

Synthesis and characterization of imprinted polymers for rare earth recovery

Abstract

This study aims to discover a novel material suitable for rare earth recycling. We explore the efficacy of a physically imprinted copolymer in sequestering cationic lanthanum from aqueous solutions. The copolymerization process with MMA, incorporating lanthanum complexes with an acrylic derivative of neocuproine, facilitates physical crosslinking. Our investigations demonstrate the copolymer's reversible lanthanum binding capability in both batch and column experiments. At laboratory scale, the copolymer achieves an impressive lanthanum retention of approximately 760 mg/g at an initial concentration (C_0) of 22 g/L in batch experiments. Regeneration of the material is achieved using HNO_3 (c), inducing alterations in its physical state. Nonetheless, subsequent washing with water preserves the copolymer's interaction capacity with lanthanum. Current efforts focus on conserving the material's physical integrity during regeneration to enable in situ regeneration in column experiments.

Keywords: rare earths, imprinted polymers, urban mining, circular economy, recycling

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Abbreviations: AA, atomic absorption; AIBN, azobisisobutyronitrile; 5-ADMP, 5-acrilamido-(2,9-dimethyl-1,10-phenanthroline); °C, degree centigrade; C_0 , initial concentration for column experience; cm, centimeters; cm^{-1} , wave number; ^{13}C -NMR, carbon-13 nuclear magnetic resonance; COSY, homonuclear correlation spectroscopy; DCCl_3 , deuterated chloroform; DCM, dichloromethane; DMF, dimethylformamide; DMSO-d6, deuterated dimethyl sulfoxide; EGDMA, ethyleneglicoldimethacrylate; FTIR, Fourier transform infrared spectroscopy; g, gram; h, hour; ^1H -NMR, protonic nuclear magnetic resonance; HLLW, high level liquid waste; HSQC, heteronuclear single quantum coherence spectroscopy; mg, milligram; MHz, megahertz; min, minutes; mL, milliliters; MMA, methylmethacrylate; mmol, millimole; P1/P2, poly(MMA-co-5-ADMP); PMMA, polymethyl methacrylate; s, second; TGA, thermogravimetric analysis; THF, tetrahydrofurane; UV, ultraviolet

Introduction

Daily life has been undergone to radical changes in recent decades, due to rapid technological advancements. Nowadays, human comfort and capabilities have significantly expanded thanks new technological applications. The effects of this disruption on daily life have been broad and deep, and take place in both, industries and homes. While the social changes brought about by these discoveries cannot yet be compared to what happened with the industrial revolution, they are increasingly pushing boundaries and the ultimate repercussions remain unknown.

These advances and the speed of their evolution are astonishing, but they shorten useful life of many devices, mostly the electronic ones.

Considering that the use of these new technologies from household appliances to computers, including lighting sources and cell phones, the widespread use of these new technologies in the daily lives of ordinary people results in a colossal global production. When premature obsolescence due to technological progress is combined with the mass distribution of these goods, a substantial amount of waste requiring proper disposal and management is created.

One of critical element in the construction of electronics and devices used in so-called “green technologies”, such as wind energy

and electric car production, is the use of elements called “rare earths”. These elements are not so “rare” as their name suggest, but the challenge lies in their low concentrations in several minerals, and it is difficult to isolate them from other elements. Access to rare earths can be achieved through direct extraction, isolation from the exploitation of other minerals or through recycling from unconventional sources. The mining of these elements is always linked to significant damage to the environment, either by erosion, such as when the crust is removed, or by the generation of large leachate lagoons that end up contaminating the soil and groundwater. Moreover, the minerals from which they are extracted, often contain some amounts of radioactive elements such as thorium (Th) and uranium (U), which is already concerning. It is estimated that for every ton of rare earths, 2000 tons of toxic waste are produced,¹ highlighting the continued need for environmental preservation in the development of new technologies. Therefore, current research must be directed not only at technological improvements themselves, but also enhancing efficiency, preservation, reuse and recycling of the materials used in different devices.

