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Regis Garcia[a]; Olivier Vigneau[a]; Catherine Pinel[b]; Marc Lemaire[a]
[a] CPE Lyon, Villeurbanne Cedex, France [b] Institut de Recherches sur la Catalyse, Villeurbanne Cedex, France

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SOLID–LIQUID LANTHANIDE EXTRACTION WITH IONIC-IMPRINTED POLYMERS

Regis Garcia,[1] Olivier Vigneau,[1] Catherine Pinel,[2] and Marc Lemaire[1],*

[1]Laboratoire de Catalyse et Synthèse Organique,
UMR 5622, CPE Lyon, 43 bd du 11 Novembre 1918,
69622 Villeurbanne Cedex, France
[2]Institut de Recherches sur la Catalyse, UPR 5401,
2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France

ABSTRACT

Different polymers were synthesized using ionic-imprinting technique in order to separate lanthanides by liquid–solid extraction as a model for actinides/lanthanides separation. Those materials were based on vinylpyridine, acrylic acid, or a diethylene triamine pentaacetic acid derivative. We have studied the influence of the structure of crosslinking agents and the use of monomeric complexing agent. A significant increase in the selectivity of complexation is obtained when the material is prepared in the presence of the target ion.

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*Corresponding author. E-mail: marc.lemaire@univ-lyon1.fr

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INTRODUCTION

The concept of molecular-imprinted polymers, which was developed by Wulff and Mosbach[1,2] more than 20 years ago, has many potential applications.

Metal-ion-imprinted polymers have received less attention than molecule-imprinted analogs.[3] However, some articles already demonstrated the possibility of preparing polymeric materials that were capable of metal-ion recognition. This concept consisted of preparation of a matrix in the presence of the ionic template. After removal of the target cation under mild conditions, the prepared solid can react with a mixture of cations from which the imprinted cation should thus be preferentially extracted from the solution. As the interactions were different from those involved in molecular imprinting, the preparation of the solids was also different and based on three techniques.

One of the first ionic template effect in the synthesis of chelating polymers was reported by Nishide et al.[4,5] in the mid-1970s. They crosslinked linear chain polymers [poly(4-vinylpyridine)] with a bifunctional reagent (dibromoalkane) in the presence of metal ions. Such rigid matrices exhibited an imprinting effect in the case of the iron/copper ion separation. We prepared Na- and Cs-imprinted acetaldehyde–resorcinol resins in order to discriminate alkali metals.[6] These resins were tested in a competitive extraction of monovalent cations ($Li^{(I)}$, $Na^{(I)}$, $K^{(I)}$, $Rb^{(I)}$, and $Cs^{(I)}$). The $Cs^{(I)}$-imprinted resin achieved a much higher selectivity in favor of the cesium cation than the $Na^{(I)}$-imprinted resin. The solid state ^{13}C NMR of the material showed a fine structure similar to that of resorcinarene known to be selective of Cs.

Recently, the concept of surface-imprinting polymers was introduced by Takagi and coworkers.[7,8] The specific solids were prepared by emulsion polymerization involving a functional host monomer (phosphoric acid derivatives), an emulsion stabilizer, a crosslinking agent, and a metal cation template, which was selectively complexed by the metal-binding groups at the aqueous–organic interface to form recognition sites. The template cation was removed by acidic stripping to yield microspheres with a metal-ion-templated surface. Using this technique, Uezu et al.[9] synthesized lanthanide-imprinted polymers to separate a mixture of lanthanides (III) (La, Dy, Ce). A selective adsorption of $Dy^{(III)}$ was achieved using the $Dy^{(III)}$-imprinted polymer at pH 2.

An alternative approach was based on the copolymerization of isolated or nonisolated monomers/ion complexes with the crosslinking agent. This approach presented a great advantage of optimizing both the ratio ligand/ion and the geometry of the cavity. Kuchen and Schram[10] tested a copper$^{(II)}$-imprinted resin in a competitive extraction of bivalent cations ($Cu^{(II)}$, $Zn^{(II)}$, $Cd^{(II)}$, $Pb^{(II)}$). This resin was obtained by the polymerization of a dimeric complex Cu-methacrylic acid/vinylpyridine in the presence of ethylene glycol dimethacrylate (EGDMA) and the resulting material was able to fix up to 70% of the Cu cation while $Zn^{(II)}$,

$Cd^{(II)}$, and $Pb^{(II)}$ cations were not adsorbed. Fish and coworkers[11,12] prepared a $Zn^{(II)}$-templated copolymer of 4-vinylbenzyl-monosubstituted-1,4,7-triazacyclononane (TACN) and divinylbenzene (DVB). The overall order of metal-ion selectivity was $Mn^{(II)} < Ni^{(II)} < Co^{(II)} \ll Zn^{(II)}$ indicating the dominance of the imprinting effect of the template. Using this approach, lead and uranyl-based selective polymers were tested as selective sequestering agents and as components of electrochemical sensors.[13] As the functional groups were covalently bound to the matrix, the life-time of the electrodes appeared to be relatively long.

For some other applications, organometallic complexes were imprinted onto the polymer matrix but the metallic center was not removed. Sharma and Borovik described the preparation of solid supports containing Co(III)-complexes and their use as selective reversible O_2 binding.[14] We copolymerized optically pure Rh-complexes and the so-prepared materials exhibited improved enantioselectivity during the reduction of acetophenone.[15]

We are involved in programs, which involves the study of the reduction of the amount of long-term radiotoxicity residue of nuclear waste by the separation of short-term radiotoxicity ions from the long-term ones. With this purpose, different approaches were developed: selective precipitation, liquid–liquid extraction, nanofiltration–complexation, etc.[16,17] However, to overcome this challenge, it is necessary to develop methods that are as efficient as possible. Recently, we reported the preparation of ion-imprinted solids, which exhibited selectivity towards $Gd^{(III)}$ with respect to $La^{(III)}$.[18,19] These two elements were chosen as models: indeed, considering only their sizes, lanthanum and gadolinium were expected to mimic some elements among lanthanides and minor actinides, respectively. Such assumption is of course questionable but we would like to demonstrate that the principle of the imprinting effect could be used in order to separate ions of similar properties. Indeed, these two cations possess very similar chemical and physical properties such as ionic charge (Ln^{3+}), hydrated ionic radii ($R_{Gd} = 4.69\,Å$, $R_{La} = 4.61\,Å$), and a lack of defined geometry as coordination numbers vary from 6 to 12.[20] In this article, we report our results on the study of influence of the different parameters involved in the preparation of the complexing polymer on the selectivity for the separation Gd/La.

