Jasco, Essex, United Kingdom) with the resolution of 4 cm^{-1} and 32 scans.

The thermal stability of Cu(II)MA and copolymers was evaluated by thermogravimetry (TG) on a Thermogravimetric Analyzer Shimadzu DTG-60H (Shimadzu Scientific Instruments, Maryland, USA) at heating rates of $10^\circ\text{C}\cdot\text{min}^{-1}$, under nitrogen atmosphere with a flow rate of $30 \text{ mL}\cdot\text{min}^{-1}$. In the analysis, it was used a sample mass around 8.0–10.0 mg and platinum crucibles. For evaluation of glass transition temperatures of the polymer materials, it was used the differential scanning calorimetry performed on a Shimadzu DSC-60 calorimeter (Shimadzu Scientific Instruments, Maryland, USA) at heating rates of $10^\circ\text{C}\cdot\text{min}^{-1}$ under helium atmosphere of $30 \text{ mL}\cdot\text{min}^{-1}$. In the analysis, it was used a sample mass in the range from 8.0 to 10.0 mg and sealed aluminum crucibles.

The X-ray diffraction (XRD) patterns of the Cu(II)MA and the precursor reagent [copper (II) carbonate] were determined on a Bruker D8 FOCUS X-ray diffractometer (Bruker AXS, Inc., Wisconsin, USA), using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, and 30 mA). The diffraction patterns were performed at a scan rate of $0.25^\circ\cdot\text{min}^{-1}$ with steps of 0.05° and values of 2θ in the

angular range of 2° – 80° . The measurements of energy-dispersive X-ray spectroscopy (EDX) for the MCM and the polymeric materials were carried out on an EDX-720 fluorescence spectrometer (Shimadzu Europa GmbH, Duisburg, Germany). The EDX spectra were acquired with steps of 0.02 and a live time of 100 s, using the Ti-U channel.

The morphology of surface of the polymeric films was observed through scanning electron microscopy (SEM) on a JEOL JSM-7001F Field Emission Scanning Electron Microscope (Jeol Ltd., Tokyo, Japan) operating at an accelerating voltage of 15 keV. Polymer film samples were previously coated with a thin layer of gold deposited by sputtering process.

The solid-state ^{13}C MAS NMR spectra were acquired on a Bruker Avance II+ 300 MHz spectrometer (Bruker do Brasil, São Paulo, Brazil). The spectra were obtained at a spinning speed of 10 kHz, 2048 scans with 3 s of recycle delay.

The fraction of copper in the Cu(II)MA monomer and Cu(II)MA-based copolymers was determined through inductively coupled plasma optical emission spectrometry on an iCAP 6300 Duo ICP optical emission spectrometer (Thermo Fisher Scientific, Cambridge, United Kingdom), equipped with a nebulizer pump (pressure of 0.16 MPa, Flush Pump Rate equal to 50 rpm, analysis pump rate of 25 rpm and relaxation time of 5 s), an axially and a radially viewed plasma, a simultaneous charge injection device detector in the ranging from 166.25 to 847.00 nm and an argon gas purge.

RESULTS AND DISCUSSION

Figure 1 shows the IR spectra of Cu(II)MA monomer and copolymers [PVAcCu(II)MA, PEACu(II)MA, and PMMA-Cu(II)MA]. The infrared spectrum of copper (II) methacrylate indicates characteristic bands at 1645, 1555, 1410, and 1000 – 900 cm^{-1} related to C=C stretching, symmetrical stretching COO^- , asymmetrical stretching COO^- , and bending of C–H e C–C, respectively. The value of Δ [where Δ is equal to (wavenumber of symmetrical stretching COO^-) – (wavenumber of asymmetrical stretching COO^-)] is 145 cm^{-1} , which is related to bridging coordination of the carboxylate ions in the complex. The characteristic band referent to Cu–O bond does not appear at IR/ATR because this band appears near to 400 cm^{-1} and the cell of ATR does not exhibits the spectra at wavenumber below 600 cm^{-1} .²²

For the PVAcCu(II)MA copolymer [Figure 1(A)], it is observed bands related to both the poly(vinyl acetate) (PVAc) and the Cu(II)MA monomer. The bands relative to Cu(II)MA are observed at 1555 cm^{-1} , 1410 cm^{-1} and some broad bands between 1000 and 900 cm^{-1} . The bands corresponding to PVAc homopolymer are noticed in the range from 2940 to 2970 cm^{-1} (symmetrical and asymmetrical stretching C–H sp^3) and 1725 cm^{-1} (stretching of C=O). The bands at 1230 cm^{-1} are related to both the Cu(II)MA and the PVAc, relative to the C–O stretching.^{15,23–25}

In particular for the PEACu(II)MA copolymeric material [Figure 1(B)], it is observed that bands related to both the poly(ethyl acrylate) (PEA) and Cu(II)MA monomer. The bands referent to Cu(II)MA are located at 1550 cm^{-1} , 1410 cm^{-1} , and some broad

bands at 1000 and 900 cm^{-1} . The bands relative to PEA are located at 3050 cm^{-1} (symmetrical and asymmetrical stretching C–H sp^3) and 1720 cm^{-1} (stretching of C=O).^{15,23–25}

Infrared spectra of PMMACu(II)MA copolymer, poly(methyl methacrylate) (PMMA) and Cu(II)MA monomer are presented in Figure 1(C). Cu(II)MA monomer exhibits characteristic bands at 1550 and 1410 cm^{-1} . The bands corresponding to PMMA are observed between 2930 and 3030 cm^{-1} (symmetrical and asymmetrical stretching C–H sp^3), 1720 cm^{-1} (stretching of C=O), 1190 cm^{-1} (O–C–O carbonyl stretching), and 1120 cm^{-1} (rocking vibration of polymeric chain).^{15,23–25}

Figure 2 shows the results of thermogravimetric analyses of PVAc, PPEA, PMMA, Cu(II)MA, and copper-containing copolymers performed in order to evaluate the thermal stability of the polymeric materials and determine the mass fraction of inorganic residue into the analyzed materials. The copper (II) methacrylate presents three important weight-losing: the first one occurs in the range from 90 to 130°C (this weight loss is probably related to the solvent evaporation), the second is observed between 160 and 230°C , and the third significant weight loss takes place in the range from 230 to 300°C . The second and the third weight losses are related to the polymeric chain degradation. The weight fraction of inorganic residue was determined to be around 38 wt %.

