

# Polymer Chemistry

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# Polymer Chemistry

## ARTICLE

### First report on phosphonate-based homopolymer combining both gadolinium chelating and thermosensitive properties: synthesis and evaluation†

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Original phosphonate-based acrylamide was first prepared in four steps including the incorporation of valuable carbamoylmethylphosphonate moiety. This monomer was then polymerized, thus leading to poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) (P(CPAAm6C)), combining both thermosensitivity and chelating properties. The influence of different parameters (polymer concentration, salt, acidity) over the P(CPAAm6C) cloud point was determined, notably considering the salting-out and salting-in effect related to the Hofmeister series. Finally, it was proved that thermosensitive P(CPAAm6C) was efficient for the complexation of gadolinium below and above the cloud point. The latter logically depended of the Gd sorption. To our knowledge, the P(CPAAm6C) polymer represents the only example reported in the literature where only one monomeric unit can allow on the one hand the complexation of rare earth elements, in particular gadolinium, and on the other hand thermo-responsiveness property. The poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) polymers open the way to new materials that could be used for the treatment of rare earth elements containing effluents, allowing their recovery while possibly recycling the homopolymer.

## Introduction

Rare earth elements (REE) are becoming increasingly important, mainly due to the transition to a green economy, with a global demand annually growing at a rate of 3.7–8.6%.<sup>1</sup> They include a group of 17 elements consisting of scandium, yttrium and the lanthanides, which showed similar chemical and specific physical properties.<sup>2</sup> REEs are used in many devices such as microelectronic industry, rechargeable batteries,<sup>3</sup> catalytic converters, magnets<sup>4</sup> and much more.<sup>5, 6</sup> Lanthanides can also be met in nuclear wastes of the nuclear industry.<sup>7</sup> So, the selective complexation of lanthanides and/or actinides from aqueous solutions is of interest to separate them before storage. Treatment of nuclear wastes is currently

achieved using different processes such as solvent extraction or the use of ion-exchange resins which are nowadays the most common processes for f-block elements separation. Even if efficient, solvent extraction or liquid-liquid extraction proved to be organic solvents high consuming and the risk of formation of a third phase remains an important drawback.<sup>8</sup> Concerning ion-exchange process, some insoluble functionalized polymer resins were reported in the literature and proved to be efficient for lanthanide/actinide separation. They are mainly based on polystyrene, grafted with different O-donor groups,<sup>9</sup> such as malonamides,<sup>10</sup> ethylenediamine tetraacetic acid (EDTA) and diethylenetriamine pentaacetic acid,<sup>11</sup> and carbamoylmethylphosphonate.<sup>12, 13</sup> This process does not use organic solvents but showed drawbacks such as a high cost, and limited accessibility to complexing groups due to the insolubility of the polymer resins. Finally, another possibility is the use of hydrophilic complexing polymers which facilitate sorption but has to be removed using expensive polymer-enhanced ultrafiltration (PEUF).<sup>14</sup>

In a general manner, advantages of common processes allowing the recovery of cations can be highlighted in the following way: (i) insoluble polymeric resins are of great interest since they can be easily removed from the water after sorption whereas (ii) water-soluble polymeric sorbents ease the sorption step since the sorption groups are directly in contact with the cationic pollution in water due to polymer hydrophilicity. As a result, new approach developed in the literature consisted in combining both advantages of the reported processes, using thermosensitive polymer enhanced

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microfiltration (TEMF).<sup>15, 16</sup> This process, carried out for the sorption of Al, Ni, Cd, and Al cations, was based in the synthesis of new thermosensitive<sup>17</sup> copolymers bearing phosphonated groups.<sup>18, 19</sup> Poly(*N-n*-propylacrylamide thermosensitive moieties led to lower critical solution temperature (LCST) values close to ambient temperature and complexing properties given by hydrolyzed (dimethoxyphosphoryl) methyl 2-methylacrylate (hMAPC1) monomer allowed the removal of specific metallic pollution from water.<sup>20-22</sup> LCST of the copolymers were controlled by the molar ratio of each monomer in the copolymers which deeply depended on the reactivity ratios of monomers.<sup>23</sup> Additionally, a good compromise had to be found to have high complexing group content while keeping the thermosensitivity property which proved to considerably limit the quantity of complexing moieties throughout the copolymer.

In the present contribution, we report for the first time in the literature the synthesis of homopolymers combining both chelating groups and thermosensitivity from a single original monomer, namely the diethyl-6-(acrylamido)hexylcarbamoyl methylphosphonate (CPAAM 6C). The latter bears carbamoylmethylphosphonate functions which proved to efficiently sorb lanthanides.<sup>24</sup> These complexing groups were directly introduced on the monomer unit which allowed the obtaining of fully functionalized polymers also showing thermosensitivity property with accurate cloud point value while having maximum complexing group content. Study of fundamental parameters influencing the cloud point and complexation with gadolinium demonstrated that poly(diethyl-6-(acrylamido) hexyl carbamoyl methyl phosphonate) (P(CPAAM6C)) was very promising material for lanthanide extraction processes.