EXPERIMENTAL SECTION

Materials

All solvents and reagents used were at least of reagent grade and were purchased from Aldrich and Acros; 55% DVB (Aldrich) was used. Elemental analysis and electrospray mass spectra were performed at "Service Central d'Analyse" (CNRS, Solaize, France). Infrared spectra were obtained on a Perkin Elmer 1720X spectrometer and the NMR spectra were obtained on a Bruker AC200 (200 MHz) spectrometer.

General Procedure for Synthesis of Imprinted Vinylpyridine/Ethylene Glycol Dimethacrylate Copolymers and Removal of the Cation

4-Vinylpyridine (0.47 g, 4.4 mmol), EGDMA (3 mL, 16 mmol), and lanthane nitrate (0.23 g, 0.53 mmol, $N/\text{metal} = 8.2$), were dissolved in methanol (3 mL). The mixture was stirred in order to have a clear solution, introduced into a tube containing the AIBN (azoisobutyronitrile) (0.04 g, 5%) and ultrasonicated until complete dissolution. The tube was flushed under argon, capped, and heated at 50°C until polymerization (48 hr). The polymers were ground, sieved, and washed with 1 *N* HCl (5 × 100 mL), 0.1 *N* NaOH (5 × 100 mL), and H_2O until neutrality was achieved (pH 5–6). The resins were dried under vacuum for 24 hr. For a nitrogen/metal ratio of eight, the yields of the imprinted polymers were as following: La-imprinted polymer: 89% (3.19 g), Gd-imprinted polymer: 92% (3.30 g). Anal. calcd (%): C, 62.9; H, 7.1; N, 1.6. Found: C, 59.6; H, 6.7; N, 1.5. FTIR (KBr, cm^{-1}): 3500 (ν_{OH}), 2991, 2959 (ν_{C-H} ring), 1730 ($\nu_{C=O}$), 1629, 1598 ($\nu_{C=N}$), 1480, 1467 ($\nu_{C=C}$ ring), 1151 ($\nu_{O=C-O-C}$), 1072 ($\nu_{O=C-O-C}$), 983 ($\nu_{\text{vinyl ester}}$). For the blank polymer: yield: 91% (3.36 g). Anal. calcd (%): C, 62.9; H, 7.1; N, 1.6. Found: C, 61.4; H, 7.3; N, 1.6. FTIR (KBr, cm^{-1}): 2991, 2958 (ν_{C-H} ring), 1729 ($\nu_{C=O}$), 1628, 1598 ($\nu_{C=N}$), 1480, 1466 ($\nu_{C=C}$ ring), 1152 ($\nu_{O=C-O-C}$), 1071 ($\nu_{O=C-O-C}$), 970 ($\nu_{\text{vinyl ester}}$).

Gadolinium Triacrylate Complex

Gadolinium oxide (8.82 g, 24.3 mmol) was added to a solution of acrylic acid (10 mL, 0.14 mol, 6 eq) in water (100 mL). The mixture was heated at 50°C under stirring for 72 hr; then cooled, filtered, and water was removed by lyophilization. The white solid was washed with diethyl ether and dried under vacuum. Yield: 87% (15.7 g); ^1H NMR (D_2O) δ (ppm): 6.68 (s large, 3H), 6.16 (s large, 6H). Anal. calcd (%) for $C_9H_9O_6Gd{\cdot}H_2O$: C, 27.8; H, 2.9; Gd, 40.5. Found: C, 28.8; H, 2.7; Gd, 39.5. ES^- *m/z* (%): 442.1 $[M + {}^-OOCCH{=}CH_2]^-$; FTIR (KBr, cm^{-1}): 3389, (ν_{OH} and $\nu_{C=CH_2}$), 1642 ($\nu_{C=O}$), 1528 (ν_{COO-}), 1434, 1374 ($\nu_{CH=CH_2}$), 1266 (ν_{C-O}), 995, 976, 916.

General Procedure for the Synthesis of Gadolinium Triacrylate/Divinylbenzene Copolymers and Removal of the Cation

Gadolinium triacrylate complex (0.52 g, 1.4 mmol) and DVB (15.3 mL, 10.8 mmol, 7.7 eq) were dissolved in a methanol/water mixture (4 mL, v/v: 9/1). The solution was introduced into a tube containing AIBN (0.01 g, 5%) and ultrasonicated until complete dissolution. A magnetic stir bar was added and oxygen was removed under argon flow. The tube was capped and heated at 50°C until polymerization (24 or 48 hr). Then the formed polymer was ground and sieved. The resins were washed with 1 *N* aqueous HCl (5 × 100 mL), 0.1 *N* aqueous NaOH (5 × 100 mL), and H_2O until neutrality was achieved (pH 5–6). The resins were dried under vacuum for 24 hr. Yield: 98% (1.8 g). Anal. calcd (%): C, 80.4; H, 6.7; Na, 5.4. Found: C, 78.6; H, 7.6; Na, 2.3; FTIR (KBr, cm^{-1}): 2962, 2927 ($\nu_{C-H\ ring}$), 1702 ($\nu_{C=O}$), 1600, 1577, 1448 ($\nu_{C=C\ aromatic}$), 992, 896, 796, 708. The blank polymer was synthesized as described previously starting from acrylic acid (0.1 g, 1.4 mmol) and DVB (15.3 mL, 10.8 mmol, 7.7 eq). Yield: 93% (2.94 g). Anal. calcd (%): C, 90.1; H, 7.6; Na, 1.0. Found: C, 88.9; H, 8.0; Na, 0.5; FTIR (KBr, cm^{-1}): 3083 ($\nu_{CH=CH_2}$), 2960, 2924, 2852 ($\nu_{C-H\ ring}$), 1075 ($\nu_{C=O}$), 1602, 1493, 1452 ($\nu_{C=C\ aromatic}$), 797, 760, 699.

