



Universidad
Carlos III de Madrid



This is a postprint version of the following published document:

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 (5), pp. 1368-1377.

DOI: [10.1016/j.eurpolymj.2008.02.006](https://doi.org/10.1016/j.eurpolymj.2008.02.006)

© Elsevier, 2008



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License.

Self-assembly of physically crosslinked micelles of poly(2-acrylamido-2-methyl-1-propane sulphonic acid-co-isodecyl methacrylate)-copper(II) complexes

Verónica San Miguel, Fernando Catalina, Carmen Peinado *

Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., CIJuan de la Cierva 3, 28006 Madrid, Spain

Abstract

Metal complexes were prepared by the reaction of Cu(II) chloride with sodium salt of random copolymers of 2-acrylamido-2-methylpropane sulphonic acid, AMPS, and isodecyl methacrylate, i-DMA. Composition was varied in the feed to obtain copolymers and their corresponding metal chelates with different content of i-DMA hydrophobic monomer. The copolymers and their metal chelates were characterized by Fourier transformed IR spectroscopy (FTIR) and scanning electron microscopy (SEM) as well as energy-dispersive X-ray spectroscopy (EDS). The X-ray diffraction studies revealed that the polymers and their chelates were amorphous. Also, the stabilities of the copolymers and their metal chelates were investigated using thermal methods such as TGA and DSC analysis. Lower thermal stability was found for the polymer-metal complexes compared to that of the copolymers.

Fluorescence spectroscopy was used to further confirm the copolymers and their Cu(II) metal complexes self-aggregate in water. Critical micellar concentrations become lower by metal complexation. A synergistic effect in self-assembly behaviour in water solutions of Cu(II) polycomplexes is attributed to the interplay between hydrophilic-hydrophobic interactions and electrostatic forces with Cu^{2+} ions. Physical crosslinking of polymeric micelles obtained by metal complexation led to more stable micelles. Sodium salt copolymers led to secondary aggregation while ionic crosslinking provided lonely micelles distributed through the substrate as seen by SEM. These results point to a mechanism in which cation-assisted-polymer-modified water structure plays a central role in the phase separation behaviour.

Keywords: Polymer-metal chelates; Water soluble polymers; Thermal properties; Self-assembly; Crosslinked micelles

1. Introduction

In the past decade metal organic polymers and coordination polymers have attracted the interest of a growing part of the scientific community for the advantages that they offer due to their attractive network structures as well as their potential applications as functional materials [1–3].

The choice of metal ion has a significant effect on these polymeric structures as well as the binding modes of the ligands. Therefore, the selection of the ligands is crucial for assembly of metal ions

* Corresponding author. Tel.: +34 915622900; fax: +34 91 5644853.

E-mail address: cpeinado@ictp.csic.es (C. Peinado).

and ligands in coordination polymers. The basis of molecular assembly is the meaningful and organized connections between molecular structures by means of covalent bonds, hydrogen bonds, π - π interaction and their combination [4]. The nature of assembly of metal-polymers is highly influenced by a number of factors, such as the coordination ability of metal ions, the structural characterization of organic ligands, solvent system, temperature, pH of the solution, ratio of metal to ligand and counter ions [5,6]. An alteration in any of these factors often results in new complexes with different structural topologies and functions.

The simplest synthetic route for synthesizing an organic polymer-metal complex is the synthesis of a macromolecular ligand and subsequent anchoring of a metal salt or complex, and is by far the most investigated strategy which has led to uncountable examples concerning in particular the use of polystyrene [7,8]. Another alternative is the incorporation of a metal by polymerization of a suitable metal containing monomer [9].

The use of organic polymers for metal complexes allows one to conjugate a controllable flexibility of the matrix with the possibility to fine-tune the physical properties (polarity, swellability, morphology, etc.) [10]. Therefore, incorporation of metals into a polymer microstructure offers unique potential for the preparation of processible materials with properties that differ significantly from those of conventional organic polymers. In solution, polymer-metal complexes form microheterogeneous regions which show different physicochemical properties as unique absorption characteristics, stability, redox reactions, catalytic activities, electrochemical reactions, etc, compared to those of low molecular weight metal complexes. Complexation of metal ion in solution is an important process in several technological areas. Therefore, it is expected that the interest in polymer-metal complexes will grow up in the next years.

The interest in metal containing polymers is primarily due to their wide use as catalyst, antifriction materials, biologically active substances, electrically conductive coatings and so forth. For example, oxidative degradation of polycyclic aromatic hydrocarbons has been investigated, using hydrogen peroxide, catalyzed by heterogeneous polymeric chelates of selected metals, Fe(II), Cu(II), and Co(II) [11]. Other area of application is in the removal of metal ions from an aqueous waste which is an important field for environmental research. The metal binding properties of poly(2-acrylamido-2-methyl-1-propane

sulphonic acid) (AMPS) were studied by the liquid-phase polymer-based retention technique, under different experimental conditions [12]. This strong polyelectrolyte showed a high retention for di- and trivalent cations at all pH. Soykan et al. [13,14] have prepared copolymers based on AMPS and their metal complexes showed antimicrobial activity.

