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Sorption properties of carbamoylmethylphosphonated-based polymer combining both sorption and thermosensitive properties: New valuable hydrosoluble materials for Rare Earth Elements sorption

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Abstract

The sorption properties of gadolinium (Gd) by an original carbamoylmethylphosphonate (cmp)-based acrylamide polymer combining both chelating and thermosensitive properties namely poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) (P(CPAAm6C)) are presented for the first time. For pH = 1 and at 20 °C, the maximum sorption capacity reached 0.6 $mmol.g^{-1}$ for the highest Gd concentrations. Different parameters influencing the sorption of Gd were studied as pH, ionic strenght and temperature. The temperature was shown to affect both the sorption and the stability of the complex cmp-Gd formed by coordination mode with C=O and P=O functions. The selectivity of the cmp group for Gd was demonstrated in Gd/Ni mixture and shows its thermosensitive polymer is very promising for the development of selective sorption processes.

Introduction

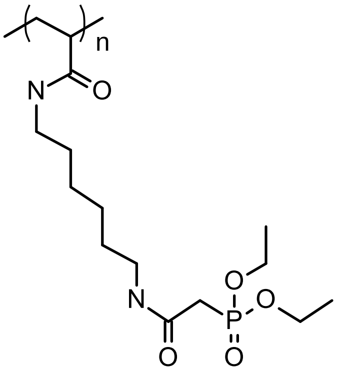
Rare earth elements (REE) are a group of elements including lanthanides (Ln), scandium (Sc) and yttrium (Y).[1] They are used in various applications in high technology as magnets, catalytic converters, battery, optical lenses, phosphors or electronic compounds.[2], [3] Most of REE are not rare as suggested by their name. Except promethium which isotopes are radioactive with short life decay period, all of REE are found all over the world and, are more abundant in the Earth’s crust than silver, gold, nickel, lead or platinum. Since their supply risk was pointed out in 2010 and because of their economic importance, these metals are considered as critical.[3], [4]

Despite REE are produced in many countries (Australia, Russia, USA), about 86% of them are still produced in China.[5]–[7] This situation of quasi-monopoly leads the European industry to develop alternative separation processes to obtain REE, and more particularly lanthanide elements, by recycling or exploitation of new mineral deposits. REEs are present in numerous minerals such as monazite (phosphates, $(Ce,La,Nd,Sm,Gd,Y,Th)PO_4$),[8], [9] samarskite (oxides, $(Y,Fe^{3+},Fe^{2+},U,Th,Ca)_2(Nb,Ta)_2O_8$),[2], [10] bastnaesite (carbonate-fluorides, $REECO_3F$)[11] and allanite (oxide, $Ca,REE,Fe^{2+},Al_2(SiO_7)$).[12] These minerals usually contain lanthanides (Ln), transition metals and small amounts of natural radioelements such as uranium (U) and thorium (Th) and can be exploited.

Another means of supply can be the exploitation of the "urban mine" *ie*. the Waste Electronic and Electrical Equipment (WEEE) recycling which contains lanthanides and transition metals.[7] For example Lamp phosphors, Nickel-metal-hybrid batteries (NiMH) and catalysts can contain 20, 10 and 3.5 % of REE respectively combined with transition metals. But nowadays less than 1 % of REE used are recycled from WEEE.[13]

In the case of both supply routes, after an initial grinding step, minerals or WEEE are leached with concentrated solutions of hydrochloric, sulfuric or nitric acids to increase the recovery of metals in solution.[14] After filtration, each element is subsequently separated and pre-concentrated using different processes such as precipitation (or fractioned crystallization), solvent extraction [5], [14] or solid phase extraction.[15], [16] Although it is the most economical and the simplest process to implement, precipitation is not always the most efficient. The disadvantage of this type of process is mainly due to co-precipitation phenomena (precipitation of a part of non-targeted cations) that makes sometimes this process poorly selective and complicated due to the presence of many successive steps. Solvent extraction or liquid-liquid extraction is usually applied to obtain high degree of purity of each elements.[14] For example, the Rhône Poulenc process had the capability of producing a purity grade about 96 % in the case of praseodymium (Pr), neodymium (Nd) and samarium (Sm). A higher purity was obtained for the other lanthanides with a grade higher than 99.5 %. This high selectivity is obtained by using selective extractants such as cationic or anionic exchangers, or chelating extractant. Concerning the selective separation of lanthanide and actinide elements, the main part of chelating functional groups contains O-donor sites like, amides,[17], [18] malonamides,[18]–[20] phosphates,[21], [22] carbamoylmethylphosphine oxides,[21] carbamoylmethyl-phosphonate, and carbamoylmethyl-phosphonic acids. [23], [24] However, despite its high efficiency and excellent selectivity, solvent extraction requires a large amount of aliphatic solvents (heptane, kerosene…), which are generally carcinogenic compounds and make them harmful for health and environment. An alternative process consists in using extraction on solid phase, which doesn't need any organic solvent. Lanthanide/actinide sorbents could be organic (resins),[25]–[35] inorganic,[36], [37] or hybrid (organic/inorganic)[35], [38]–[40] materials. Organic or hybrid materials are generally functionalized with ion exchange or solvating sites with similar complexing motifs than those used in solvent extraction.[25], [27], [29], [33]–[35] However, these materials are generally designed in eluting column and thus they are difficult to industrialize in a continuous process, on the one hand and, energy consumer on the other hand.[38] New recovery processes are now emerging such as polymer enhanced ultrafiltration or polymer assisted ultrafiltration (PEUF/PAUF), which associates a functionalized polymer (soluble or insoluble) in order to complex metals with a membrane ultrafiltration step to recover the polymer after complexation.[41], [42] For example, Ricoux et al. reported the development of a recovery process for palladium using an insoluble phosphine oxide functionalized polymer.[43],[24] Another more interesting example is the Graillot *et al.* TEMF process (Thermosensitive Enhanced MicroFiltration) that allowed to eliminate metals from water by using water soluble P(N*n*PAAm-*stat*-$_{h}$MAPC1) copolymers.[44] The N*n*PAAm showed thermosensitive properties whereas the MAPC1 monomers enabled the metal complexation.[45], [46] The use of this kind of complexing-thermosensitive polymer has two advantages: (i) the thermosensitive polymer is soluble in solution at temperature lower than the cloud point (CP) thus favoring the complexation of metals and (ii) the polymer becomes insoluble at temperature above the CP, leading to the increase of particle sizes and thus to an easier filtration step which allows energy savings.[47]–[49]