In a previous work we studied the possibility of capture lanthanides using a copolymer containing suitable ligands, to be used in HLLW's treatment.² Building on this previous experience and aiming to contribute to the “urban mining”, we performed the synthesis of a physically imprinted copolymer, using MMA and a monomer which can act as ligand of rare earths.

Based on the reported data about the formation of luminescent complexes between Eu^{3+} and 1,10-phenanthroline,³ we decided to include 2,9-dimethyl-1,10-phenanthroline in MMA copolymer, and studied its behaviour towards a specific ion, under the hypothesis that the presence of methyl groups could potentially lead to some level of selectivity the radius of different ions.

Materials and methods

General

Azobisisobutyronitrile (AIBN) was provided by Teyupa S.A. Acrylic acid, thionyl chloride and neocuproine were purchased from Merck. Sodium hydroxide, nitric and sulfuric acids were purchased from Biopack Productos Químicos. Solvents were purchased from Sintorgan S.A and distilled before used. ^1H - and ^{13}C -NMR were

recorded on a Bruker AMX-600 from Bruker Corporation (600 and 150 MHz, respectively, Universidad de Buenos Aires, Facultad de Farmacia y Bioquímica), in DCCl_3 or DMSO-d_6 . FTIR 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. UV spectra were recorded in a BIOBASE BK-S380.

Lanthanum concentrations were determined by atomic absorption, performed by the División de Servicios Analíticos de la Comisión Nacional de Energía Atómica (CNEA).

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

Synthesis of title compound was performed as described earlier,^{2,4} but in this case, the reduction of nitro compound was made using Ni/Raney as catalyst. Briefly, the nitro compound was dissolved in 2 mL of methanol (0.46 g, 1.82 mmol), and catalytical amounts of Ni/Raney (5mg) were added. Hydrogen was then bubbled through the solution while stirring constantly. The catalyst was filtered out and washed with methanol (4x1mL) and water (4x1mL). The combined filtrate and washings were concentrated, and the resulting aqueous phase was extracted with chloroform (4x1mL) to remove potential organic-soluble impurities. The residue was treated with THF and cyclohexane yield a filterable brown powder of the 5-amino derivative (0.33 g, 1.48 mmol, 81%).

For acylation, the amino compound (1.00 g; 4.48 mmol) was dissolved in 2.5 mL of pyridine, and treated with acryloyl chloride (0.50 mL, 6.19 mmol, synthesized in our laboratory from acrylic acid and thionyl chloride) in an ice water bath, with constant stirring. After 4 h of reaction at room temperature, the mixture was poured onto ice and water to obtain title compound (0.52 g, 1.88 mmol 47 %). Spectroscopic data matched previously reported results accurately.

Synthesis of $[\text{La}(5\text{-ADMP})_3]\text{Cl}_3$

In two test tubes, 0.25 g (0.67 mmol) of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and 0.56g (2.02 mmol) of 5-ADMP were dissolved separately in the minimum amount of ethanol. The 5-ADMP solution was placed in a silicone bath at 60 °C with stirring and then, solution of lanthanum was added. The mixture was heated for 8 h, evaporated, resulting in the formation of a dusty brown precipitate. (0.52 g, 0.48 mmol, 72 %).

Synthesis of poly(MMA-co- $[\text{La}(5\text{-ADMP})_3]$)

Technique A: An adaptation of the procedure described by X. Liu was applied,³ starting from 0.47 g of $[\text{La}(5\text{-ADMP})_3]\text{Cl}_3$ (0.43 mmol) and 5.85 mL (55 mmol) of MMA in DMF (10 mL), using AIBN (0.03g, 0,18 mmol) as initiator. Atmosphere was inertized with vacuum followed by refilling with N_2 (3 cycles). The reaction was carried out at 80 °C during 48 h. After that, the reaction medium was poured on fresh water, and the copolymer was obtained as a very thin precipitate (P1, 1.0 g; 17 %).

