



CORPUS PUBLISHERS

Research and Development in Polymer Science (RDPS)

Volume 2 Issue 1, 2023

Article Information

Received date : July 04, 2023

Published date: July 24, 2023

*Corresponding author

Miriam Martins Alho, Universidad de Buenos Aires, Facultad de Ingeniería, Departamento de Química, Av. Paseo Colón 85, Universidad de Buenos Aires, Facultad de Ingeniería, Laboratorio de Materiales Orgánicos (LabMOR), Instituto de Química Aplicada a la Ingeniería (IQAI), Buenos Aires, Argentina

DOI: 10.54026/RDPS/1007

Keywords

Polymer synthesis; Tailor-made polymers; Recycling; Neocuproine; HLLW

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Research Article

Synthesis and Characterization of a Poly (methyl methacrylate-co-N-(2,9-dimethyl-1,10-phenantrolin-5-yl) acrylamide) Copolymer. Preliminary Results of its Interaction with some Lanthanides in Acid Media

Agustín Alvarado¹, Valeria Pozzoli^{2,3}, Javier Eiras⁴, Miriam Martins Alho^{2,3*} and Andrea Bruttomesso⁴

¹Centro Atómico Ezeiza, Comisión Nacional de Energía Atómica, Presbítero Juan González y Aragón N° 15, 1804. CP B1802AYA - Ezeiza, Provincia de Buenos Aires, Argentina

²Universidad de Buenos Aires, Facultad de Ingeniería, Departamento de Química, Av. Paseo Colón 850, 5to. Piso. CP C1063ACV - Buenos Aires, Argentina

³Universidad de Buenos Aires, Facultad de Ingeniería, Laboratorio de Materiales Orgánicos (LabMOR), Instituto de Química Aplicada a la Ingeniería (IQAI), Av. Paseo Colón 850, 5to. Piso. CP C1063ACV - Buenos Aires, Argentina

⁴Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Orgánica, Av. Intendente Güiraldes 2160, Pabellón II, 3er. Piso, Ciudad Universitaria. CP C1428EHA - Buenos Aires, Argentina

Abstract

In this work, we synthesized a copolymer of methylmethacrylate with a monomer derived from 2,9-dimethyl-1,10-phenanthroline, in order to be tested for lanthanide uptake and possible nuclear fuel reprocessing. The incorporation of this monomer in the copolymer was confirmed by the observed results on the 1H NMR, which also allowed us to estimate the molar composition of these material. We found that feed composition does not correlate with the composition of the copolymer, which is attributed to a tendency to a preferential incorporation of methylmethacrylate instead the phenanthroline monomer by the growing chain. This behavior would indicate that methylmethacrylate have a higher reactivity, probably attributed to a steric hindrance exerted by the neocuproyl group. The copolymer is stable up to 300 °C. Using ICP we were able to determine that poly(methylmethacrylate-co-N-(2,9-dimethyl-1,10-phenantrolin-5-yl)acrylamide) shows a marginal retention of rare earth cation at the working low pH, probably due to an unfavorable spatial arrangement of the pendant aromatic groups.

Introduction

In the development of the nuclear energy cycle, one of the most interesting challenges, not only from the economic point of view but also from the best efficiency of all process, lies in the improvement and development of methods for reprocessing radioactive materials [1]. Previous studies deal with the interaction between certain ligands and rare earths, like malonamides such as DMBTDMA (N,N,N',N'-dimethyldibutyltetradecylmalonamide), and DMDOHEMA (N,N,N',N'-dimethyldioctylhexylethoxymalonamide), and diglycolamides such as TODGA (N,N,N',N'-tetra-n-octyldiglycolamide). These ligands and others with some similar compositions were used for preconcentration and chromatographic extraction of minor actinides and lanthanides, using different supporting materials [1,2]. This separation is a key step in the elimination of long-lived minor actinides and lanthanides from other fission products in high level liquid waste (HLLW). On other hand, polymers containing phenanthroline pendant groups were the focus of several investigations over the past decade, due to their fluorescent capabilities when complexing with lanthanides [3-5]. Furthermore, chloromethylated polystyrene was modified using 5-amino-1,10-phenanthroline, and used for Fe³⁺ or Ru⁴⁺ complexation. The resulting materials could be used to carried out some oxidations under mild conditions [6-7]. Considering all this background, and taking into account the capability of phenanthroline moiety to form complexes with lanthanides, we decided to synthesize a new monomer derived from 2,9-dimethyl-1,10-phenanthroline, the 5-acrylamido-2,9-dimethyl-1,10-phenanthroline (5ADMP), in order to obtain a copolymer with methyl methacrylate (MMA) for subsequent rare earth absorption tests. The obtained copolymer was thermal and spectroscopically characterized and the results of the preliminary test with several rare earths are presented.