In a previous work, the first thermosensitive-complexing homopolymer (P(CPAAm6C)) was reported.[50] The possibility to obtain both properties from a single monomer would be advantage for industry. The homopolymerization of the CPAAm6C enabled to obtain a functional rate of 100 % by free radical polymerization (chemical structure represented in scheme 1), which was not reached by using copolymerization of two monomers. Furthermore the distribution of functional sites remained unclear in the case of P(NnPAAm-*stat*-MAPC1) or P(NnPAAm-*stat*-DAAmEP) copolymerization (thermosensitive monomer *vs.* complexing monomer) as observed by Graillot.[51] With its carbamoylmethylphosphonate esters function (cmp), the P(CPAAm6C) could be used for lanthanide recovery using a process involving three successive steps: (i) complexation of lanthanide elements at a temperature lower than CP by the carbamoylmethylphosphonate (cmp) function, (ii) increase of temperature above the CP to get an insoluble polymer of higher particle size and finally (iii) filtration of the insoluble polymer complexing lanthanides. In this work, the multiparametric study of gadolinium sorption (chosen as model of lanthanides series) by P(CPAAm6C) was investigated by varying several parameters as the amounts of Gd(III) and P(CPAAm6C), pH, ionic strength and temperature during the extraction step. Thereafter, some informations about the extraction mechanism were obtained by infrared spectroscopy and the selectivity of P(CPAAm6C) regarding to gadolinium was studied in synthetic solutions containing Gd(III)/Ni(II) mixtures to mimic REE/transition metals mixtures encountered in the recycling steps consequently to the treatment of solutions coming from WEEE recycling or mining.



Scheme 1 Chemical structure of the poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) (P(CPAAm6C) obtained by free radical polymerization.

1. Experimental

1.1. Materials

1.1.1. Polymeric sorbent

Polymeric sorbent used in this study is the poly(diethyl-6-(acrylamido)hexylcarbamoyl-methylphosphonate) homopolymer (P(CPAAm6C)) obtained from the free radical polymerization of CPAAm6C as described in a previous work.[50] All details concerning the synthesis and the main characteristics of the polymer are reported in supplementary data.

1.1.2. Synthetic solutions

0.5 mol.L^{-1} stock metal solutions were prepared by dissolution of gadolinium(III) nitrate hexahydrate ($Gd(NO_3)_3$, $6H_2O$, Aldrich, metal basis trace, 99.99%) or Nickel(II) nitrate hexahydrated ($Ni(NO_3)_2$, $6H_2O$, Aldrich, metal basis trace, 99.999%) in mQ water with adjusted pH.

1.2. Analysis

1.2.1. Size Exclusion Chromatography (SEC)

SEC was used to determine the number average molecular weight (M_n) of the synthesized P(CPAAm6C). SEC was performed with a Varian 390-LC equipped with a refractive index detector. PolarGel M column was used at 60 °C with flow rate of 0.8 $mL.min^{-1}$ calibrated with triple detection method. Elution solvent used was DMF (+ 0.1 wt.% LiCl). In this work, P(CPAAm6C) was characterized by SEC in DMF using triple detection method and allowed the determination of M_n (36400 $g.mol^{-1}$) and dispersity $Đ$ (3.7).

1.2.2. Cloud point (CP) measurements

Thermosensitivity of the polymers was determined from the change in the transmittance value through the polymer solution with temperature. The measurement of the transmittance was carried out on different concentrations of polymer in aqueous solutions with a Perkin Elmer Lambda 35 UV-Visible spectrometer equipped with a Peltier temperature programmer PTP-1+1. A wavelength of 500 nm was selected for the analysis. The temperature ramp was fixed to 0.1 $°C.min^{-1}$ between 15°C and 50°C. The thermosensitivity was characterized by a sudden slope change in the transmittance curve. The CP values of the copolymers thus corresponded to the minimum of the derivative curves.

1.2.3. Dynamic Light Scattering (DLS) measurements

Light scattering measurements were recorded on a Malvern Zetasizer Nano Series equipped with a He-Ne laser (λ = 632.8 nm). Samples were introduced into the cells (pathway: 10 mm) after filtration through 0.45 µm PTFE microfilters to determine the hydrodynamic radius of polymer objects in aqueous solutions. The correlation function was analyzed *via* the general purpose method (NNLS) to obtain the distribution of diffusion coefficients (D) of the solutes. For the dynamic study, the Stokes-Einstein equation allowed to obtain the apparent equivalent hydrodynamic radius (R_H) from the Contin's method described in equation (1):

$$R_H = \frac{k_B T}{6\pi \eta_S D} \tag{1}$$

where T is the temperature of the sample (K), k_B is the Boltzmann constant ($m^2.kg.s^{-2}.K^{-1}$), η_S is the viscosity of the fluid ($kg.m^{-1}.s^{-1}$) and D is the translational diffusion coefficient at dilution infinite ($m^2.s^{-1}$).

1.2.4. Infrared spectroscopy

IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer with an ATR sampling accessory.

1.2.5. Metal analysis

The concentrations of metals were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with a SPECTRO ARCOS ICP spectrometer. The latter was calibrated with 0; 0.5; 1; 5; 10 and 15 mg.L^{-1} standard solutions (prepared by dilution of commercial standards of Gd and Ni with initial concentration of 1000 mg.L^{-1}). All samples were diluted to be within this reference range.

1.3. Method

1.3.1. Sorption using dialysis method

All sorption experiments were performed by immersing a dialysis membrane (cut-off equal to 2kDa) containing 10 mL of a solution of P(CPAAm6C) in a 100 mL of cation solution. The total volume was equal to 110 mL (dialysis methods in SI).[30] The temperature was controlled by a 6L Fisher Bioblock Scientific Cryothermostated bath. For a better fundamental understanding, this method was chosen to overcome the concentration gradients that are generally observed near the membrane in ultrafiltration processes. Moreover, it makes the titration of ions at equilibrium easier by sampling from the bulk, because polymer chains remain in the dialysis tube. Concentrations were determined by ICP-OES. When thermodynamic equilibrium was reached, the concentration of free ions in dialysis and in the bulk can be considered to be equal, *i.e.* $C_{e,bulk} = C_{e,dial}$. The initial concentration of cation C_0 was considered in the total volume of the system and was calculated from equation 2:

$$C_0 = \frac{C_{bulk} \times V_{bulk}}{V_{bulk} + V_{dial}} \qquad (2)$$

where C_{bulk} and V_{bulk} are the concentration and volume of the bulk solution (out of dialysis). V_{dial} is the volume of dialysis membrane containing the polymer solution.