The PVAcCu(II)MA copolymeric material exhibits a single weight loss that occurs in the range from 130 to 380°C with inorganic residue of 36 wt % only related to Cu(II)MA. Compared to PVAc [initial weight loss observed at 270°C , as shown in Figure 2(A)], the PVAcCu(II)MA shows a decrease in the thermal stability. The PEA-Cu(II)MA copolymer shows a large weight loss ranged from 100 to 500°C with a final residue of 32 wt %, related to Cu(II)MA and poly(ethyl acrylate). This behavior is observed because PEA forms residual coke at elevated temperatures. Compared to PEA [initial weight loss occurs at 250°C , showed in Figure 2(A)], the thermal stability of PEACu(II)MA copolymer is decreased. The PMMACu(II)MA copolymer exhibits a single weight loss observed in the range from 160 to 450°C with an inorganic residue of approximately 10 wt %, only related to Cu(II)MA precursor. In this case, the thermal stability of PMMACu(II)MA material was kept unchanged when compared to the stability behavior observed of PMMA homopolymer.

It is reasonable to assume that the thermal stability behavior observed for PVAcCu(II)MA and PEACu(II)MA copolymers is closely associated to amount of free-radical initiator BPO. According to Figure 2(B), the mentioned Cu(II)MA-based copolymers usually undergo degradation at temperature values below those observed for its correspondent homopolymers, probably due to the high initiator concentration employed in the polymerization reactions, which led to a lowering of the average molar masses of the copolymeric materials.^{3–6}

The thermogravimetric analyses can also be used to infer the monomers conversion. As depicted in Figure 2(B), the observed values of residual inorganic material were determined to be equal to 38 wt % for Cu(II)MA monomer, 36 wt % for PVAcCu(II)MA, 32 wt % for PEACu(II)MA, and 10 wt % for PMMACu(II)MA

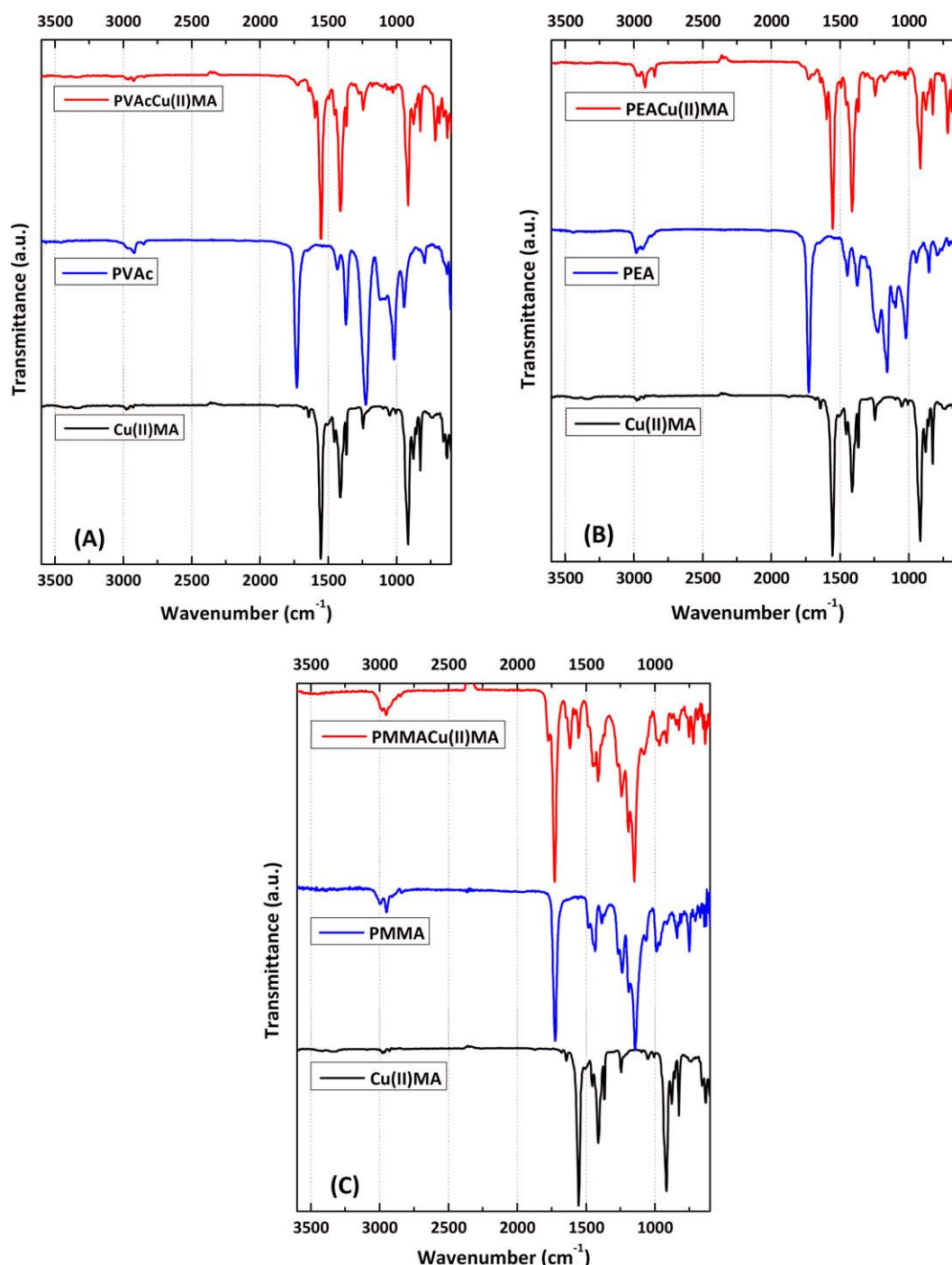


Figure 1. Infrared spectra of the Cu(II)MA-based materials. (A) PVAcCu(II)MA copolymer and PVAc homopolymer; (B) PEACu(II)MA copolymer and PEA homopolymer; and (C) PMMACu(II)MA copolymer and PMMA homopolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymers, which indicates that the reaction conversion can be presented in ascending order as follows: PMMACu(II)MA > PVAcCu(II)MA > P(EACu(II)MA). The percentage of final residue obtained for PVAcCu(II)MA and PEACu(II)MA are close to the one determined for Cu(II)MA monomer, evidencing the low conversion due to the low reactivity of both the vinyl acetate and the ethyl acrylate in the presence of copper (II) methacrylate comonomer, in contrast to the high conversion value of copolymerization in the presence of methyl methacrylate.