Experimental

Materials

Acrylic acid, azo-bis-isobutyronitrile (AIBN) and methyl methacrylate (MMA) were provided by Teyupa S.A. Thionyl chloride, oxalyl chloride and neocuproine were purchased from Merck. ¹H and ¹³C NMR were recorded on a Bruker AMX-500 from Bruker Corporation (500 and 125 MHz, respectively, Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, UMYMFOR), in CDCl₃. IR spectra were performed on a Nicolet 6700 spectrometer from Thermo Scientific (Instituto Tecnológico de Buenos Aires) and TGA analysis was recorded on a TGA-50 Shimadzu Analyzer from Shimadzu

Corporation (Universidad de Buenos Aires, Facultad de Ingeniería, ITPN) at 5 °C/min under nitrogen flow. ICP analysis were performed on a Perkin Elmer from Elan DRCII (CNEA-Comisión Nacional de Energía Atómica).

Procedures

Synthesis of 5-nitro-2,9-dimethyl-1,10-phenanthroline and 5-amino-2,9-dimethyl-1,10-phenanthroline (1)

2,9-dimethyl-1,10-phenanthroline (0.3g, x 1.44 mmoles) was dissolved in 6 ml concentrated sulfuric acid. To this stirred solution, 4 ml of nitric acid was added, while the temperature was kept around 115 °C using a sand bath. The mixture was stirred for 2 h after the nitric addition and then, basified, filtered and then extracted with ethyl acetate. Finally, the reduction was carried out with H₂, using 5% Pd/C in methanol giving compound 1. The obtained product was in good agreement with that reported in literature [8].

Synthesis of 5-acrylamido-2,9-dimethyl-1,10-phenanthroline (5ADMP) (2)

To a mixture of acrylic acid (0.35 ml) in dichloromethane, (COCl)₂ was added (0.5 ml), and then this solution was administered dropwise to a suspension of 1 (0.220 g, 0.986 mmol) in 6 ml in dichloromethane and triethylamine (1 ml) with continuous stirring at room temperature under argon atmosphere. The reaction was allowed to continue for 48 h approximately. After concentration under reduced pressure, the residue was chromatographed on a silica column with 1:1 cyclohexane:ethyl acetate as eluent. The assignment of NMR signals was made by analysis of COSY, HSQC and HMBC experiments. Pure 5ADMP was obtained as a yellowish solid (0.243 g, 89% yield). Molecule numbering for 5ADMP is shown in Figure 1. ¹H NMR (δ, 500 MHz, CDCl₃): 8.34 (s, 1H, -NH-), 8.31 (d, 1H, H₃, J_{3,4} = 8.5), 8.22 (s, 1H, H₆), 8.09 (d, 1H, H₈, J_{7,8} = 8.2), 7.49 (d, 1H, H₇, J_{7,8} = 8.1), 7.43 (d, 1H, H₄, J_{3,4} = 8.4), 6.57-6.58 (complex signal, 2H, H_{1'}+H_{3'}), 5.85 (s broad, 1H, H_{2'}), 2.91 (s, 3H, CH₃-C₉), 2.90 (s, 3H, CH₃-C₂). ¹³C NMR (δ, 125 MHz, CDCl₃): 164.55 (C=O), 159.43 (C₂), 159.20 (C₉), 145.65 (C_{10b}), 143.69 (C_{10a}), 136.30 (C₅), 136.29 (C₈), 130.76 (C_{1'}), 130.20 (C₃), 129.66 (C_{4a}), 128.46 (C_{2'}), 126.40 (C_{6a}), 123.99 (C₇), 123.19 (C₄), 119.22 (C₆), 25.74 (CH₃-C₂), 25.60 (CH₃-C₉).