Technique B: In a round bottom flask, 0.18 g of $[\text{La}(5\text{-ADMP})_3]\text{Cl}_3$ (0.17 mmol) was dissolved in 10 mL of DMF. Then 5.50 mL (52 mmol) of MMA was added and purged as described earlier, followed by the addition of 0.02 g (0,12 mmol) of AIBN dissolved in 5 mL of DMF. The reaction mixture was heated at 80°C and after 2 h, 0.20 g (0,18 mmol) of $[\text{La}(5\text{-ADMP})_3]\text{Cl}_3$ and 20 mg (0,12 mmol) of AIBN were added. Further additions of AIBN (30 mg, 0.18 mmol) were made at 30 and 48 h into the reaction. After the last addition, the

mixture was left to react for 24 more hours. After this, the mixture was then poured into fresh water, yielding a filterable solid. After vacuum dried at 60°C, 5.10 g of P2 were obtained (92 % of recovery).

P1 and P2 conditioning

Both copolymers (P1 and P2) were washed with HNO_3 (c), then with several portions of fresh water until neutrality. After that, the materials were vacuum dried at 60 °C.

Batch experiences

For these experiences, capped vials were used. In each vial an exact mass of P1 or P2 ranging from 80 and 100 mg were weighed, and they were mixed with 5.00 mL of solutions of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ of a known concentration. Each suspension was stirred for 30 s and then, left at room temperature for 30 min, then filtered and the clear solution was set aside for further analysis.

Column experiences and breakthrough curve

Based on the findings from the batch experiences, the parameters of the laboratory column, filled with P2, were selected. The specific parameters chosen were: mass of P2 (0.87 g); length (4.9 cm), diameter (2.54 cm), velocity (0.2cm/s), flow rate (0.1 mL/s) and C_0 (739.2 mg/L).

The column was moistened with distilled water drain, and then, it was loaded with 70 mL of a solution of 739.2 ppm of La. Fractions of the eluate were collected as follows: 10 mL each interval up to 30 mL, 5 mL each between 30 and 60 mL, and a final fraction of 10 mL to reach a total volume of 70 mL.

Results

In a previous report² we described the synthesis of a copolymer of MMA and 5-ADMP and analyzed its interaction with some rare earths showing a low retention capacity, but it was assayed only in low concentrations. In this work we aimed to investigate the potential impact of the relative position of the ligands in the copolymer on the retention of a given cation. Our approach involved the copolymerization in the presence of a complex between the polymerizable ligand and a selected cation, such as lanthanum.

The incorporation of this complex in the reaction medium would act as physical crosslinker through the La^{3+} , which will fix the position of ligands. Once incorporated to the polymeric matrix in a specific orientation, it would imprint an appropriate cavity for the location of the cation on the polymer.

Considering that each complex requires three polymerizable ligands, the resulting product would be a crosslinked material with a specific arrangement of these ligands in fact, a physically imprinted polymer.

The polymerization conditions used to synthesise imprinted polymers involve a high proportion of a chemical crosslinker, typically EGDMA.⁵⁻⁷ This relationship ensures the imprinting process but results in rapid polymer insolubilisation, leading to the formation of a very fine powder. This characteristic could be an obstacle in column applications, prompting the decision to use the complex as the sole crosslinking agent.

For the first attempt of copolymerization, both monomers and the initiator were mixed at once with the solvent and just a few minutes later insoluble particles appeared (P1). Despite the heating was prolonged for additional 24 h, the scent of MMA in the reaction medium was very strong and the recovery percentage was scarce (17%).

When the polymerizations were carried out in DMF, the strong solvation of monomers slowed down the reaction speed, but in this case, the precipitation seems to be the main reason for the low conversion degree. As soon as precipitate appears in the medium, many growing chains are lost. For that reason, we decide to increase the amount of AIBN and add it in portions. The cross-linking complex was also added in two portions. As result of this strategy, we could isolate the copolymer (P2) with more than 90 % of mass recovery.

