Thiacalix[4]amido-based Netty Polymers: Novel Sorbents for Heavy Metal Cations and Derivatives of Aniline

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A B S T R A C T

By reacting *p-tert*-butylthiacalix[4]arene with ethyl chloroacetate using KI as catalyst in K_2CO_3/acetone, 5,11,17,23-*tert*-butyl-25,26,27-*tri*-ethoxy-2-acetylthiacalix[4]arene and 5,11,17,23-*tert*-butyl-25,26,27,28-*tetra*-ethoxy-2-acetylthiacalix[4]arene were prepared in moderate yields. Their further reactions with *bi*-(ethyleneimine) or *tri*-(ethyleneimine) produced the first examples of four *tri*-bridged and *tetra*-bridged thiacalix[4]amido-based polymers with porous and netty architectures in yields of 81%, 84%, 86%, 89%, respectively. The structures of these polymers were confirmed by FTIR, elemental analysis, ^{1}H NMR, and SEM, etc. The M_n of these novel polymers were 18000~22000 which indicated that approximately 17~20 thiacalix[4] arene units are present in each polymer molecule. The adsorption experiments of these novel polymers showed excellent adsorption abilities for soft metal cations Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+}, but low adsorption towards hard metal cations Na^+ and K^+. Also, these novel polymers exhibited outstanding adsorption capacity for a series of aniline derivatives. The highest adsorption percentages were 93.4% and 94.2% for Cu^{2+} and *p*-nitroaniline, respectively. The saturation adsorption capacities of thiacalix[4]amido-based polymer with *tri*-(ethyleneimine) for Cu^{2+} and *p*-nitroaniline were as high as 1.51 mmol/g and 1.34 mmol/g, respectively. The adsorption percentages of novel polymers reduced sharply in pH < 4, but they can be recycled by desorption in 10% ammonia solution.

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INTRODUCTION

Calixarenes were well known as excellent building blocks to construct variety of receptors for ions and biomolecules in the past few decades [1]. With the extensive and in-depth studies of all kinds of calixarene derivatives, more and more attentions were paid to calixarene-based polymers which may be processed into materials as effective extractants for toxic heavy metals cations and polluted organic molecules from waters [2-4]. Up to now, two methods have been used to synthesize calixarenes-based polymers. One is the grafting method, i.e., immobilization of calixarene derivatives on polymer matrix such as peptide resin [5], PEG [6], polystryrene [7], dextrans [8], polysilane [9], Merrifield resin [10], and polyacrylate [11]. Another method is copolymerization of calixarene with other active bis-functional monomers, such as bisphenols [12],

styrene [13,14], vinyl acetate [15], diisocyanate [16], poly(ethylene-glycol) [17], tetraphthaloyl dichloride [18], and norbornene [19].

Also, from the literature, it may be concluded that the guest recognition abilities of calixarene-based polymers are greatly influenced by the structures and contents of calixarene units, and some of them exhibit excellent extraction or adsorption abilities for metal cations such as heavy metal cations, anions and organic molecules such as amino acid esters [4-19]. The excellent complexation abilities of these polymers for ions exhibit potential applied prospective in ionic exchange and adsorption, ionic extraction and separation technologies.

Recently, thiacalixarenes, as novel calixarene building block, have attracted much research interests compared with "classical" calixarenes, because the presence of sulphur atoms in calixarene skeleton results in many novel features such as easy chemical modification, different size and more flexible conformational behaviour, specially, the excellent complexation ability with sulphur contribution for soft metal cations [20]. However, although the "classical" calixarenes polymers have been extensively studied, only several linear or grafting thiacalixarene-based polymers are reported [18]. Moreover, to our knowledge, the existing reports on polymeric calixarenes have shown their application as ion carriers, but no investigation has been performed on adsorption of aniline derivatives, which often create serious organic pollutants in water.

In this paper, the first examples of four *tri*-bridged and tetra-bridged thiacalix[4]amido-based polymers with porous and netty architectures were synthesized by copolymerization of thiacalix[4]arene esters derivatives with poly(ethyleneimine). Their adsorption experiments showed that these novel polymers exhibit high adsorption percentages for cations Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+}, as well as outstanding adsorption percentages for a series of aniline derivatives. The saturation adsorption capacities and the role of pH were also studied. The outstanding adsorption abilities for heavy metal cations and aniline derivatives exhibited good prospects for their application in removal of polluted water and environmental protection.

EXPERIMENTAL

Materials and Measurements

^1H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 500 (Germany) instrument at room temperature, using TMS as an internal standard. Elemental analyses were performed at Carlo-Erba 1106 Elemental Analyzer (Italy). Osmometric molecular weight determinations were carried out by a Knauer vapour pressure osmometer (Germany) at concentrations of ca. 10^{-3} M in $CHCl_3$ (37°C). FTIR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer (England) as KBr pellets. The atomic absorption spectrograph employed was a WFX-II spectrometer (China). UV-vis measurements were performed on a Varian UV-VIS (USA) instrument. All solvents were purified by standard procedures before use. All other chemicals, except special instruction, were analytically pure and used without further purification. All reactions were carried out under nitrogen atmosphere.