1.3.2. Sorption kinetics

Four experiments were performed to study the kinetics, and three samples of 1 mL were collected to keep the volume change negligible (max 3%) for each series of experiments. The sorption capacity at a given time t (Q_t, expressed in mmol.g^{-1}) was then calculated from the mass balance (equation (3)) where C_t (mmol.L^{-1}) is the concentration of metal elements at the given time t (hours), V (L) and C_0 (mmol.L^{-1}) are the volume and the initial concentration of metals, respectively, and m (g) the mass of P(CPAAm6C).

$$Q_t = \frac{(C_0 - C_t)V}{m} \qquad (3)$$

1.3.3. Sorption equilibrium experiments

Sorption equilibrium was studied by varying either the concentration of metal for a given polymer mass (or concentration) in dialysis membrane, or the P(CPAAm6C) mass for a constant metal concentration. The influence of the pH and ionic strength was investigated by addition of nitric acid and sodium nitrate solutions, respectively. The influence of the temperature was studied between 10 and 40 °C. After 24 hours of stirring (optimized from kinetics experiments), the concentration of metals in solution at equilibrium, C_e (mmol.L^{-1}) was measured and the sorption capacity at equilibrium Q_e (mmol.g^{-1}) was determined from the mass balance (equation 4).

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (4)$$

where C_0 (mmol.L^{-1}) is the initial concentration of metal, m (g) is the polymer mass and V (L) is the volume of total solution.

1.3.4. Desorption experiments

Desorption of metals was studied in two steps. First, the equilibrium was reached at 20 °C to determine the sorption rate of metal by assaying 1 mL of the solution at equilibrium. Then, solutions were heated up to 35°C and, after 24 hours, the gadolinium concentration in solution was determined.

1.3.5. Selectivity studies

Sorption experiments were performed with solutions containing different total initial amounts of targeted cations $\sum_{inital} C/cmp$ with mixtures containing 50 mol.%Gd and 50 mol.%Ni. Solutions were prepared with an initial pH adjusted to 1 by addition of nitric acid (HNO_3).

2. Results and discussions

2.1. Thermosensitive behavior *vs* pH

In previous works,[50] it was demonstrated that the cloud point (CP) of P(CPAAm6C) in aqueous solution depended on the concentration of ionic species. In this work, the CP values of the polymer were measured as a function of the pH (fixed by HNO_3 concentration and ranging from 0 to 6.5) (Fig. S2†). Between pH 0 and 1 the CP increases from 5 to 32 °C. A plateau was observed at 32 °C from pH=1 to pH=2. Then, beyond pH = 2, the cloud point increased again to reach 42 °C corresponding to the polymer in solution without any addition of HNO_3. This first study allowed us to determine a suitable couple of temperature/pH values for the development of sorption experiments. Taking into account these results and in order to make the experiments at "conventional" temperatures, the study was performed for pH>1 and T=20 °C to remain before the CP.

2.2. Sorption properties

2.2.1. Sorption kinetics of Gd(III)

The time required to ensure equilibrium in the dialysis method was determined from kinetic experiments. Fig. 1 represents the sorption kinetics using P(CPAAm6C) in an aqueous solution containing gadolinium nitrate with a concentration equal to $1{,}77\times10^{-2}$ mol.L^{-1}. The pH was adjusted to 1 with nitric acid and the temperature was maintained at 20°C to keep the sorbent soluble in the bulk.

From Fig. 1, it was shown that equilibrium was reached after 20 hours (mainly due to the dialysis equilibrium system), leading to a sorption capacity of 0.6 mmol of Gd per gram of material in the presence of a large excess of Gd. Hence, all the experiments performed at equilibrium were carried out during a contact time of 24 h.

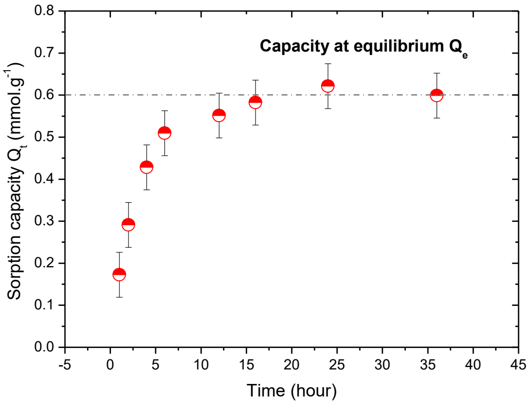


Fig. 1 Sorption kinetics obtained by contacting 50 mg of P(CPAAm6C) contained in 10 ml dialysis solution with 100 mL of bulk solution with C_0(Gd) = $1{,}61\times10^{-2}$ mol.L^{-1} (i.e. Gd/cmp = 12.3) at pH = 1 and for T = 20 °C.

2.2.2. **Sorption isotherm of Gd(III)**

The sorption capacity related to gadolinium at equilibrium was determined in fixed conditions of P(CPAAm6C) concentration (10 mL of 5 g/L of polymer in tubular membrane) was determined by sorption isotherms at 20°C and pH = 1 (Fig. 2). This pH value was selected to avoid (i) the precipitation of the polymer due to the decrease of the cloud point (at 20°C, the soluble state of the polymer is thus ensured to promote sorption), (ii) the precipitation of gadolinium hydroxide (Fig. SI4), and (iii) the protonation of carbamoylmethylphosphonate (cmp) group that will lead to the great decrease of the sorption capacity.[17] The amount of gadolinium trapped onto the P(CPAAm6C), Q_e(Gd), was shown to slowly increase at equilibrium when the free gadolinium concentration in solution increased from 0 to 15 mmol. Then, the sorption capacity of Gd sorbed tended to reach a plateau associated to a "maximum sorption capacity" of P(CPAAm6C) (Q_{max}) equal to 0.6 mmol.g^{-1}. This estimation was in accordance with the equilibrium capacity determined in the kinetic experiment with a large excess of Gd (Fig. 1). In the literature, solid adsorbent functionalized with carbamoylemethylphosphonated function had sorption capacities less than P(CPAAm6C) and comprised between 0.34 and 0.50 mmol.g^{-1}.[25], [52] Comparison shows the interest of soluble sorbent during the complexation step.