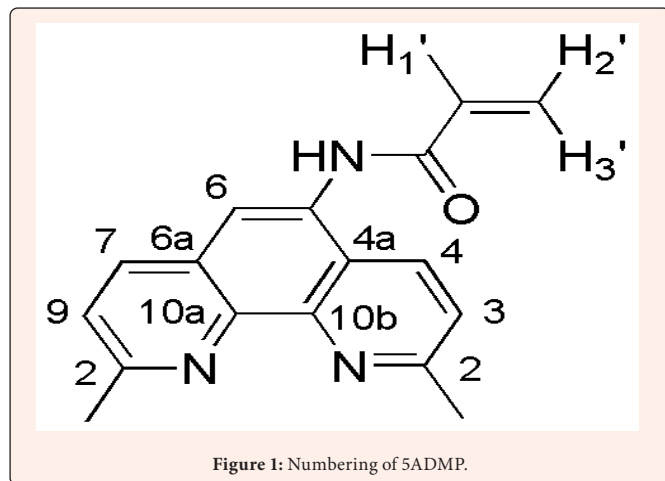


Figure 1: Numbering of 5ADMP.

Synthesis of poly(MMA-co-5ADMP)(3)

A mixture of MMA (4.70 mmol) and 5ADMP (0.58 mmol) was dissolved in DMF (10 mL) and purged with N₂ (approximated molar relationship 8:1). Then 5 mg of AIBN were added into the glass polymerization tube, and the homogeneous solution was purged again. Next, the tube was closed and heated at 80 °C for 6h. The mixture was concentrated under reduced pressure and then poured to cold water. The precipitate was filtered, dissolved in acetone and reprecipitated in 150 ml of methanol (0.380 g, 60% of conversion degree). The copolymer was spectroscopically (NMR and IR-FT) and thermally characterized (TGA, DSC). ¹H NMR (δ, 500 MHz, CDCl₃): 8.35-7.35 (aromatics), 3.95-3.30 (CH₂O- groups), 3.15-2.70 (CH₃-Ar groups), 1.84, 1.04 and 0.86 (CH₃-methacrylate groups from polymethacrylate sections, mm, mr and rr) [9]. 2.45-0.65 (-CH₂-, -CH- and CH₃- methacrylate groups neighbors to 5ADMP). IR(KBr): 3363

cm⁻¹ (N-H), 2995-2850 cm⁻¹ (C-H aliphatic), 1732 cm⁻¹ (C=O), 1671 cm⁻¹ (Amide I), 1624 cm⁻¹ (C=C), 1593 cm⁻¹ (Amide II), 1269, 1241, 1194 and 1145 cm⁻¹ (methacrylate polymers).

Interaction of poly(MMA-co-5ADMP) with some lanthanides

The copolymer was contacted with solutions of around 10 ppm of Ce, Sm, Eu, Dy and La in three different nitric acid concentrations (0.05M, 1M and 8M). For Gd, solutions of around 20 ppm were used. The mixtures were shaken in a vortex, left at room temperature overnight, and then centrifuged, and the supernatant was analyzed using ICP.

Results

NMR Characterization

NMR characterization of 5ADMP was not so simple as expected. ¹H NMR (Figure 2) showed two very close singlets (2.91 and 2.90 ppm) attributable to C₂ and C₉ methyl groups and six signals between 7.3 - 8.5 ppm region which integrates for six protons (aromatics plus amide proton), four of them as doublets and two as wide singlets. The vinyl protons showed an unusual pattern for a monosubstituted alkene, because the resonance frequencies of H_{1'} and H_{3'} are very close, so a typical first order analysis could not be carried out on these signals. The ¹³C NMR showed the presence of seventeen signals, according with the total number of carbons in the molecule. The signals at 25.74 and 25.60 ppm were assigned to C₂ and C₉ methyl groups and the peak at 164.47 was attributed to carbonyl group.

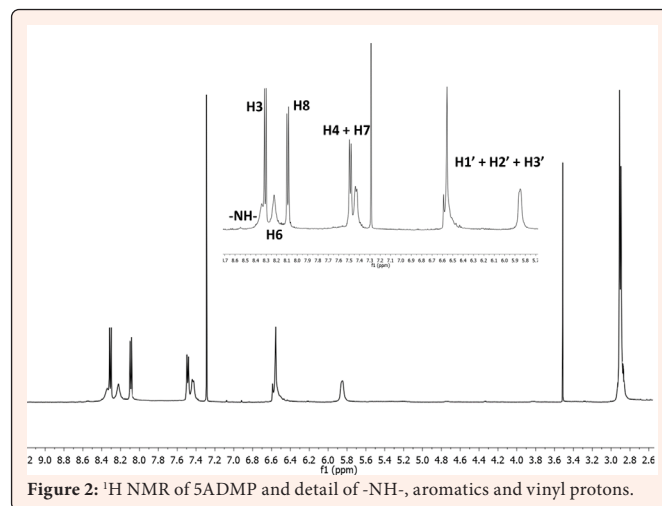


Figure 2: ¹H NMR of 5ADMP and detail of -NH-, aromatics and vinyl protons.