Synthesis of 5,11,17,23-tert-Butyl-25,26,27-*tri*-ethoxy-2-acetylthiacalix[4]arene (2) and 5,11,17, 23-*tert*-Butyl-25,26,27,28-*tri*-ethoxy-2-acetylthia-calix[4]arene (3)

Under nitrogen atmosphere, the mixture of *p-tert*-butylthiacalix[4]arene (2 mmol, 1.44 g), ethyl chloroacetate (10 mmol, 1.22 g), K_2CO_3 (10 mmol, 1.38 g) and KI (10 mmol, 1.66 g) was stirred in 100 mL refluxing acetone. The *p-tert*-butylthiacalix [4] arene was vanished by the monitor of TLC detection in 72 h. After distilling off the solvent under reduced pressure, the residue was treated with 30 mL HCl solution (10 w/v%) and extracted by 40 mL $CHCl_3$. The organic phase was separated, dried by anhydrous $MgSO_4$ and concentrated. Then the residue was purified by chromatographic column (SiO_2 100-200 mesh, CH_2Cl_2 as eluant). Compounds 2 and 3 were obtained as white powder in yields of 48% and 32%, respectively.

Compound 2: mp = 251-253°C. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.05 [s, 18 H, $C(CH_3)_3$], 1.13 (t, 3 H, CH_2CH_3), 1.27 (t, 6 H, CH_2CH_3), 1.32 [s, 9 H, $C(CH_3)_3$], 1.43 [s, 9 H, $C(CH_3)_3$], 3.97-4.79 (m, 12 H, OCH_2 and CH_2CH_3), 7.01(s, 2 H, ArH), 7.52 (bs, 4 H, ArH), 7.54 (s, 2 H, ArH), and 7.86(s, 1 H,

OH); ESI-MS m/z (%): 978.2 (M$^+$, 100).

Anal. Calcd. for $C_{52}H_{66}S_4O_{10}$: C = 63.79, H = 6.80; found: C = 63.73, H = 6.91.

The characterization of compound 3 was in accordance with the data in literature [21].

Synthesis of *tri*-Bridged Thiacalix[4]amido-based Polymers (4a and 4b)

Under nitrogen atmosphere, a mixture of thiacalix[4] arene triesters derivatives 2 (0.98 g, 1.0 mmol) and *bi*-(ethyleneimine) or *tri*-(ethyleneimine) (1.7 mmol) was stirred and refluxed in 30 mL toluene/methanol (v/v= 1/1) for 24 h until the materials were utterly disappeared by monitoring with TLC. After evaporating off the solvent under reduced pressure, the residue was treated with distilled water (50 mL) and extracted with CHCl$_3$ (50 mL). The organic layer was separated and dried over MgSO$_4$. After evaporating off the solvent to dryness, the powder was washed by a small amount of acetone to remove small molecules. Polymers 4a and 4b were obtained in 81% and 84% yields, respectively.

Polymer 4a: straw yellow powder, ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.03 [bs, 18 H, C(CH$_3$)$_3$], 1.30 [s, 9 H, C(CH$_3$)$_3$], 1.41 [s, 9 H, C(CH$_3$)$_3$], 3.90-4.77 (m, 18 H, OCH$_2$ and NCH$_2$), 6.98-7.52 (m, 8 H, ArH), 8.28 (bs, 6 H, OH and NH); IR (KBr) ν: 3431 (OH and NH), and 1655 (C=O) cm^{-1}.

Polymer 4b: yellow powder, ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.04[bs, 18 H, C(CH$_3$)$_3$], 1.31 [s, 9 H, C(CH$_3$)$_3$], 1.40 [s, 9 H, C(CH$_3$)$_3$], 3.92-4.82 (m, 24 H, OCH$_2$ and NCH$_2$), 6.96-7.51(m, 8 H, ArH), 8.31(bs, 7 H, OH and NH); IR (KBr) ν: 3430 (OH and NH), 1654 (C=O) cm^{-1}.

The elemental analyses and osmometric M$_n$ data of polymers 4a and 4b are shown in Table 1.

Synthesis of *tetra*-Bridged Thiacalix[4] amido-based Polymers (5a and 5b)

Under nitrogen atmosphere, a mixture of thiacalix[4] arene tetraesters derivatives 3 (1.1 g, 1.0 mmol) and *bi*-(ethyleneimine) or *tri*-(ethyleneimine) (2.2 mmol) was stirred and refluxed in 30 mL toluene/methanol (v/v= 1:1) for 24 h until the materials were utterly disappeared by the monitor of TLC. After evaporating off the solvent under reduced pressure, the residue was treated with distilled water (50 mL) and extracted with CHCl$_3$ (50 mL). The organic layer was separated and dried over MgSO$_4$. After evaporating off the solvent to dryness, the powder was washed by a small amount of acetone to remove small molecules. Polymers 5a and 5b were obtained in 86% and 89% yields, respectively.

Polymer 5a: yellow powder, ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.15 [bs, 36 H, C(CH$_3$)$_3$], 3.87-4.80 (m, 24 H, OCH$_2$ and NCH$_2$), 7.12-7.28 (m, 8 H, ArH), 8.67 (bs, and 6 H, NH); IR (KBr) ν: 3401 (NH), 1654 (C=O) cm^{-1}.