(*N*,*N*′)-Ethylenebis(Acrylamide)

Ethylenediamine (2 mL, 30 mmol) and 4-polyvinylpyridine (13.6 g, 4 eq) were added to dichloromethane (40 mL) and the reaction mixture was cooled to 0°C. The acryloyl chloride (5.35 mL, 2.2 eq) was added dropwise. After total addition, the mixture was stirred for 24 hr at room temperature. The solution was filtered and the solid was washed with dichloromethane (3 × 25 mL) and then with methanol (25 mL). The combined organic phases were dried on $MgSO_4$, filtered, and concentrated under vacuum. Five percent of hydroquinone was added in order to avoid the polymerization during the evaporation of the solvent. The solid was washed with ether and dried under vacuum. Yield: 2.71 g (54%). ^1H NMR (CD_3OD) δ (ppm): 6.22 (d, 4H, $J = 7.1$ Hz), 5.64 (t, 2H, $J = 7.04$ Hz), 3.4 (s, 4H). ^{13}C NMR (CD_3OD) δ (ppm): 170.1, 133.6, 128.4, 41.6. ES^+: *m/z* (%): 191 $[M + Na]^+$; FTIR (KBr, cm^{-1}): 3248 (ν_{NH}), 1656, 1555 ($\nu_{C=O}$), 1620 ($\nu_{C=C}$), 1400 ($\nu_{CH=CH_2}$), 1303 (ν_{C-N}), 990, 936 (ν_{C-H}). Anal. calcd (%) for $C_8H_{12}N_2O_2$: C, 57.1; H, 7.2; N, 16.7. Found: C, 56.8; H, 7.3; N, 17.9.

(*N*,*N*′)-Propylenebis(Acrylamide)

Starting from propylenediamine (741 mg, 10 mmol), 900 mg of (*N*,*N*′)-propylenebisacrylamide was obtained (yield: 50%). ^1H NMR (CD_3OD) δ (ppm):

6.23 (d, 4H, $J = 7.2$ Hz), 5.65 (t, 2H, $J = 7.14$ Hz), 3.29 (t, 4H, $J = 6.9$ Hz), 1.75 (qt, 2H, 6.9 Hz); ^{13}C NMR (CD_3OD) δ (ppm): 168.5, 132.3, 126.9, 38.2, 30.4. ES^+: *m/z* (%): 205.1 $[M + Na]^+$; FTIR (KBr, cm^{-1}): 3268 (ν_{NH}), 1649, 1562 ($\nu_{C=O}$), 1602 ($\nu_{C=C}$), 1401 ($\nu_{CH=CH_2}$), 1246 (ν_{C-N}), 990, 966 (ν_{C-H}). Anal. calcd (%) for $C_9H_{14}N_2O_2$: C, 59.3; H, 7.7; N, 15.4. Found: C, 59.3; H, 7.8; N, 15.5.

General Procedure for the Synthesis of Gadolinium Triacrylate Complex/(*N*,*N*′)-Alkylenebis(Acrylamide) Copolymers and Removal of the Cation

Gadolinium triacrylate complex (220 mg, 0.6 mmol) and (*N*,*N*′)-methylenebis(acrylamide) (926 mg, 6 mmol) were dissolved in a mixture of methanol/water (4 mL, v/v: 9/1). The clear solution was introduced into a tube containing the AIBN (4 mg, 4%) and ultrasonicated until complete dissolution. A magnetic stir bar was added and oxygen was removed under argon flow. The tube was capped and heated at 50°C until polymerization (48 hr). The formed polymer was ground and sieved. The resins were washed with 1 *N* HCl (5 × 100 mL), 0.1 *N* NaOH (5 × 100 mL), and H_2O until neutrality was achieved (pH 5–6). The resins were dried under vacuum for 24 hr. Yield 93% (1.02 g). Anal. calcd (%): C, 50.9; H, 5.9; N, 16.0; Na, 3.7. Found: C, 50.3; H, 6.7; N, 15.9; Na, 2.5; FTIR (KBr, cm^{-1}): 3500 (ν_{H_2O}, N—H), 3085, 2944 ($\nu_{OH\ acid}$), 1700 ($\nu_{C=O\ acid}$), 1654, 1533 ($\nu_{C=O\ amide}$), 1451, 1394 ($\nu_{CH=CH_2}$), 1349 (ν_{C-N}), 1283, 1217 (ν_{C-O}), 1115, 963, 724. The corresponding blank polymer was synthesized starting from acrylic acid (124 μL, 1.8 mmol), and (*N*,*N*′)-methylenebis(acrylamide) (925.4 mg, 6 mmol). Yield: 97% (1.02 g). Anal. calcd (%): C, 52.0; H, 6.0; N, 15.4; Na, 3.8. Found: C, 51.0; H, 6.7; N, 14.9; Na, 2.3; FTIR (KBr, cm^{-1}): 3500 (ν_{H_2O}, N—H), 3085, 2944 ($\nu_{OH\ acid}$), 1700 ($\nu_{C=O\ acid}$), 1654, 1533 ($\nu_{C=O\ amide}$), 1451, 1394 ($\nu_{CH=CH_2}$), 1349 (ν_{C-N}), 1283, 1217 (ν_{C-O}), 1115, 963, 724.