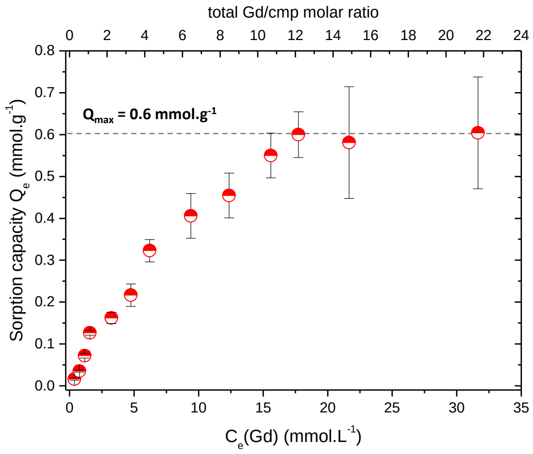


Fig. 2 Sorption isotherm obtained when contacting 50 mg of P(CPAAm6C) contained in 10 mL of dialysis solution with 100 mL bulk solution containing various gadolinium concentrations at pH = 1 and for T = 20°C.

2.3. Influence of concentrations conditions on Gd(III) sorption

2.3.1. Influence of the polymer concentration in the dialysis membrane

The impact of the polymer concentration on the sorption of Gd(III) was studied for a given initial gadolinium concentration of 7.98×10^{-4} mol.L^{-1}. The variation of the percentage of gadolinium sorbed on P(CPAAm6C) at pH = 1 as a function of the polymer concentration (0.25 to 10 g.L^{-1} , *i.e.* 0 to 100 mg of P(CPAAm6C) in 10 mL) is reported in Fig. 3 . From this figure, the amount of Gd sorbed by the polymer increased from 2.5 to 9.5% when increasing the polymer concentration from 0.25 to 1 g.L^{-1} in the dialysis membrane, as a result of the increase of the sorption sites related to gadolinium. Then, the amount of sorbed gadolinium decreased down to 2.5% for concentrations between 1 and 10 g.L^{-1}. So, these results clearly showed an effect of the concentration of P(CPAAm6C) on the gadolinium uptake. This decrease could result from the modification of the density of the sorbent solution, leading to closer polymer chains (which could favor polymer-polymer interactions thus decreasing the number of polymer-Gd(III) interactions) and a higher viscosity (which could lead to a more difficult ion transfer from the bulk solution).

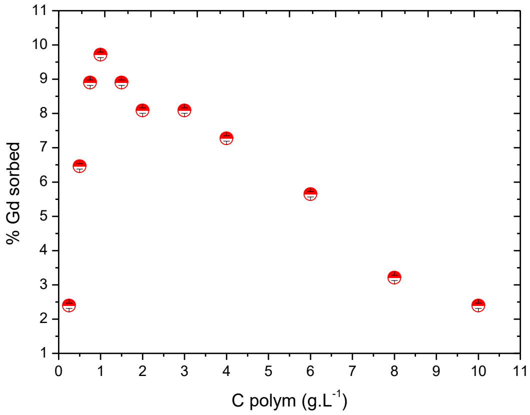


Fig. 3 Variation of the rate of sorbed gadonium (%) *vs* concentration of P(CPAAm6C) contained in the 10 mL dialysis membrane and with $C_0(Gd) = 7.98\times10^{-4}$ mol.L^{-1}, pH = 1 and T = 20 °C.

2.3.2. Effect of ionic strength and nitrates

The presence of salts can affect the interaction between cations and sorbent through the increase of the ionic strength. So, the influence of the ionic strength was studied at pH = 1 with given amounts of P(CPAAm6C) and gadolinium. Adding different amounts of $NaNO_3$ in the solution allowed to modify the ionic strength (I), which was determined from equation (5) where c_i is the molar concentration of ion i ($mol.L^{-1}$) and z_i the charge number of the ion. In the absence of $NaNO_3$, the ionic strength was equal to 0.16 $mol.L^{-1}$ due to the presence of gadolinium species, proton and nitrate ions.

$$I = \frac{1}{2}\sum_{i=1}^{n} c_i z_i^2 \qquad (5)$$

The sorption capacity of Gd at equilibrium *vs* the ionic strength (Fig. 4) showed two trends: (i) the amount of Gd trapped increased slowly and quasi-linearly from 0.40 to 0.86 $mmol.g^{-1}$ for an ionic strength ranging from 0.16 to 1.16 $mol.L^{-1}$ with a slope equal to 0.50 (ii) then, a more pronounced increase of the sorption capacity (from 0.86 to 1.93 $mmol.g^{-1}$) when increasing the ionic strength from 1.16 to 2.16 $mol.L^{-1}$. Ligands as cmp cannot form electrostatic bond (by charge exchange/ion exchange) because they do not have any acid site. The increase of the ionic strength led to an increase of the transfer of the free Gd contained in solution to the functionalized polymer and confirmed the participation of NO_3^- in the sorption mechanism. This behaviour was in agreement with a mechanisms of extraction of metals by solvation effect observed in solvent extraction[53], [54] and explained the general increase of Q_e *vs* ionic strength. Concerning the break of slope (from 0.5 to 1.07), it may be related with a change in polymer solvation. Referring to previous works, $NaNO_3$ also had a “salting-in” effect on the P(CPAAm6C).[50] At a concentration about 1.0 $mol.L^{-1}$, corresponding to the change of slope in the Q_e *vs* C_{NaNO_3} curve, the CP tended towards a maximum plateau which traduced a “maximum” solvation induced by the effect of "salting in". In this condition, the polymer was more "relaxed" in the solution and the complexing sites were more accessible for Gd(III) ions. The combination of the effects of $NaNO_3$ on gadolinium hydration and on the polymer solvation promoted the interactions between the ligand and the lanthanide, the sorption capacity of the P(CPAAm6C) was consequently more improved.