In order to characterize both copolymers, we try to perform their NMR. However, they were only partially soluble in DCCl_3 , resulting in a spectrum identical to poly MMA. $^1\text{H-NMR}$ of P2 in DMSO-d_6 exhibit some aromatic signals around 8 ppm. Additionally, for methyl groups at positions 2 and 9 of the heterocycle were detected at 3.03 and 2.98 ppm, as singlets (Figure 1).

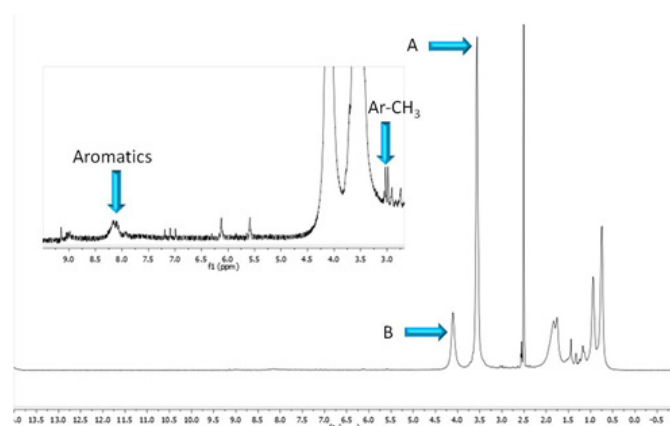


Figure 1 $^1\text{H-NMR}$ for P2 a 600 MHz in DMSO-d_6 .

Two signals at 3.56 and 4.10 ppm were also detected (A and B) likely $-\text{OCH}_3$ and H_2O . As the last one (B) showed no correlation with any carbon in the HSQC spectrum (Figure 2) it was assigned to water. The reported resonance frequency for water in DMSO-d_6 is 3,33 ppm,⁸ suggesting potential confinement, as described before for another MMA-neocuproine copolymer.²

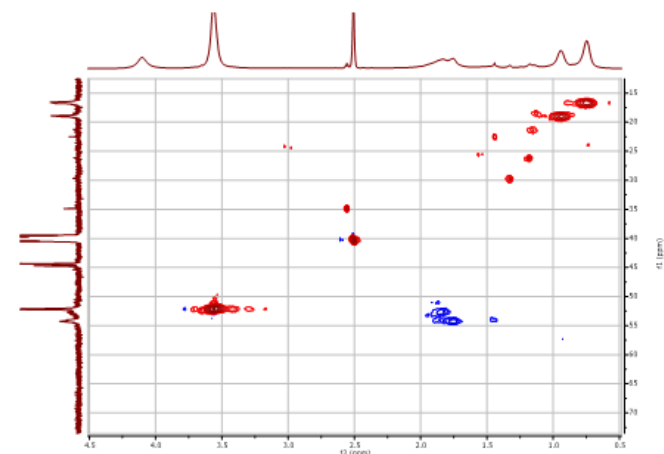


Figure 2 HSQC for P2 in DMSO-d_6 . No H-C correlation was observed for signal at 4.1 δ .

The low intensity of aromatic signals in NMR spectrum is due to the feed composition and polymerization conditions, with a molar ratio close to 140:1 of MMA. Considering the likelihood that not all the complex was incorporated into P2, the NMR spectrum matched expectations.

Because of this relationship, the FTIR of P2 is almost the same than for PMMA,⁹ but some differences were observed. The absorption band at 1386 cm^{-1} for P2 is wider compared to PMMA, with a new absorption detected at 1365 cm^{-1} . Additionally, a less intense but more significant absorption at 1205 cm^{-1} is observed. This little band is located just in the middle of the four absorption bands pattern, typical of methacrylate polymers (Figure 3). All these differences allow us to conclude that P2 is not exclusively PMMA, because even when they could not be assigned to neocuproine core, the observed alterations take place into the fingerprint zone, which differs of pure PMMA.

