Synthesis and Properties of Calixcrown Telomers

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The synthesis and complexation properties of a series of novel calixcrown telomers **6–9**, and characteristics of the calixcrown siloxane telomer **9** as a GC stationary phase are described.

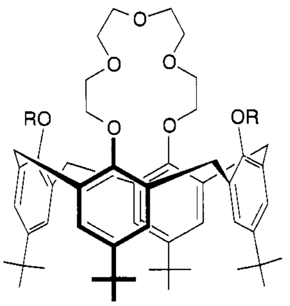
Recently, calixarenes have received increasing attention in supramolecular chemistry.[1,2] Various methods for functionalizing calixarenes have been developed and numerous calixarene derivatives have been synthesized in the past two decades.[3] The calixcrowns, which are calixarenes bridged by a polyethylene glycol chain, were found to be a new class of potassium-selective ionophores.[4,5] Compared with calixarene monomers, calixarene polymers are a much more recent innovation. Only a few examples have been reported: a polystyrene-immobilized calix[6]arene as a uranophile,[6] a polymer of calix[4]arene methacrylate as an Na^+ ionophore,[7] and a silica gel-immobilized calixarene as a liquid chromatography stationary phase.[8] Here we report the synthesis and properties of a series of novel calixcrown telomers **6–9**.

Refluxing a mixture of *p-tert*-butylcalix[4]arene and tetraethylene glycol ditosylate in benzene in the presence of K_2CO_3 afforded *p-tert*-butylcalix[4]crown-5 **1**. Treatment of **1** with NaH followed by ethyl bromoacetate in dioxane gave *p-tert*-butylbis(ethoxycarbonylmethoxy)calix[4]crown-5 **2** in 78% yield after purification by recrystallization from ethanol, mp 218–220 °C. The calixcrown ester **2** was converted (NaOH, H_2O) into *p-tert*-butyldicarboxymethoxycalix[4]crown-5 **3** in 89% yield, mp 264–266 °C. *p-tert*-Butyldiundecenylcalix[4]crown-5 **4** was obtained in 82% yield after purification by column chromatography from the reaction of **1** with undecenyl tosylate (NaH, benzene). The structures of compounds **2–4** were confirmed by IR, MS and ^1H NMR spectra and elemental analyses. The ^1H NMR spectra showed that all these compounds exist in a cone conformation.[9]

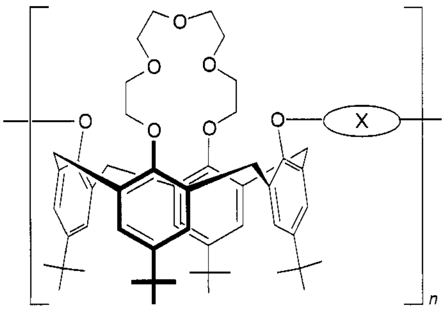
p-tert-Butylcalix[4]crown-5 **1** was treated sequentially with NaH and triethylene glycol ditosylate in a minimum amount of dioxane to give the calixcrown ether telomer **6** after purification by reprecipitation from a chloroform–methanol system, $\bar{M}_n$ = 5400 (vapour phase osmometer). The calixcrown ester telomer **7** ($\bar{M}_n$ = 6300) was prepared from **1** and decanedioyl chloride by a similar precedure. Mixing the calixcrown acid **3** with 1,10-decanediamine in ethanol afforded the corresponding ammonium salt, which was heated under reduced pressure to give the calixcrown amide telomer **8** ($\bar{M}_n$ = 7100) after purification by reprecipitation from a dichloromethane–methanol system. The calixcrown siloxane telomer **9** ($\bar{M}_n$ = 4900) was prepared by hydrosilylation of *p-tert*-butyl-diundecenylcalix[4]crown-5 **4** with dichloromethylsilane in the presence of H_2PtCl_6–Pr^iOH, which afforded the disilylcalixcrown **5**, which was then polycondensed with silanol-terminated dimethyl silicon oil ($\bar{M}_n$ = 500) in a molar ratio of 1 : 3.3, and was finally treated with excess chlorotrimethylsilane.

The structures of the calixcrown telomers **6–9** were characterized by IR and ^1H NMR spectra and elemental analyses. The elemental analysis and ^1H NMR spectrum indicated that the calixcrown content in **9** is 0.25 mmol per gram of the calixcrown siloxane telomer. We deduced that the calix[4]arene units in the calixcrown telomers **6–9** all exist in a cone conformation from their ^1H NMR spectra and the structures of the calixcrown monomers.

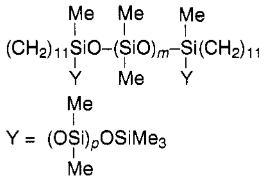
Results of two-phase extraction measurements[10] with the calixcrown telomers and Li^+, Na^+, K^+, NH_4^+ picrates are summarised in Table 1; data obtained with two calixcrown monomers are included for comparison purposes. The results demonstrate that the phase-transfer efficiency and selectivity of the calixcrown telomers are related to the type of chain linking the calixcrown units. The calixcrown ether telomer **6** and the calixcrown amide telomer **8** have much higher phase-transfer efficiencies than the calixcrown ester telomer **7** and the calixcrown siloxane telomer **9**, because the inter-calixcrown bridges provide additional binding sites in the former two telomers, which are not available in the latter two. Efficiency for K^+ increased in the order **9** < **7** < **6** < **8** and the K^+/Na^+ selectivity increased in the reverse order. The calixcrown ether telomer **6** showed an unusual higher phase transfer efficiency for NH_4^+ than all the other calixcrown telomers and monomers, due to the inter-calixcrown tri(oxyethylene) bridge in **6**. All the calix[4]crown-5 telomers and monomers examined showed selectivity for K^+ and poor efficiency for Li^+. The phase transfer