The fraction of copper, determined through ICP measurements, assumed the following values: 38.0 wt % for Cu(II)MA monomer, 29.99 wt % for PVAcCu(II)MA, 25.4 wt % for PEACu(II)MA, and 11 wt % for PMMACu(II)MA copolymers. ICP results agree very well with the fraction of inorganic material determined via thermogravimetric analysis. The small difference observed for PVAcCu(II)MA and PEACu(II)MA copolymers can be attributed to the formation of relatively small amounts of carbon residue during the copolymer degradation.

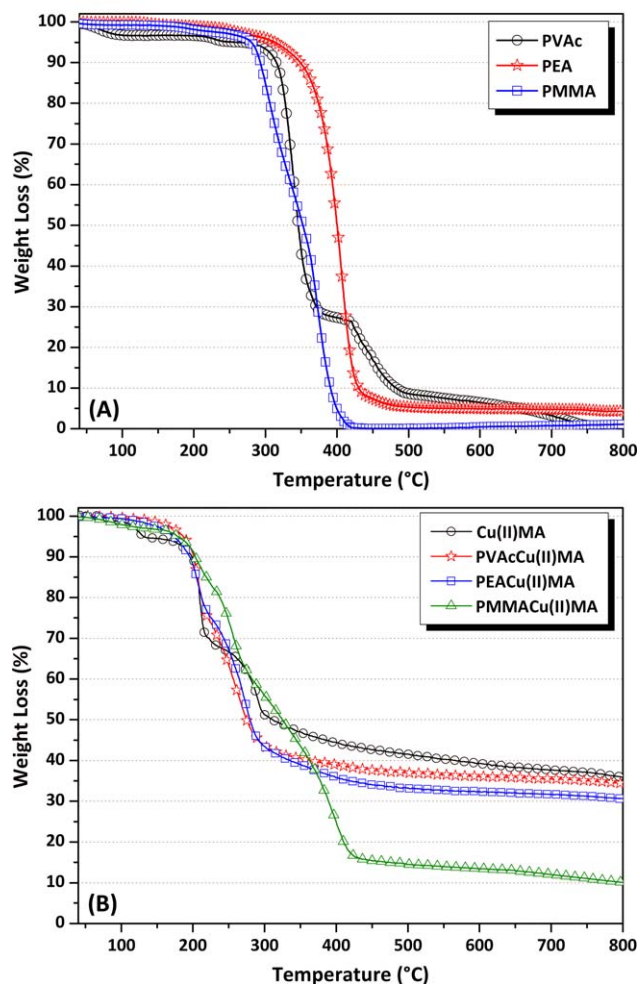


Figure 2. Thermal stability of the precursor Cu(II)MA and the Cu(II)MA-based copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In order to characterize the copolymer structure, ^{13}C MAS NMR analyses have been carried out; however, it was not possible to observe a resolved spectrum for PVAcCu(II)MA and PEACu(II)MA because of the high fraction of the inorganic monomer into the copolymer matrix. The acquired spectra profile showed a suppression of the NMR signal, due to the presence of antiferromagnetic or paramagnetic species of copper. It is well-known that some copper salts, such as nitrates and sulfates, have a large positive magnetic susceptibility and hinder the NMR signal.²⁶ As PMMACu(II)MA copolymer exhibited the highest conversion of the organic part, and consequently the lowest amount of copper species, a relatively well-resolved NMR spectrum was observed (see Figure S1 in Supporting Information).

Based on the copper fraction from ICP analyses, the thickness of the copolymer films was determined as $0.52\ \mu\text{m}$ for PVAcCu(II)MA, $0.58\ \mu\text{m}$ for PEACu(II)MA, and $0.89\ \mu\text{m}$ for PMMACu(II)MA copolymers. As a matter of the fact, the electrode performance is closely related to both the film thickness and the mass fraction of copper in the copolymer material (Figure S2 in Supporting Information). Additionally, the weight

fraction of copper can be used to determine the overall conversion, considering the theoretical value of 100% of conversion of both monomers, which corresponds to a final copper content in the copolymer of approximately 6.33 wt % (N.B. 38.0 wt % for Cu(II)MA monomer corresponds to a fraction of vinyl monomer equal to zero). In this case, the final vinyl monomer (VAc, EA, and MMA) fraction (x_{VM}^{CM}) were determined as follows: 5.4 wt % for PVAcCu(II)MA, 9.9 wt % for PEACu(II)MA, and 49.1 wt % for PMMACu(II)MA copolymers, considering only the total incorporation of vinyl monomer molecules (the reader is referred to Supporting Information for a more detailed description of protocol used to calculate these amounts). As an additional information, the fraction of copper (II) methacrylate monomer ($x_{Cu(II)MA}^{CM}$) in the final copolymer is equivalent to 78.7 wt % for PVAcCu(II)MA, 66.8 wt % for PEACu(II)MA, and 28.9 wt % for PMMACu(II)MA copolymers.

Figure 3 illustrates the thermal transition behaviors of the Cu(II)MA-based copolymers and the homopolymers and Table I exhibits the values of glass transition temperatures (T_g). It can be observed that the T_g of Cu(II)MA-based copolymers increase in comparison to the T_g determined for the MMA, VAc, and AE homopolymers, which is related to the increase of the polymeric chain rigidity, as a result of the metal inclusion into the molecular structure of the copolymeric chains (infrared spectra of the materials in Figure 1 indicated a bridging coordination mode).

Figure 4 shows the typical diffractograms of Cu(II)MA monomer and basic copper (II) carbonate. The main peaks of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ are observed at $2\theta = 11.9^\circ, 14.7^\circ, 16.1^\circ, 17.6^\circ, 18.9^\circ, 24.0^\circ, 29.4^\circ, 29.9^\circ, 31.2^\circ, 32.1^\circ, 35.6^\circ, 36.3^\circ, 37.0^\circ, 38.2^\circ,$ and 41.3° ; whereas for Cu(II)MA monomer, the main peaks are located at $2\theta = 7.4^\circ, 9.1^\circ, 10.2^\circ, 11.2^\circ, 11.9^\circ, 13.9^\circ, 14.0^\circ, 14.7^\circ, 15.9^\circ, 16.1^\circ, 17.6^\circ, 21.6^\circ, 22.4^\circ, 24.0^\circ, 25.7^\circ, 27.7^\circ, 28.5^\circ, 29.1^\circ, 30.2^\circ, 31.6^\circ, 32.6^\circ,$ and 33.7° . Cu(II)MA monomer and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ diffractograms present similar peaks at $2\theta = 11.9^\circ, 14.7^\circ, 16.1^\circ, 17.6^\circ,$ and 24.0° . It can also be observed in Figure 4 that Cu(II)MA monomer is highly crystalline, once the peaks presented in the diffractogram are very sharp and well defined.