Diethylenetriamine-*N*,*N*′-Diacetamidostyrene Triacetic Acid

Diethylenetriaminepentaacetic dianhydride (8 g, 22.4 mmol) was added to anhydrous dimethyl formamide (DMF) (160 mL), and heated at 80°C until dissolution. A solution of 4-vinylaniline (15.5 g, 0.13 mol, 5.8 eq) in anhydrous DMF (120 mL) was added dropwise, and the mixture was heated at 80°C for 48 hr. The solution was cooled, filtered, and concentrated. The residue was dissolved in a small amount of DMF, diethyl ether was added, and the precipitate was filtered and dissolved in hot methanol. The filtrate was concentrated under vacuum and the residue was recrystallized ($CHCl_3$/MeOH), to give a white product after 12 hr. Yield: 5.9 g (44%). ^{1}H NMR (DMSO *d*6) (dimethylsulfoxime) δ (ppm): 10.14 (s, 3H), 8.32 (s, 2H), 7.65 (d, 4H, $J = 8.55$ Hz), 7.37 (d, 4H, $J = 8.57$ Hz), 5.16 (d, 2H, $J = 11.2$ Hz), 3.55 (s, 8H), 3.05 (s large, 4H), 2.96 (s large, 4H). ^{13}C NMR (DMSO *d*6) δ (ppm): 172.7, 172.6, 137.9, 135.9, 132.3, 126.3, 119.4, 112.8, 57.8, 54.9, 54.7, 52.5, 49.8. Anal. calcd (%) for $C_{30}H_{37}N_5O_8$: C, 60.5; H, 6.3; N, 11.8. Found: C, 59.9; H, 5.9; N, 11.6. ES$^-$ *m*/*z* (%): 594.2 $[M - H]^-$; FTIR (KBr, cm^{-1}): 3450 (ν_{NH}), 3000 (ν_{OH}), 2958 ($\nu_{CH\ ring}$), 1710 ($\nu_{C=O}$), 1650 ($\nu_{C=C}$), 1530 ($\nu_{C=O\ amide}$), 1480 ($\nu_{C=C\ aromatic}$), 1200 ($\nu_{C=O}$), 1000 (ν_{C-N}), 990 ($\delta_{C-H\ vinyl}$), 870, 754.

Diethylenetriamine-(*N*,*N*′)-Diacetamidostyrene Triacetic Acid/Divinylbenzene Copolymers and Removal of the Cation

As described previously,[19] the synthesis of the blank polymer was performed in methanol (5 mL), with diethylene triamine-(*N*,*N*′)-diacetamidostyrene triacetic acid (0.50 g, 0.84 mmol), DVB (1.95 mL, 13.4 mmol), sodium nitrate (215 mg, 2.52 mmol), and AIBN (4 mg, 5%) After 48 hr, the polymer was washed once with MeOH (100 mL), 1 *N* HCl (5 × 100 mL), and H_2O until neutrality was achieved (pH 5–6). The resins were dried under vacuum for 24 hr. Yield: 2.1 g (95%). Anal. found (%): C, 82.5; H, 7.7; N, 2.2; Na, <100 ppm; FTIR cm^{-1} (KBr): 3450 (ν_{N-H}), 3000 (ν_{OH}), 2958 ($\nu_{CH\ ring}$), 1700 ($\nu_{C=O}$), 1660 ($\nu_{C=C}$), 1610 ($\nu_{C=N}$), 1550 ($\nu_{C=O\ amide}$), 1474 ($\nu_{C=C}$), 995, 931, 880, 790. The Gd-imprinted polymer was synthesized from diethylenetriamine-(*N*,*N*′)-diacetamidostyrene triacetic acid (0.5 g, 0.84 mmol), $Gd(NO_3)_3{\cdot}6H_2O$ (0.39 g, 0.84 mmol), DVB (1.9 mL, 13.4 mmol), AIBN (4 mg, 5%) in methanol (4 mL). Yield: 2.18 g (98%). Anal. found (%): C, 85.0; H, 7.8; N, 1.6; Gd, 1.6; FTIR cm^{-1} (KBr): 3440 (ν_{N-H}), 3005 (ν_{OH}), 2960 ($\nu_{CH\ ring}$), 1691 ($\nu_{C=O}$), 1657 ($\nu_{C=C}$), 1605 ($\nu_{C=N}$), 1550 ($\nu_{C=O\ amide}$), 1471 ($\nu_{C=C}$), 992, 951, 894, 790 cm^{-1}.

General Procedure for Competitive Extraction

After washing and drying the materials it was determined by chemical analysis that except for the diethylene triamine pentaacetic acid (DTPA)-based polymer, less than 6% of the metal was still present in the matrix. In order to evaluate the performance of the resin, the determination of the initial and final concentrations of both cations (Gd^{3+} and La^{3+}) was realized by the inductively coupled plasma–atomic emission spectroscopy (ICP–AES) analysis (Table 1).

After the removal of the template, the resin was evaluated by a competitive extraction test. Aqueous solution of lanthanide salts ($C_{La} \approx C_{Gd} \approx 1 \times 10^{-4}$ mol L^{-1}) was prepared from $Gd(NO_3)_3{\cdot}H_2O$ (99.9% purity) and $La(NO_3)_3{\cdot}H_2O$

Table 1. Instrumental Conditions for the Determination of Ln(III) by ICP–AES

Inductively Coupled Plasma Source	27.12 MHz
Sample injection	
Nebulizer	Cross-flow
Sample uptake	Peristaltic pump
Spectrometer	
Focal length (m)	0.5
Grating, grooves (mm^{-1})	2400
Slit width input/output (μm)	10/25
Exposure time (sec)	3
Wavelength (nm)	342.247 (Gd), 379.478 (La)
Experimental conditions	
Sample flow rate ($mL\,min^{-1}$)	3
Rf power (kW)	2.5

(99.9% purity). Such solutions (initial pH 6) were stable over a long period and no lanthanide precipitation was analyzed. In a flask, the appropriate amount of polymer (typically 120–240 mg) was added to 10 mL of the lanthanides solution. The mass of the polymer and the volume of the solution were adjusted to get $10 < \%E < 85$ for each cation in order to avoid a large discrepancy on the selectivity. The suspension was shaken vigorously for 24 hr at 20°C. The solution was then filtered through a Millipore filter (0.45 μm) and the filtrate was analyzed by ICP–AES.

In the case of the DTPA-based polymer, the behavior of the blank and imprinted polymers greatly differed. An amount of 20 mg of blank polymer was shaken for 24 hr with 10 mL of lanthanides solution. Analysis of the solution showed that 18% of the lanthane and 60% of the gadolinium have been extracted. At the same time, 390 mg of the imprinted polymer was shaken for 24 hr with 10 mL of lanthanides solution from which less than 1.5% of lanthane and 22% of gadolinium were extracted.