In this spectrum there were several signals which could be assigned by comparison with model compounds, like 159.40 and 159.12 ppm (C-2 and C-9) or 145.63 and 143.70 (10a and 10b), but for a more accurate assignments HSQC combined with HMBC were carried out. From HSQC experiment we confirmed that all signals initially attributed to quaternary carbons had not correlation with any proton. On the other hand, amide proton was assigned to a broad singlet at 8.34 ppm with no correlation with any carbon. The other broad singlet (8.23 ppm) correlated with 119.25 signal; therefore, these signals were assigned to H-6 and C-6 respectively. Peak at 128.47 ppm correlated with two proton signals (6.56 and 5.85 ppm), so it was attributed to vinyl CH₂. As no vinyl coupling constant could be measured, we can not affirm which of them corresponds to H_{2'} or H_{3'}, but as signal at 5.85 ppm is narrower, we assume that it could have the two smaller coupling constants of this system (J_{cis} and J_{gem}), and it was tentatively attributed to H_{2'}. The superposition of H_{1'} and H_{3'} signals do not allow further analysis, but its correlation led us to assign signal the for C_{1'} (130.76 ppm). As H₆ and C₆ were individualized by the HSQC, the correlation of C₆ with a doublet at 8.10 ppm in the HMBC experiment let us to assign this signal to H₇, which also correlated with signals at 126.40, 143.71 and 159.12, assigned to C_{6a}, C_{10a} and C₉, respectively. The doublet at 7.49 ppm shows an HMBC correlation with C₉, so it was assigned to H₈ (C₈ = 124.00 from HSQC). From HMBC, H₈ shows a correlation with 25.60 ppm which was attributed to CH₃-C₉ (2.91 ppm CH₃-C₉), consequently, the signal at 25.74 ppm was assigned to CH₃-C₂ (2.90 ppm CH₃-C₂).

Doublet at 8.31 ppm showed correlation with three quaternary carbons: 129.72, 145.71 and 159.40 ppm, which were assigned to C4a, C10b and C2, respectively, so, this doublet could be attributed to H3 as well as to H4. As the signal at 7.43 ppm (123.23 ppm) shows no correlations in HMBC, the ambiguity persists. Taking into account values reported for C3 and C4 for neocuproine derivatives, values for H3 and H4, and consequently for C3 and C4, were provisionally assigned. The ¹H NMR spectrum of the copolymer 3 showed the presence of aromatic protons, which confirms the incorporation of 5ADMP. The signals integration of the corresponding to 5ADMP methyl group and the MMA methoxy group (Figure 3) allowed us to estimate the proportion of 5ADMP in the copolymer, using Equation (1).

$$\frac{m}{n} = \frac{2A}{B} \quad (1)$$

The values *m* and *n* represent the number of moles of MMA and 5ADMP monomers incorporated into the polymer, respectively, while *A* and *B* represent the values of the integrals for the signals of the -OCH₃ group of MMA and of the methyl group for 5ADMP. As results of this calculation, we estimated that the copolymer has an approximate molar composition of 25:2 (MMA:5ADMP), which represent a 7.4 % molar ratio of 5ADMP.

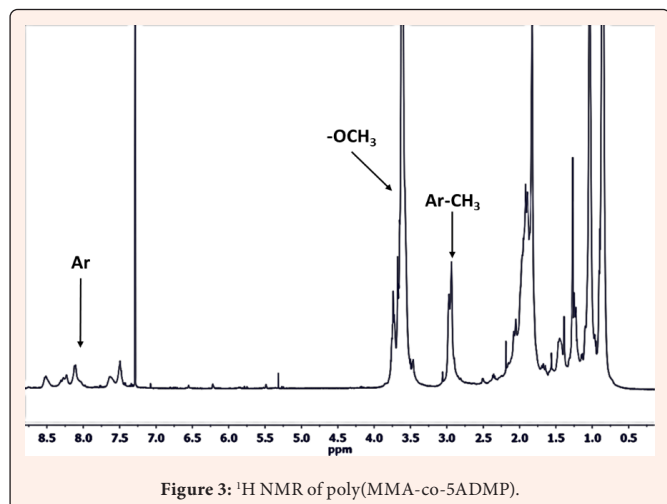


Figure 3: ¹H NMR of poly(MMA-co-5ADMP).