This paper is a continuation of the previous work concentrating on preparing hydrophobically modified polyelectrolytes by radical copolymerization of 2-acrylamido-2-methylpropane sulphonic acid, AMPS, and isodecyl methacrylate [15]. The removal of single metal ions and *m*-cresol from aqueous solutions in equilibrium dialysis experiments by means of the copolymers was investigated. Also, their micellization behaviour was pH-dependant becoming interesting stimuli-responsive copolymers and thus they have potential application as polymeric surfactants in micellar enhanced ultrafiltration processes for water purification. Physical stability of nanoparticles is a fundamental requirement for its application. Cross-linking of the shell or core of hydrophobic micelles is a promising strategy to increase the micelle stability. Recently, it has been shown that the physical stability of polymeric micelles can be improved by introducing a crystalline structure (e.g. in the form of stereocomplexes) in their cores [16]. The innovation of this paper is to prepare physically shell-crosslinked micelles from metal polycomplexes of copolymers based on 2-acrylamido-2-methylpropane sulphonic acid, AMPS, and isodecyl methacrylate.

The aim of this study was to investigate the stability and self-assembling behaviour in water of the metal complexes of hydrophobically modified polyelectrolytes, copolymers of 2-acrylamido-2-methylpropane sulphonic acid, AMPS, and isodecyl methacrylate. The synthesis was carried out by cation exchange with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at neutral pH using 1:2 (metal:polymer) stoichiometry. Their thermal characterization was carried out by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Moreover, their micellization behaviour in aqueous solutions was investigated using a fluorescence probe method and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Isodecyl methacrylate (i-DMA), purchased from Aldrich, was distilled under reduced pressure prior

to use. 2-Acrylamido-2-methylpropane sulphonic acid (AMPS), from Eastman Kodak, copper (II) chloride dihydrate and *m*-cresol, from Aldrich, and sodium dodecyl sulphate (SDS), Scharlau, were used as received without further purification.

2,2'-Azobis-isobutyronitrile (AIBN), from Across, was purified by recrystallization from ethanol, prior to be used as initiator of the polymerization. *N,N'*-Dimethylformamide, from Scharlau, was dried and then, distilled under reduced pressure. Amberlite IR-120 ion-exchange resin was purchased from Aldrich.

Fluorescent probe 4-(*N,N*-diethyl)amino-7-nitrobenz-2-oxa-1,3-diazole (NBD-NEt₂) was synthesized as previously described [17]. All the solvents used on our fluorescence studies were of spectroscopic grade, from Merck. Water was Milli-Q grade, having an initial resistivity of 18.2 mΩ cm.

2.2. Copolymerization

The synthesis of the copolymers has been described elsewhere [15]. The comonomers (total monomer concentration, 1 mol/L), 2-acrylamido-2-methylpropane sulphonic acid and isodecyl methacrylate, were copolymerized at 70 °C ± 0.1 °C under N₂ atmosphere using AIBN (0.3 wt.%) in purified *N,N'*-dimethylformamide as solvent.

2.3. Preparation of polymer metal chelates

Copper complexes of the chelating copolymers AMPS_{co}(*x*) were prepared according to the following procedure. For preparation of AMPS/Cu(II) complexes, the aqueous solutions of copolymers AMPS_{co} (concentration 0.045 mol repeating unit/L) and CuCl₂ · 2H₂O (concentration 0.02 mol/L) were mixed at a volume ratio 1:1. The mixing was maintained overnight at ambient temperature and then, solvent was removed by liophilization. A green solid was obtained and then washed with methanol and acetone several times and dried under vacuum to constant weight. Thus, the uncomplexed metallic ions Cu(II) can be removed with the filtrate and ion concentration was determined gravimetrically. The difference between Cu²⁺ in the feed solution and free Cu²⁺ corresponds to the chelated copper ions.

2.4. Characterization

¹H NMR spectra were recorded in D₂O solution on a Bruker AM-400 instrument operated at

400 MHz. IR spectra were recorded on a Perkin–Elmer FTIR-spectrophotometer and polymeric samples were examined in KBr matrix. *Elemental analysis*: nitrogen and sulphur contents were determined by elemental analysis in a Micro Carlo Erba equipment, model EA 1108.

Wide-angle X-ray diffraction (WAXS) patterns were recorded in the reflection mode at room temperature by using a Rigaku ROTAFLEX RTP300 rotating anode X-ray generator with a Cu target and a Ni filter produced Cu Kα (λ = 0.154 nm) X-rays, connected to a computer. The diffraction scans were collected continuously over a period of 20 min (exactly 30 min) in the range of 2*q* values from 5° to 35°, using a sampling rate of 1° min⁻¹. The goniometer was calibrated with a silicon standard.

2.4.1. Scanning electron microscopy

The surface of specimens was analyzed using an environmental scanning electron microscope, ESEM Philips XL30, operated at 25 kV, equipped with a energy-dispersive X-ray analyzer (EDX). Specimens were dried at room temperature prior to scanning.

2.4.2. Thermal analysis

Thermogravimetry (TGA) measurements were performed in a Perkin–Elmer thermobalance, model TGA 7. Measurements were carried out using 5 mg of sample and heated at a rate of 10 °C per minute under nitrogen atmosphere. *Differential scanning calorimetry (DSC)*. The glass transition temperatures of the copolymer and their complexes were measured by a differential scanning calorimeter (Perkin–Elmer DSC 7) at a cooling and heating rate of 10 °C/min with a cell purged with nitrogen. The second scan is considered that reflects the properties of the systems.

UV spectra were recorded by means of a Perkin–Elmer UV-35 spectrophotometer.