Figure 5 shows the EDX spectra of copper (II) methacrylate and Cu(II)MA-based copolymers. Strong characteristic peaks are observed at 8.04 keV, related to $\text{CuK}\alpha$, and at 8.90 keV, related to $\text{CuK}\beta$, both associated to Ti-U channel. All analyzed samples present percentage of copper above 99%, indicating a high purity of these samples.

Figures 6–9 show the morphology of the copper (II) methacrylate monomer and copper (II) methacrylate-containing copolymers, considering two conditions: (i) monomer and copolymeric materials from the reactor system after removal of the ethanol used as dispersed medium, as illustrated in Figures 6–8; and (ii) films of the copolymeric materials prepared in accordance with the experimental procedure described in the experimental section of the voltammetry studies, as depicted in Figure 9. According to Figure 6, copper (II) methacrylate monomer presents a very irregular morphology with average particle size ranging approximately from 0.01 to $70\ \mu\text{m}$. In accordance with Figures 7 and 8, copper (II) methacrylate-

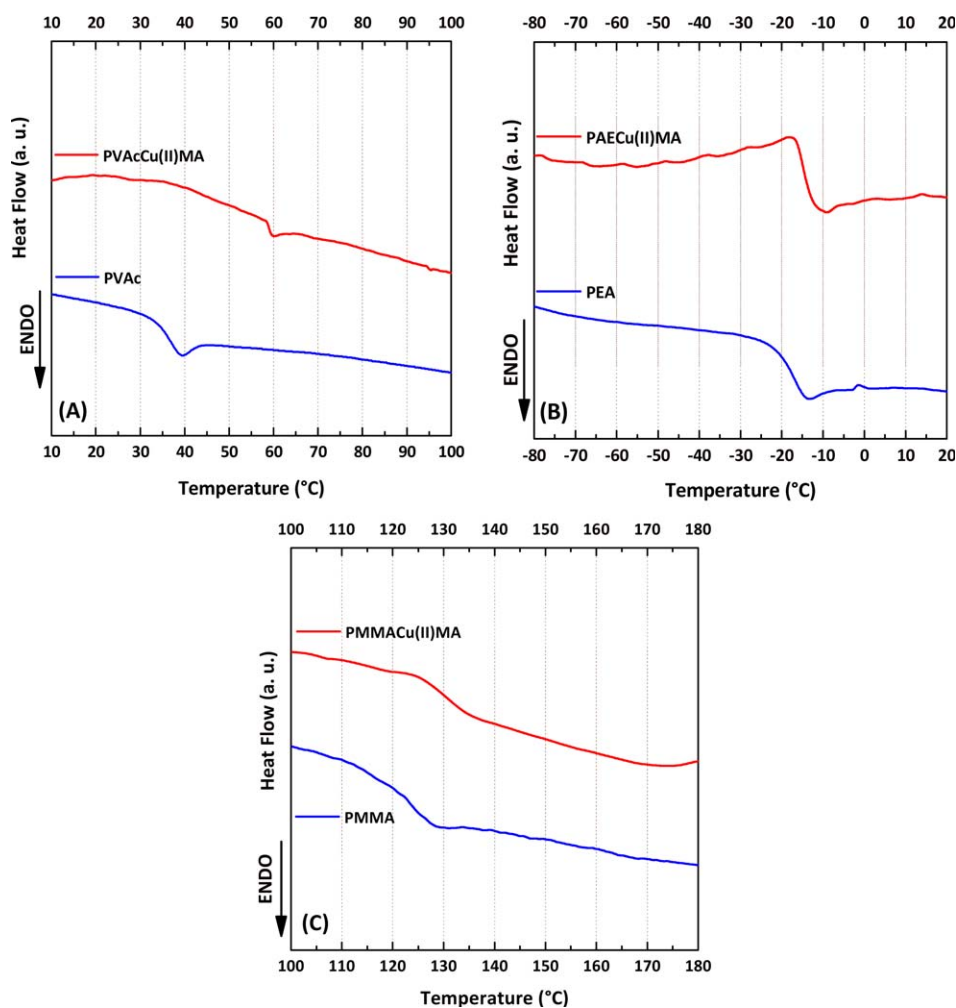


Figure 3. Differential scanning calorimetry of homopolymers and copper-containing copolymers. (A) PVAcCu(II)MA and PVAc; (B) PEACu(II)MA and PEA; and (C) PMMACu(II)MA and PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

based copolymers formed after removal of ethanol exhibit a uniform surface morphology. It is interesting to observe the morphological formation concerning the PVAcCu(II)MA copolymer, which results from polymer chains reorganization during ethanol evaporation. DRX analyses of the copper (II) methacrylate-containing copolymers (Figure S3 in Supporting Information) showed that the crystalline nature of the Cu(II)MA monomer was preserved in the copolymers, which exhibited very sharp and well-defined peaks.

In order to reproduce the film formation on the surface of the glassy carbon electrode, the surface morphology of copper (II) methacrylate-based copolymers were evaluated, as can be seen

in Figure 9. Typically, all copolymeric films displayed smooth surface morphology.