R
1 H
2 CH_2CO_2Et
3 CH_2CO_2H
4 $(CH_2)_9CH{=}CH_2$
5 $(CH_2)_{11}SiCl_2Me$



X
6 $CH_2(CH_2OCH_2)_2CH_2$
7 $CO(CH_2)_8CO$
8 $CH_2CONH(CH_2)_{10}NHCOCH_2$

9


$$(CH_2)_{11}\underset{Y}{\overset{Me}{Si}}O{-}(\underset{Me}{\overset{Me}{Si}}O)_m{-}\underset{Y}{\overset{Me}{Si}}(CH_2)_{11}$$

$$Y = (O\underset{Me}{\overset{Me}{Si}})_pOSiMe_3$$

efficiency for K^+ of the telomers **6–9** is comparable to that of the corresponding monomer **1** or **2**, while the selectivity is somewhat lower.

Transport experiments for LiCl, NaCl, KCl, NaSCN and KSCN were carried out with a $H_2O–CHCl_3–H_2O$ liquid membrane system[11] using the calixcrown telomers **6–9** as cation carriers. The results of the cation transport experiments are in good agreement with those of the two-phase extraction measurements.

Though McKervey and Böhmer have mentioned using *p-tert*-calix[8]arene as a stationary phase in a review,[2] no paper concerning calixarenes as the stationary phase in gas chromatography has yet been published, as far as we know. Our group had synthesized a series of crown ether-containing polysiloxanes and successfully used them as GC stationary phases.[12] The calixcrown siloxane telomer **9** should also be suitable for use as a GC stationary phase. A fused-silica capillary column, which was coated with a 0.5% solution of the telomer **9** in dichloromethane by the static method, showed very high column efficiency (number of effective plates n = 4500 m^{-1}, determined using naphthalene at 120 °C). A wide range of compounds (both polar and non-polar) such as aromatics, alcohols and hydrocarbons can be separated effectively on this column. This column showed excellent separation abilities for positional isomers. For example, the capacity factors (k') for *o*-, *m*- and *p*-chlorophenol (at 170 °C) are 0.284, 0.782 and 0.974, respectively; k' for *o*-, *m*- and *p*-benzenediol (at 190 °C) are 0.462, 0.939 and 1.612, respectively; k' for *o*-, *m*- and *p*-xylene (at 80 °C), are 1.098, 1.892 and 1.239, respectively. Most calixarene derivatives are unsuitable for use as stationary phases in capillary GC because of their very high melting points and the difficulty in coating them onto a capillary column. But the calixcrown siloxane telomer **9** is a very good stationary phase in GC due to its low glass transition temperature (as a gum at room temperature), excellent chemical and thermal stability, and both hydrophilic and lipophilic cavities which can interact with various types of compounds. Details of the calixcrown siloxane telomer **9** and another non-crown calix[4]arene siloxane telomer as GC stationary phases will be published elsewhere.

Table 1 Percentage extraction of picrate salts in $CHCl_3$ at 25 °C[a]

	Calixcrown telomer					
Picrate salt	1	2	6	7	8	9
Li^+	0.08	0.3	3.2	0.4	1.2	0.4
Na^+	0.3	5.4	7.3	0.7	21.5	0.4
K^+	11.8	41.5	33.5	9.2	40.7	7.6
NH_4^+	1.5	0.4	12.6	0.8	1.6	0.5

[a] 1.00 ml of a 0.005 mol dm^{-3} receptor solution in $CHCl_3$ was shaken (10 min) with 1.00 ml of a 0.005 mol dm^{-3} picrate salt solution in H_2O and the percentage extraction was measured from the resulting absorbance at 380 nm.

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References

1 E. van Dienst, W. I. I. Bakker, J. F. J. Engbersen, W. Verboom and D. N. Reinhoudt, *Pure Appl. Chem.*, 1993, **65**, 387.

2 M. A. McKervey and V. Böhmer, *Chem. Br.*, 1992, 724.

3 J.-D. van Loon, W. Verboom and D. N. Reinhoudt, *Org. Prep. Proced. Int.*, 1992, **24**, 437.

4 P. J. Dijkstra, J. A. J. Brunink, K.-E. Bugge, D. N. Reinhoudt, S. Harkema, R. Ungaro, F. Ugozzoli and E. Ghidini, *J. Am. Chem. Soc.*, 1989, **111**, 7567.

5 E. Ghidini, F. Ugozzoli, R. Ungaro, S. Harkerma, A. A. El-Fadl and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1990, **112**, 6979.

6 S. Shinkai, H. Kawaguchi and O. Manabe, *J. Polym. Sci., Polym. Lett.*, 1988, **26**, 391.

7 S. J. Harris, G. Barrett and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, 1991, 1224.

8 J. D. Glennon, K. O'Connor, S. Srijaranai, K. Manley, S. J. Harris and M. A. McKervey, *Anal. Lett.*, 1993, **26**, 153.

9 C. D. Gutsche, B. Dhawan, J. A. Levine, K. Y. No and L. J. Bauer, *Tetrahedron*, 1983, **39**, 409.

10 G. M. Lein and D. J. Cram, *J. Am. Chem. Soc.*, 1985, **107**, 448.

11 J. D. Lamb, J. J. Christensen and R. M. Izatt, *J. Chem. Educ.*, 1980, **57**, 227.

12 X.-C. Zhou, C.-Y. Wu, X.-R. Lu and Y.-Y. Chen, *J. Chromatogr.*, 1994, **662**, 203.