Fluorescence emission spectra were recorded on a Perkin–Elmer LS-50B spectrofluorimeter. All measurements were performed at ambient temperature. To improve accuracy in the determination of maximum wavelengths first derivative spectra were obtained in all the wide emission bands. As employed fluorescent probe exhibits low solubility in water, stock solutions were prepared in ethanol. The stock solutions (2.2 × 10⁻³ M) were added into the examined polymer water solutions of a given concentration in amount lower than 1.5% (v/v). The effective concentration of probe was maintained

constant at 4×10^{-6} M in all the aqueous solutions. Fluorescence emission spectra of the probe were recorded in the range 490–700 nm using a fixed excitation wavelength of 477 nm. Under such conditions, only one single fluorescence emission peak was observed. All the spectra were corrected using the response curve of the photomultiplier.

3. Results and discussion

3.1. Synthesis and characterization

The preparation of hydrophobically modified polyelectrolyte by radical copolymerization of 2-acrylamido-2-methylpropane sulphonic acid, AMPS, and isodecyl methacrylate, i-DMA, under nitrogen at 70 °C using azo-bis-isobutyronitrile (AIBN) as initiator in *N,N'*-dimethylformamide (DMF) as solvent was achieved as previously described [15]. Feed composition was changed to obtain copolymers with different hydrophobic content. In the text below, they will be referred as $\text{AMPS}_{\text{co}}(x)$ where x denotes the molar percentage content of the i-DMA in the copolymer. The structure of the copolymers is shown in Fig. 1. The copolymer composition was estimated from elemental microanalysis and from ^1H NMR using the characteristic integral values of the respective monomers.

The Cu^{2+} chelates of the copolymers were prepared using stoichiometric relationship 1:2 of $\text{CuCl}_2/\text{AMPS}_{\text{co}}(x)$ in water solutions at room temperature. The stoichiometry of polycomplexes formed between the copolymers $\text{AMPS}_{\text{co}}(x)$ and copper ions was determined gravimetrically. Table 1

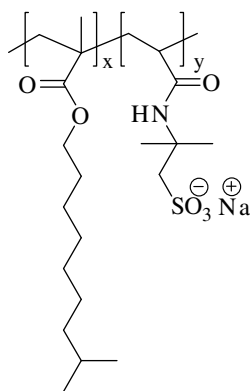


Fig. 1. Structure of the copolymers of 2-acrylamido-2-methyl-1-propane sulphonic acid and isodecyl methacrylate, $\text{AMPS}_{\text{co}}(x)$, where x denotes the percentage of isodecyl methacrylate.

Table 1
Concentration of copper (II) chloride dihydrate and the final percentage of Cu^{2+} in the chelates

Copolymer	M_n	M_w/M_n	$[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]_{\text{feed}}$ (mM)	% $\text{Cu}^{2+}_{\text{chelated}}$
$\text{AMPS}_{\text{co}}(11)$	24,480	2.50	20	100
$\text{AMPS}_{\text{co}}(20)$	19,500	3.13	18	98
$\text{AMPS}_{\text{co}}(30)$	24,300	2.36	17	95

shows the concentration of copper (II) chloride dihydrate in the feed and the final percentage of Cu^{2+} in the polymer chelate. Both copolymers and their chelates were soluble in water and insoluble in common organic solvents such as hexane, toluene, acetone, DMF, THF and ethanol.

The metal contents in all the polycomplexes were consistent with the employed 1:2 (metal:ligand) stoichiometry, since one metal ion was coordinated by two polymer ligands. The percentage of chelated divalent copper ions diminished as hydrophobic content increased in the copolymers. This order can be explained by Pearson's proposal [18], hard acids prefer to combine with hard base and a soft acid prefers to combine with a soft base. Therefore, the selectivity of polymeric ligand for an acidic metal ion will be increased by the number and basicity of charged oxygen groups, this is for the $\text{AMPS}_{\text{co}}(11)$ copolymer with the highest content of AMPS. The metal complexing activity of the polymers depends not only on the nature of the ligands groups but also on their accessibility toward the metal ions. Steric hindrance and hydrophobic nature are known to limit the chelating reaction [19]. Therefore, increasing the i-DMA hydrophobic content leads to a reduction of chelation, as observed in Table 1 from $\text{AMPS}_{\text{co}}(11)$ to $\text{AMPS}_{\text{co}}(30)$.

Absorption spectra of copolymer $\text{AMPS}_{\text{co}}(x)$, copper (II) chloride dihydrate and $\text{AMPS}/\text{Cu}(\text{II})$ complex solutions were recorded on a UV-vis spectrometer. The $\text{Cu}(\text{II})$ absorption band observed at $\lambda_{\text{max}} = 814$ nm for the salt is shifted to 788 nm wavelength after complexation with the copolymer AMPS. This spectral shift can be attributed to the interaction of AMPS_{co} with Cu^{2+} ions.