Table I. Glass Transition Temperatures of Homopolymers and Copper-Containing Copolymers

Homopolymer	T_g (°C)	Copolymer	T_g (°C)
PVAc	35	PVAcCu(II)MA	59
PEA	-18	PEACu(II)MA	-14
PMMA	125	PMMACu(II)MA	135

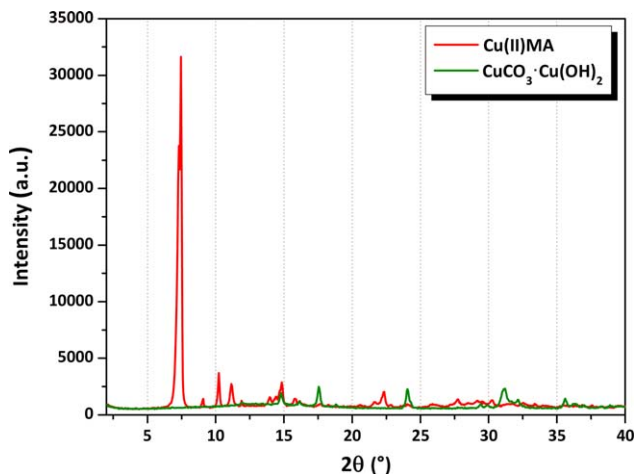


Figure 4. X-ray diffraction of copper (II) methacrylate and precursor $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

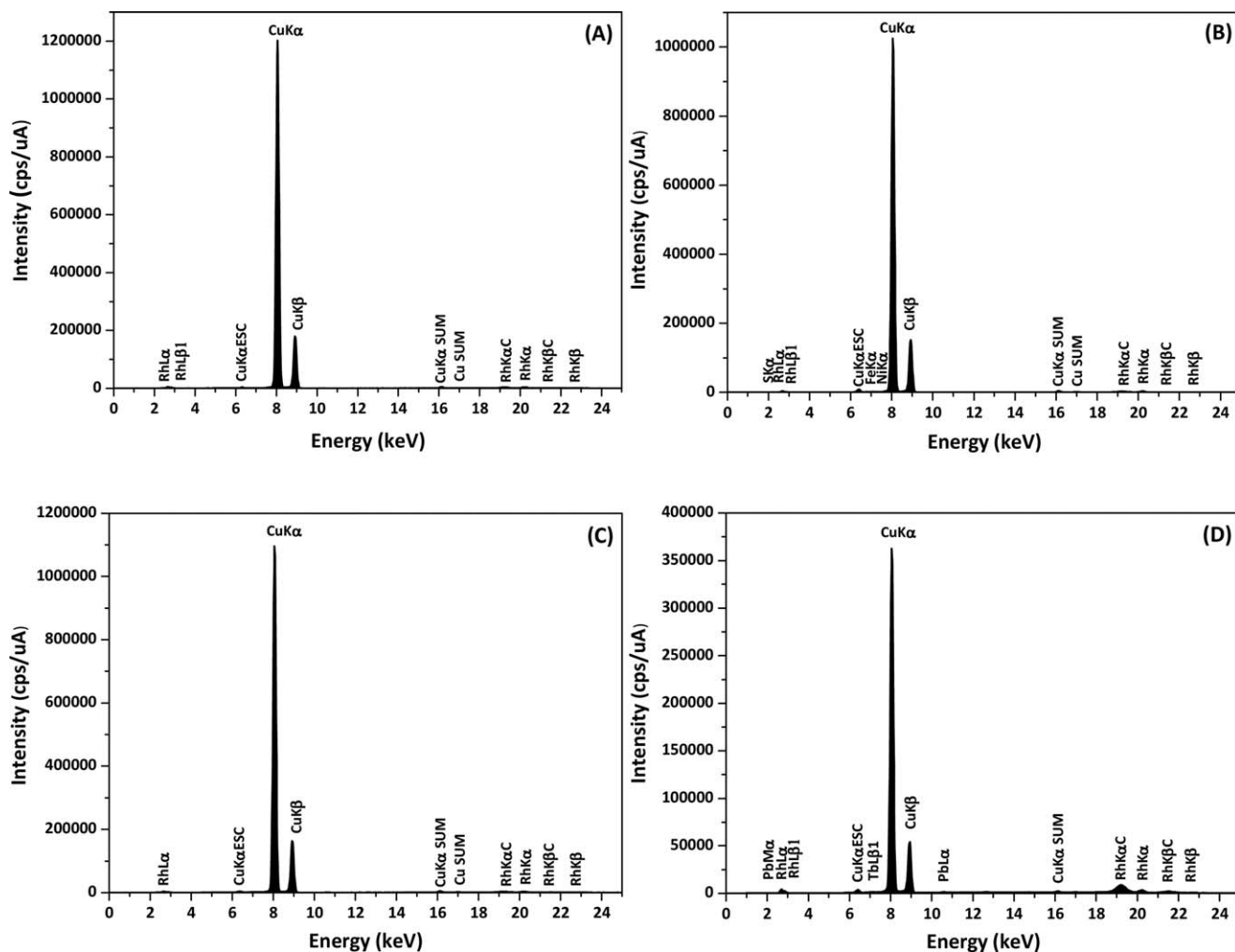


Figure 5. Energy-dispersive X-ray spectra of (A) Cu(II)MA monomer; (B) PVAcCu(II)MA copolymer; (C) PEACu(II)MA copolymer; and (D) PMMA-Cu(II)MA copolymer.

The Cu(II)MA-based copolymers were tested as modifiers films of glassy carbon surface to electroanalytical application. In order to study the electrochemical performance, each polymer was deposited on a glassy carbon electrode (GCE) by coating drop technique. The GCE-modified electrode was tested in cyclic voltammetry assays, which correspond to an essential step to deter-

mine the potential application of the polymeric materials in the fabrication and/or development of electrochemical sensors. In Figure 10 is shown cyclic voltammograms for $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ in 0.1 mol L^{-1} KCl solution using GCE and GCE modified with Cu(II)MA copolymers. As can be observed, the GCE presented an oxidation peak at a potential of 0.34 V and a

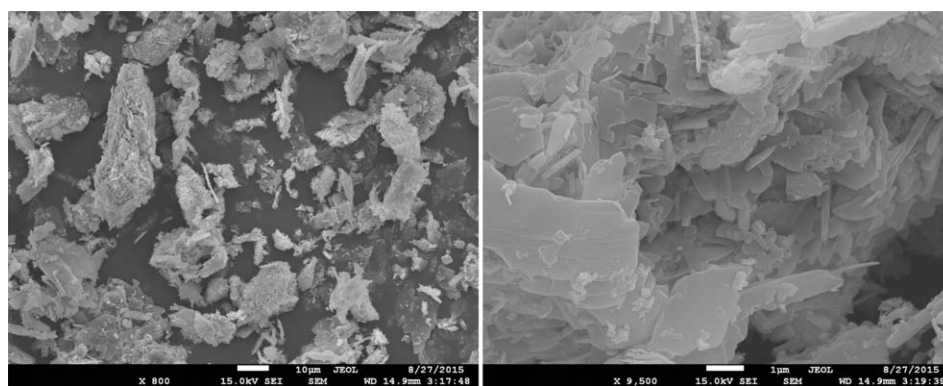


Figure 6. Scanning electron microscopy of the copper (II) methacrylate monomer.