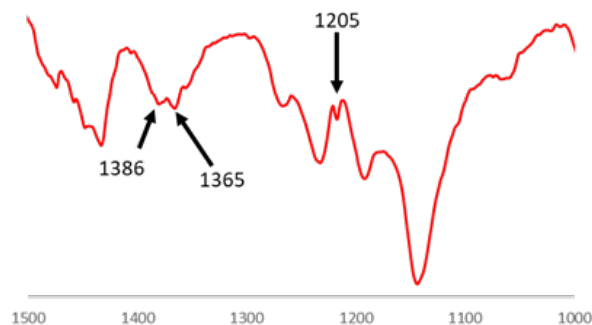


Figure 3 Detail of FTIR of polymer P2.

Taking into account the NMR signal superposition and the substantial difference in the molar monomer composition, the relative proportion of both monomers cannot be estimated accurately determinate by this analytical method. By the assuming total incorporation of the added monomer (0.36 mmol) to the total amount of recovered polymer, maximum level of lanthanum recovery of 9.8 mg/g of polymer is established. The UV spectra showed a common absorption pattern for neocuproine in N-methylpyrrolidone shows at 275 nm. Through UV analysis of spectra for P1 and P2, we can ensure that both, P1 and P2 have incorporated 5-ADMP, at least in part. Also, we made a calibration curve by measuring the absorption at 275 nm of neocuproine solutions of known concentration, and then with data analysis, the proportion of 5-ADMP in P2 was estimated. As result of this, we could estimate that the composition of P2 was of 0.7% molar of $[\text{La}(5\text{-ADMP})_3]\text{Cl}_3$ (7.1 % weight), which correspond to a retention capacity of 9.2 mg La/g of polymer, aligning closely with theoretical values.

Thermogravimetric analysis highlighted some disparities between P1 and P2 (Figure 4).

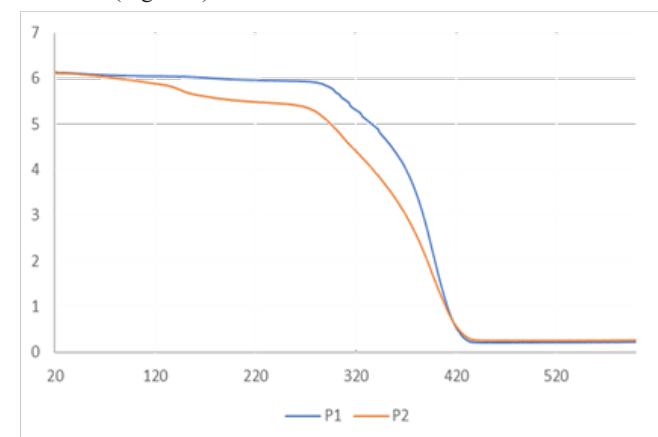


Figure 4 Thermogravimetric behavior for P₁ and P₂.

As shown in Figure 4, P2 has a higher loss of weight than compared to P1 before reaching 100 °C (3 vs 1.4%). P1 is characterized as a more stable material with insignificant weight loss until exceeding 285 °C (less than 5%). Beyond this temperature, a decomposition process initiates and concludes around 440 °C. P2 demonstrates good thermal stability up to roughly 140 °C, followed by a gradual weight reduction (5.4% of the initial mass). Subsequently, a decomposition phase initiates leading to a 4% mass loss, followed by stability with only

a 3% reduction until 267 °C. At 445 °C, a substantial decomposition occurs, leaving 4% of the original mass as residue.

To evaluate the synthesized materials against lanthanum solutions, samples of P1 and P2 were contacted with the same volume of lanthanum solutions of different concentrations, under isothermal conditions.

The concentration was determined by AA, before and after the interaction with the copolymers. The outcomes are shown in Table 1.

