

# Modification of Poly Acrylic Acid Using Calix[4]arene Derivative for the Adsorption of Toxic Heavy Metals

Abdol Reza Hajipour,<sup>1,2</sup> Sakineh Habibi,<sup>2</sup> Arnold E. Ruoho<sup>1</sup>

<sup>1</sup>Department of Pharmacology, University of Wisconsin, Madison, Wisconsin 53706-1532

<sup>2</sup>Pharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, IR, Iran

Received 14 February 2009; accepted 6 February 2010

DOI 10.1002/app.32246

Published online 26 May 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly acrylic acid (PAA) was grafted with *p*-*t*-butyl calix[4]arene diamine (distal cone) (2) to adsorb toxic heavy metal and alkali metal cations. The grafting method includes the amidation reaction of PAA with calixarene diamine derivative 2 which was carried out in *N,N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP) as solvents. The modified PAAs (PAA-C1 and PAA-C2) were characterized by FTIR, <sup>1</sup>H-NMR, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). PAA-C1 and PAA-C2 were used to evaluate the sorption properties of some toxic heavy metal cations (Co<sup>2+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>,

Hg<sup>2+</sup>), alkali metal cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>), and Ag<sup>+</sup>. Results showed that the modified PAAs were good sorbents for heavy metal and alkali metal cations. The main goal of this project is to design hydrophobically modified PAA that is suitable for ion selective membranes and chemical sensor devices for adsorption of toxic heavy metals. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 818–826, 2010

**Key words:** calixarenes; ionophore; poly(acrylic acid); amidation; sorption; toxic heavy metals; hydrophobically modification

## INTRODUCTION

The importance of controlling the levels of environmental pollutants has generated increasing interest<sup>1–4</sup> in the development of novel sensors such as calixarene-based ion-selective electrodes or chemically modified field-effect transistors for the detection of heavy metals. Toxic heavy metals are dangerous because of their accumulative and persistent character in the environment. Some of these metals such as cadmium, mercury, copper, and lead are toxic and pose a threat to human health.<sup>5</sup> From an environmental and economic viewpoint, there remains a need to discover more selective and effective extractants for such toxic heavy metals.<sup>6–8</sup>

Heavy metal ion removal from waters has been the subject of extensive technological research and recovering processes.<sup>9</sup> Several different types of materials have been studied for the treatment of aqueous streams contaminated with heavy metals, among them polymers,<sup>10–12</sup> amorphous silica,<sup>13,14</sup> clays,<sup>15–17</sup> and zeolites.<sup>18,19</sup> Nevertheless these materials have shown several problems like low mechanical and thermal stability, weak chemical union with the metals, poor removal efficiency, high cost, etc. These factors have led the scientific community to develop new techniques to remove heavy metals

from the environment. The majority of the effective and economic methods are based on adsorption process, so the synthesis of adsorbents for the removal of toxic heavy metal ions from wastewater is a continuing research objective of environmental pollution control processes.

Recently PAA has found wide range of applications by surface modification with functional polymers and specific molecules.<sup>20,21</sup> PAA grafted porous membranes can be used for example in drug delivery systems where the membranes act as selective filters changing the pore size by external chemical signals.<sup>22,23</sup>

Calixarenes have generated considerable interest<sup>24</sup> as useful building blocks for the synthesis of receptors for cations, anion and neutral molecules. During the last decades, they have attracted much attention<sup>25</sup> as a type of key receptor in super-molecular receptors. The increasing interest for these compounds is stimulated by the simple, large scale synthesis of calixarenes and the different ways that they can selectively be functionalized at the lower (phenolic groups) or upper rim (aromatic nuclei).<sup>26,27</sup> Modified Calix[4]arenes have been found to be extremely useful in host-guest chemistry due to their tendency to form complexes with metal cations and neutral molecules. Based on this property, specific ligands for analytical chemistry,<sup>28</sup> membranes,<sup>29</sup> decontaminating agents for waste water,<sup>30,31</sup> dendrimers and star polymers from calixarene core<sup>32,33</sup> and catalysts for polymer synthesis<sup>34</sup> have been prepared. Chemical modifications of calix[4]arenes can

Correspondence to: A. R. Hajipour (Haji@cc.iut.ac.ir).

also be exploited to keep macrocycle into a fixed conformation and at the same time to provide a special reactivity.<sup>35</sup>

Because of the commercial availability and industrial importance of PAA, and the easy preparation of calixarenes in large scale, we selected calixarene derivative 2 as a good ionophore and distributed this compound in the PAA chain. To the best of our knowledge, no report concerning this topic has been published to date. This article firstly reports the preparation, characterization, and sorption properties towards some selected heavy metal ( $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ ), silver and alkali metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Ag}^+$ ) of calix[4]arene-grafted PAA.

## EXPERIMENTAL

### Materials

PAA with average molecular weight of 2000 g/mol was purchased from Aldrich Co. The other materials were from Merck Co. and used without further purification. DMF was purified with distillation under reduced pressure and stored over the molecular sieve. NMP was distilled under reduced pressure over calcium hydride and stored over the molecular sieve. Reactions were monitored by TLC on silica gel. *p*-*tert*-Butyl calix[4]arene was prepared as described.<sup>36</sup>  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{CsNO}_3$ ,  $\text{AgNO}_3$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ , and  $\text{Hg}(\text{NO}_3)_2$  were purchased from Merck and were used as received. All aqueous solutions were prepared with deionized water.

