Synthesis, Extraction, and Adsorption Properties of Calix[4]arene-poly(ethylene-glycol) Crosslinked Polymer

Weipu Zhu, Pengfei Gou, Kui Zhu, Zhiquan Shen

Key Laboratory of Macromolecule Synthesis and Functionalization of Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

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ABSTRACT: Novel calix[4]arene-poly(ethylene glycol) crosslinked polymer (CCP) has been synthesized by the polycondensation reaction between a *p-tert*-butylcalix[4]-arene derivative and dihydroxyl capped poly(ethylene glycol) (DHPEG, M_n = 1000) catalyzed by neodymium tosylate. The hydrogel, consisted of 66.9% water and 33.1% CCP, can selectively extract aromatic organic molecules from aqueous solution according to the diameter of the guest molecules, which infers that the diameter of the calix-[4]arene cavity is about 5.4 Å and the conformation of calix[4]arene units altered from cone conformation to 1,3-alternate conformation during the polycondensation reaction. Furthermore, CCP can also adsorb naphthalene from gas phase, showing much higher capacity than active carbon does, which may have some potential applications in the field of separation and environment protection. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1968–1973, 2008

Key words: adsorption; crosslink; calix[4]arene; extraction; hydrogels

INTRODUCTION

Nowadays, water and air pollution generated by industrial effluents owning organic molecules such as aromatic chemicals and halides have been a serious problem all around the world. To have ecologically sustainable growth, it is necessary to explore separation materials to treat with effluent water and gas. Crosslinked polymers formed by three-dimensional and elastic networks can allow other molecules to be trapped inside the interstitial spaces. They have found many useful applications in the field of separation science and technology.[1–4]

Macrocyclic compounds such as calixarenes, cyclodextrins, and crown ethers have been developed for the purpose of creating stable complexes with a target guest molecule.[5–10] Calixarenes can be easily prepared by base-induced condensation of certain *p*-substituted phenols with formaldehyde, which are of great interest because of their basket-shaped structure providing unique cavity capable of including various guest molecules.[11] The cavity size of calixarenes can be adjusted by the number of phenol units. The monomeric calixarenes have been frequently reported as extractant to extract organic molecules and metal ions.[12–15] However, researches on the polymeric calixarenes are still limited. Only a few calixarene-containing polymers have been developed as adsorption materials.[16–18] These reports are all concerning about the adsorption behaviors toward metal ions such as alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+) and heavy metal cations (Ag^+, Cu^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}) via liquid–liquid extraction method. This article reports a novel crosslinked hydrophilic polymer containing calix[4]arene units, which can extract organic molecules from both aqueous solution and gas phase.

Correspondence to: Z. Shen (zhiquan_shen@163.com).

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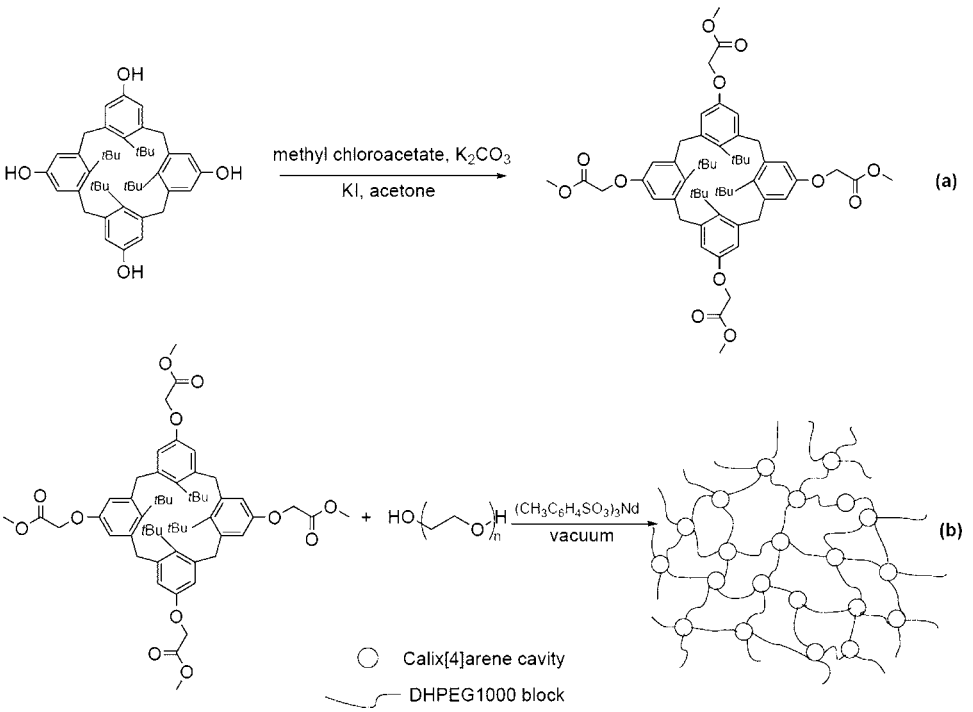
EXPERIMENTAL