Table 1 Results of the isothermal interaction of P1 and P2 with lanthanum solutions, at constant time

Batch	P1 (mg)	C _i	C _f	R	Batch	P2 (mg)	C _i	C _f	R
1	102,3	124	50	3,62	1	93,70	161	63	5,23
2	98,1	194	76	6,01	2	100,4	197	72	6,23
3	101,7	218	73	7,13	3	86,10	249	91	9,15
4	98,3	264	100	8,34	4	90,70	333	120	11,74
5	100,5	714	270	22,09	5	80,40	888	320	35,32
6	100,4	1360	500	42,83	6	85,40	1388	490	52,58
7	103,2	2380	870	73,16	7	85,10	2234	780	85,43
8	101,0	7930	2600	263,9	8	92,40	6945	2400	245,9
9	101,4	15300	5300	493,1	9	86,70	15100	5300	565,2
10	97,6	21450	11000	535,4	10	92,50	21940	7900	758,9

C_i = initial concentration in ppm, C_f = final concentration in ppm, R = retention of lanthanum in mg/g of polymer

Considering all these results and knowing that the behavior in column of P2 could be less effective than in batch experiences, we estimated the volume of (milliliters) of solution needed required to reach the breakthrough point (0.1 C₀, about 40 mL of 739 ppm solution). Three 10 ml aliquots of the effluent were collected, followed by six of 5 ml each and finally one of 10 ml, to obtain multiple more points where the breaking point would occur. The obtained experimental breakthrough curve is shown in Figure 5.

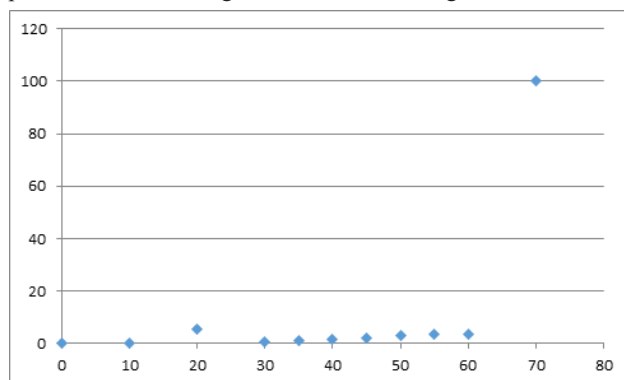


Figure 5 C/C₀ (%) vs mL for P2 column experience.

Discussion

The behavior of P1 is consistent with that typically seen in crosslinked polymers, as it exhibits high thermal stability and low solubility in common solvents, even in the reaction medium (DMF). Adding 5-ADMP gradually during the synthesis of P2 prevented an early crosslinking of the materials, leading to the consequent insolubilization of the product and reducing chain extinction., while additional AIBN improved mass recovery rates. P1 and P2 showed the capability of retain lanthanum, and its capacity depends on the initial concentration of the cation, as in common in adsorptive process. The data related to isothermal interaction of P1 and P2 with different concentrations of lanthanum are presented in Figure 6.

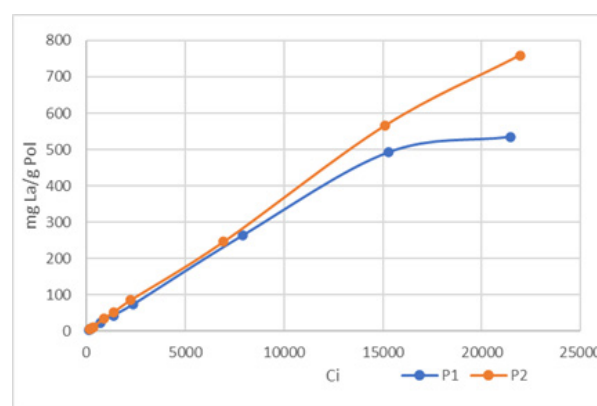


Figure 6 Retained lanthanum (in mg/g of P1 or P2) vs initial concentration (C_i in ppm).

As previously mentioned, the maximum lanthanum retention capacity by P2, only by coordination, would be 9.8 mg of lanthanum per gram of polymer. Both materials exhibited lanthanum retention values below the estimated threshold up to near C_i of 255 ppm, and surpassing the estimated limit as C_i increased, although remaining far from saturation.