### Instrumentation

IR spectra were recorded on a FT/IR-680 plus spectrophotometer using KBr pellets. Band intensities are assigned as weak (w), medium (m), and strong (s). Band shapes assigned as shoulder (sh), sharp (s), and broad (br).  $^1\text{H-NMR}$  spectra were recorded on 500 MHz instrument, using  $\text{DMSO-d}_6$  as solvent and tetramethylsilane as a chemical shift reference (tube diameter 5 mm). Thermal gravimetric analysis (TGA) was obtained by a Mettler TGA-50 under air atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ . Differential scanning calorimetry (DSC) was obtained by a Mettler DSC-30 under nitrogen atmosphere at a rate of  $10^\circ\text{C}/\text{min}$ .

### Synthesis of calix[4]arene dinitro derivative (1)

A mixture of *p*-*t*-butyl calix[4]arene (10.000 g, 0.015 mol), anhydrous  $\text{K}_2\text{CO}_3$  (2.430 g, 0.0176 mol) and *p*-nitrobenzyl bromide (6.670 g, 0.0307 mol) in  $\text{CH}_3\text{CN}$  (80 mL) was refluxed for 20 h. The solvent was removed under reduced pressure, the mixture was

treated with  $\text{CH}_3\text{Cl}$  (200 mL) and filtered. The filtrate was concentrated under reduced pressure (50 mL). Then  $\text{CH}_3\text{OH}$  (100 mL) was added and the pale yellow crystals appeared gradually. After a few hours the crystals were filtered under vacuum and washed with cold methanol to give 12.9 g (91.6%) of the pure compound 1. m.p. =  $148\text{--}149^\circ\text{C}$ .

FTIR (KBr,  $\text{cm}^{-1}$ ): 3434 (s, br), 3113 (m), 3047 (m), 2959 (s), 2906 (s), 2866 (s), 1606 (m), 1524 (s), 1483 (s), 1461 (s), 1393 (m), 1366 (s), 1348 (s), 1347 (s), 1297 (m), 1193 (s), 1123 (m), 1109 (m), 1031 (m), 946 (m), 919 (w), 824 (s), 852 (s), 819 (m), 796 (m), 780 (m), 736 (s), 699 (w), 650 (w), 629 (w), 578 (w), 552 (m), 530 (m)  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta$  0.96 (s, 18H), 1.29 (s, 18H), 3.34 (d, 4H,  $J = 13.0$  Hz), 4.23 (d, 4H,  $J = 13.0$  Hz), 5.17 (s, 4H), 6.83 (s, 4H), 7.08 (s, 4H), 7.26 (s, 2H), 7.91 (d, 4H,  $J = 8.5$  Hz), 8.17 (d, 4H,  $J = 8.6$  Hz). Elemental analysis: Calculated for  $\text{C}_{58}\text{H}_{66}\text{N}_2\text{O}_8$ : C (75.79%), H (7.24%), N (3.05%); Found: C (75.81%), H (7.23%), N (3.06%).

### Reduction of compound 1 (2)

To a mixture of 1 (4.500 g, 0.0049 mol), Raney-Ni (5.490 g), ethyl acetate (80 mL), and MeOH (40 mL) was added gradually  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  (11.50 mL). The reaction mixture was stirred at room temperature for 1 h, and was then refluxed for 2 h with continuous stirring. Then the solvent was evaporated under vacuum and toluene (300 mL) was added and heated to its boiling point. The hot mixture was filtered and after concentrating the solvent, the white crystals appeared. The crystals were filtered and washed with cold methanol to give 3.00 g (71.43%) of compound 2. m.p. =  $278^\circ\text{C}$ .

FTIR (KBr,  $\text{cm}^{-1}$ ): 3551 (m), 3469 (m), 3415 (m), 3176 (m, br), 3048 (m), 3026 (m), 2954 (s), 2906 (s), 2869 (s), 1637 (m), 1617 (m), 1481 (s), 1456 (m), 1384 (m), 1361 (m), 1304 (m), 1284 (m), 1257 (w), 1250 (m), 1199 (s), 1157 (m), 1124 (m), 1102 (m), 946 (w), 889 (w), 870 (m), 815 (m), 781 (s), 729 (m), 709 (m), 695 (m), 673 (m), 619 (m), 591 (m), 552 (w),  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ ,  $25^\circ\text{C}$ ):  $\delta$  0.91 (s, 18H), 1.16 (s, 18H), 1.8 (brs, 4H), 3.20 (d, 4H,  $J = 13.0$  Hz), 4.18 (d, 4H,  $J = 13.0$  Hz), 4.61 (s, 4H), 7.01–7.26 (m, 18H). Elemental analysis: Calculated for  $\text{C}_{58}\text{H}_{70}\text{N}_2\text{O}_4$ : C (81.08%), H (8.21%), N (3.26%); Found: C (80.80%), H (8.40%), N (3.00%).