Materials

p-tert-Butyl-calix[4]arene and neodymium tosylate [$Nd(O_3SC_6H_4CH_3)_3$] were prepared according to the procedures reported previously.[15,19] Reaction solvents were purified in an usual way prior to use. Commercial methyl chloroacetate, potassium carbonate, potassium iodide, and other reagents (analytical reagent) were used without further purification.

Synthesis of calix[4]arene tetraesters ($C_{56}H_{72}O_{12}$)

As shown in Scheme 1(a), a mixture of *p-tert*-butyl-calix[4]arene (0.65 g, 1 mmol), methyl chloroacetate



Scheme 1 Synthesis of calix[4]arene tetraesters (a) and CCP (b).

(0.86 g, 8 mmol), K_2CO_3 (1.38 g, 10 mmo1), KI (12.7 mg, 0.1 mmol), and anhydrous acetone (50 mL) was stirred under argon atmosphere and refluxed for 72 h. After removing acetone, the residue was suspended in $Na_2S_2O_3$ aqueous solution (5%, 30 mL) for 30 min and then extracted with dichloromethane (15 mL × 3). The organic extract was dried over magnesium sulfate, filtered, and concentrated to 10 mL. Upon addition of methanol, calix[4]arene tetraesters are precipitated to give 0.80 g white powder (0.854 mmol, 85% yield). Melting point: 216–218°C. MS for $C_{56}H_{72}O_{12}$: m/z = 960 ($M + Na^+$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.00 (s, 36H, $C(CH_3)_3$), 3.69 (s, 12H, CH_3), 3.12, and 4.88 (d, 8H, $ArCH_2Ar$), 4.74 (s, 8H, $ArOCH_2$), 6.71 (s, 8H, ArH).

Synthesis of CCP

As shown in Scheme 1(b), calix[4]arene tetraesters (0.937g, 1 mmol) and DHPEG (M_n = 1000, 2.0 g, 2 mmol) were dissolved in anhydrous xylene (50 mL) in a 100-mL, three-necked, round-bottomed flask equipped with a magnetic stirrer, an argon inlet, and a distillation column, and then neodymium tosylate (6.6 mg, 0.01 mmol) was added as a catalyst. The polycondensation reaction between calix[4]arene tetraesters and DHPEG was carried out at 160°C for 2 h under argon flow with continuous removal of the solvent and released methanol. Then, the reaction was continued at 250°C under 0.5–1 mbar vacuum for 3 h. The product was washed by THF several times to remove the catalyst, dried in vacuum to a constant weight, and the transparent amorphous CCP was prepared.

Preparation of hydrogel from CCP

CCP (0.225 g) was added into 100 mL fresh distilled water. CCP was swelled by absorbing water to a constant weight of 0.679 g after 8 h, and the hydrogel containing 33.1% CCP and 66.9% water was obtained.