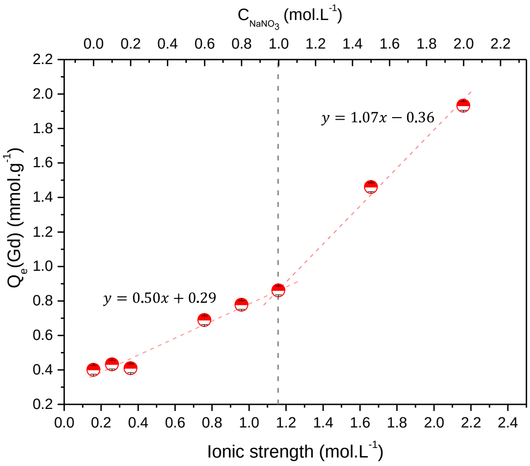


Fig. 4 Variation of the sorption capacity of gadolinium on P(CPAAm6C) versus the ionic strength (adjustment with the help of $NaNO_3$) with C_0(Gd) = 9.88×10^{-3} mol.L^{-1}, P(CPAAm6C) = 50 mg in 10 mL dialysis tube, (Gd/cmp = 7.54), pH = 1 and T = 20 °C

2.3.3. pH influence

The influence of the pH on the sorption of gadolinium was studied for pH < 3.5 to avoid the precipitation of gadolinium hydroxide. The variation of sorption capacity of P(CPAAm6C) regarding to gadolinium *vs* the pH of the solution is presented in Fig. 5 for a gadolinium concentration of 5.45×10^{-3} mol.L^{-1} (corresponding initial molar ratio Gd/cmp of about 4.18). Two trends were observed when pH decreased from 3.2 down to 1: (i) first the increase of Gd sorption was observed when the pH varied from 3.5 to 1.75, and then (ii) a tray towards a value of 0.27 mmol.g^{-1} was obtained for lower pH. However, the addition of nitric acid was associated to the increase of the ionic strength. As described in 2.3.2, this increase was found to promote the uptake of gadolinium by P(CPAAm6C) and could thus explain the increase of Q_e(Gd) with decreasing pH from 3.5 to 1.5. Additionally, for pH < 1.5, the proton concentration was high enough to induce the competition between the protonation of the cmp groups and the complexation of Gd(III). Indeed, from a concentration [HNO_3] = 1 mol.L^{-1} (pH=0) all amide groups are mono-protonated.[25], [55] A competition between the complexation of the Gd and the protonation was observed in the literature in the case of chelating resins.[25]

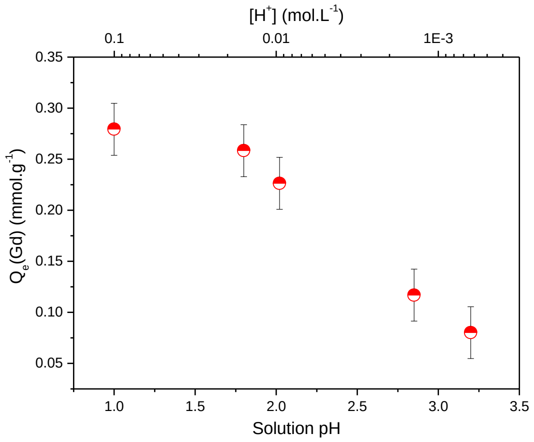


Fig. 5 Variation of the sorption capacity of P(CPAAm6C) regarding to gadolinium versus the pH of the solution, with C_0(Gd) = 5.45×10^{-3} mol.L^{-1}, P(CPAAm6C) = 50 mg in 10 mL dialysis tube, (Gd/cmp = 4.18) and T = 20 °C.

2.4. Temperature influence

Because the P(CPAAm6C) has thermosensitive properties, its solubility and organization in aqueous solution change as a function of temperature. These modifications could affect the sorption properties when they occur before the sorption process or could destabilize the *cmp*-Gd complex formed. For this reason, we studied the influence of temperature before and after the complexation step.

2.4.1. Physical state depending of temperature

The change in the organization of polymer chains in aqueous solutions was highlighted by plotting the particle sizes distribution of the polymer *vs*. temperature solution from 25 to 41 °C. Measurements were carried out by DLS in the whole temperature range with gadolinium concentrations corresponding to Gd/cmp ratios equals to 0 (polymer only), 0.54 and 10.5 and a polymer concentration equal to 5 g L^{-1} in the 10 mL dialysis tube (Fig. 6). Two trends were observed for initial Gd/cmp ratios equal to 0.54 and 10.5: (i) for temperatures lower than the CP value (T < 33°C), the particle size ranged between 10 and 25 nm for Gd/cmp =0 and 0.54, and from 10 to 1000 nm for Gd/cmp = 10.5; (ii) around the CP value (33°C) and in a narrow temperature range (33 °C to 42 °C), a strong increase of the particle sizes was observed leading to values higher than 1000 nm for both Gd/cmp ratios. When the temperature was lower than the CP value, the polymer chains were dispersed in the solution and the particle sizes corresponded to the hydrodynamic volume of the chains in aqueous solution. At temperatures close to the CP value, the thermosensitive properties of the P(CPAAm6C) promoted polymer-polymer interaction and led to the polymer chains aggregation, thus explaining the increase of the particle size that overcame 1000 nm. The precipitation/aggregation of polymer, which occurred at 33 °C (polymer only) and at 31 °C for Gd/cmp = 0.54 and 10.5, could induce a water rejection[56] and a competition between the polymer-polymer interactions by hydrogen bonding (with –NH and C=O and P=O) and the complexation.

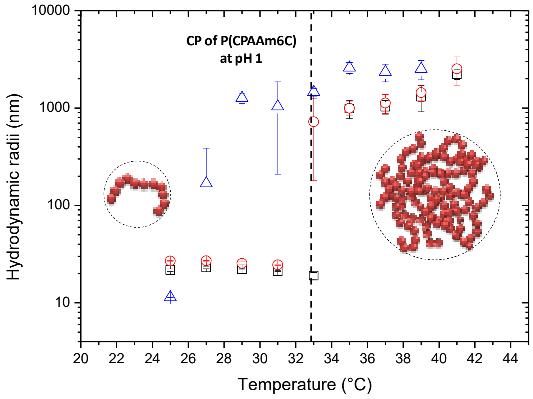


Fig. 6 Variation of the P(CPAAm6C) particle size vs the temperature of the solution. [P(CPAAm6C)] = 5 g.L^{-1}, pH = 1. Experiments with polymer only (☐), with Gd/cmp = 0.54 (○) and with Gd/cmp = 10.5 (△)

2.4.2. Influence of temperature on the sorption process

The behavior and solubility of P(CPAAm6C) depend on temperature, due to the thermosensitive behavior of the polymer. The sorption capacity of gadolinium was determined at different temperatures of the solution, *i.e.* 10, 20, 25, 30 and 50 °C (Fig. 7) with red plots. For these experiments all the concentrations were kept constant (C_0(Gd)= 1.51×10^{-2} mol.L^{-1} and mass of polymer = 50 mg in 10 mL dialysis solution, Gd/cmp=11.5, [$NaNO_3$] = 0 mol.L^{-1} and pH = 1). The "bulk" solutions were warmed up before the incorporation in the polymer dialysis tube. The cloud points for 5 g.L^{-1} of P(CPAAm6C) in 0.1M HNO_3 is represented with black dash line.