### Grafting procedures: reaction of PAA with compound 2

#### METHOD 1

In a typical modification reaction, 0.84 g (11.66 mmol) of PAA was dissolved in 20 mL of NMP at  $60^\circ\text{C}$  over a period of 2 h. Then, 0.50 g (0.58 mmol) of compound 2 and 0.123 g of dicyclohexyl

carbodiimide (DCC) (0.65 mmol), separately dissolved in 10 mL of NMP, were introduced successively into the PAA solution under vigorous stirring. The temperature was maintained at 60°C for 24 h. The system was then cooled to room temperature and the dicyclohexyl urea crystals were removed by filtration. The precipitate was washed with hot (60°C) NMP (2 × 10 mL) and methanol (2 × 50 mL) and finally dried at 80°C for 4 h under reduced pressure to obtain 0.45 g of white powder (PAA-C1).

FTIR (KBr): 3000–3590 (s, br), 2956 (s), 2867 (m), 1756 (m), 1679 (s), 1603 (m), 1481 (s), 1384 (s), 1362 (s), 1306 (m), 1285 (m), 1257 (m), 1240 (m), 1200 (s), 1158 (m), 1123 (m), 1090 (m), 976 (w), 945 (m), 926 (w), 915 (w), 891 (m), 874 (s), 836 (m), 817 (s), 782 (s), 739 (m), 709 (m), 675 (m), 619 (m), 603 (m), 591 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>, 25°C): δ 0.98 (s, 18H), 1.24 (s, 18H), 1.78 (m, 2H), 1.85 (m, 2H), 2.01 (m, 2H), 2.18 (m, 2H), 2.78 (m, 2H), 3.21 (d, 4H), 4.12 (d, 4H), 4.60 (s, 4H), 6.80–7.00 (m, 18H).

## METHOD 2

0.84 g (11.66 mmol) of PAA and 0.50 g (0.58 mmol) of compound 2 were dissolved in 30 mL of DMF at 60°C over a period of 2 h. Then, the solution was stirred at 140°C for 2 h and at 60°C overnight. The reaction mixture was then cooled to room temperature and added 50 mL of methanol. The precipitate was washed with methanol (2 × 50 mL) and finally dried at 80°C for 4 h under reduced pressure to obtain 0.48 g of white powder (PAA-C2).

## SORPTION STUDIES

### Preparation of metal picrates

Heavy metal picrates were prepared by the addition of a 1.0 × 10<sup>-2</sup> M solution of metal nitrates to a 2.5 × 10<sup>-5</sup> M aqueous picric acid solution and shaken at room temperature for 1 h. The alkali picrates were the solutions containing 2.5 × 10<sup>-5</sup> M of picric acid and 1.0 × 10<sup>-3</sup> M of metal nitrate salt.

### Picrate extraction procedure

Picrate extraction experiments were performed following the Cram procedure.<sup>37–39</sup> 10 mg of PAA-C1 or PAA-C2 was mixed with 10 mL of an aqueous solution containing the metal picrate solution and was shaken at room temperature for 30 min in a stoppered glass flask. The sorbent was removed by filtration before measurements. The concentration of the picrate remaining in aqueous phase after the sorption was determined spectrophotometrically using a Perkin–Elmer Lambda 6 spectrophotometer equipped with integrating sphere.

The percent sorption of ion (S%) has been calculated as

$$S(\%) = \left[ \frac{C_i - C_e}{C_i} \right] \times 100 \quad (1)$$

where C<sub>i</sub> and C<sub>e</sub> are the initial and final concentration of metal picrates before and after sorption, respectively.

### Determination of acid number

Acid number for PAA, PAA-C1 and PAA-C2 was determined according to ASTM D 1045. The procedure was as follows:

0.1 g PAA was weighed into a 100 mL Erlenmeyer flask and dissolved in 25 mL of absolute ethanol. Then a few drops of bromthymol blue indicator were added and the solution was titrated with a solution of 0.01 N NaOH. Also the blank titration was made on 25 mL of the solvent used to dissolve the sample. The acid number expressed as the milligrams of NaOH per gram of the sample, as follows:

$$\text{Acid number} = \{(A - B)N \times 56.1\} / C$$

where

A = NaOH or KOH solution required for titration of the sample, mL,

B = NaOH or KOH solution required for titration of the blank, mL,

N = normality of the NaOH or KOH solution, and

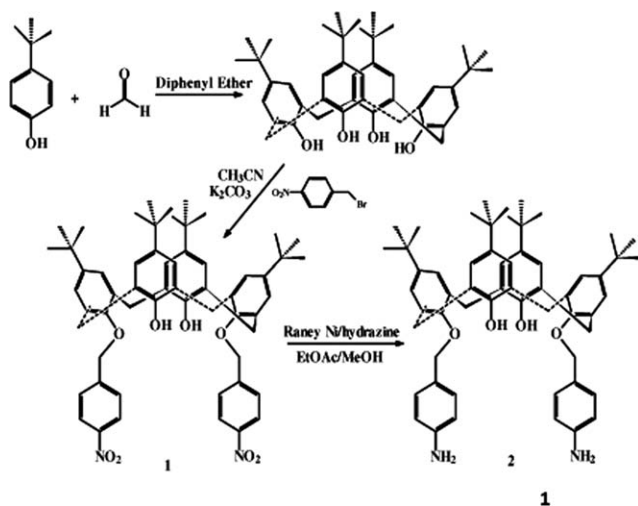
C = sample used, g

For measuring the acid number of PAA-C1 and PAA-C2, we used the above procedure but due to insolubility of PAA-C1 and PAA-C2 in ethanol, we dissolved 0.05 g of the sample in 5 mL of DMF and then diluted the solution with ethanol to 25 mL. The acid number for PAA, PAA-C1, and PAA-C2 was 435.2, 352.0, and 332.0 respectively. These values showed that about 20% of carboxylic acid groups were substituted with amide groups bearing calixarene units and the grafting percentage for PAA-C1 and PAA-C2 was 19.12 and 23.71% respectively.