Extraction measurements

CCP hydrogel (0.3 g) and 5.0 mL of freshly prepared aqueous solution of toluene (700 ppm, $A_{261\ nm}$ = 1.157, the maximum UV absorbance of toluene is at 261 nm) were added into a small airproof vial (10 cm^3) equipped with a stirring bar. After 48-h adsorption process, 1.5 mL of the solution was taken out for UV measurement to determine the decrease of toluene concentration. And, the final concentration of toluene in aqueous solution was estimated by eq. (1) as follows:

$$C_{\text{final}} = C_{\text{initial}} \times \frac{A_{261\,\text{nm, final}}}{A_{261\,\text{nm, initial}}} \quad (1)$$

where C_{initial} and C_{final} represent the initial and final concentration of toluene in aqueous solution, while $A_{261\ \text{nm,initial}}$ and $A_{261\ \text{nm,final}}$ represent the initial and

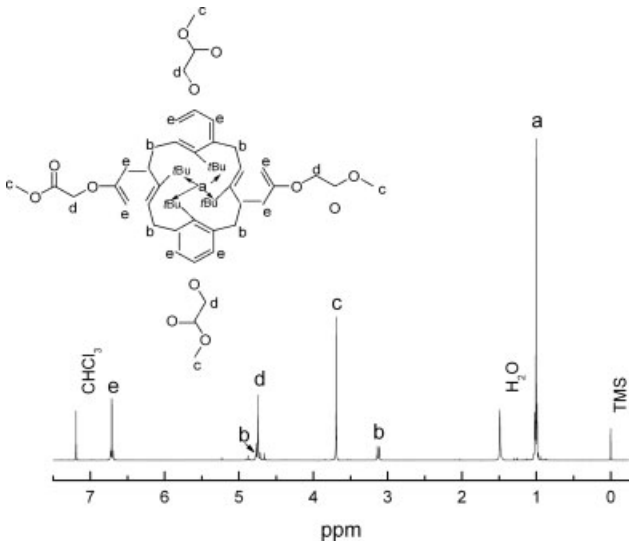


Figure 1 ^{1}H NMR spectrum of calix[4]arene tetraesters.

final UV absorbance at 261 nm. The concentration of toluene in the hydrogel was calculated according to eq. (2) as follows:

$$C_{\text{hydrogel}} = (C_{\text{initial}} - C_{\text{final}}) \times \frac{W_{\text{solution}}}{W_{\text{hydrogel}}} \qquad (2)$$

where C_{hydrogel} represents the final concentration of toluene in the hydrogel, and W_{hydrogel} and W_{solution} represent the weight of the hydrogel and solution, respectively.

As a comparison, the extraction of toluene by 23 mg monomeric *p-tert*-butylcalix[4]arene owning the same amount of claix[4]arene unit with 0.3 g CCP hydrogel was carried out by the same way. And, the extractions of other aromatic molecules such as benzene (550 ppm, $A_{253\ \text{nm}} = 0.737$), chlorobenzene (700 ppm, $A_{263\ \text{nm}} = 0.386$), and nitrobenzene (700 ppm, $A_{241\ \text{nm}} = 1.234$) from aqueous solutions by CCP hydrogel and monomeric *p-tert*-butylcalix[4]-arene were operated by similar method.

Adsorption measurements

CCP (0.1 g) was placed into a closed chamber (50 mL) with 5.0 g of naphthalene comparted by a grid. The process of the naphthalene adsorption by CCP was measured by the weight addition of the CCP. The adsorption of naphthalene by active carbon as a comparison was performed as earlier.

Apparatus

^{1}H NMR spectrum was recorded on a Bruker Avance DMX500 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. Absorption spectra measurements were performed on a UV–vis spectrophotometer (756PC, Shanghai Spectrum Instruments). Differential scanning calorimetric (DSC) curve was taken on a TA Q100 apparatus (TA Instruments). The samples were cooled to −50°C and heated to 100°C twice with a heating rate of 10°C/min. ESI-positive MS was performed using Bruker Esquire 3000 plus spectrometer with an ESI interface.