The copolymers and their metal chelates were also characterized by X-ray diffraction. The results indicate that both the copolymers and their metal complexes were amorphous. Fig. 2 shows X-ray diffraction patterns of metal chelate of copolymer $\text{AMPS}_{\text{co}}(11)$ and the cupric salt. The appearance of crystallinity in metal polycomplexes may be due

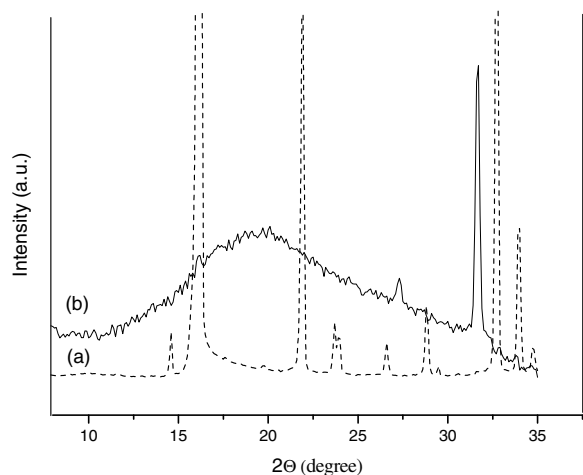


Fig. 2. XRD diffraction of (b) AMPS_{co}(11)/Cu chelate and (a) CuCl₂ · 2H₂O.

to the inherent crystalline nature of the metallic ions. The shift of the diffraction peaks at $2\theta = 26.6^\circ$, 28.9° and 32.7° in the CuCl₂ · H₂O to 27.3° and 31.7° in the metal polychelate, AMPS_{co}/Cu, indicated also the complexation of Cu²⁺ with the water soluble random copolymer.

SEM micrographs of solid films showed any characteristic pattern. The EDS analysis showed the presence of Cu(II) in the metal chelates which was distributed homogeneously in the sample.

3.2. FTIR spectroscopy

FTIR spectra of AMPS_{co} were compared with that of its metal complex in Fig. 3. The spectra of the polycomplexes showed similar features than those of pure copolymers. However, the shift of certain bands confirmed the incorporation of metal ions into the polymer chain. It can be seen that the intensity of the absorption band associated with *i*-DMA carbonyl vibrations at 1716 cm^{-1} of the polycomplexes was significantly reduced in comparison with spectra of pure copolymers. Moreover, the absorption band associated with AMPS amide group at 1660 cm^{-1} decreased slightly in intensity. This fact can be explained since the AMPS carbonyl moiety is located on the same chain as the ligand binding site. The sharp peak at 1040 cm^{-1} was assigned to the SO₃⁻ symmetric stretch, which is known to exhibit narrow bands in other complexes [20], while (amorphous) polymer modes are generally much broader. The decrease of the intensity of the band at 1040 cm^{-1} associated to SO₃⁻ group

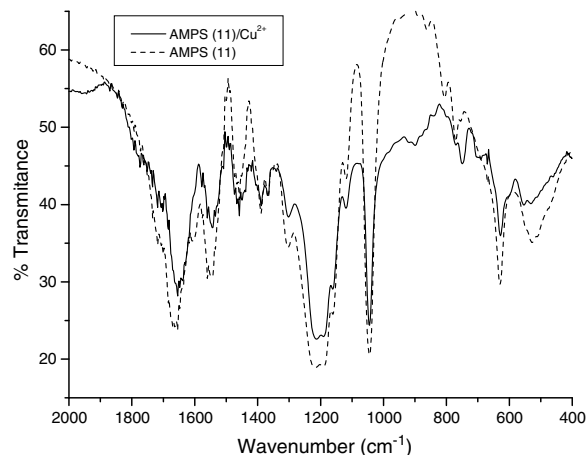


Fig. 3. FTIR spectra of AMPS_{co}(11)/Cu chelate and the corresponding pure copolymer.

also confirmed the interaction between sulphonic moieties and Cu²⁺ ions and the involvement of this moiety as one of the coordination groups. This decrease was partially hindered by the formation of a new band at 905 cm^{-1} . We noted that the SO₃⁻ stretch band exhibited no inhomogeneous profile or splitting in these systems. This indicates that all the SO₃⁻ groups were subject to the same single environment, which was likely in the form of an ionic pair, both in the sodium salt copolymer and its Cu(II) complex. It was also observed a shift of the absorption bands to lower wavenumbers (from 1716 to 1708 cm^{-1}) for C=O_{*i*-DMA} and from 1660 to 1642 cm^{-1} for C=O_{AMPS}). The carbonyl stretching of the keto group was shifted to lower frequencies due to the charge transfer from the carbonyl oxygen to the Cu²⁺ ion. These shifts would be consistent with bonding to the metal being through the sulphonic, carbonyl and nitrogen of amide groups, favouring the arrangement of these groups to coordinate with copper ions. The strong $\nu(\text{CH})$ absorption observed as an intense and sharp band at 770 cm^{-1} in the copolymer splitted in an asymmetric doublet, $770(\text{s})$ and $747(\text{m})\text{ cm}^{-1}$. The incorporation of metal ions to the polymers caused an inversion of the intensities of such doublet on the spectrum; indicating that the ligands presented a chelating coordination mode. The absorption band (not showed in Fig. 3), assigned to NH free and associated by hydrogen bonding, at 3480 cm^{-1} became broader by metal chelation and shifted to lower wavenumbers. This feature indicated the formation of intermolecular hydrogen bonds and the presence of

coordinated water molecules in the Cu(II) complexes.

3.3. Thermal behaviour

The thermal degradation behaviour of the copolymers and their complexes was studied in the range of 50–700 °C. The TGA thermograms are shown in Fig. 4 together with the derivative TGA. The decomposition of the random copolymers showed a maximal decomposition rate between 345 and 358 °C, depending on their composition. Increasing the AMPS content in the copolymer led to a slight increase on the temperature decomposition. However, two decomposition stages at lower temperatures were observed for AMPS_{co}(20) at 274 and 329 °C, probably due to the lower molecular weight and higher polydispersity compared to those of the copolymers AMPS_{co}(11) and (30).