## Experimental

**Materials.** 1,6-diaminohexane (Sigma Aldrich), diethylphosphonoacetic acid (Sigma Aldrich, 95%), trifluoroacetic acid (Sigma Aldrich, 99%), acryloyl chloride (Aldrich, 97%), di-*tert*-butyl dicarbonate (Fulka, 99%), dicyclohexylcarbodiimide (DCC) (Aldrich, 99%), dimethylaminopyridine (DMAP) (Aldrich 99%), nitric acid (Carlo Erba 65%), sodium nitrate (Alpha Aesar), sodium chloride (Carlo Erba), anhydrous ethanol (Aldrich, 98%) and cerium nitrate hexahydrate (Aldrich, 99,99% metal basis) were used as received. 2,2'-azobisisobutyronitrile (AIBN) (Aldrich, 98%) was used after recrystallization in methanol. Triethylamine (Aldrich, 99%) was dried by means of a molecular sieve adsorbent. All solvents were purchased from Aldrich and were used without further purification.

## Characterizations.

**Nuclear Magnetic Resonance (NMR).** Bruker Advance DRX 300 (300Hz) was used to record <sup>1</sup>H, <sup>31</sup>P NMR spectra with CDCl<sub>3</sub> or D<sub>2</sub>O as deuterated solvents purchased from Eurisotop. For <sup>1</sup>H NMR, chemical shifts were referenced to the corresponding hydrogenated solvent residual peaks at 7.26 ppm and 4.79

ppm, for CDCl<sub>3</sub> and D<sub>2</sub>O, respectively. H<sub>3</sub>PO<sub>4</sub> was used as reference for <sup>31</sup>P NMR.

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

**Cloud points measurements.** Thermosensitivity of the polymers was estimated by a change in the transmittance through the polymer solution with temperature. The measurement of the transmittance was carried out on different concentrations of polymer 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. The temperature ramp was 0.1 °C per minute.

**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 allows to obtain the apparent equivalent hydrodynamic radius (R<sub>H</sub>) from the Contin's method:

$$R_H = \frac{k_B T}{6\pi\eta_s D}$$

T is the temperature of the sample, k<sub>B</sub> is Boltzmann constant, η<sub>s</sub> is the viscosity of the fluid and D is the translational diffusion coefficient at finite dilution.

**Size Exclusion Chromatography (SEC).** 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<sup>-1</sup> calibrated with poly(methyl methacrylate) (PMMA) standards. Elution solvent used was DMF (+ 0.1%<sub>w</sub> LiCl).

## Synthesis of carbamoylmethylphosphonate-functionalized acrylamide monomer CPAAM6C

**Synthesis of 6-(*tert*-butoxycarbonylamino)hexylamine (1).** 6-(*tert*-butoxycarbonylamino)hexylamine was prepared in 70% yield using known procedure.<sup>25</sup> Compound **1** was obtained by extraction with diethylether. No further purification step was necessary.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 1.19 (s, 2H, NH<sub>2</sub>), 1.26-1.52 (m, 8H, CH<sub>2</sub>), 1.42 (s, 9H, CCH<sub>3</sub>), 2.68 (t, 2H, HNCH<sub>2</sub>), 3.12 (q, 2H, H<sub>2</sub>NCH<sub>2</sub>), 4.56 (br, 1H, NH).

IR: ν<sub>max</sub> (cm<sup>-1</sup>): 1694 (C=O<sub>NHBOC</sub>), 2929 (C<sub>tert</sub>-H), 3365-3230 (N-H<sub>amine/amide</sub>).

**Synthesis of diethyl-6-(*tert*-butoxycarbonylamino)hexyl carbamoylmethylphosphonate (2).** To the compound **1** (8.19 g, 37.86 mmol) dissolved in anhydrous dichloromethane (20 mL) were consecutively added dimethylaminopyridine (DMAP)

(4.63 g, 37.89 mmol), diethylphosphonoacetic acid (6.19 g, 31.56 mmol), and dicyclohexylcarbodiimide (DCC) (7.83 g, 37.95 mmol), all dissolved in anhydrous dichloromethane (3 × 10 mL). The mixture was allowed to stir at 25 °C during 24 hours and then cooled to the freezer during the night. After filtration, the mixture was washed with HCl 2N (4 × 50 mL), water (4 × 50 mL), Na<sub>2</sub>CO<sub>3</sub> 10% (4 × 50 mL), and brine (2 × 50 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. After evaporation of the solvent, transparent yellow oil was obtained in 81% yield (10.10 g).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 1.36 (t, 6H, CH<sub>3</sub>), 1.43 (s, 9H, CCH<sub>3</sub>), 1.30-1.54 (m, 4H, CH<sub>2</sub>), 2.85 (d, 2H, OCCH<sub>2</sub>PO), 3.12 (m, 2H, CH<sub>2</sub>NH), 3.28 (q, 2H, HNCH<sub>2</sub>), 4.18 (q, 4H, OCH<sub>2</sub>), 4.56 (br, 1H, NH), 6.75 (br, 1H, NH).

<sup>13</sup>P NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 23.30 (s, 1P, PO(OEt)<sub>2</sub>).

IR ν<sub>max</sub> (cm<sup>-1</sup>): 1246 (P=O), 1657 (C=O<sub>amide</sub>), 1710 (C=O<sub>NHBoc</sub>), 2929 (C<sub>tet</sub>-H), 3305 (N-H<sub>amide</sub>).

**Synthesis of hexyl-6-(diethylcarbamoylphosphonate)-1-amonium trifluoroacetate salt (3).** Trifluoroacetic acid (35 mL) was slowly added to a solution of compound **2** (7.00 g, 16.48 mmol) dissolved in anhydrous dichloromethane (15 mL). Resulting mixture was stirred during 4 hours at 25 °C. Then, dichloromethane and trifluoroacetic acid were removed by cryo-distillation at 50 °C. Water (100 mL) was added and resulting mixture was filtered to remove the DCC/DCU traces of the previous step. Finally, water was removed by lyophilization. Viscous oil was obtained in quantitative yield (6.72 g).