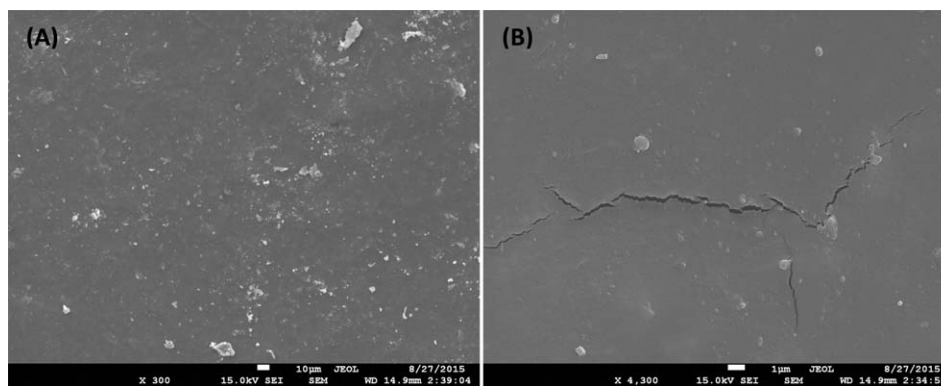


Figure 7. Scanning electron microscopy of the Cu(II)MA-based copolymers. (A) PEACu(II)MA copolymer and (B) PMMACu(II)MA copolymer.

reduction peak at a potential of 0.10 V attributed to the $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox pair. When the modified electrode was immersed in a solution of potassium hexacyanoferrate (III), $\text{K}_3[\text{Fe}(\text{CN})_6]$, a pair of redox peaks appeared at potential of 0.68 – 0.72 V attributed to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ pair in the complex $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ formed within the polymeric film. Several works reported the application of copper polymeric films in determination of sulfite²⁷ and nitrite²⁸ but problems with repeatability and control of the amount of copper deposited on the electrode surface limits its use.²⁹ In this work, Cu(II)MA-based copolymers are presented as excellent option to manufacture of GCE modified with copper polymer that allows to increase the amount of copper on the electrode surface, which could improve the sensibility, lifetime, repeatability, and precision of the electroanalytical method.

The performance of the chemically modified electrodes is closely related to the amount of copper in the copolymer chains. In this sense, it is expected that the copolymers presenting low conversion allow for the improvement of the signal as the concentration of Cu^{2+} is maximized, generating a high current magnitude. A poor incorporation of the vinylic monomers, as for instance, VAc and AE, implies in an increase in the numbers of Cu^{2+} ion incorporated into the copolymeric chains, rising the conductivity and the electrode effective area; and thus, positively contributing to the oxidation and reduction of iron ions, as illustrated in Figure 10. When compared with the bare GCE, the PVAcCu(II)MA copolymer film showed an increased current in both oxidation and reduction peaks. The oxidation peak was increased 2.8 times and the reduction peak 1.5 times. The well-defined and increased peaks in the modified electrode can

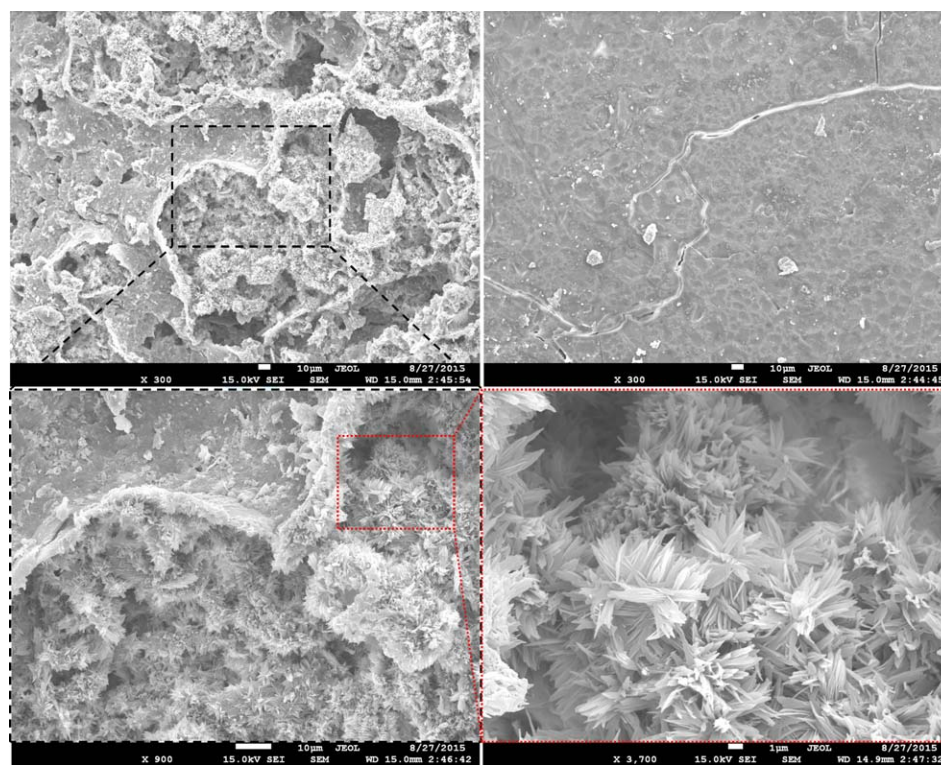


Figure 8. Scanning electron microscopy of the PVAcCu(II)MA copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