The decomposition of the Cu²⁺ polycomplexes involved multiple steps which began at lower tem-

peratures than those of their corresponding random copolymers. The first stage of decomposition (200–260 °C) was due to the release of bounded molecules of water. The second stage of decomposition was broad and showed overlapping of several processes, likely release of residual water and anhydride formation. The shift of this stage to a lower temperature range may be due to dissociation of intramolecular hydrogen bonds of AMPS_{co} due to complex formation. The third decomposition stage of polycomplexes appeared in the same temperature range than pure copolymers and should correspond to the release of unsaturated products, CO₂ and CO. This last process occurred at the maximum decomposition rate in pure copolymers whereas in the polycomplexes the highest decomposition rate was observed in the second stage. All these results clearly indicated the lower thermal stability of the polycomplexes compared to that of the pure copolymers. Table 2 compiled the temperatures at different percentages of weight loss and the residual weight at 700 °C. The values of residual weight at 700 °C varied between 23% and 41%.

Several factors may contribute to the lower thermal stability of polycomplexes. The presence of the Cu(II) metallic ions may enhance thermal conductivity and facilitate heat transfer from the surroundings to the core of polymer leading to the thermal degradation of the polymeric chain. Coordination water also may play a role to favour heat conduction and reduce the thermal stability of polycomplexes. Moreover, the chelation of the organic polymers modified the chemical structure. As FTIR spectra showed, hydrogen bonding between carbonyl and amide groups were partially disrupted due to the complex formation, reduction of intramolecular hydrogen bonding may reduce the thermal stability of these polymers.

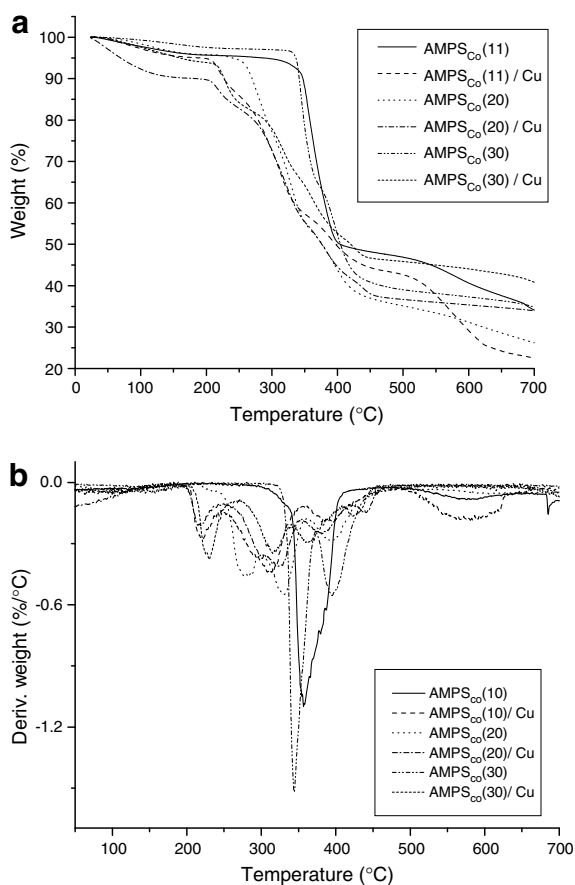


Fig. 4. (a) TGA thermograms and (b) derivative TGA curves of pure copolymers and their corresponding Cu²⁺ chelates.

Table 2
Temperature (°C) at weight loss (%) of 5–50% and residual weight at 700 °C

Samples	Temperature (°C) at weight loss of				Weight (%) at 700 °C
	5 (%)	20 (%)	40 (%)	50 (%)	
AMPS _{co} (11)	286	358	380	404	35
AMPS _{co} (11)/Cu	190	279	333	397	23
AMPS _{co} (20)	239	292	337	376	26
AMPS _{co} (20)/Cu	69	272	333	376	34
AMPS _{co} (30)	336	348	385	404	34
AMPS _{co} (30)/Cu	158	289	365	420	41

Table 3

Glass transition temperatures of the random copolymers AMPS_{Co} and their Cu(II) polycomplexes

Copolymer	T_g ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
	Copolymers	Cu(II) polycomplexes
$\text{AMPS}_{\text{Co}}(11)$	136	135
$\text{AMPS}_{\text{Co}}(20)$	82	121
$\text{AMPS}_{\text{Co}}(30)$	133	130

Thermal behaviour was also studied by differential scanning calorimetry. The glass transition temperatures were determined from the second DSC run as the midpoint of the transition region and are shown in Table 3. All the synthesized copolymers showed a single glass transition temperature which indicated the formation of random copolymers. T_g values were higher than that reported [15] for the homopolymer poly(AMPS) (124°C). The relatively high T_g in the random copolymers are due to the amide and sulphonic groups attached to the backbone of the polymers facilitating entanglement of the polymer chains. As the i-DMA hydrophobic content increased T_g decreased and an exceptional low value of T_g was found for $\text{AMPS}_{\text{Co}}(20)$ due to its lower molecular weight and higher polydispersity. The glass transition temperature showed slight changes with the incorporation of Cu^{2+} ions to the polymers and the polycomplexes exhibited also a single glass transition. A different behaviour was observed for $\text{AMPS}_{\text{Co}}(20)$, the glass transition temperature increases from 82°C to 121°C by metal complex formation. Metallic ions may act as crosslinkers between polymer chains, reducing the segmental mobility and changing physical properties (increasing T_g).