<sup>1</sup>H NMR (D<sub>2</sub>O, 300MHz) δ (ppm): 1.31 (t, 6H, CH<sub>3</sub>), 1.25-1.38 (m, 4H, CH<sub>2</sub>), 1.44 (m, 2H, CH<sub>2</sub>), 1.51 (m, 2H, CH<sub>2</sub>), 2.97 (t, 2H, CH<sub>2</sub>NH), 2.94-3.02 (d, 2H, OCCH<sub>2</sub>PO), 3.18 (t, 2H, HNCH<sub>2</sub>), 4.19 (q, 4H, OCH<sub>2</sub>).

<sup>13</sup>P NMR (D<sub>2</sub>O, 300MHz) δ (ppm): 24.58 (s, 1P, PO(OEt)<sub>2</sub>).

<sup>19</sup>F NMR (D<sub>2</sub>O, 300MHz) δ (ppm): -75.62 (s, 3F, CF<sub>3</sub>COO<sup>-</sup>).

IR ν<sub>max</sub> (cm<sup>-1</sup>): 1142 (C-F), 1200 (P=O), 1653 (C=O<sub>amide</sub>), 1778 (C=O<sub>TFA</sub>), 2942 (C<sub>tet</sub>-H), 3284 (N-H<sub>amide</sub>).

**Synthesis of diethyl-6-(acrylamido)-hexylcarbamoylmethyl phosphonate (CPAAM6C) (4).** Compound **3** (17.43g, 37.96 mmol) was dissolved in anhydrous acetonitrile (80 mL) under nitrogen. Dried triethylamine (28.8 mL, 192.6 mmol) was added at 0 °C and resulting mixture was allowed to stir during 4 hours at room temperature. Then, acryloyl chloride (4.5 mL, 53.7 mmol) in anhydrous acetonitrile (40 mL) was added dropwise at 0 °C. Reaction was stirred during 5 minutes at 0 °C and 20 hours at room temperature. Solvent was removed in reduced pressure and 250 mL of water was added. The solution was basified with Na<sub>2</sub>CO<sub>3</sub> to pH=9. The product was extracted with dichloromethane (3 × 50 mL) and organic phase was dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent, an orange oil (CPAAM6C) was obtained in 77% yield (11.29 g).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 1.35 (t, 6H, -CH<sub>3</sub>), 1.30-1.37 (m, 4H, -CH<sub>2</sub>-), 1.58 (m, 4H, -CH<sub>2</sub>-), 2.28-2.79 (d, 2H, OCCH<sub>2</sub>PO),

3.22-3.35 (m, 4H, HNCH<sub>2</sub>), 4.18 (q, 4H, OCH<sub>2</sub>), 5.56-5.63 (dd, 1H, =CH, J = 10.33 Hz), 6.06-6.30 (dd, 2H, CH<sub>2</sub>=).

<sup>13</sup>P NMR (D<sub>2</sub>O, 300MHz) δ (ppm): 23.23 (s, 1P, PO(OEt)<sub>2</sub>).

IR ν<sub>max</sub> (cm<sup>-1</sup>): 1243 (P=O), 1626 (C=C), 1655 (C=O<sub>amide</sub>), 2932 (C<sub>tet</sub>-H), 3282 (N-H<sub>amide</sub>).

**Free radical polymerization of carbamoylmethylphosphonate monomer. Synthesis of poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) P(CPAAM6C).** Monomer **4** (6.60 g, 18.95 mmol) and AIBN (18.7 mg, 0.95.10-4 mol) were dissolved in dimethylsulfoxide (40 mL). The mixture was deoxygenated by three freeze-pump-thaw cycles and placed under nitrogen. The Schlenk tube was then immersed in a thermostated oil bath at 80 °C for 16 hours. The polymer was purified by dialysis in water, performed with regenerated cellulose membrane with a cut off 2000 Da during five days. The resulting aqueous solution was lyophilized leading to P(CAAM6C) as a white solid M<sub>n,SEC</sub> = 31000 g.mol<sup>-1</sup>, Đ = 2.1).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 1.18-1.63 (m, -CH<sub>2</sub>- and -CH<sub>3</sub>), 2.81-3.33 (m, HNCH<sub>2</sub> and CO-CH<sub>2</sub>-PO), 4.08-4.22 (m, OCH<sub>2</sub>).

<sup>13</sup>P NMR (CDCl<sub>3</sub>, 300MHz) δ (ppm): 23.05 (s, 1P, PO(OEt)<sub>2</sub>).

IR ν<sub>max</sub> (cm<sup>-1</sup>): 1237 (P=O), 1644 (C=O<sub>amide</sub>), 2931 (C<sub>tet</sub>-H), 3287 (N-H<sub>amide</sub>).

**Complexation of Gd(NO<sub>3</sub>)<sub>3</sub> with P(CPAAM6C) polymer.** A solution of P(CPAAM6C) (0.5 g, 1.44 mmol) in water (5 mL) was added in a solution of gadolinium nitrate in water (5 mL) at appropriate concentrations at 15 °C. Resulting mixture was stirred for 24 hours. Then, temperature was raised to room temperature resulting in the formation of insoluble P(CPAAM6C) which was filtered and washed with warm water before being characterized by infrared measurements.