Polymer 5b: yellow powder, ^{1}H NMR (500 MHz, CDCl$_3$) δ: 1.17 [bs, 36 H, C(CH$_3$)$_3$], 3.83-4.93 (m, 32 H, OCH$_2$ and NCH$_2$), 7.06-7.36 (m, 8 H, ArH), 8.89 (bs, 8 H, NH); IR (KBr) ν: 3412 (NH), 1653 (C=O), 3430 (OH and NH), and 1654 (CONH) cm^{-1}.

The elemental analyses and osmometric M$_n$ data of polymers 5a and 5b are shown in Table 1.

Adsorption Percentages of Polymers 4 and 5

According to the published method [22], 10 mg of polymer was added to 10 mL of an aqueous solution of metal cation (1.0×10^{-3} mol/L). After stirring for 24 h at 25°C, the mixture was filtered. The concentration of metal cation after adsorption in filtrate was examined by atomic absorption spectroscopy. The percentage of cations adsorbed by polymers was

Table 1. Elemental analysis (%) and molecular weight of polymers 4 and 5.

Polymer	C (%) Found (calcd.)	H (%) Found (calcd.)	N (%) Found (calcd.)	M$_n$
4a	62.71(62.73)	6.72(6.78)	6.37(6.32)	18342
4b	62.28(62.30)	7.05(7.13)	7.98(7.92)	19279
5a	61.78(61.86)	6.86(6.86)	7.79(7.72)	20134
5b	61.42(61.41)	7.16(7.22)	9.51(9.55)	22026
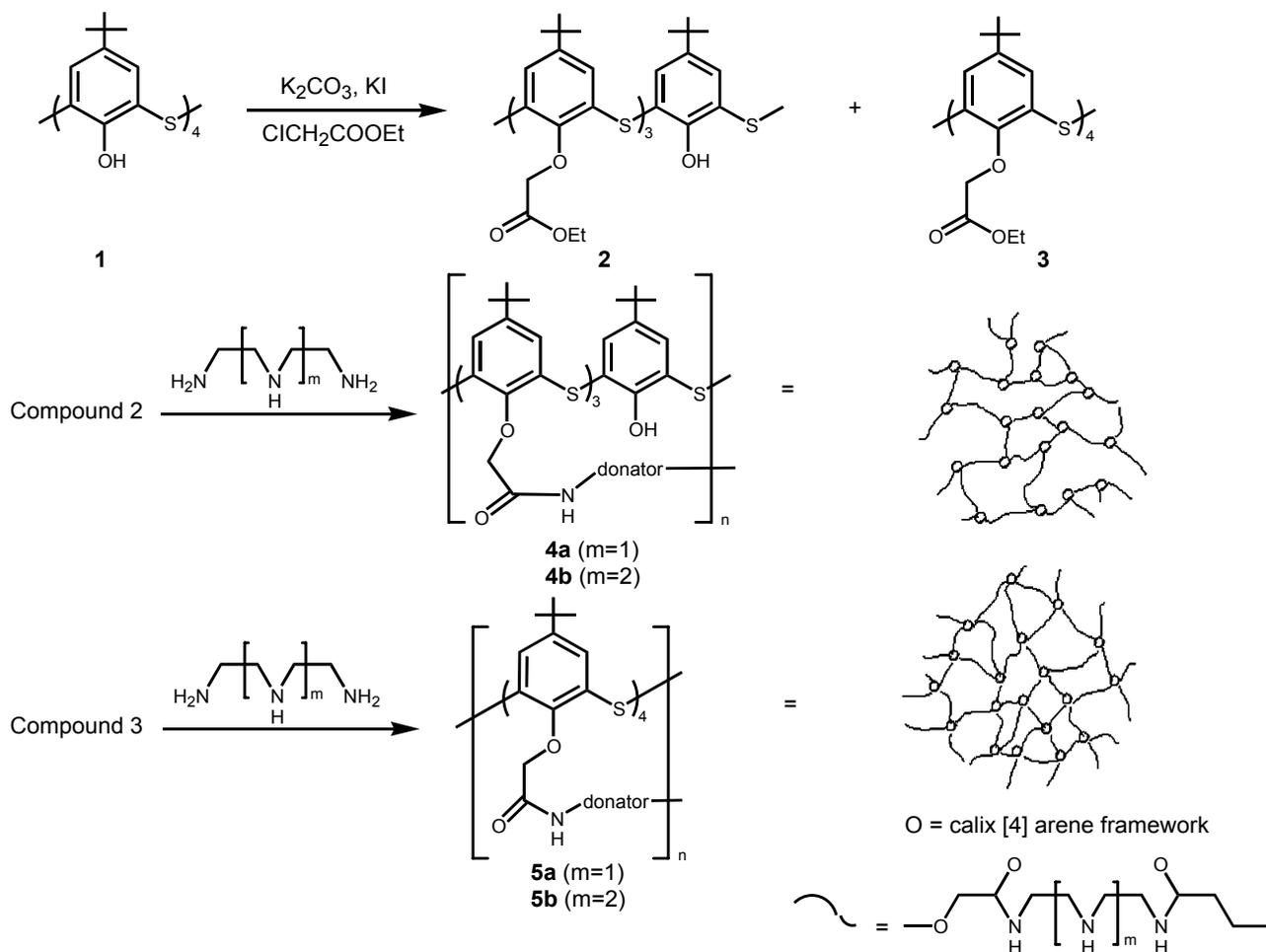
Scheme I. The synthetic routes of *tri*-bridged (4a and 4b) *tetra*-bridged (5a and 5b) thiacalix[4] amido-based polymers.