3.4. Self-assembly behaviour of the metal polycomplexes in water solution

The amphiphilic nature of the copolymers, consisting of hydrophilic AMPS and hydrophobic i-DMA, provides an opportunity to form micelles in water. We used several fluorescent probes, ICT (Intramolecular Charge Transfer) and organic salts, to determine the minimum micellar concentration of the random copolymers in a previous work [15]. In this study, a NBD amino derivative was selected as extrinsic fluorescent probe for studying the associative behaviour of the amphiphiles AMPS_{Co} and their metal complexes in water. Fig. 5 plots the variation of the ratio ϕ_f/ϕ_{f_0} versus the polymer

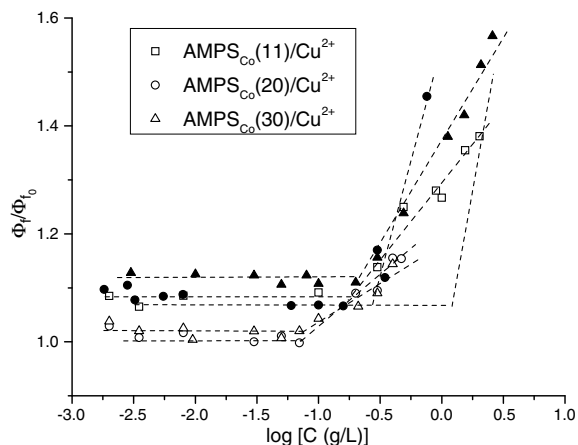


Fig. 5. Plot of ϕ_f/ϕ_{f_0} versus the polymer concentration of $\text{AMPS}_{\text{Co}}/\text{Cu}$ chelates compared to the corresponding pure copolymers. Open and solid symbols correspond to polycomplexes and pure copolymers, respectively.

concentration, where ϕ_{f_0} is the fluorescence quantum yield of the probe in pure water and ϕ_f is the same in polymeric solutions. In all cases, there was a strong increase of the ϕ_f/ϕ_{f_0} ratio that corresponded to the onset of the self-assembly behaviour which is typical for amphiphilic polymers in water solutions. Then, for all the copolymers a sharp fluorescence change occurred at minimum micellar concentration (cmc) which was the minimum concentrations for the formation of the hydrophobic microdomains (Table 4). The formation of hydrophobic microregions (domains) in aqueous media and the penetration of NBD derivative into these domains led to the increase of fluorescence intensity emission accompanied by a solvatochromic shift.

Characteristic features of aqueous solutions of polymers under study were the low cmc which became lower by the incorporation of Cu(II) ions. Cmc values determined in this way were of appr. $0.07\text{--}1.2\text{ g/L}$. The higher was the content of hydrophobic units, the lower the cmc value. In comparison with the pure copolymers, their Cu(II) chelates

Table 4

Critical micellar concentrations determined for AMPS_{Co} copolymers and their metal chelates

Copolymers	cmc (g/L)	cmc (g/L)
	Copolymers	Cu(II) polycomplexes
$\text{AMPS}_{\text{Co}}(11)$	1.20	0.16
$\text{AMPS}_{\text{Co}}(20)$	0.32	0.08
$\text{AMPS}_{\text{Co}}(30)$	0.25	0.07

Effect of their hydrophobic chain contents.

exhibited a lower cmc. A synergistic effect in self-assembly behaviour in water solutions of Cu(II) polycomplexes was attributed to the interplay between hydrophilic–hydrophobic interactions and electrostatic forces with Cu^{2+} ions. The transition range, where ϕ_f/ϕ_{f_0} value increased with concentration, became broader for the $\text{AMPS}_{\text{co}}(11)/\text{Cu}$ than that of $\text{AMPS}_{\text{co}}(11)$. This feature indicates that self-assembly behaviour in water solutions of these hydrophobically modified polyelectrolytes seems to be governed by electrostatic interactions and the exchange of Na^+ by Cu^{2+} modifies the electrostatic forces. This feature was confirmed by the highest reduction of critical micellar concentration (7.5-fold, from 1.2 g/L to 0.16 g/L) by incorporation of Cu^{2+} to the $\text{AMPS}_{\text{co}}(11)$ which behaves mainly as a polyelectrolyte. However, the reduction of cmc for the $\text{AMPS}_{\text{co}}(30)$, which had the highest hydrophobic level, was the lowest (3.6-fold). Therefore, the crosslinking induced by copper ions led to the formation of hydrophobic microdomains which were different from that formed for the pure copolymer. Crosslinked micelles provided for a host system that is capable of differentiation of guest (fluorescent probe) locations from encapsulation within the core, through partitioning at the interface, to binding within the shell or at the surface. Therefore, partitioning of the organic fluorescent probe was different for the Cu(II) polycomplexes than that of pure copolymers as shown in Fig. 5 when polymer concentration was higher than cmc.

The apparent crystalline regions in the polycomplexes may also play a role hindering the hydrophobic regions to the fluorescent probe. This was also reflected in the shift of maximum wavelength. While hypsochromic shift was observed for the random copolymers at concentrations higher than cmc, the maximum emission wavelength changed slightly as polycomplexes concentration increased, at least in the studied concentration range (Fig. 6). This may be explained considering that the probe was located in a polar microenvironment even though self-assembly occurred inducing solubilisation of this organic compound in water solutions.