IR characterization

From the IR-FT spectra of copolymer we can observe some interesting absorptions in the carbonyl zone. The strongest band was assigned to the contribution of carbonyl ester of acrylate monomer (1732 cm⁻¹). Smaller absorptions were also observed at lower wave numbers and were assigned to the Amide I, Amide II and C=C bands, indicating the presence of 5ADMP in the copolymer (Figure 4). Around 3300 cm⁻¹ a broad band could be observed. This can be attributed to N-H stretching but also can be assigned to moisture contained in the polymer, as it was confirmed by thermogravimetric analysis. Due to the low 5ADMP contribution to the whole polymer, the IR between 1100 and 1300 cm⁻¹ shows two double bands, characteristic of methacrylate polymers.

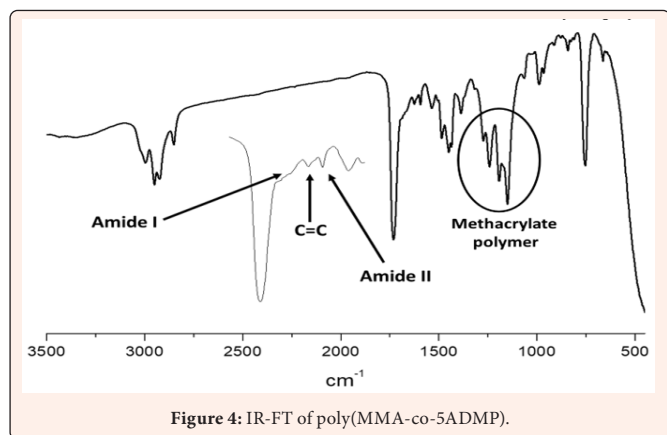


Figure 4: IR-FT of poly(MMA-co-5ADMP).

Thermal characterization

After an initial little loss of mass, occurred below 100°C (loss of water, 3.44%), poly(MMA-co-5ADMP) is stable up to 300°C, where a decomposition process starts with a point of inflection at 350°C, which matches with an exothermal event in DSC (375°C). TGA shape is similar to PMMA, except by the amount of residual material at 500°C. At this temperature, PMMA is completely decomposed while for poly(MMA-co-5ADMP) there is still 20% of the original mass. Two events (T = 295 and 325°C) consistent with glass transitions in DSC were observed (Figure 5).

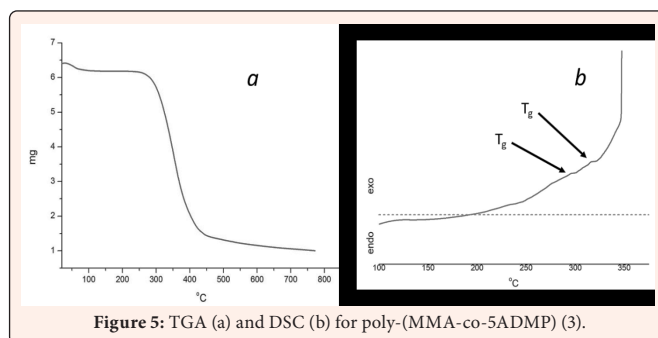


Figure 5: TGA (a) and DSC (b) for poly-(MMA-co-5ADMP) (3).

Discussion

Based on ¹H NMR estimations, the incorporation of both monomers to the copolymer is not consistent with the feed composition. Taking into account that the feed composition was 8:1 (11.1 % molar ratio of 5ADMP), we can conclude that 5ADMP result less reactive than MMA, because in the growing copolymer chain there is a slight tendency to incorporate MMA monomer than 5ADMP. A similar effect was observed for copolymers of MMA and *N*-1-naphthylacrylamide (NAM) and it was attributed to the steric hindrance of the aromatic moiety [10], so, the observed behavior for 5ADMP could be attributed to the same reason. In that particular case, feed composition was approximately conserved in the resulting copolymer when molar amount of NAM was lower than MMA, and the lack of reactivity of NAM was observed in a molar feed composition of 50%. Even though a similar behavior could be expected for 5ADMP, it is notable that it is evidenced by molar compositions of less than 10% of the aromatic monomer. This behavior could indicate a higher steric hindrance for 5ADMP than for NAM. The percentage of 5ADMP in the copolymer 3 is higher than the reported composition for *N*-(1,10-phenanthroline-5-yl)acrylamide-MMA copolymer [3]. Based on these results, we can conclude that the incorporation of two methyl groups in the phenanthroline core did not affect the possibilities of incorporation on an MMA copolymer. This is a reasonable thought, because the modification is produced far from the vinyl group, and there is no extra steric hindrance.