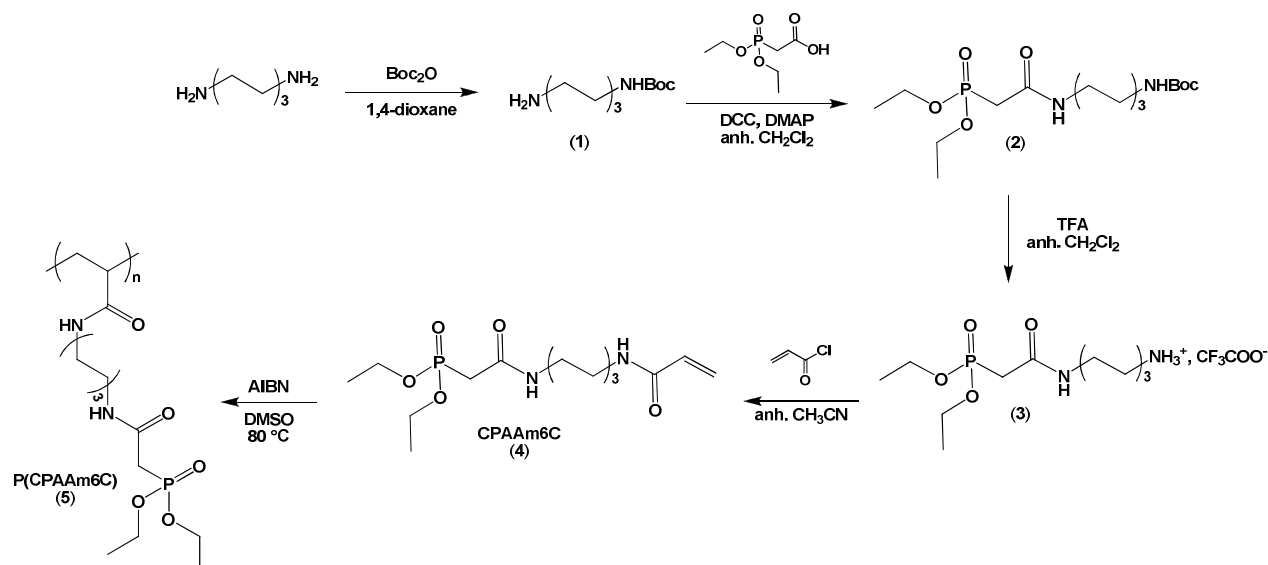
**Nitric acid resistance.** P(CPAAM6C) (50 mg) was dissolved in 2 mol.L<sup>-1</sup> solution of nitric acid (5 mL) and stirred during 48 hours. After 24 hours. Nitric acid was then removed by dialysis. Finally, water was removed by freeze-drying.

## Results and discussion

### Synthesis of the carbamoylmethylphosphonate-based polymer

Synthesis of the diethyl-6-(acrylamido)hexylcarbamoylmethyl phosphonate monomer (**4**) (CPAAM6C) was achieved in four steps from 1,6-diaminohexane (Scheme 1). Concerning the general reactional pathway developed, acrylamide function was chosen due to its better stability than the ester one in heavy acidic processes generally used for the treatment of nuclear wastes (leaching of lanthanides oxide or monazites, for instance). Carbamoylmethylphosphonate group was selected as it already proved to be efficient for the complexation of lanthanides in liquid-liquid process or grafted to resins.<sup>12,13,26,</sup>

<sup>27</sup> First step of the synthesis dealt with the monoprotection of



**Scheme 1** Reactional pathway describing the synthesis of the diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate (CPAAm6C) monomer (4), and the resulting poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) (PCPAAm 6C) polymer (5).