These findings suggest the presence of multiple mechanism of lanthanum retention in these materials. Moreover, the behavioral disparity between the two polymers, notably at higher concentrations, is evident. P1 behaves like monolayer adsorption, reaching saturation at an initial concentration near 15,000 ppm, in contrast, P2 shows no signs of saturation at almost 22,000 ppm. In fact, P2 was tested with a C_i of 35,000 ppm without reaching saturation.

According with the data from batch experiments, we attempt to predict the breakthrough point using P2 in the column modality, adjusting the velocity of flow to align closely with the contact time for batch experiences. The previous calculations estimated this point around 40 mL of solution, but it actually occurs when 61 or 62 mL of the effluent was collected (610-620 secs from the start). From

these data, the experimental capacity calculated for P2 in a column experience at laboratory scale is about 52 mg La/g.

Both experiences, batch and column, shows that P2 has a higher retention capacity than the calculated or anticipate, supporting the theory of multiple retention mechanism of lanthanum.

As can be deduced from the NMR spectra in DCCl_3 and DMSO-d_6 , P2 seems to be a composite material: PMMA and a crosslinked copolymer including 5-ADMP. The PMMA within in P2 was synthesized in the presence of lanthanum:5-ADMP complex. One plausible hypothesis is that the PMMA growing around the complex (which would be incorporated later in other growing chains), creates an impression or cavity, with suitably oriented methacrylate groups. As consequence, the lanthanum could interact with these groups, enhancing the material's retention capacity.

The polymer regeneration is significant challenge. A small amount of P2 used in batch experiments was regenerated through treatment with HNO_3 , washed with distilled water, and then tested with three different C_i of lanthanum. Results showed no significant differences compare to the initial use. However, the observed behavior during regeneration hinders direct column regeneration. During the acid treatment the polymer structure collapses, turning it into a sticky mass (Figure 7) as a consequence of lanthanum removal. As the imprinting was made through a physical interaction, with the complex acting as trifunctional monomer, the removal of the central cation affects the polymer structure. When this solid is washed with distilled water until neutrality and dried, it recovers its original shape.



Figure 7 P2 after HNO_3 (c) treatment and after washing with distilled water and drying.

One possible explanation is that in a strong acidic environment not only the lanthanum is removed, but also pyridine rings could also become protonated, and may lead to repulsion between the ligands and losing the original architecture (Figure 8). When the material is washed with water, it could allow coordinate with the heterocycles, enabling them to revert to their original configuration. This empirical observation would match with the observation of confined water in the $^1\text{H-NMR}$.

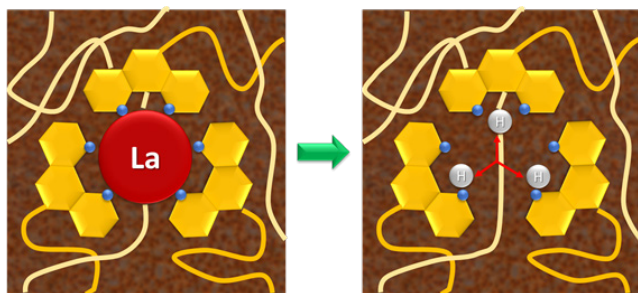


Figure 8 Lanthanum removal and neocuproine protonation.

As result of this evidence, we are now working in a new copolymer including some chemical crosslinkers in order to preserve the polymer architecture during the regeneration process.

Conclusion

In this work we synthesized two MMA:5-ADMP copolymers and tested against solutions of lanthanum. As the observed behavior of P2 was nearly linear for low concentrations we could estimate that the La^{3+} capture for 10 ppm solutions, must be around 0.4 mg/g. Even though the conditions were not exactly the same, the unprinted polymer captured only 0.1 mg/g of material, and this could mean a difference between both polymers. Moreover, P2 is able to retain an amount of cation superior than the maximum calculated based on complex content, depending on the initial concentration of solution.

The obtained results on the polymer re-utilization are more than promising, and we are now improving the structural integrity of the polymer during regeneration. The selectivity of P2 against other cations and its performance against acidic cationic solutions will soon be tested.

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None.

Conflicts of interest

Authors declare that there are not conflict of interest.

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