calculated as follows:

$$E(\%) = (C_0 - C) / C \times 100$$

where E is the adsorption percentage of polymers, C_0 is the known concentration of cations before adsorption and C is the concentration of cations after adsorption. The data obtained were the average of two independent experiments. Blank control experiments in the absence of the calixarene polymers showed that the change of concentration before and after stirring for 24 h at 25°C was less than 1%.

According to the similar procedures for cations, the adsorption experiments for aniline derivatives were carried out in the water-ethanol (V/V: 8/2) solutions of aniline compounds. The concentration in the filtrate was examined by UV spectroscopy.

Saturated Adsorption Capacity of Polymer 5b
According to a reported method [23], the approach of changing the volume of cation solution was employed to examine the saturated adsorption capacity. A sample of polymer 5b (10 mg) was added in sequence into Cu^{2+} or *p*-nitroaniline solutions (1×10^{-3} mol/L) of which the volumes were 5, 10, 15, 20, 25, 30, 35, and 40 mL, respectively. Each mixture was stirred for 24 h at 25°C and then it was filtered. The concentration in the filtrate was determined by atomic absorption or UV spectroscopy methods. The adsorption capacity was calculated as follows:

$$Q = (C - C^*)V / W$$

where Q is the adsorption capacity, C is the initial concentration before adsorption, C^* is the concen-

tration after adsorption, V is the volume of solution and W is the mass of the polymer.

Adsorption Percentages at Different pH Values

According to a reported method [23], samples of polymer (10 mg) and solutions of cation (1×10^{-3} mol/L, 10 mL) at different pH values were mixed and stirred for 24 h at 25°C. After filtration, the concentration of cation was examined by atomic absorption spectroscopy and the adsorption percentage was calculated.

RESULTS AND DISCUSSION

Synthesis and Characterizations

The synthetic routes of the novel polymers 4a, 4b, 5a and 5b are shown in Scheme I. Compound 1 was synthesized according to published method [24]. Akdas et al. [21] and Iki et al. [25] had reported the synthesis of *tetra*((ethoxycarbonyl)- methoxy) thiacalix[4] arene (3) by reacting *p-tert*-butylthiacalix[4]arene with ethyl bromoacetate. However, in our experiments, using ethyl chloroacetate instead of ethyl bromoacetate and KI as catalyst, *tri*((ethoxycarbonyl)methoxy)-thiacalix[4]arene (2) and tetra ((ethoxycarbonyl)-methoxy) thiacalix[4]arene (3) were obtained in K_2CO_3/acetone system with 48% and 32% yields, respectively. Further, the ammonolysis of compounds 2 or 3 with poly(ethyleneimine) afforded novel polymers 4a, 4b, 5a and 5b in high yields. Since compounds 2 and 3 possessed three or four esters groups and the esters are easily ammonolyzed by poly(ethyleneimine), polymers 4a, 4b, 5a and 5b are not linear but tridimensional netty *tri*-bridged or tetra-bridged polymers. The structures of polymers 4a, 4b, 5a and 5b were confirmed by IR spectra, elemental analysis, ^{1}H NMR spectra, SEM images, etc.

The elemental analysis data and molecular weight of polymers 4 and 5 are shown in Table 1. The molecular weight for polymers was determined by vapour pressure osmometric measurements. The M_ns of polymers 4 and 5 are 18000~22000 which indicate that there are approximately 17~20 thiacalixarene units in each polymer molecules.

The structures of polymers 4 and 5 were confirmed
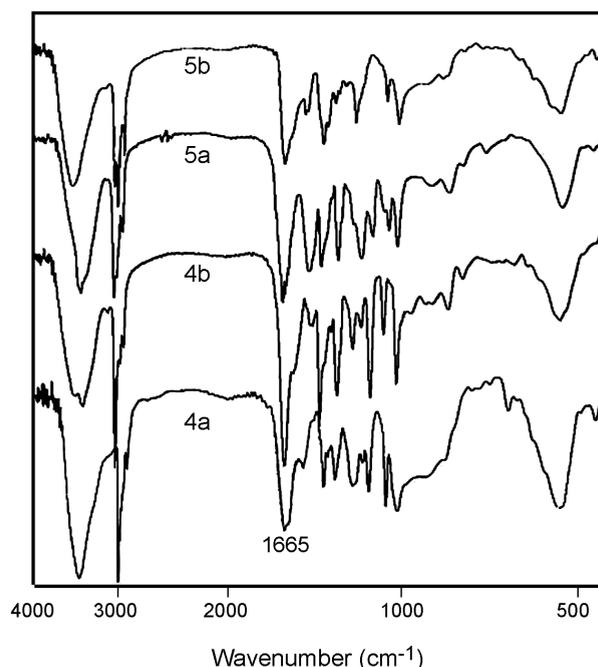
Figure 1. FTIR spectra of *tri*-bridged (4a and 4b) *tetra*-bridged (5a and 5b) thiacalix[4] amido-based polymers.