To study the influence of sorption on thermosensitivity, the cloud point of 5 g.L^{-1} at pH = 1 after sorption equilibrium reached with an initial concentration of Gd C_0(Gd) = 1.51×10^{-2} mol.L^{-1} was measured and represented by the red dash lines in Fig. 7. The higher Gd sorption capacities (around 0.6 mmol.g^{-1}) were obtained for temperatures below the cloud point. Once the temperature overcame the cloud point, the amount of sorbed gadolinium was shown to decrease to finally reach about 0 mmol.g^{-1} at 50°C. Such variation of the sorption properties with temperature could be linked to the physical state of the thermosensitive polymer. When the P(CPAAm6C) precipitated at temperatures beyond the cloud point, the cmp chelating sites were less accessible. A part of the cmp was involved in polymer-polymer interactions to form particles. So, Gd ions can be complexed only on the free cmp located at the surface of the precipitate formed at T > CP and allowed to a decrease of sorption capacity. Additionally, a shift of about 3 °C between the CP values obtained with and without gadolinium (black and red dash line) showed that the presence of gadolinium induced a modification of the cloud point. It is therefore important to consider all ions in solution for the optimization of the sorption step temperatures in the process. In the next paragraph, the influence of the temperature on the physical properties of the P(CPAAm6C) was therefore investigated after a sorption step to check if it could induce a desorption of the complexed Gd.

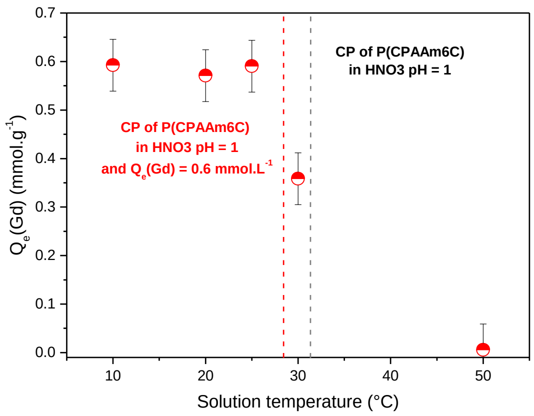


Fig. 7 Sorption of Gd with P(CPAAm6C) vs the temperature of experiment. C_0(Gd)= 1.51×10^{-2} mol.L^{-1}, P(CPAAm6C) = 50 mg in 10 mL dialysis, pH = 1, T = 20 °C. In black dash line is represented the cloud point of the P(CPAAm6C) = 5 g.L^{-1} and for pH = 1. The red dashed line represents the solution of P(CPAAm6C) = 5g.L^{-1} with in pH =1 and C_e(Gd) = 1.49×10^{-2} mol.L^{-1} after the equilibrium was reached at 20 °C, Q_e = 0.6 mmol.L^{-1}.

2.4.3. Impact of the increase of temperature after the complexation process

Due to the break of hydrophobic hydration at temperatures beyond the CP, it is known that polymer-polymer interactions are favored comparing to polymer-cation interactions, thus it would be possible to lead to cation desorption. It has been checked whether the aggregation/precipitation of the P(CPAAm6C) happening for temperatures beyond the CP could imply a desorption of the cations sorbed onto the polymer in the previous step. The sorption-desorption experiments were carried out in two steps: (i) sorption equilibrium was reached at 20°C after 24 hours (ii) then, during 24 hours, the temperature was maintained at 40 °C to overcome the cloud point. This increase of temperature induced the insolubility of the thermosensitive sorbent. Fig. 8 shows the distribution of the gadolinium after 24 h at 40 °C. The red and blue histograms represent the mol percentage of Gd desorbed from polymer and the amount of Gd that was still sorbed onto the polymer, respectively. Whatever the amount of Gd sorbed at equilibrium at 20°C (between 0.02 and 0.55 mmol.g^{-1}), the increase of the temperature above the CP induced the desorption of a fraction of Gd previously sorbed by the polymer. From Fig. 8 the amount of Gd desorbed is linked to the amount of initial amount of Gd sorbed at 20 °C, except for the highest value (0.55 mmol.g^{-1}). The desorption rate tended to decrease with increasing the initial amount of Gd trapped at 20 °C. The lower desorption of Gd as the sorption capacity increases at 20 °C could be explained by the increase of the ionic strength induced by the gadolinium ions. Indeed, the higher sorption capacities corresponded to the higher ionic strength which favored the formation of the Gd(III)-cmp complex.

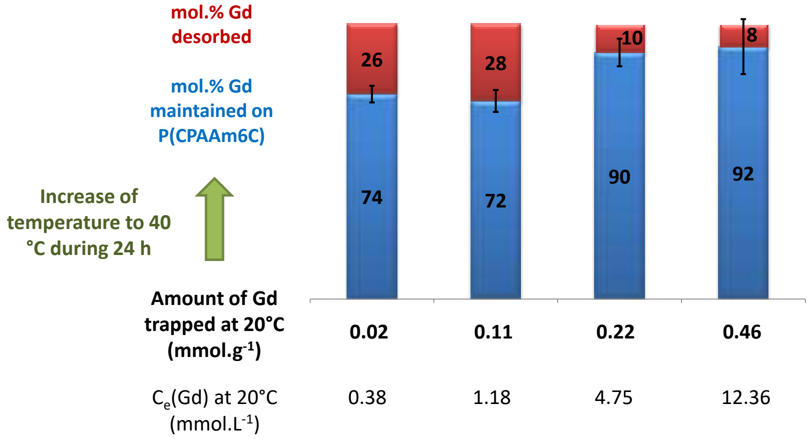


Fig. 8 Distribution of desorbed / sorbed gadolinium (expressed in mol percents) after 24h of contacting time at a temperature of 40 °C and as a function of the sorption capacity obtained after the first sorption step at 20 °C. 🟦: Gd sorbed*:* 🟥 Gd desorbed

2.5. Study of mechanism of sorption

In order to study the chemical interactions between Gd(III) and polymer at the origin of the sorption mechanism, a multi-scale approach was carried out:

(i) at the macroscopic scale, by analyzing the organization of the polymer in solution versus the sorption of gadolinium and,

(ii) at the microscopic (spectroscopic) scale, by focusing on the interactions between the metal and the ligand.