RESULTS AND DISCUSSION

Many parameters have to be considered to testify the quality of resins. Obviously, they must be selective for a metal in the presence of other ones. In this article, all the described tests were performed under competitive conditions, with two cations present simultaneously in the solution. The determination of initial and final concentrations [C_A^i ($mg\,L^{-1}$) and C_A^f ($mg\,L^{-1}$), respectively] of both cations was performed by ICP–AES analysis. Preliminary studies showed that after 8 hr of shaking of the polymer in solution, the concentration of the two cations was constant but to ensure that the equilibrium was attained, the suspension was shaken for 24 hr. Considering these data, different parameters were calculated: the extraction capability defined as $E_{\mathrm{A}}\,(\%) = (C^{\mathrm{i}}_{\mathrm{A}} - C^{\mathrm{f}}_{\mathrm{A}}) \times 100/C^{\mathrm{i}}_{\mathrm{A}}$; the distribution coefficient, $D_{\mathrm{A}}\,(\mathrm{mL\,g^{-1}}) = (C^{\mathrm{i}}_{\mathrm{A}} - C^{\mathrm{f}}_{\mathrm{A}})/C^{\mathrm{f}}_{\mathrm{A}} \times V/m$, where V is the volume of the extracted solution and m, the mass of resin; and finally, the extraction selectivity of the resin, $S_{\mathrm{A/B}} = D_{\mathrm{A}}/D_{\mathrm{B}}$.

In a preliminary study, different copolymers were prepared using various monomer ligands (4-vinylpyridine, 2-hydroxyethyl methacrylate, acrylic acid, and acryoyl propanediamide) and crosslinking agents (DVB, EGDMA, acryoyl propanediamide). All these reagents differed mainly in their hydrophilicity and none of them was known to have intrinsic selectivity towards lanthanides. Whatever the material tested, the values of selectivity ($S_{\mathrm{Gd/La}}$) were similar (2.4 ± 0.3). This value was obtained after testing more than 10 different materials with several experiments for each of them. We assumed that this average extraction selectivity achieved with blank resins, depends only on the properties of the lanthanide salts itself and mainly on their desolvatation energy.[21] Under this assumption, we shall consider that an imprinted effect will be effective only if $S_{\mathrm{Gd/La}} < 2.1$ or $S_{\mathrm{Gd/La}} > 2.7$. To determine the selectivities, the uncertainty of each experimental measurement must be taken into account. Particularly, the accuracy of the selectivity was largely affected by the final concentration of both cations. So, the uncertainty ($\sigma S_{\mathrm{Gd/La}}$) was calculated for each extraction value according to the following formula established from the literature:[22]

$$\sigma S_{\mathrm{Gd/La}} = \left\lfloor \frac{(C^{\mathrm{i}}_{\mathrm{Gd}} - C^{\mathrm{f}}_{\mathrm{Gd}})C^{\mathrm{f}}_{\mathrm{La}}}{(C^{\mathrm{i}}_{\mathrm{La}} - C^{\mathrm{f}}_{\mathrm{La}})C^{\mathrm{f}}_{\mathrm{Gd}}} \right\rfloor \sqrt{\frac{0.16}{(C^{\mathrm{i}}_{\mathrm{Gd}} - C^{\mathrm{f}}_{\mathrm{Gd}})^2} + \frac{0.16}{(C^{\mathrm{i}}_{\mathrm{La}} - C^{\mathrm{f}}_{\mathrm{La}})^2} + \frac{0.04}{(C^{\mathrm{f}}_{\mathrm{Gd}})^2} + \frac{0.04}{(C^{\mathrm{f}}_{\mathrm{La}})^2}}$$

Special care was taken to remove the template efficiently. After synthesis, the polymers were ground and washed five times with 1 *N* HCl to eliminate the cation. It was confirmed by elemental analysis that the chemical structure of the blank and the imprinted polymers were identical.

In a previous work, it was shown that commercial polyvinylpyridine–DVB resins extract lanthanides despite having low binding constants.[23] We synthesized materials based on these monomers using the concept of metal-ion-imprinted polymers with different vinylpyridine/metal ratio (8 and 20), but no ionic template effect was observed.

The efficiency of those materials was low, and this is probably due to the hydrophobic nature of the DVB. Ethylene glycol dimethacrylate was widely used as a crosslinking agent in the preparation of molecular-imprinted polymers.[24] In order to obtain a more hydrophilic polymer, we used EGDMA instead of DVB (Fig. 1).

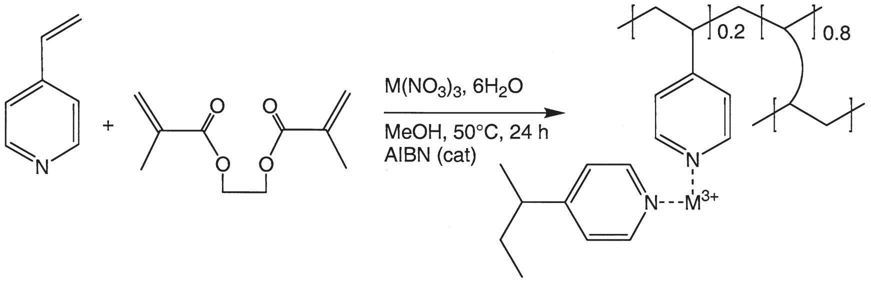

Figure 1. Synthesis of Ln-imprinted polymers.

We synthesized polymers, with different metal-ion templates (Gd^{3+} or La^{3+}). A blank polymer was synthesized in a similar way. Very good yields were achieved (>90%). Polymers were tested in a competitive Gd^{3+}/La^{3+} extraction with 240 mg of copolymer and using 10 mL of solution ($C_{Ln} \sim 1 \times 10^{-4}$ mol L^{-1} each). The initial pH of the solution was 6.