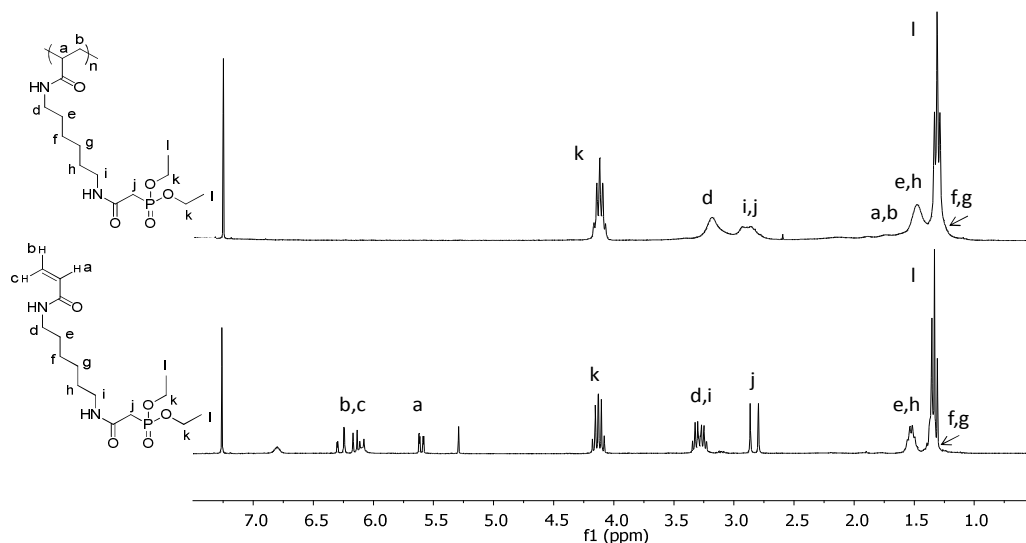
the 1,6-diaminohexane using di-tert-butyl dicarbonate ( $\text{Boc}_2\text{O}$ ) in 1,4-dioxane.<sup>28</sup> Monoprotected compound was recovered by extraction with diethylether with 70% yield and was characterized by  $^1\text{H}$  NMR in deuterated chloroform. Then, second step consisted in coupling the monoprotected amine with diethylphosphonoacetic acid in the presence of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) as catalysts in anhydrous dichloromethane. Compound (2) was obtained with 81% yield after washing of the organic layer. Dicyclohexylurea (DCU) was not completely removed by washing as shown in the  $^1\text{H}$  NMR spectrum (Fig. S1†) with a signal between 1 and 2 ppm corresponding to the methylene of the cyclohexyl rings of the DCU. This was not a problem for the global synthesis as this by-product was fully eliminated in the following step of the synthesis. Deprotection of tert-butyloxycarbonyl group was achieved with an excess of trifluoroacetic acid to lead to the corresponding ammonium trifluoroacetate salt (3). Furthermore, the addition of water allowed removing DCU which precipitated and was then easily removed by filtration as confirmed by  $^1\text{H}$  NMR (Fig. S2†). Salt was obtained in quantitative yield. Finally, polymerizable group was introduced using acryloyl chloride in the presence of triethylamine. Diethyl-6-(acrylamido) hexylcarbamoylmethyl phosphonate monomer (4) was recovered after a versatile extraction with 77% yield. To conclude, we succeeded in preparing an original acrylamide monomer bearing lanthanides chelating functions. Monomer was fully characterized by  $^1\text{H}$  and  $^{31}\text{P}$  NMR in deuterated chloroform.  $^1\text{H}$  NMR (Fig. 1) notably showed signals corresponding to the acryloyl function at 6.06–6.30 and 5.56–5.63 ppm, and to the methylene group in  $\alpha$  of the phosphonate functions at 2.28–2.79 ppm.  $^{31}\text{P}$  NMR showed a signal at 23.05 ppm, logically attributed to the phosphorus of the phosphonate function. Finally, an important

characteristic of the reactional pathway is the easy purification steps at each stage allowing a versatile synthesis of such monomer in high scale. radical polymerization of diethyl-6-(acrylamido)hexyl carbamoylmethylphosphonate was carried out under nitrogen in dimethylsulfoxide at  $80^\circ\text{C}$  during 16 hours using 0.5% of AIBN as initiator. Resulting polymer (5) was purified by dialysis in water, performed with regenerated cellulose membrane (cut off 2000 Da) in order to obtain very pure material for evaluation of its properties. The resulting aqueous solution was lyophilized leading to P(CAAm6C) as a white solid. Characterization by size exclusion chromatography in DMF using PMMA standards permitted to determine a molecular weight ( $M_n$ ), and a dispersity ( $\mathcal{D}$ ) equal to 31000  $\text{g}\cdot\text{mol}^{-1}$  and 2.1, respectively.  $^1\text{H}$  NMR confirmed the efficiency of the polymerization reaction and of the purification step by dialysis as signals were broader and acryl protons have disappeared between 5.5 and 6.5 ppm.

#### Influence of the polymer concentration on the cloud point and size

As poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) proved to be thermosensitive, first work dealt with the study of the influence of different parameters on the cloud point, especially the concentration (Fig. 2). For such purpose, five solutions of different concentrations (5, 10, 15, 20 and 30  $\text{g}\cdot\text{L}^{-1}$ ) were prepared in deionized water. It appeared that varying the polymer concentration led to a small decrease of the cloud points going from 42.5 to  $41^\circ\text{C}$ , when concentration increased from 5 to 30  $\text{g}\cdot\text{L}^{-1}$ , respectively. This demonstrated that the cloud point was not really dependant of the polymer concentration. It is also important to mention that, at a same concentration, the difference of cloud point values between



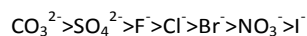


**Fig. 1**  $^1\text{H}$  NMR spectra in deuterated chloroform of a) below: the diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate (CPAAM6C) monomer (4), and b) top: the resulting poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) (PCPAAM6C) polymer (5).

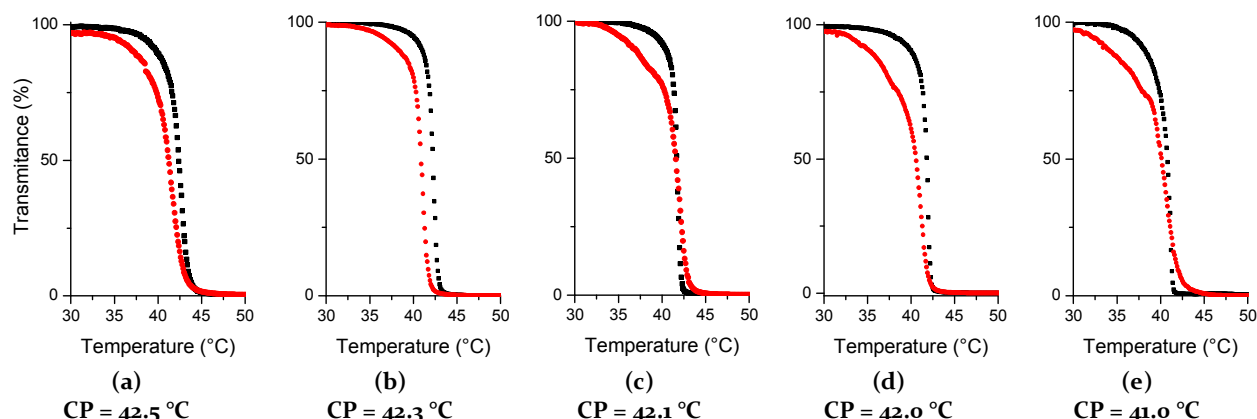
increasing and decreasing the temperature was lower than 10%, demonstrating that the thermo-responsiveness was reversible. The thermosensitive behavior of P(CAAM6C) was illustrated by DLS measurements (Fig. S3<sup>†</sup>). Below the cloud point, hydrodynamic radius ( $R_H$ ) was around 50 nm whatever the concentration. On the reverse, 5 °C above the cloud points, radii depended on the polymer concentration. At high concentration (30 g.L<sup>-1</sup>), the  $R_H$  was measured at 859 nm whereas it was 214 nm for the lowest one (5 g.L<sup>-1</sup>). As the temperature increased, P(CAAM6C) chains became hydrophobic and eventually collapsed. At high concentration, interactions between polymer chains were more favored leading to the formation of larger aggregates. On the other hand, at low concentrations, polymer chains were better separated and could hardly aggregate, which resulted in smaller sizes. Same behavior was described in the literature in the case of copolymers based on poly(N-isopropylacrylamide).<sup>29</sup>