The major driving force behind self-association of amphiphilic copolymers is the decrease of free energy of the system due to removal of hydrophobic fragments from the aqueous surroundings with the formation of micelle core stabilized with hydrophilic blocks exposed into water [21]. The lower is the cmc value of a given amphiphilic polymer, the more stable are micelles even at low concentration of an

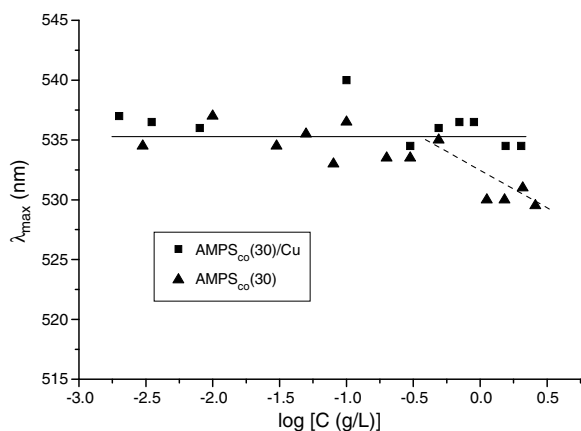


Fig. 6. Plot of λ_{max} versus the polymer concentration of $\text{AMPS}_{\text{co}}(30)/\text{Cu}$ chelate compared to that of its corresponding pure copolymer.

amphiphile in the medium. Therefore, micelles from polycomplexes showed higher stability than those from the corresponding copolymers. This is especially important from the application point of view, since upon the dilution with the large volume of the water only micelles with low cmc value still exist, while micelles with high cmc value dissociate into unimers.

The kinetic stability of micelles was studied by monitoring the decrease of fluorescence intensity as a function of time after the addition of THF to the copolymer solutions (Fig. 7). We observed that AMPS_{Co} micelles fell apart as seen by the steeply

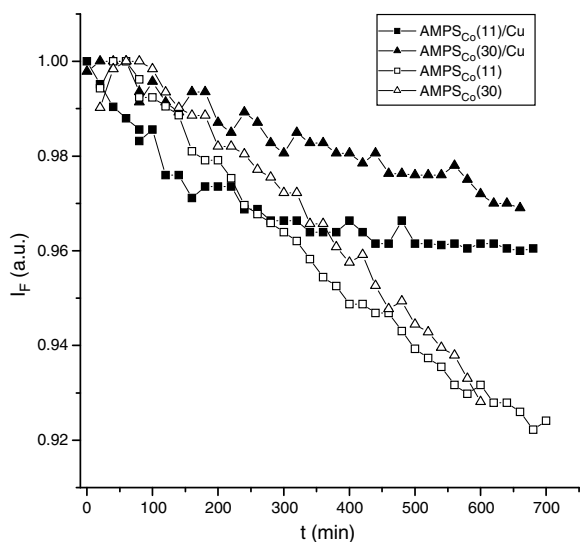


Fig. 7. Plot of the fluorescence intensity as a function of time after the addition of THF to the copolymer solutions (1 g/L).

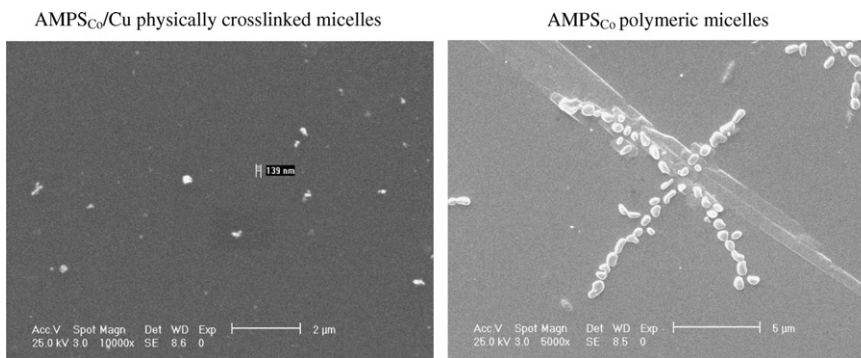


Fig. 8. SEM images of (a) AMPS_{Co}/Cu physically crosslinked micelles and (b) AMPS_{Co} polymeric micelles.

decrease of fluorescence intensity. In contrast, upon addition of THF to crosslinked micelles fluorescence intensity decreased steadily during the first 200 min and then reached a plateau thus indicating the presence of intact structures at this time. This behaviour demonstrates that ionic crosslinking hampers micelles disintegration and crosslinked micelles of AMPS_{Co}/Cu exhibited inherently higher stability.