by their FTIR spectra which showed similar changes. Figure 1 shows the FTIR spectra of polymers 4a, 4b, 5a and 5b. In the FTIR spectra, the characteristic absorption peak of C=O (ester groups of compounds 2 and 3) at 1760 cm^{-1} disappeared completely and the strong absorption peak of C=O (amido groups of polymers 4 and 5) appeared at 1665 cm^{-1}. These observations in FTIR spectra certainly suggest that the ester groups were ammonolyzed completely by poly(ethyleneimine).

Also, the signals of ^{1}H NMR spectra of polymers 4 and 5 were assigned to appropriate protons. However, it was difficult to deduce the conformation of thiacalix[4]arene units in polymers 4 and 5 due to the absence of -CH$_2$- groups on thiacalix[4] arene skeleton and the overlapped signals for ArH. These results might indicate that they adopted the alternate or mixed conformations, which are in accordance with the conformation studies of the compounds 2 and 3 [21,24]. The alternate or mixed conformation was favourable for intermolecular bridging which resulted in cross-linked polymeric structures.

The surface structures of polymers 4 and 5 were also observed by scanning electron microscopy

(a)

(c)

(b)

(d)
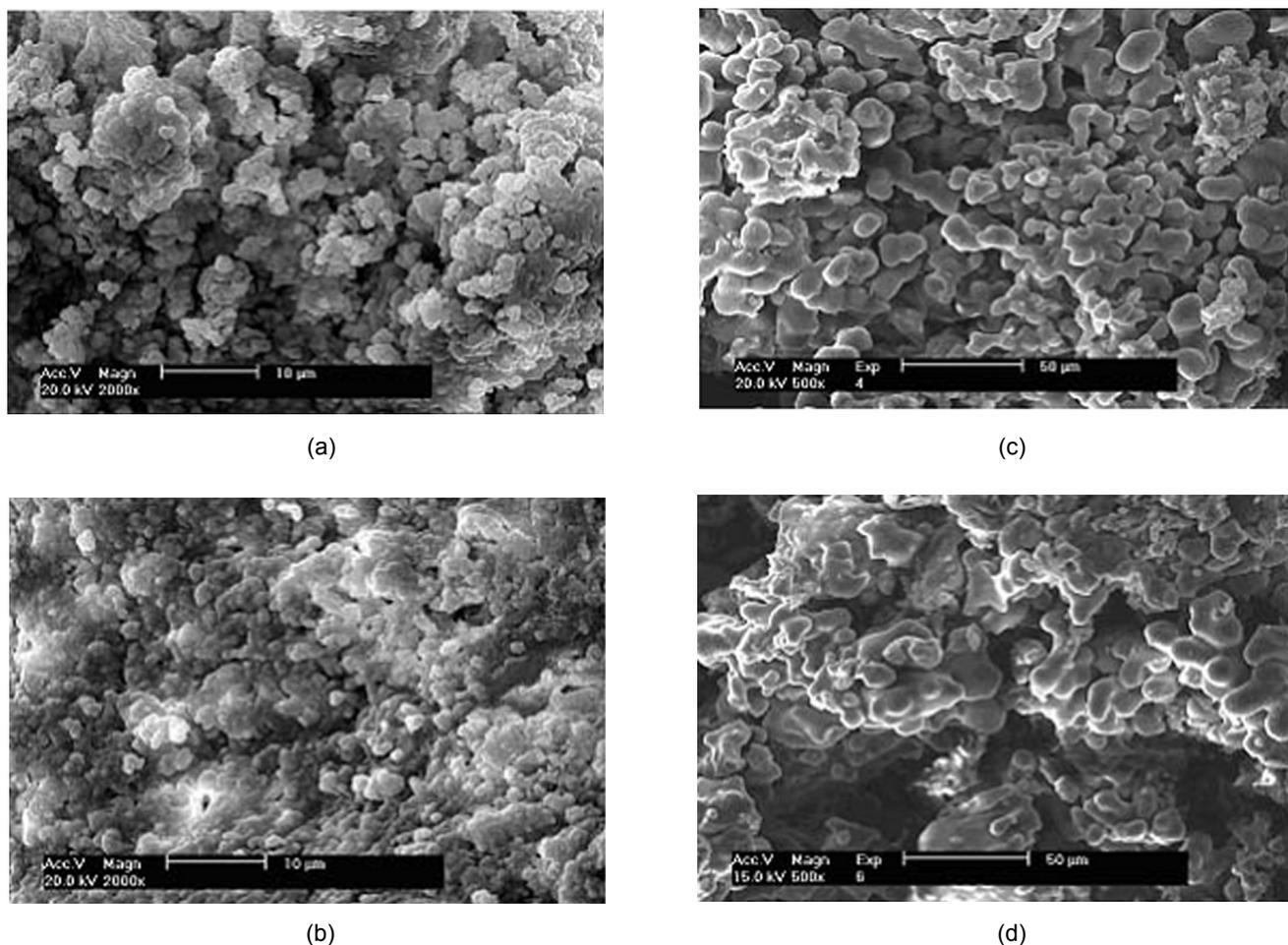
Figure 2. SEM micrographs of *tri*-bridged (a and b) *tetra*-bridged (c and d) thiacalix[4] amido-based polymers.