## RESULTS AND DISCUSSION

### Synthesis

Calixarenes have been widely used as three-dimensional building blocks for the construction of artificial molecular receptors capable of recognizing neutral molecules, cations and more recently anions.<sup>24–26</sup> Thus, having chosen the *p*-*tert*-butyl calix[4]arene as the basis for derivatives, synthetic way had to be developed to enable the derivatization of the molecule. In this work, *p*-*tert*-butylcalix[4]arene has been



**Scheme 1** Synthesis of calix[4]arene dinitro and diamino derivatives 1 and 2.

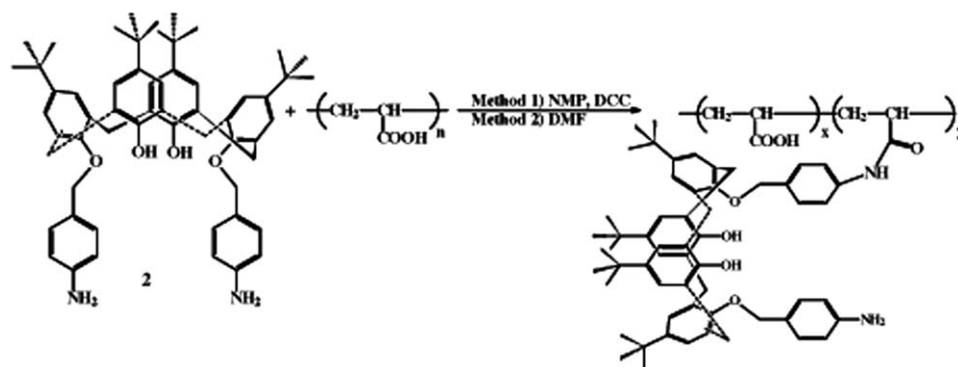
treated with *p*-nitrobenzyl bromide in dry acetonitrile in the presence of potassium carbonate to obtain the cone conformer of 1 in 91.6% yield. The preparation of the compound 1 has been reported in literature but we have prepared it in higher yield. A reduction of the nitro groups of 1 by Raney-Ni/ $N_2H_4 \cdot H_2O$  gave the amino derivative 2 in 71.4% yield (Scheme 1). Completion of the reaction was followed by IR spectroscopy, which showed the disappearance of the band because of the nitro groups at 1524 and 1348  $cm^{-1}$  and appearance of the new bands at 3551 and 3469  $cm^{-1}$  for the amino groups. The compounds 1 and 2 were characterized by FTIR,  $^1H$ -NMR and elemental analysis.

The modification of PAA with compound 2 was performed using two methods: in a system of dry NMP/DCC and in dry DMF as a solvent (Scheme 2). We investigated the best conditions for the reaction of PAA with calix diol. The grafting yield in DMF (method 2) was higher than in method 1. We performed the reaction by varying temperature, the reaction time and the amount of solvent. Also we changed the ratio of 2 to PAA and finally we could

find the best conditions. We could reduce the molar ratio of 2/PAA to 1/20 while maintaining the good extraction ability which is comparable to the calix[4]-arene diamine 2. This result is much valuable. It means that we can use much smaller amount of ionophore with good extraction yield. Thus, these modified polymers are superior to the monomer 2 in ion extraction.

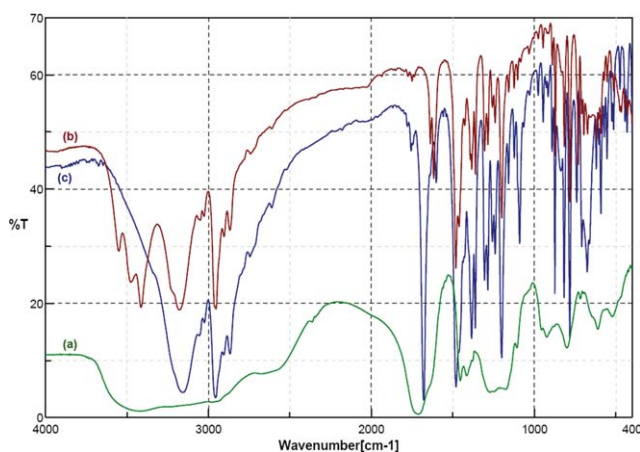
FTIR spectra of PAA, calix diamine 2 and PAA-C were demonstrated in Figure 1. Comparing with IR spectra of them showed distinct absorption peaks especially for amide and phenyl groups, which indicated that the calixarene diamine derivative had been grafted with PAA successfully. We followed the reaction with IR spectroscopy and compared the intensity of the peak at 1680  $cm^{-1}$  (the characteristic absorption peak of amide group) in each run. For comparison, FTIR spectra of PAA-C1 and PAA-C2 have been shown in Figure 2. As seen in IR spectra, the peak of amide group is more intense in the case of PAA-C2 which verified the higher grafting yield in method 2.