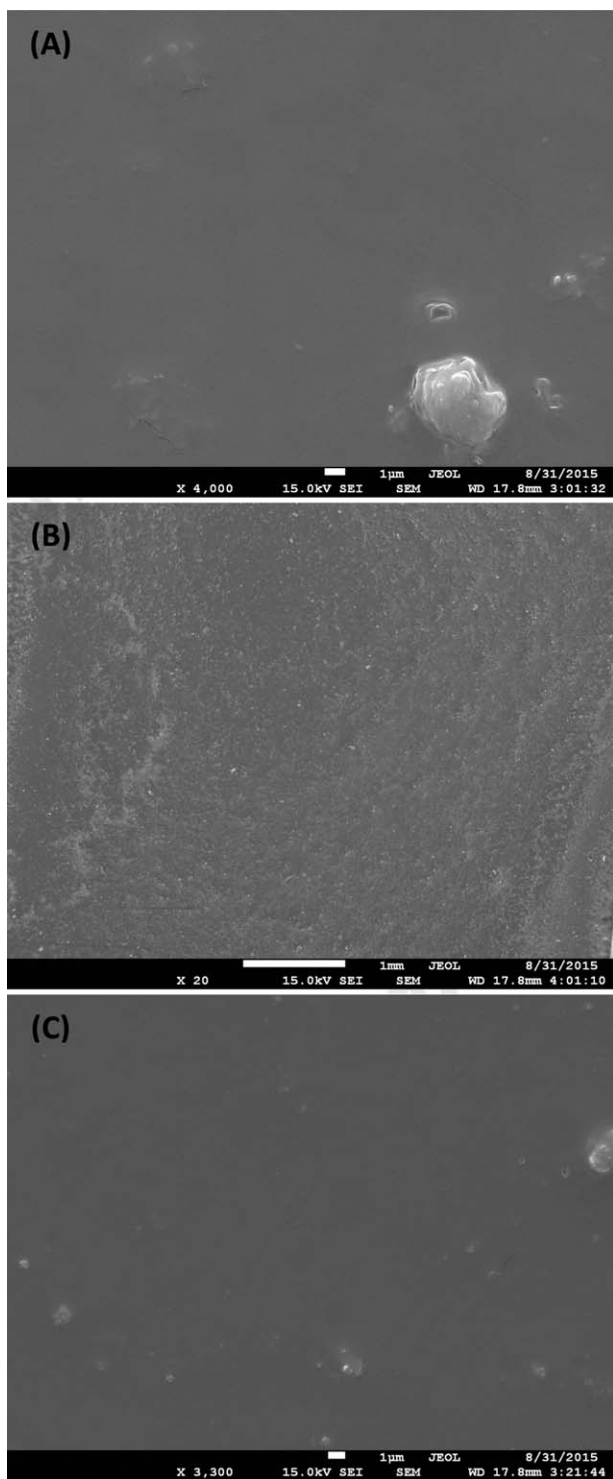


Figure 9. Scanning electron microscopy of films of the Cu(II)MA-based copolymers. (A) PVAcCu(II)MA copolymer, (B) PEACu(II)MA copolymer, and (C) PMMACu(II)MA copolymer.

improve the sensibility and decrease of detection limits in electroanalytical determinations.

It is very important to take into account that the homogeneous distribution of copper on the electrode surface is the main challenge. Ideally, the electrode modifier exhibiting the highest cop-

per concentration is the most preferable. To perform low conversion copolymerizations with vinyl monomers, such as ethyl acrylate and vinyl acetate, is of fundamental importance, as the final copolymer ensures the proper film formation and consequently the homogeneous dispersion of copper on the electrode surface. In this scenario, Cu(II)MA homopolymer should be avoided, as the resulting material is completely insoluble in traditional solvents such as THF.

The experimental results presented in Figure 10 clearly indicate that the Cu(II)MA-based copolymers are promising materials to be applied in the manufacture of electrochemical sensors to determine electrochemically molecules of high analytical interest. As a matter of fact, because PVAcCu(II)MA copolymer exhibited the best results, additional tests have been carried out, as illustrated in Figure 11. Despite this, it is worth to emphasize that all Cu(II)MA-based copolymers synthesized here are highly recommended to be employed in electroanalytical determinations, as the reaction conversion, and consequently the concentration of copper ions, can be properly controlled. Film and/or adhesive properties of the copolymers have to be considered as key factors during the step related to polymeric film coating on the electrode surface. Additionally, the layer thickness of the copolymer should also be taken into account as the diffusion rate of electroactive ions through copolymer matrix is highly impacted by the film layer.¹⁸

Figure 11 shows the stability test for PVAcCu(II)MA copolymer. The stability test consists of observing cyclic voltammograms (scans) in sequence. As can be observed, the intensity of signal is kept almost constant (stable) after the twentieth scan, showing that this copolymer achieves its stability in few cycles and that the same signal behavior is maintained for a total of 60 performed scans. After these scans, the modified electrode can be used as sensor in electroanalytical determinations. So it can be concluded that electrode life time is good. It is reasonable to assume that the loss of reproducibility may occur due to the modification of the structure, degradation, or loss of copolymer.

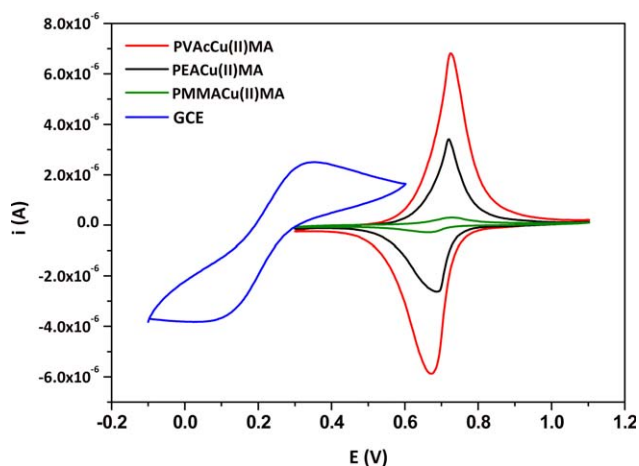


Figure 10. Cyclic voltammograms of copper-containing copolymers and glassy carbon electrode for 10^{-3} mol L^{-1} $K_3[Fe(CN)_6]$ in 0.1 mol L^{-1} KCl solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

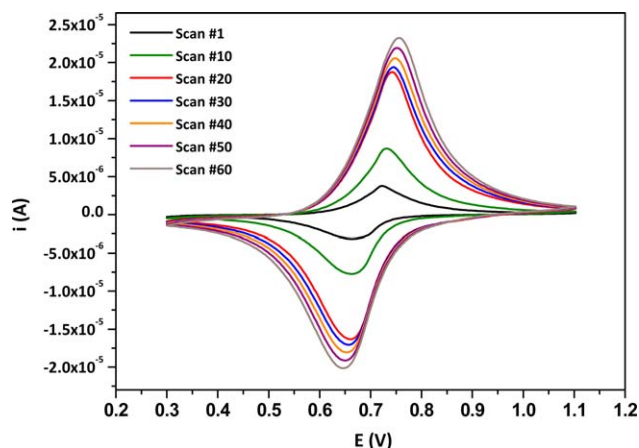


Figure 11. Electrochemical stability of PVAc-Cu(II)MA at GCE for a 10^{-3} mol L^{-1} $K_3[Fe(CN)_6]$ solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Despite this, based on the experimental results, no degrading events have been observed after 60 scans.