(SEM). Figure 2 shows the SEM micrographs of polymers 4 and 5. As expected, it can be seen that both polymers 4 and 5 were sparsely porous and cross-linked netty architectures. To the best of our knowledge, polymers 4 and 5 were the first examples of thiacalixarene-based cross-linked netty polymers.

Adsorption Percentages of Polymers 4a, 4b, 5a, and 5b
The binding abilities of calixarene derivatives were decided by the macrocyclic ring sizes, their conformations and the nature of the functional groups [1]. Polymers 4 and 5 possessed abundant amido groups, which are favourable for binding to metal cations and amino organic compounds. Thus, the adsorption abilities of polymers 4 and 5 have been studied for a series of metal cations and aniline derivatives which are common water pollutants. The adsorption results are shown in Tables 2 and 3.

From the adsorption data given in Table 2, it is evident that polymers 4 and 5 show remarkable adsorption percentages towards all the metal cations, especially, the very high adsorption percentages for heavy and transition metal cations Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+}. The tetra-bridged polymers 5a and 5b showed higher adsorption percentages than those of *tri*-bridged polymers 4a and 4b. *Tri*(ethyleneimine) polymers 4b and 5b showed higher adsorption percentages than those of *bi*(ethyleneimine) polymers 4a and 5a. These results may be attributed to the presence of sulphur and amido groups in polymers where they prefer to form complexes with heavy and transitional metal cations through cation-p interactions according to the concept of "hard and soft acids and bases" introduced by Pearson, and the more amido groups in polymers, resulting in stronger adsorption abilities for cations.

In Table 3, it is observed that polymers 4 and 5

Table 2. Metal cations adsorption percentages of polymers 4 and 5.

Polymer	Na$^+$	K$^+$	Ag$^+$	Hg^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}
4a	14.2	15.2	52.5	57.6	67.4	59.8	70.9	53.2	64.8
4b	17.9	28.5	66.2	76.8	83.6	64.4	88.2	69.0	82.2
5a	16.1	23.9	80.1	84.8	91.3	78.5	76.9	79.6	76.3
5b	24.8	29.2	88.5	90.2	93.4	86.7	92.2	84.2	86.7

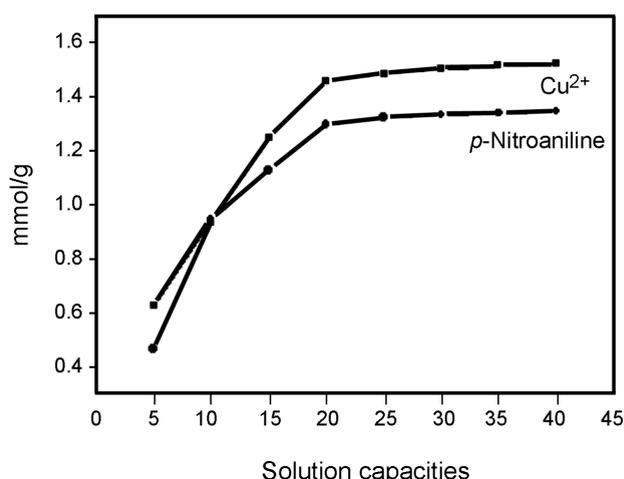**Table 3.** Aniline derivatives adsorption percentages of polymers 4 and 5.

| Material	4a	4b	5a	5b
Aniline	46.7	48.8	52.4	65.5
o-Phenylendiamine	53.4	63.2	64.7	70.2
m-Phenylendiamine	52.8	56.7	63.1	72.9
p-Phenylendiamine	58.8	69.9	78.6	86.8
o-Nitroaniline	64.7	72.5	79.9	84.5
m-Nitroaniline	53.3	62.3	78.4	88.9
p-Nitroaniline	85.7	88.6	91.2	94.2

show excellent adsorption percentages for series of aniline derivatives. The adsorption results for series of aniline derivatives are similar to those of cations, i.e., the more amido groups in polymers, the stronger adsorption abilities for aniline derivatives. The high adsorption percentages for aniline derivatives might be due to the π-π stack action of the phenyl groups and the hydrogen bond action between amido groups of polymers and amino groups of aniline derivatives. In contrast, it could be seen that the adsorption selectivity of polymers 4 and 5 for both cations and aniline derivatives is low. Yilmaz et al. have reported that the good complexation selectivity is due to stable cone conformation in calixarene polymers [26,27]. The low adsorption selectivity of polymers 4 and 5 might be attributed to the mixed or alternate conformations of thiacalix[4]arene units in polymers 4 and 5 as described above. It is worth mentioning that the adsorption abilities for aniline derivatives are studied for the first time in supramolecular chemistry.