#### Influence of salts and acidity on the cloud points

The effect of a series of sodium salts (NaI, NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>) on the cloud point of P(CPAAM6C) was also investigated as it is known that salts disrupted the hydration structure surrounding the polymer chains, modifying the demixing temperature.<sup>30</sup> We first studied the influence of the anions, highlighting the evolution of the CP as a function of the concentration of salts ranging from 0 to 1 mol.L<sup>-1</sup> (Fig. 3a)). For such purpose, the Hofmeister effect, which was first reported in the case of the solubility of proteins in aqueous medium, was considered. The typical order of the Hofmeister series for some anions is:<sup>31, 32</sup>



Additionally, it was reported in the literature that polymer solvation in the presence of salt could be explained by three different interactions: (i) anions can polarize an adjacent water molecules involved in hydrogen bonding with the amide groups borne by the polymer, (ii) anions can interfere with the hydrophobic hydration of the macromolecule by increasing the surface tension of the cavity surrounding the polymer backbone, and (iii) anions can directly bind to the polyacrylamide. The two first effects lead to the salting-out (decrease of the CP) whereas the third one causes salting-in (increase of the CP) of the polyacrylamide.<sup>31</sup> In the case of poly(diethyl-6-(acrylamido) hexylcarbamoylmethyl phosphonate), the evolution of the cloud points as a function of all salt concentrations was not linear as curves showed two distinct behaviors. First, below a salt concentration of 0.028 mol.L<sup>-1</sup>, corresponding to a salt/amide ratio equal to 1 (taking into account that there was two amide per repetitive monomeric unit), the CP drastically decreased in all cases. This was attributed to a salting-out phenomenon specifically due to interactions between salt and water molecules involved in the hydrogen bonding with amide functions. This effect was similar for all salt as cloud points measured were about the same, except for sodium nitrate (Fig. 3, inlet). Slightly lower values for NaNO<sub>3</sub> were probably due to its higher charge density. Above the 0.028 mol.L<sup>-1</sup> salt concentration, two different behaviors were seen. Higher decrease of the CP was obtained in the case of CO<sub>3</sub><sup>2-</sup> kosmotrope ion. Indeed, we assumed that the water layer was “busy” solvating the kosmotrope, preventing the solvation of the polymer surface. Water thus became a poorer solvent and the polymer attempted to minimize its solvent exposed surface area by becoming more compact, becoming more and more insoluble



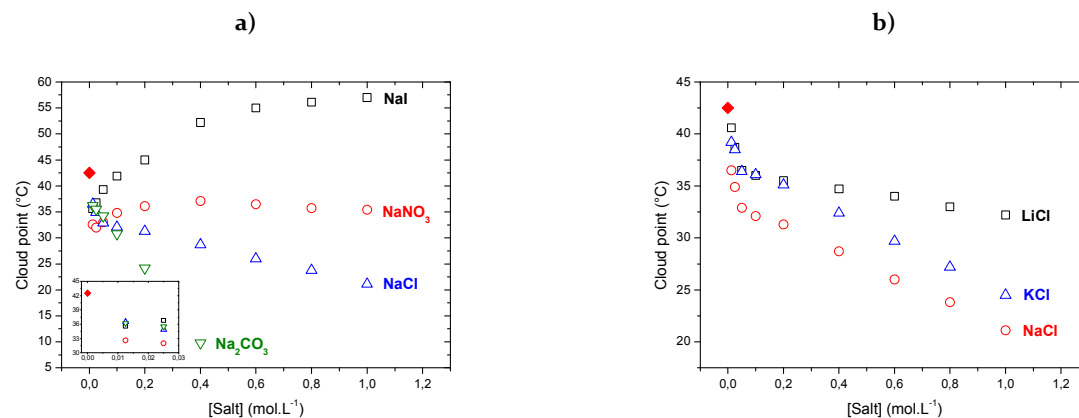
**Fig. 2** Determination of the cloud point for different P(CAAM6C) concentrations: (a) 5 g.L<sup>-1</sup>, (b) 10 g.L<sup>-1</sup>, (c) 15 g.L<sup>-1</sup>, (d) 20 g.L<sup>-1</sup>, (e) 30 g.L<sup>-1</sup>. CP: cloud points. Black plots: increasing temperature, red plots: decreasing temperature.