Also the  $^1H$ -NMR spectra of calix diamine 2, PAA and PAA-C confirmed the grafting of 2 with PAA.  $^1H$ -NMR spectrum of PAA showed the characteristic signals of  $-CH_2$  and  $-CH$  groups in the region of 1–2.1 and 2.2–2.6 ppm respectively. In  $^1H$ -NMR spectrum of calix diamine 2 the characteristic signals of four *t*-butyl groups appeared as two sharp peaks at 0.91 and 1.16 ppm. The typical signal patterns (two doublets) at 3.20 and 4.18 ppm were assigned to the equatorial and axial protons of the methylene bridges of the calix[4]arene in the cone conformation. The protons of hydroxyl and phenyl groups appeared in the region of 7.01–7.26 ppm. In the  $^1H$ -NMR spectrum of PAA-C the characteristic signals of both PAA and calix units appeared: the signals of *t*-butyl groups at 0.98 and 1.24 ppm, methylene groups of PAA at 1.78–1.85 ppm, methyne groups of PAA at 2.18 and 2.78 ppm, doublets of methylene bridge in calix moieties at 3.21, 4.12 ppm and the signals of calixarene phenyl groups in the region of 6.80–7.00 ppm. These results verified the



**Scheme 2** Grafting of calix[4]arene diamine derivative 2 onto PAA.



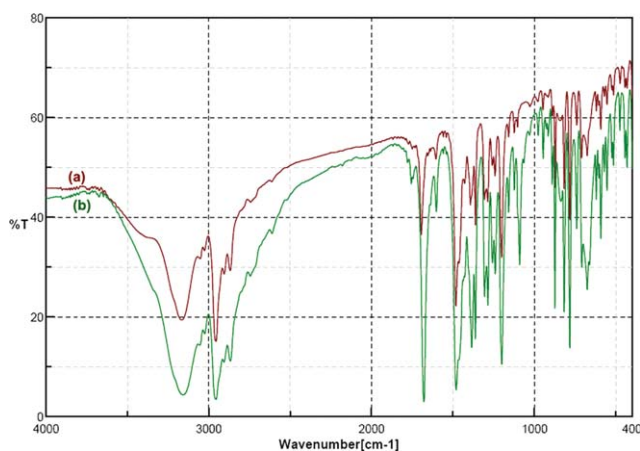


**Figure 1** FTIR spectra of (a) PAA, (b) calix diamine 2 and (c) PAA-C2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

incorporation of calix[4]arene diamine 2 onto PAA (Fig. 3).

Unfortunately,  $^1\text{H-NMR}$  spectrum of PAA-C1 was not as good as the spectrum of PAA-C2, because PAA-C1 is less soluble than PAA-C2 in  $\text{DMSO-d}_6$ . So we couldn't investigate and compare the grafting yield of the polymers. Therefore we use the acid number determination procedure to estimate the grafting yield of PAA-C1 and PAA-C2. The acid number value of PAA-C2 is larger than the value of PAA-C1 which indicates the higher grafting yield for PAA-C2.

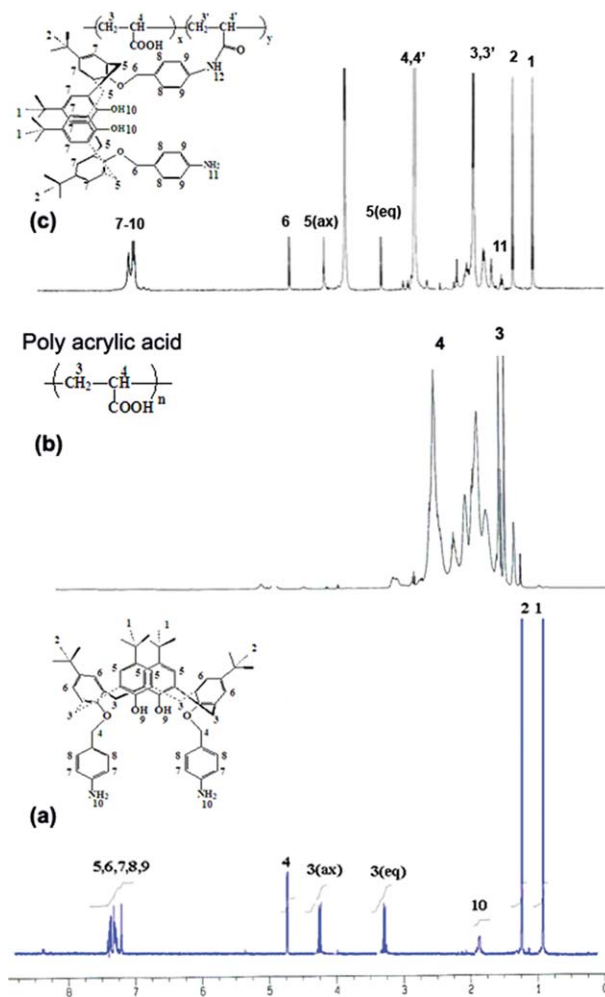
The solubility of PAA was changed after modification with compound 2. PAA is soluble in water, MeOH and polar aprotic solvents like DMF, DMSO, DMAc and insoluble in common organic solvents like benzene, cyclohexane, dichloromethane and chloroform, but PAA-C1 and PAA-C2 are hydrophobic and only soluble in polar aprotic solvents. Because of the introduction of the calix diamine 2 as