Saturated Adsorption Capacities of Polymer 5b
Polymer 5b exhibits the highest adsorption percentages for Cu^{2+} among metal cations and for p-nitroaniline among aniline derivatives, Thus, its saturated adsorption capacities towards Cu^{2+} and

p-nitroaniline were studied and the results are shown in Figure 3. It can be seen that the saturation adsorption capacities of polymer 5b for Cu^{2+} and p-nitroaniline are as high as 1.51 mmol/g and 1.34 mmol/g, respectively. These saturation adsorption results reveal that an approximate average of 1.51 equiv Cu^{2+} or 1.34 equiv p-nitroaniline were adsorbed by each thiacalix[4]amido units in polymer 5b. The outstanding adsorption abilities

Figure 3. Saturated adsorption curves of 5b for Cu^{2+} and p-nitroaniline.
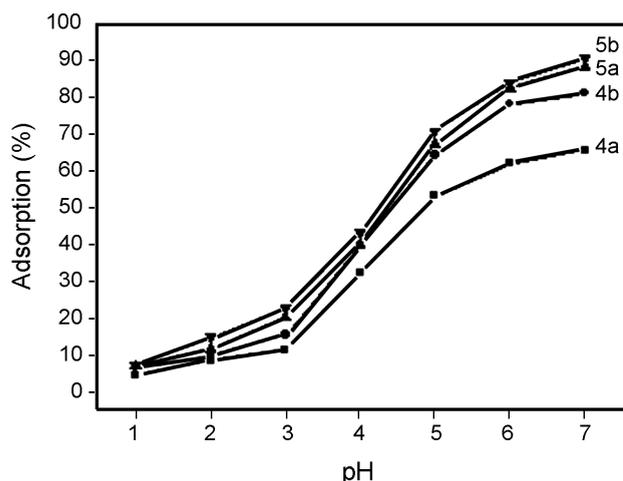
Figure 4. Effects of pH values on adsorption percentage of Cu^{2+}.

for heavy metal cations and derivatives of aniline demonstrate promising perspectives for their application in disposal of polluted water and environmental protection.

Influence of pH Value on Adsorption Percentages

Because the complexation capabilities of amido groups are greatly influenced by pH of the medium, the adsorption percentages of polymers 4a, 4b, 5a and 5b towards Cu^{2+} at different pH values were studied and the data are presented in Figure 4 (the test for aniline derivatives cannot be carried out because of the protonation of aniline derivatives at acidic medium). It can be seen that the adsorption percentages of these polymers are reduced sharply when pH < 4, which can be attributed to the protonation of amido groups of polymers and gradual loss in complex abilities in the strong acid medium.

Recycling Property

Due to the high adsorption capabilities of Cu^{2+} on polymers 5b, this polymer was selected as a representative to evaluate the recycling ability of the novel polymers. After saturated adsorption of Cu^{2+}, the polymer 5b was desorbed by 10% ammonia, washed adequately by distilled water and dried under vacuum. Then the polymer was reused for Cu^{2+} adsorption, again. Five times the adsorption percentages were tested and the results obtained are 93.4%, 90.1%, 86.6%, 82.7%, 78.3%, respectively,

which indicates that polymer 5b has good recycling properties.

CONCLUSION

This paper has described the synthesis of the first examples of *tri*-bridged and *tetra*-bridged thiacalix[4] amido-based polymers (4a, 4b, 5a and 5b) with porous and netty architecture. Their adsorption data showed that these novel polymers exhibit high adsorption percentages for cations such as Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Zn^{2+}, as well as outstanding adsorption percentages for a series of aniline derivatives. The saturation adsorption capacities of polymer 5b towards Cu^{2+} and *p*-nitroaniline were as high as 1.51 and 1.34 mmol/g, respectively. The adsorption percentages of these polymers are reduced sharply when pH < 4 and they can be reused by desorption of 10% ammonia. The outstanding adsorption abilities for heavy metal cations and aniline derivatives have exhibited good prospects for disposal application of polluted water and environmental protection.

REFERENCES

1. Asfari Z, B.hmer V, Harrowfield J, Vicens J, Saadioui M, *Calixarenes 2001*, Kluwer Academic, Dordrecht, Ch 1, 2001.
2. Uysal G, Memon S, Yilmaz M, Synthesis and binding properties of polymeric calix[4]arene nitriles, *React Funct Polym*, **50**, 77-84, 2001.
3. Memon S, Tabakci M, Roundhill DM, Yilmaz M, A useful approach toward the synthesis and metal extractions with polymer appended thioalkyl calix[4]arenes, *Polymer*, **46**, 1553-1559, 2005.
4. Gungor O, Memon S, Yilmaz M, Roundhill DM,

Synthesis of alkyl nitrile and alkyl benzonitrile derivatives of calix[4]arene and their polymer supported analogues: a comparative study in two-phase extraction systems, *React Funct Polym*, **63**, 1-9, 2005.

5. Kang Y, Rudkevich DM, Polymer-supported calix[4]arenes for sensing and conversion of NO_2/N_2O_4, *Tetrahedron*, **60**, 11219-11224, 2004.