as the NaNO<sub>3</sub> concentration increased (salting-out). In contrast, I<sup>-</sup> chaotrope ion were much less hydrated, leading to a better solvation of the polymer surface by the water. The solution thus became a better solvent and the polymer maximized its solvent accessible surface area, thus increasing the solubility of the polyacrylamide (salting-in). Other chaotrope nitrate anion showed the same tendency than iodide, even if the change in the CP values were less pronounced. Finally, Cl<sup>-</sup> even if considered as chaotrope anion, led to other behavior as cloud points decreased as a function of the salt concentration. In theory, such anions should behave as I<sup>-</sup> according to the Hofmeister series but chloride is known to often show different behaviors. In addition, recent contribution reported in the literature highlighted the higher complexity of the salt effect<sup>33</sup> and concluded that direction and magnitude of the salt effect depended on both the nature of the ion and the nature of the polymer. For instance, it is important to notice that, in the case of poly(methyl 2-acetamidoacrylate-co-methyl methacrylate), a slight augmentation of the LCST was noticed in the presence of NaNO<sub>3</sub> while with NaCl temperature led to a linear decreasing, with a salt concentration ranging from 0 to 0.6 mol.L<sup>-1</sup>,<sup>34</sup> which was in accordance with our results.

The effect of the cations was also considered using lithium, potassium, and sodium chloride (Fig. 3b)) with an increase of salt concentration going from 0 to 1 mol.L<sup>-1</sup>. This study permitted to determine the influence of alkaline cation on the thermosensitivity property. First, it is important to mention that cations proved to have a stronger affinity with the polymer whereas anions bind weakly with the polymer.<sup>35</sup> Studies with molecular dynamics for poly(N-isopropylacrylamide) solution showed that the cation interacted with the oxygen of the amide, which is a donor group.<sup>36</sup> Experimentally, in the case of the P(CPAAM6C) synthesized, CP first drastically decreased with the salt concentration and became quite linear above a salt/amide ratio superior to 1. This could be once again explained by a salting-out effect due to interactions between water molecules

involved in hydrogen bonding with amide function of the polymer and salt. Side to this anion effect, cations can also interact with oxygen of both the C=O and the P=O bonds. Salting-out effect was more pronounced with NaCl than KCl and LiCl, following Fajans's rules which classified ionic bond in the following order: NaCl > KCl > LiCl. Sodium chloride is the most dissociable salt and afforded the higher amount of interactions with water, which was not "available" anymore to solubilize the polymer, thus leading to a lower solubility of the latter (salting-out).

Last environmental parameter which was taken in consideration before studying the complexation of gadolinium was the acidity as the latter proved to also have an impact onto thermosensitivity property. We first studied the stability of P(CPAAM6C) in acidic medium as it is known that polymers can be hydrolyzed in acidic medium, especially poly(meth)acrylates,<sup>37</sup> explaining that treatments in basic media are often advised.<sup>38</sup> P(CPAAM6C) polyacrylamide was more stable due to its amide linkage. However, phosphonate moieties could be possibly hydrolyzed resulting in phosphonic acid groups. Influence of nitric acid concentration was determined using a 2 mol.L<sup>-1</sup> acid solution during 48 hours at room temperature. Then, the nitric acid was removed by dialysis and polymer dried by freeze-drying. <sup>1</sup>H NMR spectrum carried out after treatment still demonstrated the presence of the diethyl of the phosphonate moiety, with signals at 1.25 and 4.05 ppm corresponding to the methyl and methylene groups, respectively (Fig. S4†). Cloud points were then determined as a function of the nitric acid concentration (Fig. S5†) ranging from 0 to 2 mol.L<sup>-1</sup>. CP decreased with the HNO<sub>3</sub> content and became linear from 0.1 mol.L<sup>-1</sup> of acid. As previously mentioned for the influence of salt, this curve-break corresponded to the HNO<sub>3</sub>/amide ratio equal to 1. As a consequence, we concluded that totally dissociated<sup>39</sup> nitric acid interacted with P(CPAAM6C) in the same manner than salt anions or cations, leading to a similar decrease of the cloud point. Comparison of results obtained with NaNO<sub>3</sub> and HNO<sub>3</sub>



**Fig. 3** a) Influence of salt, in particular anion: cloud points as a function of different salt concentrations (NaI, NaNO<sub>3</sub>, NaCl, Na<sub>2</sub>CO<sub>3</sub>). The inset represents a zoom at the salt concentration ranging from 0 to 0.03 mol.L<sup>-1</sup>; b) Influence of salt, in particular cation: cloud points as a function of different salt concentrations (LiCl, KCl, NaCl). ♦ represents the cloud point measured in deionized water. [P(CPAAm6C)] = 5 g.L<sup>-1</sup>.

(Fig. 3a) and S5<sup>+</sup>, respectively) on the CP values highlighted the non-negligible influence of proton on the variation of cloud points. Indeed, for a salt and acid concentration equal to 1 mol.L<sup>-1</sup>, cloud points were measured at 35.4 and 19.5 °C, respectively.