With regard to the macroscopic view, DLS measurements were performed to measure the hydrodynamic radius R_H of polymer/Gd systems corresponding to different points of the isotherm. The R_H values are reported in Table 1 for different initial Gd/cmp molar ratios. Different tendencies may be observed from the variation of R_H values depending on the part of the isotherm considered. For $Q_e < 0.10$ mmol.g^{-1} (corresponding to initial Gd/cmp ratio < 0.94

and sorbed Gd/cmp < 0.036), the particle sizes after Gd sorption (R_H =26.86 nm) are larger than that of the polymer solely (R_H = 22.27 nm). On the reverse, over Q_e = 0.10 mmol.g^{-1} (initial Gd/cmp ≥ 0.94; sorbed Gd/cmp ≥ 0.036), the particle size decreased as the Q_e increased (or initial ratio Gd/cmp increase) to reach a R_H value of 12.36 nm, lower than the particle size of the polymer before sorption. When sorption capacities Q_e are below the maximum sorption capacity of the P(CPAAm6C) (Q_{max} = 0.6 mmol.g^{-1}), corresponding to the lowest quantities of Gd (Gd/cmp < 0.036), the presence of complexed Gd increased the polarity and thus the solvation of the polymer in water, leading to more relaxed polymer chains and thus to higher R_H than that of the only polymer(see scheme on Fig. 9). Concerning the CP values listed in Table. 1, they remained constant and equal to 33°C for Q_e ≤ 0.10 mmol.g^{-1} because the concentration of free Gd in solution C_e(Gd) was too low to induce a salting-in or salting-out effect. Above the maximum sorption capacity, from Q_e = 0.10 mmol.g^{-1}, the R_H decreased (26 nm for Q_e = 0.10 mmol.g^{-1}; 23 nm for Q_e = 0.41 mmol.g^{-1} and 12 nm for Q_e = 0.60 mmol.g^{-1}) meaning a retraction of P(CPAAm6C) chains. This phenomenon was associated to a CP decrease from 33 to 26°C. In a previous work, it was shown that the CP decrease observed when increasing gadolinium nitrate concentration may be explained by a salting out effect[50] for the higher gadolinium concentrations. In particular, when Q_e was getting closer to Q_{max}, the C_e became sufficiently high (cf Fig. 1) to enable a predominant salting out effect compared to the polarization phenomenon of the chains. As a consequence, the chains are desolvated and retracted, involving R_H and CP decrease. Because of the desolvation, the polymer chains could collapse.

So, the increasing of the Q_e (with the increasing of Gd amount) led to the solvation and relaxation of the polymer chain until the Q_{max} was reached. When Q_e ≥ Q_{max} it was suggested that the excess of Gd (with high increasing of C_e(Gd)) allowed the desolvation of the polymer chains and a possible salting out effect that resulted in the decrease of R_H and CP.

Table. 1 Values of R_H before the CP for different Gd/cmp ratios in the case of 50 mg of P(CPAAm6C) in 10 mL dialysis membrane at pH=1 immersed in 100 mL of gadolinium solution at pH = 1 (total volume : 110 mL)

Initial Gd/cmp	C_e(Gd) (mmol.L^{-1})	Q_e(Gd) (mmol.g^{-1})	Gd/cmp sorbed ratio	R_H for T < CP (nm)	CP (°C)
0.00	0	0.00	0.000	22.27 ± 0.61	33
0.30	0.38	0.02	0.006	26.86 ± 0.06	33
0.60	0.76	0.04	0.012	26.86 ± 0.19	33
0.94	1.18	0.10	0.036	26.20 ± 0.16	32
7.34	9.40	0.41	0.141	22.48 ± 0.07	29
12.14	15.6	0.60	0.192	12.36 ± 0.42	26

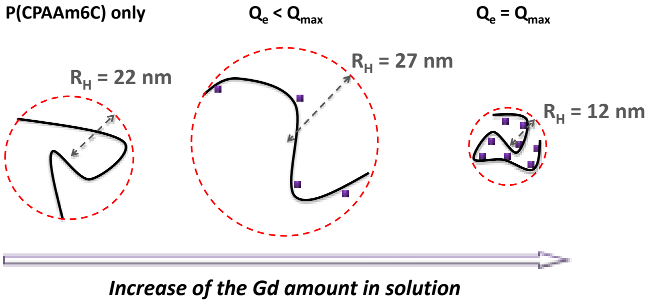


Fig. 9 Schematic representation of the polymer arrangement with different ratios of Gd trapped with the increase of Gd in solution before the CP red dash-line: hydrodynamic sphere, black line: polymeric chain, purple ball: Gd trapped

To provide information on the interaction mechanism of the complexation, all polymer solutions used for sorption equilibrium experiments were heated at +5 °C beyond the cloud point to induce the polymer precipitation. After precipitation, polymers were filtrated, dried at 60 °C and analyzed by infrared spectroscopy. Spectra normalized at 1019 cm^{-1} are shown in Fig. 10. IR spectra obtained for various Gd/cmp molar ratios (0.6, 0.96, 7.84 and 12.1) clearly demonstrated the complexation of gadolinium with the cmp site. Indeed, in comparison with the infrared spectrum of P(CPAAm6C) (absence of gadolinium sorption), the bands corresponding to P-O vibration of the phosphonated ester and C-O vibration of amides were progressively shifted from 1238 to 1201 cm^{-1} and from 1644 to 1634 cm^{-1}, respectively, when increasing the Gd/cmp molar ratio. The decrease of the P-O band at 1238 cm^{-1} compared to 1201 cm^{-1} with the presence of an isosbestic point allowed us to assign them to free P=O (1238 cm^{-1}) and P=O functions involved in gadolinium coordination (1201 cm^{-1}), respectively. By the same way, the bands located at 1644 and 1634 cm^{-1} could be assigned to free and bounded C=O amides, respectively. The presence of a shoulder on the amide band at 1625 cm^{-1} could correspond to the second amide function found in the P(CPAAm6C) (acrylamide chain) which was not modified by the gadolinium complexation.