RESULTS AND DISCUSSION

Characterization

Figure 1 shows the ^{1}H NMR spectrum of calix[4]-arene tetraesters. The singlet at 6.71 ppm due to the signal of ArH and one pair of doublets at 3.12 and 4.88 ppm due to the signal of CH_2 group connecting phenol units indicate the cone conformation of the calix[4]arene tetraesters.[20]

Figure 2 shows the DSC curves of CCP and DHPEG (M_n = 1000). The melting peak of PEG1000 block shifts from 35.8 to 14.8°C, and a cold crystallization peak at −15.5°C is detected, which attributes to the restriction of PEG1000 block indicating the network structure.

Extraction of aromatic guest molecules from aqueous solution

The hydrophilic PEG blocks and unique cavity of the calix[4]arene units enable the CCP hydrogel to extract guest molecules from aqueous solution. Figure 3 shows the UV spectra of the aromatic aqueous solutions before and after the extraction by CCP hydrogel. The UV spectra of the aqueous solutions extracted by monomeric *p-tert*-butylcalix[4]arene under the same conditions are also exhibited as comparisons. The original concentrations of benzene,

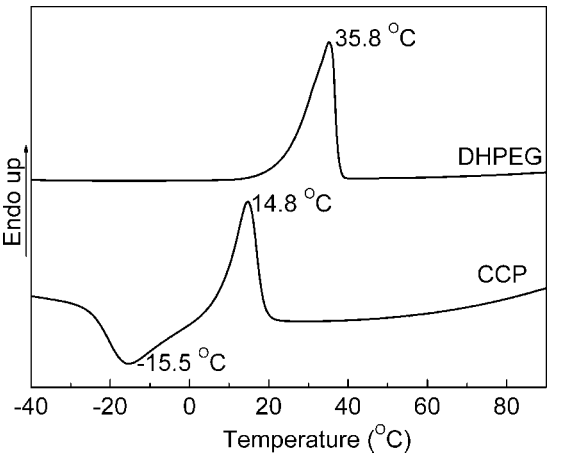


Figure 2 DSC curves of DHPEG (M_n = 1000) and CCP (second heating, 10°C/min).