**Figure 2** FTIR spectra of (a) PAA-C1 and (b) PAA-C2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

a rigid and bulky pendent group in the PAA backbone, we expected these solubility properties for PAA-C1 and PAA-C2. Of course, PAA-C1 is slightly soluble in polar aprotic solvents like DMF, DMAc and DMSO. For this reason, we couldn't take a good  $^1\text{H-NMR}$  spectrum for this compound. It seems that less solubility of PAA-C1 in these solvents is attributed to slight crosslinking between two PAA chains and one calix diamine. The solubility of the modified polymers and compound 2 has been shown in Table I. These results are much valuable, so that we can use these hydrophobically modified polymers as ion selective polymers in aqueous ionic media for separation of toxic heavy metal cations.

Thermogravimetric analysis (TGA) and DSC of PAA and PAA-C were determined and the TG, DTG, and DSC curves were presented in Figure 4. Both samples exhibited good resistance to thermal decomposition up to  $200^\circ\text{C}$  and began to decompose gradually above that temperature. PAA had four



**Figure 3**  $^1\text{H-NMR}$  (400 MHz) spectra of (a) calix diamine 2, (b) PAA and (c) PAA-C2. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE I  
Solubility of Compound 2, PAA, PAA-C1, and PAA-C2<sup>a</sup>

Polymer	H <sub>2</sub> O	MeOH	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	Acetone	THF	DMF	DMSO	DMAc
Compound 2	–	–	±	±	–	–	+	+	+
PAA	+	+	–	–	+	+	+	+	+
PAA-C1	–	–	–	–	–	–	±	±	±
PAA-C2	–	–	–	–	–	–	+	+	+

<sup>a</sup> Concentration: 5 mg mL<sup>-1</sup>; +: Soluble at room temperature; ±: slightly soluble; –: Insoluble.

thermal decomposition steps with thermal decomposition temperature of 278.0, 314.7, 490.7, and 626.3°C and the corresponding weight loss of 13.3, 8.4, 50.6 and 31.7% in each steps. TGA curve of PAA-C1 and PAA-C2 were similar to each other. As an example, PAA-C2 showed three thermal decomposition steps with thermal decomposition temperature of 212.0, 402.7, 710.7°C and weight loss of 8.15, 77.26, and 12.93%, respectively. As can be seen from these curves there is an endothermic peak at about 230°C and there are two exothermic peaks at around 360°C and 450°C for PAA. The peak at 230°C can be attributed to formation of PAA anhydride. The two exothermic peaks can be ascribed to the degradation of PAA anhydride and thermal decomposition. In DSC

curve of PAA-C there are two endothermic peaks at 230 and 342°C which can be attributed to minor anhydride formation by residual PAA and thermal degradation.  $T_{5\%}$ ,  $T_{10\%}$  and char yield of PAA-C1 and PAA-C2 has been shown in Table II.

### Evaluation of sorption capabilities

Calix[n]arenes are well-known to act as ligands or to host various species including small organic molecules, metal cations, and some anions. For example, compounds bearing four ether groups at lower rim showed good binding properties towards alkali metal cations but were inert towards alkaline earth metal ions, divalent, and trivalent metal cations.<sup>37,41,42</sup> This binding selectivity was related both to the macrocycle ring size and its conformation. However a fine tuning of the cation binding was possible by varying the alkoxy groups at the lower rim.<sup>43</sup> The complexation of transition metals has been reported to be favored by the introduction of functional groups containing soft donor atoms such as nitrogen, sulfur, and phosphorus.<sup>44,45</sup> Alkoxy lower rim substituted calix[4]arene derivatives have been shown to bind silver cations.<sup>42</sup> In this case, a cation- $\pi$  interaction appeared to be operative<sup>46</sup> since the silver ion was bound in a sandwich-like manner between two opposite phenyl rings. The selective Ag<sup>+</sup> recognition is an important requisite for several technological and biomedical applications such as photographic materials and radioimmunotherapy.<sup>47</sup>

The main goal of this study was the evaluation of sorption ability towards toxic metal cations by

TABLE II  
Some Thermogravimetric Analysis Results of PAA, PAA-C1 and PAA-C2

Polymer	$T_{5\%}$ (°C) <sup>a</sup>	$T_{10\%}$ (°C) <sup>b</sup>	Char yield (%) <sup>c</sup>
PAA	245	280	28.57
PAA-C1	205	320	25.32
PAA-C2	212	355	26.76

<sup>a</sup> Temperature at which 5% weight loss was recorded by TG at heating rate of 10°C/min in N<sub>2</sub>.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TG at heating rate of 10°C/min in N<sub>2</sub>.

<sup>c</sup> Percentage weight of material left undecomposed after TG analysis at maximum temperature 600°C in N<sub>2</sub>.