#### Complexation of gadolinium nitrate (Gd(NO<sub>3</sub>)<sub>3</sub>) onto the P(CPAAm6C) carbamoylmethylphosphonate-based polymer

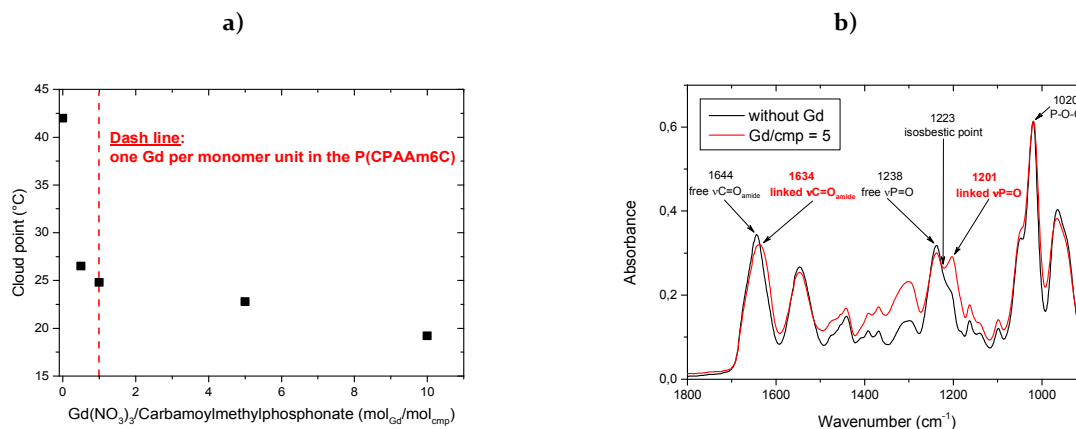
Last part of the work was devoted to the complexation of gadolinium nitrate with poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate). First, cloud points were determined as a function of the gadolinium nitrate concentration (Fig. 4a)). The number of mol of carbamoylmethylphosphonate was calculated dividing the P(CPAAm6C) mass by the molecular weight of the CPAAm6C monomeric unit. Once again, the evolution of the CP was the same than what was determined for salt concentration. The main difference was that in the present case, the important decrease of the cloud point values was obtained below a gadolinium/monomeric unit ratio equal to 1, corresponding to a Gd/amide ratio equal to 0.5. This demonstrated that Gd probably only complexed the carbamoylmethylphosphonate groups. Above, the cloud point continued diminishing but more reasonably going from 24.8 to 19.2 °C. To prove that the complexation occurred on the carbamoylmethylphosphonate function below and above the cloud point, P(CPAAm6C) and gadolinium nitrate were mixed with a Gd/monomeric unit ratio equal to 5 at 15 °C. Resulting mixture was stirred for 24 hours. The presence of gadolinium cations decreased the cloud point, and in these conditions, the CP value was 22.8 °C. As a consequence, the polymer became insoluble when temperature was raised at room temperature. So, P(CPAAm6C) was filtered and washed with water before being characterized by infrared measurements (Fig. 4b)). IR spectrum in the presence of the lanthanide clearly demonstrated the complexation of Gd with the carbamoylmethylphosphonate group. Indeed, in comparison with the infrared spectrum of

P(CPAAm6C), bands corresponding to both P=O and C=O at 1238 and 1644 cm<sup>-1</sup> were shifted to 1201 and 1634 cm<sup>-1</sup>, respectively. The shift was more obvious for the P=O band than for the C=O one, as a carbonyl of the other amide function found in the P(CPAAm6C) polymer was not modified by the complexation with gadolinium. To conclude, the infrared results were in accordance with the evolution of the cloud point values and proved that the complexation of gadolinium was still efficient even when the P(CPAAm6C) became insoluble in water. Further experiments are currently carried out to determine the sorption rate of different lanthanides including gadolinium. First results are promising as interesting sorption rates and selectivity of gadolinium onto P(CPAAm6C) material, determined from gadolinium nitrate, were already obtained.

#### Conclusions

In the present contribution, we reported the first example of an original homopolymer showing both thermosensitivity and complexing properties. Appropriate monomer, namely the diethyl-6-(acrylamido)hexyl carbamoylmethyl phosphonate, was first easily prepared in four steps and then polymerized by free radical polymerization, thus leading to poly(diethyl-6-(acrylamido)hexylcarbamoylmethylphosphonate) material. The latter was thermosensitive, as numerous polyacrylamide, and the influence of different parameters over the cloud point was determined. The addition of salt or acid proved to considerably decrease the cloud point values below a salt or acid/amide ratio inferior to 1. Then, CP continued diminishing but the effect was limited. Finally, gadolinium nitrate was added to P(CPAAm6C) water solutions. We demonstrated that Gd efficiently complexed the polymer *via* the carbamoylmethyl phosphonate function and that complexation strongly influenced the cloud point for gadolinium/carbamoylmethylphosphonate ratio below 1. Homopolymers combining both thermosensitivity and lanthanides complexing properties





**Fig. 4** a) Cloud point as a function of the gadolinium nitrate/monomer unit in the P(CPAAm6C) ratio; b) Infrared of the P(CPAAm6C) with or without complexation with gadolinium nitrate. cmp: carbamoylmethylphosphonate.

will be of great interest as (i) they are soluble in water, thus leading to an efficient complexation which (ii) modulate the cloud point, allowing an easy separation step at room temperature whilst keeping the complexation, thus (iii) permitting the recovery of gadolinium and a possible recycling of the material under acidic conditions. A more detailed study of the complexation of different lanthanides with poly(diethyl-6-(acrylamido)hexyl carbamoylmethylphosphonate), and corresponding mono or diacid derivatives, taking into account the selectivity, will be reported in a forthcoming publication.

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# Polymer Chemistry

## ARTICLE

### Graphical abstract

**First report on phosphonate-based homopolymer combining both gadolinium chelating and thermosensitive properties: synthesis and evaluation†**

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