6. Jain VK, Handa A, Pandya R, Shrivastav P, Agrawal YK, Polymer supported calix[4]arene-semicarbazone derivative for separation and pre-concentration of La(III), Ce(III), Th(IV) and U(VI), *React Funct Polym*, **5**, 101-110, 2002.

7. Memon S, Akceylan E, Sap B, Tabakci M, Roundhill DM, Yilmaz M, Polymer supported calix[4]arene derivatives for the extraction of metals and dichromate anions, *J Polym Environ*, **11**, 67-74, 2003.

8. Akkus GU, Memon S, Gürkas DE, Aslan S, Yilmaz M, The synthesis and metal cation extraction studies of novel polymer-bound calix(aza) crowns, *React Funct Polym*, **68**, 125-133, 2008.

9. Engrand P, Regnouf-de-Vains JB, A bifunctional calixarene designed for immobilisation on a natural polymer and for metal complexation, *Tetrahedron Lett*, **43**, 8863-8866, 2002.

10. Memon S, Tabakci M, Roundhill DM, Yilmaz M, Synthesis and evaluation of the Cr(VI) extraction ability of amino/nitrile calix[4]arenes immobilized onto a polymeric backbone, *React Funct Polym*, **66**, 1342-1349, 2006.

11. Mendrek B, Trzebicka B, Synthesis and characterization of well-defined poly(*tert*-butyl acrylate) star polymers, *Eur Polym J*, **45**, 1979-1993, 2009.

12. Kitano H, Hirabayashi T, Ide M, Kyogoku M, Complexation of bisphenol A with calix[6]arene-polymer conjugates, *Macromol Chem Phy*, **204**, 1419-1427, 2003.

13. Mendes AR, Gregório CC, Barata PD, Costa AI, Prata JV, Linear and crosslinked copolymers of *p-tert*-butylcalix[4]arene derivatives and styrene: new synthetic approaches to polymer-bound calix[4]arenes, *React Funct Polym*, **65**, 9-21, 2005.

14. Barata PD, Costa AI, Granja P, Prata JV, The synthesis of novel polymer-bound calix[4]arenas,

React Funct Polym, **61**, 147-152, 2004.

15. Wang L, Shi X, Jia P, Yang Y, Preparation of calixarene-containing polymer with proton transport ability, *J Polym Sci Pol Chem*, **42**, 6259-6266, 2004.

16. Dondoni A, Marra A, Rossi M, Scoponi M, Synthesis and characterization of calix[4]arene-based copolyethers and polyurethanes. Ionophoric properties and extraction abilities towards metal cations of polymeric calix[4]arene urethanes, *Polymer*, **45**, 6195-6170, 2004.

17. Zhu Y, Gou P, Zhu K, Shen Z, Synthesis, extraction, and adsorption properties of calix[4]arene-poly(ethylene-glycol) crosslinked polymer, *J Appl Polym Sci*, **109**, 1968-1973, 2008.

18. Tabakci B, Beduk AD, Tabakci M, Yilmaz M, Synthesis and binding properties of two polymeric thiacalix[4]arenes, *React Funct Polym*, **66**, 379-386, 2006.

19. Yang Y, Swager TM, Main-chain calix[4]arene elastomers by ring-opening metathesis polymerization, *Macromolecules*, **40**, 7437-7440, 2007.

20. Lhotak P, Chemistry of thiacalixarenes, *Eur J Org Chem*, **8**, 1675-1687, 2004.

21. Akdas H, Mislin G, Graf E, Hosseini MW, Cian AD, Fischer J, Synthesis and solid state structural analysis of conformers of tetrakis ((ethoxycarbonyl)methoxy)tetrathiacalix[4]arene, *Tetrahedron lett*, **40**, 2113-2116, 1999.

22. Yang FF, Guo HY, Cai XQ, Chen XL, Syntheses and adsorption properties of novel calixarene polymers: calix[6]-1,4-crown-4-based netty polymers, *React Funct Polym*, **64**, 163-169, 2005.

23. Yang FF, Chen XL, Guo HY, Cai XQ, Supramolecular chelating resins-design, synthesis and adsorption properties of cellulose grafted with calyx[4]arene, *Acta Polym Sinica*, **6**, 896-902, 2005.

24. Chu HH, Wang J, Pan ZC, Hu XJ, Gu JY, Shi XF, Synthesis and characterization of *p*-tert-Butylthiacalix[4]arenes and their derivatives, *Chin J Org Chem*, **11**, 1255-1259, 2003.

25. Iki N, Morohashi N, Narumi F, Fujimoto T, Suzuki T, Miyano S, Novel molecular receptors based on a thiacalix[4]arene platform. Preparations of the di- and tetra-carboxylic acid derivatives and their binding properties towards

transition metal ions, *Tetrahedron lett*, **40**, 7337-7340, 1999.

26. Memon S, Uysal G, Yilmaz M, Syntheses and binding properties of polymeric calix[4]crown-4, *React Funct Polym*, **47**,165-174, 2001.

27. Tabakci M, Memom S, Yilmaz M, Roundhill DM, Synthesis and evaluation of extraction ability of calix[4]-crown-6 cone conformer and its oligomeric analogue, *React Funct Polym*, **58**, 27-31, 2004.