

Synthesis and Absorption Properties of Calix[6]amides-based Polymers

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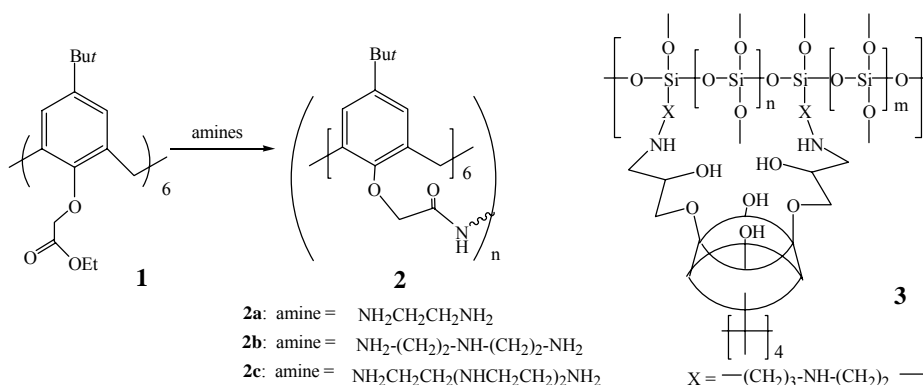
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Abstract: Reacting calix[6]arene hexaesters with poly(ethyleneimine), a series of calix [6]amides-based polymers were obtained for the first time. It is found that they show high absorption capacities towards soft cations comparing to hard cations, and the absorption abilities enhanced with the increasing of calixarene content, which may indicates the cavity of calixarene plays crucial role in absorption. Polymer **2c** shows good selective absorption capability towards Ag^+ among the tested cations.

Keywords: Calix[6]arene, polymer, absorption.

Calixarene-based polymers play an important role in all kinds of calixarene derivatives. They have been applied in many research fields, such as catalyst¹, CE², gas chromatogram³, ion chromatogram⁴. Although all kinds of calix[4]arene polymers and their recognition properties have been reported, however, only few papers concerned calix [6]arene polymers. Shinkai's group⁵ and Glenmon's group⁶ have reported several calix [6]-based polymers and found that some of these polymers showed remarkable recognition abilities towards alkali metal ions and UO_2^+ , etc. Considering the size of cavity of calixarene can greatly influence the complexation abilities of calixarene polymers, herein, we wish to report the synthesis and absorption properties of a series of calix[6]amides-based polymers for the first time.



Experimental

IR spectra were measured on AVATAR 360 spectrophotometer. Elemental analyses were carried out with Carlo-Erba1106 analyzer. Atomic absorption was measured on WFX-11 spectrograph. Compound **1** was synthesized according to the literature method⁷.

Compound **1** was refluxed with poly(ethyleneimine) (4 equiv.) in methanol-toluene (1:1, V/V) solution for 10 h. After removing of the solvent, the residue was dissolved in CHCl₃, washed by water for three times and the CHCl₃ was evaporated, polymers **2** were obtained as straw yellow powders. **2a**: Selected IR(KBr, cm⁻¹): $\nu(\text{N-H})=3302\text{br}$ and 1537s , $\nu(\text{C=O})=1664\text{s}$; Elemental analysis found: N, 6.25; C, 71.95; H, 7.92, the content of calix in per gram of polymer is 0.72mmol after calculation. **2b**: IR(KBr, cm⁻¹): $\nu(\text{N-H})=3301\text{br}$ and 1540s , $\nu(\text{C=O})=1664\text{s}$; Elemental analysis found: N, 8.46; C, 70.80; H, 8.24, the content of calix in per gram of polymer is 0.65mmol after calculation. **2c**: IR(KBr, cm⁻¹): $\nu(\text{N-H})=3292\text{br}$ and 1542s , $\nu(\text{C=O})=1664\text{s}$; Elemental analysis found: N, 10.35; C, 69.75; H, 8.50, the content of calix in per gram of polymer is 0.59 mmol after calculation.

Results and Discussion

The structures of polymers **2a-c** were characterized by IR and elemental analyses. In their IR spectrum, the strong absorb peaks at 3300 cm⁻¹ and 1540 cm⁻¹ indicated the presence of N-H bonds and the absorb peaks of esters were disappeared which means almost all of the ester groups were exchanged by amines. On the other hand, from the results of elemental analyses, the calixarene content in **2a-c** can be calculated by the percent of oxygen in these polymers. The calixarene content in **2a-c** are 0.72, 0.65, 0.59 mmol per gram, respectively.

Normally, the calixarene polymers were synthesized by connecting calixarene or functional calixarene with polymers such as siloxane polymers and chloromethylated polystyrene. The calixarene content in these kinds of polymers were low (0.01-0.1 mmol/g in most literatures⁸). In this paper, calix[6]arene was copolymerized with enamines directly, the obtained polymers **2a-c** possess high calixarene contents which are very favorable for using cavities of calixarene to recognize guests. Thus, the absorption capabilities of polymer **2a-c** towards some cations had been studied and the results were shown in **Table 1** (polymer **3** as reference compound).

From **Table 1**, it can be seen that polymer **2a-c** showed high absorption capacities towards soft cations (Ag⁺, Hg²⁺) comparing with that towards hard cations (Na⁺, K⁺). This results are in accord with the characteristic of amide group which is easily to bind soft cations but difficult to hard cations. On the other hand, it can be seen that the absorption capacities towards cations show the change: **2a** > **2b** > **2c**, which may indicates that the cavities of calix[6]arene play crucial role in binding cations, *i.e.* the change of calixarene content per gram of telomer is **2a** > **2b** > **2c**, so the complexation capabilities show similar change¹¹. Comparing with the absorption capacities of calix[4]amides-based polymer **3**, it can be seen that polymer **2** possess very high absorption capacities towards Ag⁺ but low absorption capacities towards Cu²⁺. These

results may also support that the cavities of calix[6]arene play crucial role in binding cations. Because the radius of Ag^+ (126 pm) is larger than that of Cu^{2+} (72 pm), so the larger cavity of calixarene is more favorable for binding Ag^+ , which also indicate the size of cavity of calixarene can greatly influence the complexation abilities of calixarene polymers. It is worthy to note that **2c** exhibit high selective absorption capability towards Ag^+ among the tested cations, which is very outstanding in the calixarene polymers, although some calix[4]-based polymer showed high selective binding abilities towards cations with small radius, such as Li^+ ¹².

Table 1 Absorption capacities (10^{-5} mmol/mg) of polymers **2a-c** and polymer **3** towards cations at concentration of 2×10^{-4} mol/L^a

cations	2a	2b	2c	3 ^b
Ag^+	38.5	35.5	32.9	< 1
Hg^{2+}	31.7	14.3	4.4	11.7
Cu^{2+}	10.6	10.3	9.3	19.6
K^+	4.9	4.5	1.2	/
Na^+	3.2	2.8	0.9	/

^a according to the method described in literature⁹; adding 20 mg polymer to 10 mL of 2×10^{-4} mol/L cation solution, then the solution was stirred 4 h at 30°C. After filtration, the concentration of cations was measured by atomic absorption spectrograph. The absorption capacities were calculated by formula $Q = (C_{\text{cation}} - C'_{\text{cation}})V_{\text{cation}}/W_{\text{telomer}}$.

^b These data quoted from Ref.10.

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