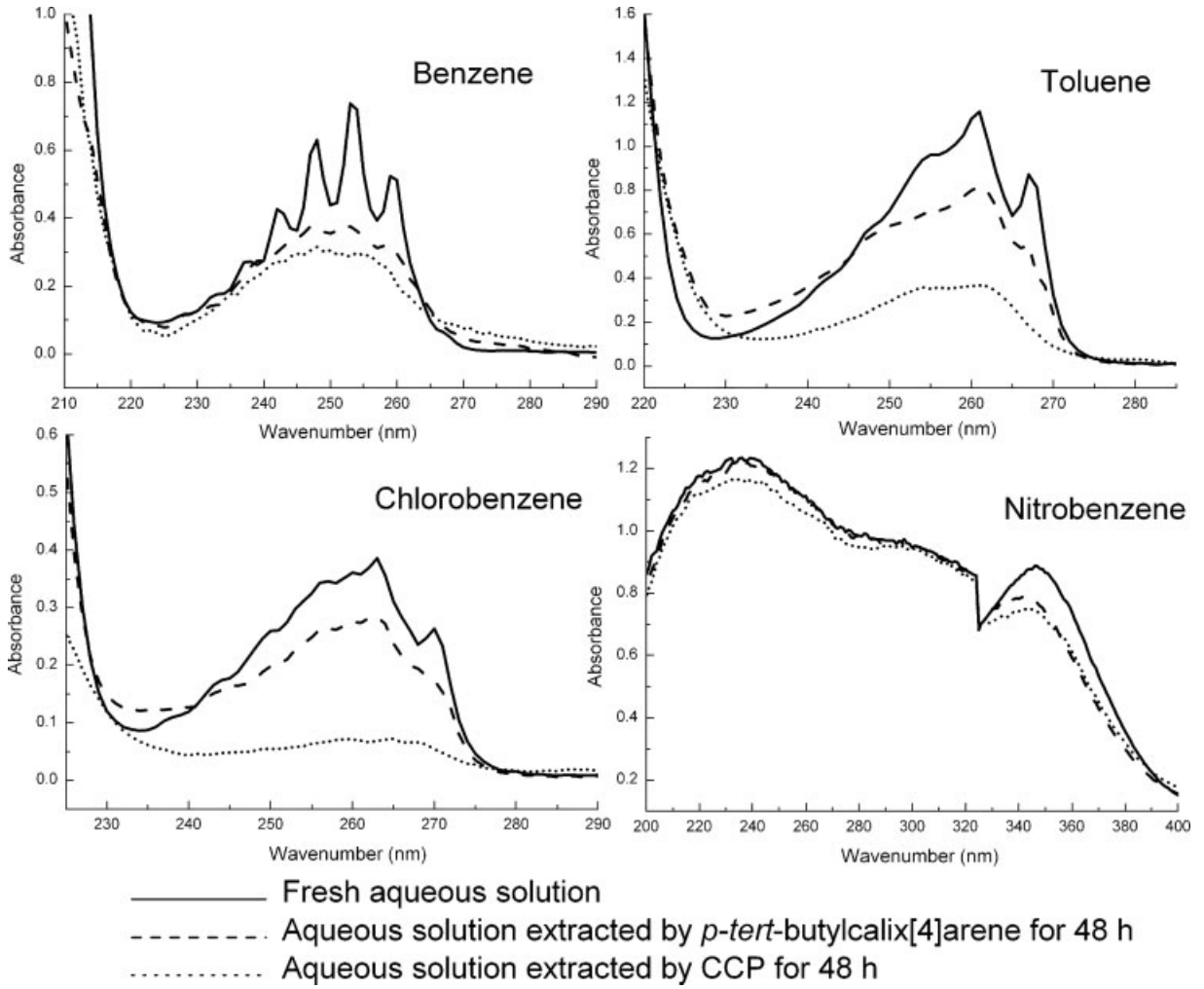


Figure 3 The decrease of UV absorbance of benzene, toluene, chlorobenzene, and nitrobenzene in aqueous solutions extracted by CCP and monomeric *p-tert*-butylcalix[4]arene for 48 h.

toluene, chlorobenzene, and nitrobenzene are 550, 700, 700, and 700 ppm, respectively. Based on eq. (2), after 48 h extraction by CCP hydrogel, the final concentrations are 223, 221, 128, and 643 ppm, respectively. The CCP hydrogel extracts toluene and chlorobenzene molecules from aqueous solution better than benzene, and almost cannot extract nitrobenzene. The data are shown in Table I.

Runs 1–3 in Table I also shows that $C_{hydrogel}$ is much higher than C_{final}, which indicates that toluene, chlorobenzene, and benzene molecules could be extracted into the calix[4]arene cavity of CCP hydrogel from aqueous solution, while nitrobenzene molecule cannot. As shown in Figure 4, the diameter of the calix[4]arene cavity is smaller than that of nitrobenzene, which results in the rejection of nitroben-

TABLE I
Extraction of Aromatic Molecules from Aqueous Solution

Run	Guest molecule	Maximum UV absorbance	Diameter (Å)[a]	$C_{initial}$ (ppm)	C_{final} (ppm)[b]	$C_{hydrogel}$ (ppm)[c]
1	Nitrobenzene	241 nm, 1.234	5.59	700	657	717
2	Toluene	261 nm, 1.157	5.41	700	221	7,983
3	Chlorobenzene	263 nm, 0.386	5.39	700	128	9,533
4	Benzene	253 nm, 0.737	5.01	550	223	3,783

[a] Diameter of the guest molecule from Ref. 21.
[b] Estimated by eq. (1).
[c] Calculated by eq. (2).