To gain a better understanding how physically crosslinked micelles behave in an aqueous media, micelles were also studied by scanning electron microscopy (SEM). Fig. 8 shows the morphology of polymeric micelles of polychelates and their corresponding random copolymers obtained by solvent casting. The self-assembly of copolymers in water provided spherical assemblies composed of poly(isodecyl methacrylate) core domains, encased within a poly(2-acrylamido-2-methyl-1-propane sulphonic acid) shell. It is likely that micelles expanded in solutions and collapsed on the coating surface upon drying and were visualized as flattened images. This shape-adaptable character of these nanostructures was imparted by the poly(isodecyl methacrylate) core soft material. Non-crosslinked polymeric micelles AMPS_{Co} exhibited aggregation giving rise to curious morphologies as illustrated in Fig. 8, whereas the physically crosslinked micelles appeared randomly distributed along the substrate, independently of hydrophobic content. This feature may be explained taking into account the role of water structure in polymer solutions. According to the effects of ions in water structure they are classified as structure forming ions (WSF ions) and the opposite types water structure breaking ions (WSB ions) [22]. The effect of cations was observed on the phase behaviour of sodium (structure making) and copper (structure breaking) ions. The attraction

or repulsion between two solute species in water depends on the compatibility of the structures in their hydration shells. As seen by FTIR, formation of intermolecular hydrogen bonds and the presence of coordinated water molecules were favoured in the Cu(II) complexes as a consequence of the rate of exchange between the hydration shell and bulk water (structure breaking ions decrease its energy of activation). Therefore, secondary aggregation is prevented in water Cu(II) polychelates solutions. However, the sodium ions provided for an ice-like water structure, screening the electrostatic interactions, weakening repulsive forces between random copolymers and allowing that secondary interactions between micelles were present. These results point to a mechanism in which cation-assisted-polymer-modified water structure play a central role in the phase separation behaviour.

Complexes of random poly(2-acrylamido-2-methyl-1-propane sulphonic acid-co-isodecyl methacrylate) and a divalent metal cation (Cu²⁺) can be utilized as micellar templates for the synthesis of the crosslinked micelles. They may find applications in similar areas than conventional micelles, but potentially exhibiting enhanced performance due to their inherently higher stability.

4. Conclusions

The complex formation of random poly(2-acrylamido-2-methyl-1-propane sulphonic acid-co-isodecyl methacrylate) was investigated by several methods. FTIR spectra confirmed the interaction of AMPS copolymers and Cu(II) ion. The incorporation of Cu²⁺ ions to the random copolymers AMPS_{Co} brings about a decrease in the thermal stability of these hydrophobically modified polyelectrolytes.

Self-assembly behaviour of the polymer chelates in water solutions was studied by fluorescence. The critical micelle concentration of chelates was diminished compared to that of their corresponding copolymers. Moreover, the behaviour was dependent on the charge content/hydrophobic level. The obtained results indicated that a synergistic effect in their self-assembly behaviour existed between the electrostatic and hydrophobic interactions as the two interactions occurred in a chelate manner. Moreover, ionic crosslinking enhanced the stability of micelles in water solutions.

Finally, the effect of cation in the micellization behaviour was explained in basis on a mechanism in which cation-assisted-polymer-modified water structure play a central role.

Acknowledgements

The authors would like to thank the Plan Nacional I+D+I (Ministerio de Educación y Ciencia) for financial support (MAT2006-05979) as well as the Comunidad Autónoma de Madrid for the funding through I+D Program (S0505/MAT-0227).

References

- [1] Moulton B, Zaworotko MJ. *Chem Rev* 2001;101:1629.
- [2] Janiak C. *Dalton Trans* 2003:2781.
- [3] Robin AY, Fromm KM. *Coord Chem Rev* 2006;250:2127.
- [4] Madhu V, Das SK. *Polyhedron* 2004;23:1235.
- [5] Jung OS, Kim YJ, Lee YA, Park JK, Chae HK. *J Am Chem Soc* 2000;122:9921.
- [6] Pan L, Woodlock EB, Wang X, Lam KC, Rheingold AL. *Chem Commun* 2001:1762.
- [7] Leadbeater NE, Marco M. *Chem Rev* 2002;102:3217. , and references therein.
- [8] McNamara CA, Dixon MJ, Bradley M. *Chem Rev* 2002;102:3275. , and references therein.
- [9] Pomogailo AD, Savost'yanov VS. *Polymerization of metal containing monomers*. CRC Press; 1994.
- [10] Mastroilli P, Nobile CF. *Coord Chem Rev* 2004;248:377.
- [11] Baldrian P, Cajthaml T, Merhautová V, Gabriel J, Nerud F, Stopka P, et al. *Appl Catal B: Environ* 2005;59:267.
- [12] Rivas BL, Maureira A, Geckeler KE. *J Appl Polym Sci* 2006;101:180.
- [13] Soykan C, Coskun R, Kirbag S. *Eur Polym J* 2007;43:4028.
- [14] Coskun R, Soykan C, Delibas A. *Eur Polym J* 2006;42:625.
- [15] Peinado C, Catalina F, San Miguel V. *J Appl Polym Sci* 2007;106:1982–91.
- [16] Kang N, Perron ME, Prud'homme RE, Zhang YB, Gaucher G, Leroux JC. *Nano Lett* 2005;5:315–9.
- [17] Fery-Forgues S, Fayet JP, Lopez AJ. *J Photochem Photobiol A: Chem* 1993;70:229.
- [18] Pearson RG. *Coord Chem Rev* 1990;100:403.
- [19] Lizzi A, Cobianco S, Roggero A. *J Polym Sci Part A: Polym Chem* 1994;32:1877.
- [20] Brodin A, Mattsson B, Nilsson K, Torell LM, Hamarab J. *J Solid State Ion* 1996;85:111.
- [21] Jones M-C, Leroux J-C. *Eur J Pharm Bio-Pharm* 1999;48:101–11.
- [22] Marcus Y. *Ion solvation*. Chichester: Wiley; 1985.