As shown in Table 2, the influence of the stripping and the washing steps on the polymers prepared from EGDMA is of great importance. When the blank polymer is washed only with water, the resin does not extract any cations. But when the resin is submitted to acidic washing steps followed by basic treatments, some extraction is observed and the level of extraction increases with the number of acidic treatments. We suppose that acidic washing steps partly hydrolyze ester groups into carboxylic acids, which should complex the lanthanides. When identical treatments are performed on the blank polymers and on the imprinted ones (five acidic washings), similar results are achieved, whatever in terms of extraction or selectivity. In that case, no imprinting effect can be detected, as the number of nonselective sites (carboxylic groups) is much higher than the number

Table 2. Metal Ion Adsorption in Gd^{3+}/La^{3+} Separation with Vinylpyridine–Ethylene Glycol Dimethacrylate Copolymers. Influence of Acidic Washings on Selectivity

		Extraction (%)		
Imprinted Ion	Stripping and Washing Steps	La^{3+}	Gd^{3+}	$S_{Gd/La} \pm \sigma S_{Gd/La}$
—	Unwashed	0	0	—
—	1 × HCl (1 *N*)	2	7	Out of margin of error
—	5 × HCl (1 *N*)	21	36	2.2 ± 0.3
La^{3+}	5 × HCl (1 *N*)	36	56	2.3 ± 0.2
Gd^{3+}	5 × HCl (1 *N*)	29	48	2.3 ± 0.3

of the selective ones (vinylpyridine). It must be noted that in scientific literature, most of the templates were removed with organic washings, which cannot produce cleavage of the ester bonds.

With this problem in mind, we chose to use a less-hydrolyzable crosslinking agent focusing on different functionalized monomers. For a better control of the definition of the materials, we performed the polymerization of the isolated lanthanide triacrylate complexes. First, we studied the effect of the crosslinking ratio on Gd^{3+}/La^{3+} separation selectivity. Materials with composition acrylate/divinylbenzene/styrene ($x/y/z$) varying from 14/24/62 to 15/85/0 were synthesized (Fig. 2). The cation/diluent ratio was kept constant but we modified the proportion of the crosslinking agent.

The blank polymers do not fix any cation independent of the DVB/(DVB + styrene) ratio and the number of washing steps (Table 3). Ionic imprinting has an influence on the efficiency of the material, indeed, the Gd^{3+}-imprinted polymers fix the two cations. As shown in Table 3, the level of the extraction vary slightly according to the amount of DVB involved, with a maximum achieved when approximately 50% of the crosslinking agent was used. Selectivity increases with the percentage of DVB, and it reaches 3.5 when no styrene is used (Fig. 3). This could be explained by the increased rigidity of the matrix and consequently a better definition of imprinted cavities after the removal of the template ion.

To achieve satisfactory efficiency and selectivity, we continued the study using only DVB as the diluent. We evaluated the influence of DVB/Gd-dimethacrylate ratio. It was observed that when the template ion was too diluted in the matrix (<0.025 Gd/DVB), the resin had a similar behavior to the blank polymer and did not extract any cations. When the cations' concentration was higher in the matrix, no influence on the selectivity was observed (Table 4).

The influence of the nature of the crosslinking agent was studied using the isolated lanthanide triacrylate salts. To avoid hydrolysis during the washing steps

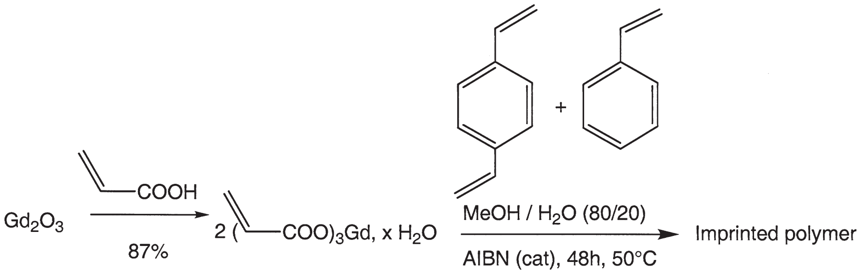

Figure 2. Synthesis of acrylate/divinylbenzene/styrene copolymer.

Table 3. Metal Ion Adsorption in Gd^{3+}/La^{3+} Separation with Vinylpyridine–Divinylbenzene–Styrene Copolymers. Influence of the Crosslinking Ratio

Polymer	% Divinylbenzene	Extraction (%)		$S_{Gd/La} \pm \sigma S_{Gd/La}$	Loading of the Polymer[a]
		La^{3+}	Gd^{3+}		
Blank	85	0	0	—	—
Blank	24	0	0	—	—
Gd-imprinted	85	29	58	3.5 ± 0.3	7
Gd-imprinted	65	53	77	3.0 ± 0.2	10
Gd-imprinted	45	57	79	2.7 ± 0.3	10
Gd-imprinted	24	25	46	2.5 ± 0.3	5.5

[a] (mol fixed Ln/COOH) × 100.

of the materials, (*N*,*N*′)-alkylenebis(acrylamides) were used as a hydrophilic crosslinking agents. These types of crosslinkers exhibited both hydrophilic character[25] and stability during acidic washing steps. The (*N*,*N*′)-methylenebis(acrylamide) was commercially available. The (*N*,*N*′)-ethylenebis(acrylamide) and the (*N*,*N*′)-propylenebis-(acrylamide) were synthesized starting from the corresponding diamines, acryloyl chloride, in the presence of polyvinylpyridine.[26]

The copolymerization of the lanthanide carboxylate complexes was completed in $MeOH/H_2O$, at 50°C for 48 hr, in the presence of (*N*,*N*′)-alkylenebisacrylamide (Fig. 4, yield $> 90\%$). Then, polymers were tested in a competitive Gd^{3+}/La^{3+} extraction with 10 mL of solution ($C_{Ln} \approx 1 \times 10^{-4}$ $mol\,L^{-1}$).

No evolution of the ion-exchange capacity was observed after several washing sequences of the blank material. In Fig. 5, the evolution of the extraction efficiency of La and Gd with respect to the nature of the crosslinking agent as well as the corresponding selectivity for Gd/La was depicted.