zene molecule into the calix[4]arene cavity. As compared with benzene, the cavity size is too large, and the molecule cannot be fixed in the cavity leading to a low extraction capacity. However, toluene and chlorobenzene molecules just fit the size of cavity, which leads to a high extraction capacity attributing to the formation of a stable complex. Thus it could be concluded that CCP hydrogel can selectively extract guest molecules from aqueous solution into its calix[4]arene cavity according to the molecule diameter. And, the diameter of the calix[4]arene cavity is inferred to be about 5.4 Å close to that of toluene or chlorobenzene molecules. This cavity size coincides well with the cavity diameter of calix[4]-arene having 1,3-alternate conformation determined by X-ray,[22] which indicates that conformation of calix[4]arene units altered from cone conformation to 1,3-alternate conformation during the polycondensation reaction. Furthermore, as Figure 3 shows, the extraction efficiencies of monomeric *p-tert*-butylcalix[4]arene under the same conditions are significantly low, which may be due to the hydrophobicity and strong hydrogen bonding of monomeric *p-tert*-butylcalix[4]arene leading to a conglomeration in aqueous solution.

Adsorption of naphthalene from gas phase

The CCP can also adsorb guest molecules from gas phase. As shown in Figure 5, the weight of naphthalene adsorbed by 500 mg CCP is 92.2 mg after 48 h. Nevertheless, 500 mg active carbon only adsorbs 24.9 mg naphthalene under the same condition. The inclusion capacities of calix[4]arene units in the polymer toward naphthalene molecules[23] may provide the driving force of adsorption behavior leading to the directional transfer from gaseous phase into the polymer.

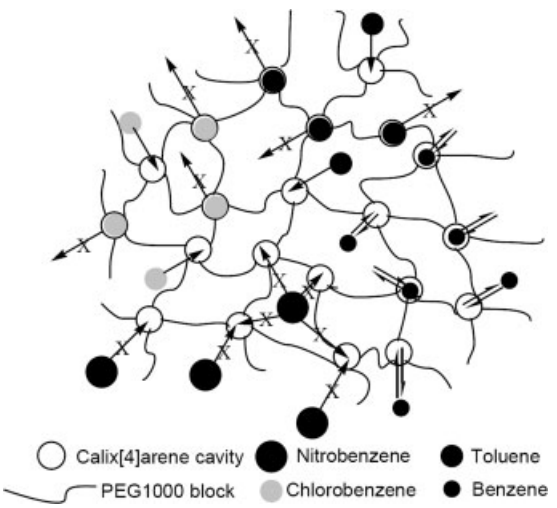


Figure 4 Conceivable mechanism of selectively extracting guest molecules from aqueous solution into the calix[4]-arene cavities.

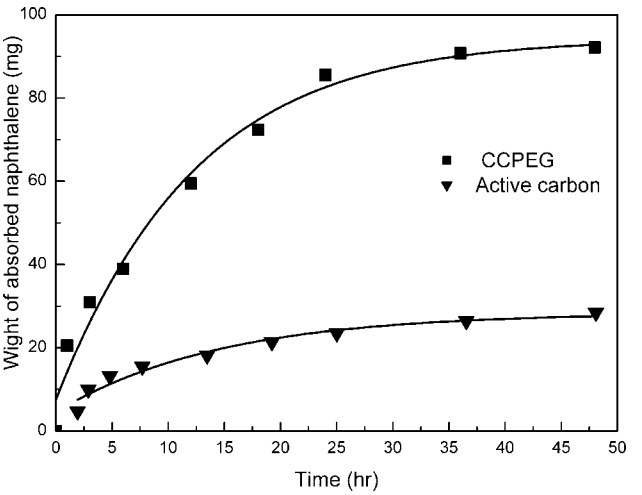


Figure 5 The weight of naphthalene adsorbed by CCP (500 mg) and active carbon (500 mg) from gas phases versus time.

CONCLUSIONS

Novel CCP containing calix[4]arene cavity and elastic networks has been synthesized. The hydrogel prepared from CCP can selectively extract aromatic molecules according to their diameters into the calix[4]-arene cavity from aqueous solution. Thus, the diameter of the calix[4]arene cavity could be inferred by the extracted molecule. Furthermore, CCP can also adsorb naphthalene from gas phase showing significantly high capacity than active carbon.

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