From thermal analysis, we conclude that this copolymer is able to be used in process under temperatures below 290°C, without softening. This limit is relatively far from room temperature, and make this material suitable for use in relatively hot environments. Taking into account the estimated composition of poly(MMA-co-5ADMP) obtained from its ¹H NMR and the content of water from TGA, we can determinate the molar relationship between water and heterocycles present in the material. From this data, we found a striking 3:1 relationship, so, and assuming that all the water molecules are interacting with the neocuproine, each heterocyclic moiety should be surrounded by three molecules of water.

Table 1: Mass of cation uptake by g of copolymer in three HNO₃ concentrations.

Cation	[C]0 (ppm)			mg of cation by g of copolymer		
	0,05M	1M	8M	0,05M	1M	8M
Ce	10.5	10.2	9.8	0.11	0.08	0.03
Sm	10.2	9.8	9.5	0.11	0.08	0.03
Eu	10.1	10.5	9.7	0.11	0.08	0.01
Gd	20.6	20.1	19.3	0.21	0.16	0.04
Dy	10.1	9.8	9.4	0.1	0.06	0.01
La	10.1	10	9.5	0.1	0.09	0.02



As lanthanides tend complexing with phenanthroline in a 1:3 ratio, therefore, taking into account the approximate polymer composition, the maximum rare earth uptake calculated should be of 30 to 36 mg/g of polymer. When we run some preliminary experiments, we verify that the experimental cation uptakes were far below this limit, but some tendencies were observed, as shown in Table 1. Based on these preliminary assays with some lanthanides, the amount of retained cation seems to be dependent on the initial concentration in solution: for Gd a 20 ppm solution was used, and the measured Gd uptake is higher than the other for all assayed cations in the three different acid concentration. As a first hypothesis, it could be expected that retention could be lower for those cations with higher ionic radius, due to the steric hindrance exerted by C2 and C9 methyl groups, however, at 0.05 M of acid concentrations, no large differences were observed between them, except those already attributed to the initial concentration of the cation. According with ICP data, the lack of capacity for cation retention is directly related with the acid concentration: for higher the acid concentration, the lower cation retention is observed, but the behavior is not the same for all cations. As only a preliminary study was made, we cannot exactly quantify the loss of material uptake increasing the acid concentration, but we can see that for Dy and Eu, at HNO₃ 8M, the material shows a cation uptake of approximately 10% of the amount retained when the acid concentration was 0.05 M. On other hand, for Ce and Sm at 8M of acid concentration, a retention of around 30% of the uptake at 0.05 M was observed. This behavior could probably be related with different values of the corresponding constants of each complex formation.

Conclusion

Even when 5ADMP monomer shows a low reactivity with MMA, the use of DMF as solvent and the prolongation of the reaction time with respect to similar copolymerization reported in the literature allowed us to a considerably increase the incorporation of complexing agents in the copolymer [3-5]. As it was early mentioned, the retention of the cations by poly(MMA-co-5ADMP) is marginal. In a first approximation, this low level of cation retention could be attributed to a protonation of the heterocyclic nitrogen, diminishing its coordination capacity. Nevertheless, this poor interaction could also be attributed to other facts. As the synthesis was carried out by a single free radical solution polymerization, the location of neocuproine moieties is irregular, and this could affect negatively the cation interaction. Taking into account that each cation interacts with three ligands, the possibility to find three neocuproine for complexation in the same neighborhood is very low. On the other hand, the fact that the retention capacity is apparently linked to the ion concentration in solution, suggests that the observed retention could be attributed to common adsorptive processes instead to a cationic complexation. Even if this particular copolymer did not match our expectations, we will use this experience to continue designing new materials for rare earths recovery and HLLW reprocessing.

Acknowledgment

We would like to thank University of Buenos Aires for partial financial support (UBACyT N° 2002012010384). We also thank to Dra. M. I. Errea for her invaluable help.

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