In literature, closer values where observed in the case of the formation of neodymium-CMPO bonds in Nd-CMPO-HDEHP complexes [57]. Lumetta *et al.* observed that the C=O bands shifted from 1643 to 1634 cm^{-1} and the P=O band shifted from 1231 to 1211 cm^{-1}. According to the literature, the complexation mechanism between Gd and cmp groups of P(CPAAm6C) is similar in nature to those observed in liquid-liquid extraction for Nd-CMPO complexation.

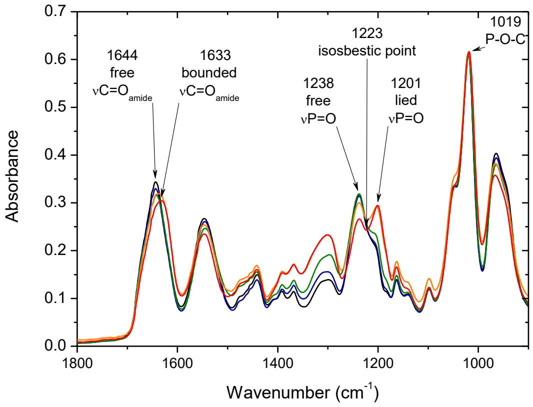


Fig. 10 IR-TF spectra of P(CPAAm6C) precipitated beyond the cloud point with and without different Gd/cmp ratios in solution. — without Gd — Gd/cmp= 0.60 — Gd/cmp = 0.94 — Gd/cmp = 7.84 and — Gd/cmp = 12.1

2.6. Selectivity studies in Gd/Ni mixture

Additional experiments were carried out with equimolar mixtures of gadolinium and nickel (50 mol. % of each cation in the initial solution) for investigating the selectivity between Gd(III) and Ni(II) encountered in the leaching mixture of electronic compounds or ores containing lanthanides and transition metals at pH = 1 in order to evaluate the selective sorption of cations on the cmp group. The distribution (expressed in mol. %) of the sorbed cationic species on the P(CPAAm6C) at equilibrium is shown in Fig. 11a) with increasing $\sum_{inital} C/cmp$ mole ratios. With the increase of $\sum_{inital} C/cmp$, the speciation of cations was modified leading to the preferential sorption of gadolinium onto the sorbent. Indeed, the percentage of sorbed gadolinium increased from 87% for $\sum_{inital} C/cmp$ of 0.3 to 94% and 98% for $\sum_{inital} C/cmp$ of 4.9 and 18.8 mol.mol^{-1}, respectively. Simultaneously, the ratio of complexed Ni(II) decreased from 13% to 2%. The higher fraction of sorbed Gd, whatever the $\sum_{inital} C/cmp$ ratio suggested that the complexing cmp site had a greater affinity for the trivalent lanthanides than for divalent transition metals, in agreement with the literature.[25] On the other hand, the modification of the distribution of sorbed species with the increase of $\sum_{inital} C/cmp$ to reach 98% of sorbed Gd could be due to the fact that lanthanides are considered as hard Lewis acids, while nickel is classified in the borderline Lewis acids and carbamoylmethylphosphonate group is a hard base with a strong electron density according to the Pearson's classification.[58]–[60] The hard acids form more stable interactions with O-donor groups than soft acids leading to a better affinity of cmp regarding to Gd(III) in Gd/Ni mixture.

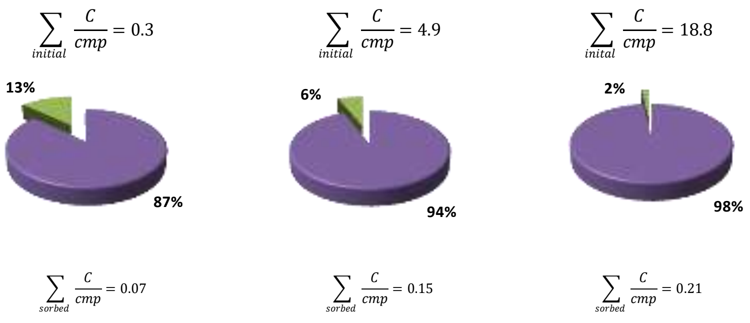


Fig. 11 Molar percentage of the cationic species loaded on P(CPAAm6C) for different initial C^{n+}/cmp ratios at 20 °C, 10 mL of 5 $g.L^{-1}$of P(CPAAm6C) immersed in 100 mL of bulk, pH = 1 and [$NaNO_3$] = 0 $mol.L^{-1}$: starting from 50 mol.% Gd and 50mol.% Ni di-components solution 🟪: Gd 🟩: Ni

Conclusions

A new homopolymer functionalized with cmp groups and combining both thermosensitive and chelating properties toward Gd and Th cations was investigated for lanthanide purification. The cloud point of the synthesized polymer ranged from 5 to 42 °C as a function of pH. The experimental conditions were chosen to obtain a low CP which provides significant cost reduction for the separation of the insoluble polymer-metal complexes from the solution, and would lead to the simplification of the separation processes. First, the sorption properties of the P(CPAAm6C) toward Gd(III) were evaluated with various gadolinium and polymer concentrations, pH values, ionic strengths and temperatures. The best sorption capacities were obtained at temperatures lower than the CP (when polymer is soluble in solution), in acidic medium (pH = 1) and for high ionic strength conditions. The thermosensitive character allowed obtaining particles having a diameter close to 1000 nm above CP, but this aggregation/precipitation induced the partial loss of gadolinium initially complexed at 20 °C. The gadolinium desorption ranged from 8 to 28%, depending on the initial gadolinium concentration in nitric acid media during the sorption phase. According to the DLS and IR analyses of the polymer with and without sorbed gadolinium, macroscopic and spectroscopic sorption mechanisms were proposed, involving the variation of the conformation of the polymer chains as a function of the Gd/cmp ratio and coordination bonds interactions between Gd and the carbonyl and phosphonate functions of the polymer. Finally, Gd/Ni equimolar model solutions at pH =1 showed that cmp groups were selective for Gd in mixtures containing gadolinium and nickel.

In order to get a better understanding of the systems, it should be necessary to study more precisely the sorption capacity of cmp regarding to gadolinium in mixtures containing gadolinium and nickel. However, the results reported in this paper clearly evidenced yet very promising properties in the field of the purification of lanthanide elements for extraction from ores or WEEE recycling. It would be also helpful to develop extensive experiments devoted to the sorption capacity and properties of P(CPAAm6C) regarding to other mixtures containing gadolinium, thorium and uranium to look for selectivity in the presence of natural actinides from monazite for example.

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