Figure 12 illustrates the effect of the film thickness on the glassy carbon electrode performance. According to the experimental results, voltammetry measurement carried out with $0.445 \mu m$ copolymeric film do not exhibit oxidation or reduction processes, indicating that the amount of polymer was insufficient to improve the redox processes of Fe^{III} . Copolymeric film of thickness equal to $0.890 \mu m$ led to the best results, exhibiting a well-defined signal. According to Figure 12, as the film thickness on the electrode surface is increased (1.781 and $2.671 \mu m$), the analytical signal is decreased, leading to a reduction of the electron transfer. It is expected that the resistivity sensor is increased, which is accompanied with an increase in capacitive current. It seems that the insulating effect (resistivity) of the copolymer films with thickness higher than $0.890 \mu m$ is more important than the conducting effect of the copper.

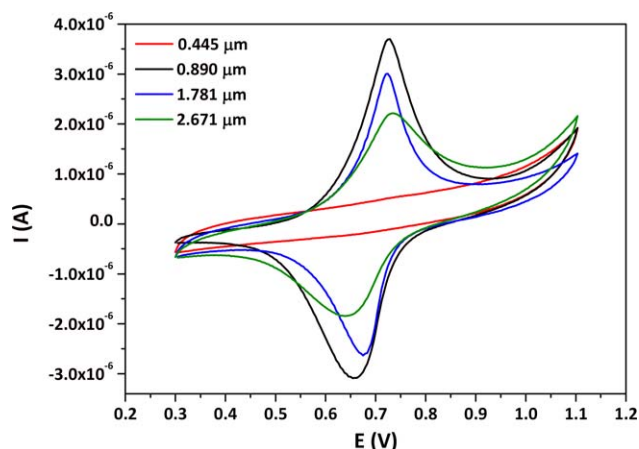


Figure 12. Cyclic voltammograms of PVAc-Cu(II)MA for evaluation of the film thickness on the glassy carbon electrode performance for a 10^{-3} mol L^{-1} $K_3[Fe(CN)_6]$ solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

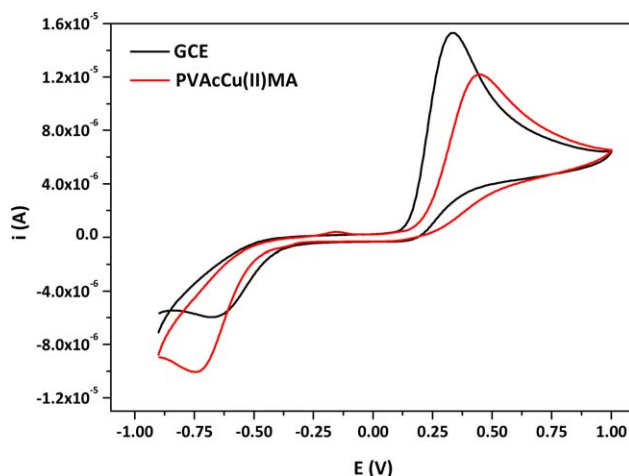


Figure 13. Cyclic voltammograms for bare GCE and PVAcCu(II)MA/GCE for ascorbic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Two other assays have been carried out to evaluate the potential of modified electrode for detection of organic molecules. In Figure 13, it is shown cyclic voltammograms for a 1.0×10^{-3} mol L^{-1} ascorbic acid in 0.1 mol L^{-1} KCl solution using GCE and chemically modified electrode with PVAcCu(II)MA. The PVAcCu(II)MA modifier is more suitable, exhibiting performance similar to the one obtained for bare GCE. The cathodic peak current was increased 2.2 times when compared with bare GCE and this could increase the sensibility in an electrochemical determination; therefore, the GCE modified could be used to monitoring of ascorbic acid by measures on the cathodic peak. In the example presented in Figure 13, as PVAcCu(II)MA copolymer showed good adhesives proprieties, it is expected that signal response might be significantly improved as result of the presence of metallic nanoparticles (NPTs), carbon nanotubes (CNTs), graphene, or black carbon homogeneously dispersed on the polymeric film. When these modifiers are used on GCE, it is necessary to use a material support that allows its attachment on CGE surface. It was reported in the literature that chitosan, dihexadecyl hydrogen phosphate (DHP), and polyamine are used as common material supports. These modifications (modifiers and its material support) to improve the signal will be doing in future works. In spite of that, the experimental results of Figure 13 can be regarded as very promising. PVAcCu(II)MA dry on the GCE is a stable, homogenous, and conductor film; thus, it is possible to replace another polymers used for the modification of GCE.^{20,30,31}

CONCLUSIONS

Copolymers consisting of vinyl monomers (vinyl acetate, ethyl acrylate, and methyl methacrylate) and copper (II) methacrylate are successfully obtained in copolymerization reactions carried out in a pseudodispersion polymerization process. The Cu(II)MA-based copolymeric materials were employed as surface modification agents in glassy-carbon electrode for quantification of organic and inorganic analytes, such as ascorbic acid and potassium hexacyanoferrate (III). The preliminary results showed that this new class of copolymer can be considered as

promising materials intend to be used as sensors in electrochemical quantifications.

Thermal characterization of materials demonstrated that these materials are less stable to temperature changes, when compared to the homopolymers of vinyl monomers. The polymeric chains are more rigid compared to the homopolymer, which reflects an increase at glass transition temperature of the Cu(II)MA-based copolymers.

Based on voltammetry analyses, it can be concluded that the Cu(II)MA-based copolymer materials are very promising to be applied in electroanalytical quantification of organic and inorganic compounds.

Although there is a great potential to detect organic and inorganic compounds, one should keep in mind that the dispersion of the polymer film on the electrode surface plays a fundamental role on performance of the chemically modified electrode. A homogeneous dispersion, combined with a good control of film thickness, is determinant to the optimization and signal reproducibility. The concentration of the metal ions in the copolymer is a key factor because it may effectively affect the signal response.

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APPENDIX A: SUPPORTING INFORMATION

Details on the experimental characterization of copper (II) methacrylate-based copolymers based on solid-state ^{13}C MAS NMR, X-ray diffraction analyses, and film thickness determination.

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