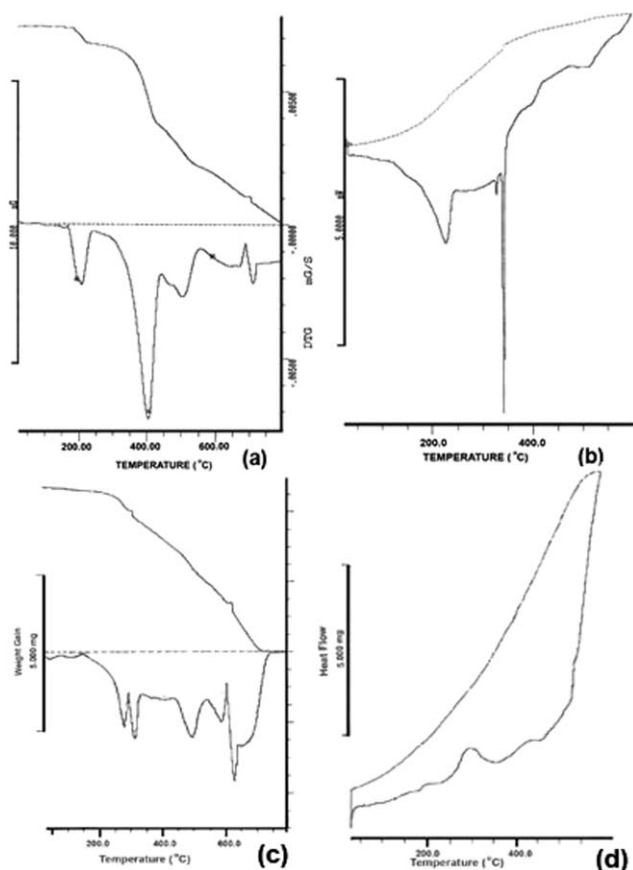


Figure 4 (a) TGA/DTG thermogram of PAA-C2, (b) DSC thermogram of PAA-C2, (c) TGA/DTG thermogram of PAA, (d) DSC thermogram of PAA.

**TABLE III**  
Extraction Values of Calix Diamine 2, PAA-C1 and PAA-C2 for Silver and Alkali Metal Cations

		Cations <sup>a</sup>			
		Ag <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Cs <sup>+</sup>
Compound 2	Initial absorbance ( $A_0$ )	0.372	0.345	0.292	0.230
	Final Absorbance ( $A$ )	0.213	0.140	0.131	0.229
	Extraction Percentage <sup>b</sup> (S%)	42.74	59.42	55.14	-
PAA-C1	Initial absorbance ( $A_0$ )	0.372	0.345	0.292	0.230
	Final Absorbance ( $A$ )	0.321	0.241	0.192	0.231
	Extraction Percentage <sup>b</sup> (S%)	13.71	30.14	34.25	0.00
PAA-C2	Initial absorbance ( $A_0$ )	0.372	0.345	0.292	0.230
	Final Absorbance ( $A$ )	0.202	0.139	0.167	0.231
	Extraction Percentage <sup>b</sup> (S%)	45.70	59.71	42.81	0.00

<sup>a</sup> Concentration:  $1.0 \times 10^{-3}$  M of alkali nitrate salts in aqueous solution containing  $2.0 \times 10^{-5}$  M of picric acid.

<sup>b</sup> 10 mg of modified PAA (solid phase) in 10 mL of aqueous picrate solution (aqueous phase) at 25°C for 30 min.

modified PAA. We grafted calix[4]arene derivative 2 as a good ionophore for silver, alkali metal, and transition metal cations to PAA as a useful industrial polymer. The extraction ability of calix diamine 2, PAA-C1, and PAA-C2 towards metal cations (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, and Hg<sup>2+</sup>) was measured using the Cram picrate method in a solid-liquid system. The sorption ability data of calix diamine 2, PAA-C1 and PAA-C2 are collected in Tables III and IV. These data have been obtained by using a 10 mg of the polymers for sorption of metal cations from aqueous solution. The equilibrium concentration of picrate in the aqueous phase has been determined spectrophotometrically.

From the results, it was observed that both PAA-C1 and PAA-C2 were effective sorbents for all mentioned cations especially for Cd<sup>2+</sup>. Hence these extraction abilities have to be ascribed to the complexation ability of the calixarene macrocycle in the polymer backbone. The higher sorption ability for modified PAA towards transition metal cations was

due to the presence of amide groups, providing an appropriate binding environment for these cations. The amide derivatized calixarenes are effective sorbents for these cations. Because the amide group is preferable to complex the more polarizable transition metal ions especially Cu, Cd, Co, and Hg due to cation- $\pi$  interactions. PAA-C2 was better sorbent than PAA-C1. This is due to the higher grafting yield for PAA-C2 as seen in FTIR spectra. The sequence of sorption efficiency of PAA-C1 and PAA-C2 for mentioned metal cations was Cd<sup>2+</sup> > Co<sup>2+</sup> > Cu<sup>2+</sup> > K<sup>+</sup> > Na<sup>+</sup> > Hg<sup>2+</sup> > Ag<sup>+</sup> and Na<sup>+</sup> > Cd<sup>2+</sup> > Cu<sup>2+</sup> > Co<sup>2+</sup> > Ag<sup>+</sup> > K<sup>+</sup> > Hg<sup>2+</sup> respectively. The calix[4]arene based PAA was a good ionophore especially for Cd<sup>2+</sup>. Overall these results demonstrate that PAA-C has the highest selectivity for absorbing Na<sup>+</sup> and good sorption ability towards Cd<sup>2+</sup>, Co<sup>2+</sup>, and Cu<sup>2+</sup>. Also PAA-C1, PAA-C2 and calix diamine 2 had no sorption ability towards Cs<sup>+</sup> ion. This result showed that the binding ability of the compound 2 and PAA-C is related to the macrocycle ring and metal