It is clear that as the length of the chain between the two amide groups increases, the hydrophobic character of the material increases, and the extraction efficiency decreases, whatever the type of solids (blank or imprinted) and the cations involved. At the same time, the selectivity for the Gd/La separation is almost constant for the reference solids, whereas it increases slightly for the Gd-imprinted ones. While no significant ionic-imprinted effects could be claimed with (*N*,*N*′)-methylenebis(acrylamide) and (*N*,*N*′)-ethylenebis(acrylamide)-based copolymers, the selectivity reaches 3.6 with the (*N*,*N*′)-propylene bis(acrylamide)-based imprinted resins. When the length of the chain between the two amide groups increases, so does the flexibility of the polymer as well as the selectivity for the separation of Gd/La. That is to say, the rigidity of the solid is

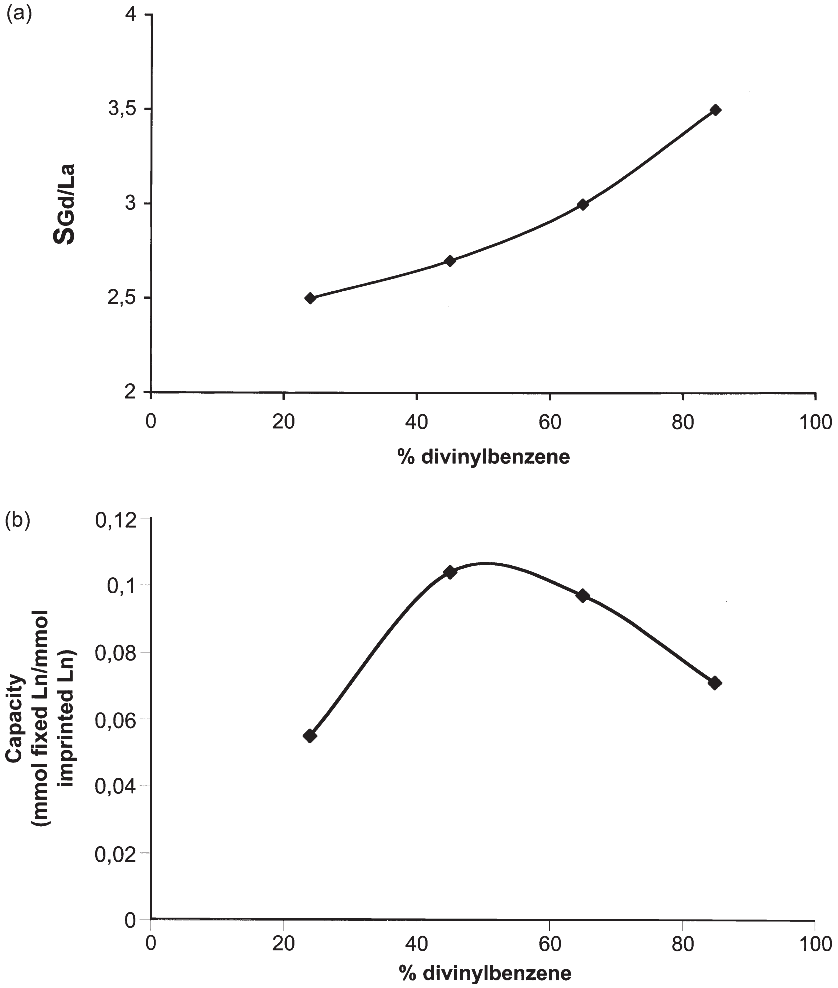

Figure 3. Influence of the degree of crosslinking on the selectivity for Gd/La.

not the only factor, which modifies the selectivity; the structure of the complexing monomer also plays a prominent role, and in this particular case, the propylene bridge derivative fits better with gadolinium than the methylene or ethylene bridge.

This study allowed a slight increase in the selectivity of materials for the separation of Gd/La. However, the highest value of the selectivity did not exceed four. So, we chose to use the derivatives of a complexing agent known to have a

Table 4. Influence of the Gd/Divinylbenzene Ratio on the Selectivity of the Templated Resins

		Extraction		
Gd/Divinylbenzene	m_{polymer} (mg)	La^{3+}	Gd^{3+}	$S_{\text{Gd/La}} \pm \sigma S_{\text{Gd/La}}$
0.13	240	46	72	3.2 ± 0.3
0.06	502	81	97	3.5 ± 3.3
0.05	624	55	82	3.6 ± 0.4
0.025	1122	<5	<5	—

high efficiency for lanthanides complexation. In this type of material, the free ligand already had a high constant for association and exhibited a certain selectivity between the studied cations. The imprinting effect should allow an improvement of the selectivity as previously shown, but in this case, this selectivity must be carefully compared to that observed with the blank material (i.e., the observed selectivity resulted from both specific selectivity of the ligand and the imprinting effect).

Our choice was based on a polymerizable derivative of DTPA because this pentacarboxylic acid was known to form complexes with lanthanide.[27] Very high formation constants of the Ln/complexes were achieved in aqueous media. Furthermore, the difference between the La and Gd formation constants was very large (19.48 and 22.46 in log, respectively). The imprinting effect was established with this ligand as the imprinted polymer exhibited a selectivity towards gadolinium that was three times higher than that of the blank.[18]

We synthesized the DTPA derivative from the commercially available diethylenetriamine pentaacetic dianhydride and *p*-vinylaniline with 70% yield. In our hands, no crystal of the corresponding lanthanide complex could be isolated and analyzed by x-ray. The polymerization was carried out for 72 hr in methanol in the presence of AIBN with a ratio of the ligand to the metal equal to 1 (Fig. 6). The blank resin was prepared in the presence of sodium nitrate in order to solubilize the complexing monomer but without inducing preorganization, and the imprinted polymer was synthesized using Gd^{3+} as the template.

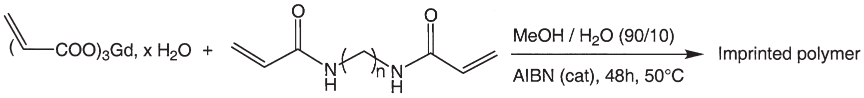

Figure 4. Copolymerization of isolated complexes with (*N*,*N*′)-alkylenebis(acrylamide).

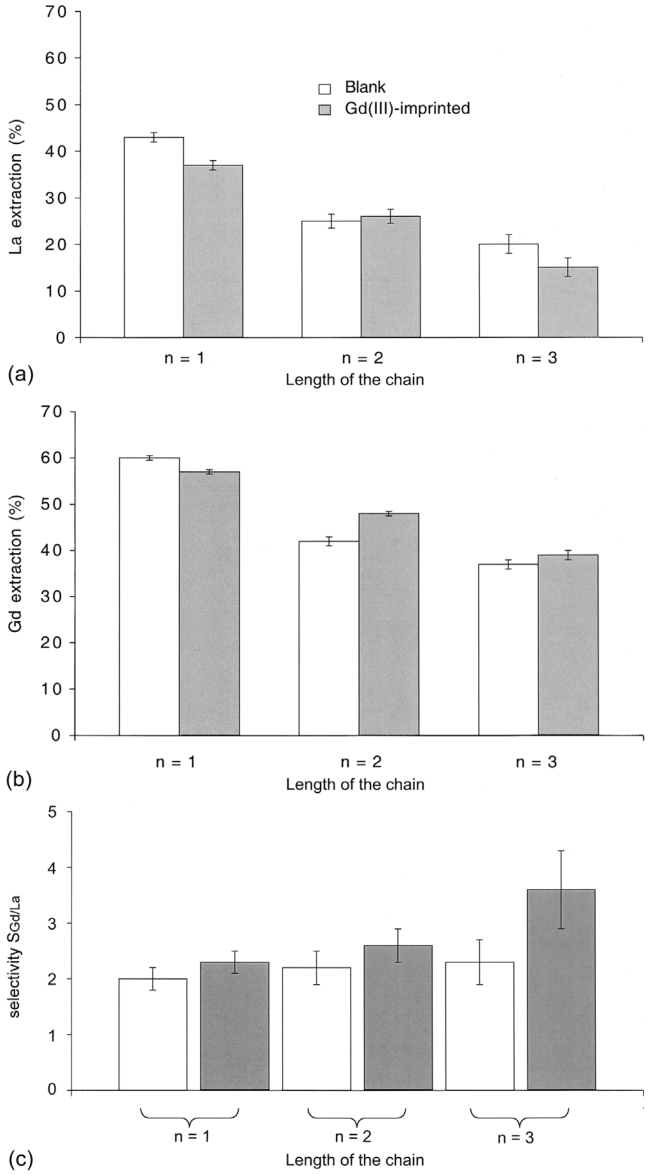

Figure 5. Extraction of (a) La and (b) Gd and (c) selectivity as a function of the length of the chain of Gd(III)-imprinted and blank polymers based on (*N*,*N*′)-alkylenebis(acrylamide).

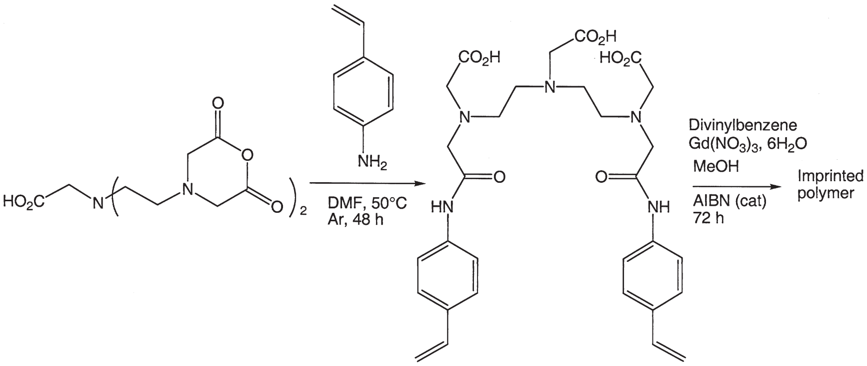

Figure 6. Synthesis of Gd(III)-imprinted polymer DTPA derivative/divinyl benzene.

The copolymers diethylenetriamine-*N*,*N''*-diacetamidostyrene triacetic acid/DVB, were washed with methanol, 1 *N* HCl, and finally with H_2O until neutrality was achieved. We verified by chemical analysis that the washed imprinted resin still contained 1.6% of gadolinium. This was attributed to inaccessible complexing sites. In comparison, no sodium was present in the blank polymer after washing.

A competitive extraction of lanthanides was performed on blank polymers and imprinted resins and the average values for each material are shown in Table 5.

Surprisingly, the blank polymer exhibits a very high capacity with a moderate selectivity, which is due to the intrinsic affinity of DTPA towards the gadolinium. Imprinting resin with Gd produces dramatic changes both on capacity and on selectivity. The former one strongly decreases and this can be partly attributed to the fact that the gadolinium used as a template is not fully eliminated and to the fact that the free complexing sites are not easily accessible. On the other hand, as expected, the selectivity is greatly enhanced. We do not observe any change in lanthanum concentration before and after extraction in

Table 5. Extraction with Polymerized DTPA Derivatives

		Extraction (%)			
Polymer	m_{polymer} (mg)	La^{3+}	Gd^{3+}	$S_{Gd/La} \pm \sigma S_{Gd/La}$	Loading of the Polymer[a]
Blank 1	20	18	60	7 ± 0.4	11
Gd-Imprinted 1	390	<1.5	22	>20	<0.1

[a] (mol fixed Ln/mol complexing monomer) × 100.

those conditions, that is to say, less than 1.5% of La is complexed due to the accuracy of the ICP–AES apparatus. The corresponding calculated selectivity is only 20 but we suppose that the real selectivity is much higher and further experiments are in progress to confirm this hypothesis.

CONCLUSION

In conclusion, we have shown that an imprinting effect enhances selectivity during the separation of two lanthanide salts. However, special care needs to be taken to minimize experimental artifacts in the results: the determination of the margin of error of the extraction values, the use of the same washing treatments for the blank and the imprinted resins, the influence of the solvent on the ionic radii, and the influence of the counter-ion used during the polymerization and the extraction, etc. Considering all of these parameters, we prepared imprinted polymers from vinylpyridine or acrylic monomers exhibiting a slightly higher ionic recognition than the blank resins. A stronger imprinting effect was achieved using polymers synthesized from DTPA derivatives, known to have strong association constants with lanthanides. This shows that an imprinting effect may be used in order to further increase selectivities of intrinsic ion-selective material.

The study of the influence of the nature of the ionic template and of the selectivity towards other cations is under way and will be published elsewhere. Attempts to isolate lanthanide complexes before polymerization are also in progress.

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