**TABLE IV**  
Extraction Values of Calix Diamine 2, PAA-C1 and PAA-C2 for Heavy Metal Cations

		Cations <sup>a</sup>			
		Cu <sup>2+</sup>	Co <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>
Compound 2	Initial absorbance ( $A_0$ )	0.232	0.234	0.242	0.236
	Final absorbance ( $A$ )	0.130	0.191	0.190	0.156
	Extraction percentage <sup>b</sup> (S%)	43.96	18.37	18.80	28.11
PAA-C1	Initial absorbance ( $A_0$ )	0.232	0.234	0.242	0.236
	Final absorbance ( $A$ )	0.111	0.124	0.107	0.162
	Extraction percentage <sup>b</sup> (S%)	36.64	41.45	48.03	30.08
PAA-C2	Initial absorbance ( $A_0$ )	0.232	0.234	0.242	0.236
	Final absorbance ( $A$ )	0.147	0.137	0.119	0.152
	Extraction percentage <sup>b</sup> (S%)	52.15	47.68	53.27	35.59

<sup>a</sup> Concentration:  $1.0 \times 10^{-2}$  M of transition metal nitrates in aqueous solution containing  $2.0 \times 10^{-5}$  M of picric acid.

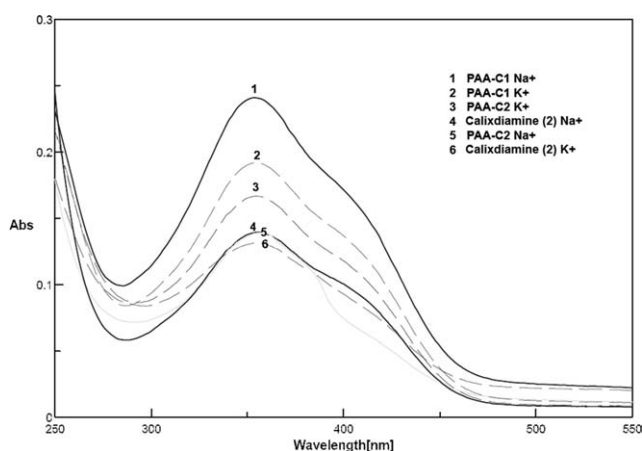
<sup>b</sup> 10 mg of modified PAA (solid phase) in 10 mL of aqueous picrate solution (aqueous phase) at 25°C for 30 min.

ion size. Figures 5 and 6 show the UV curves for final picrate solutions of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  respectively.

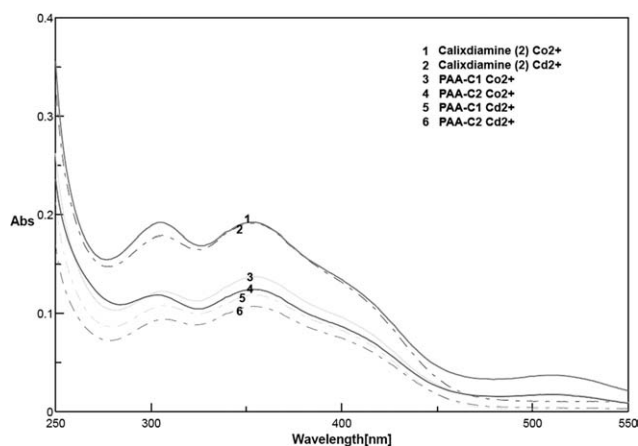
Comparing the extraction ability of PAA-C1, PAA-C2 and calix[4]arene diamine 2 shows that the modified PAA is better sorbent than the monomeric compound 2. On the other hand, upon grafting calix[4]arene diamine 2 to PAA, the compound 2 was distributed through the PAA chain. We could use much smaller amount of ionophore by decreasing molar ratio of 1/PAA to 1/20. This is worthy and economically important. On the other hand, in industry when we use a sorbent for metal ion extraction, we need a surface activator to remove a specific ion, but the carboxylic acid groups in the PAA backbone act as a surface activator and we do not need to use an additive for metal ion extraction. This modified polymer is a good candidate for using as ion selective polymer for removing silver, alkali metal and heavy metal cations. Consequently, it was clearly found out that modification of PAA with compound 2 was useful approach for toxic heavy metal sorption.

## CONCLUSION

The preparation and characterization of calix[4]arene diamine derivative (2) and modification of PAA with this calix[4]arene derivative was achieved. The sorption studies of some heavy metal, silver and some alkali metal cations were performed by the compound 2, PAA-C1, and PAA-C2 as sorbent materials. From the sorption results of heavy metal cations, it was revealed that the modified PAAs exhibited excellent sorption properties and PAA-C2 was more effective sorbent than PAA-C1. The main advantages of grafting calix diamine derivative 2 onto PAA were industrial and economical importance, reducing the amount of ionophore for metal



**Figure 5** UV curves for final aqueous solutions containing  $\text{Na}^+$  and  $\text{K}^+$ .



**Figure 6** UV curves for final aqueous solutions containing  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$ .

ion sorption with excellent sorption capabilities, hydrophobically modification, so using in aqueous ionic media for ion sorption and high thermal stability of modified PAA. These modified polymers are good ionophores for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$  and toxic heavy metal cations.

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