Syntheses and characterizations of two copolymers containing cone conformations of calix[4]arenes in the polymer backbone

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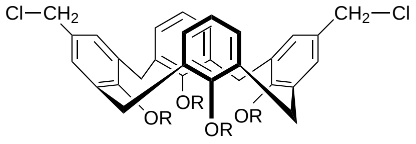
Two new polymers containing calix[4]arenes in the cone conformation were synthesized *via* condensation reactions.

Calix[4]arenes are cyclic tetramers of *tert*-butylphenol and formaldehyde which can be synthetically manipulated to assume rigid, cone-like structures which possess an upper rim defined by the *para*-positions of the aromatic rings, and a lower rim defined by the oxygen atoms. This conformation of calix[4]arenes is highly preorganized and forms complexes with neutral molecules or metal ions.[1] In order to enhance the affinity of calix[4]arenes towards certain metal ions (in particular sodium) ionophoric groups containing carbonyl or ether functionality may be appended to the lower rim.[2]

We report a new application for the well established binding properties of calix[4]arenes that involves incorporating them into polymers. These new polymers may then be processed into materials suitable for chemical sensor devices such as ion-selective electrodes and filtration/extraction membranes. Previously reported sensor devices based on calixarenes have been fabricated by blending the calixarene molecules into polymer melts or other membrane composites.[3,4] Blending methods have several drawbacks including non-uniform ordering of the calixarene units, leaching, and difficulty in reproducing a given set of properties in the blend.

Calixarene-based polymers have just begun to receive attention, and of the few reported, the calixarene moieties have been appended to the polymer *via* the lower rim of the calixarene monomers.[5] A calixarene-based water soluble polymer has also been reported in which the upper rim of the calixarene was used as the site of attachment to the polymer.[6] Until very recently, no polymers have been reported in which the calixarenes were part of the polymer backbone. Dondoni *et al.* have successfully copolymerized a calixarene monomer in the 1,3-alternate conformation with Bisphenol A to yield a calixarene-based polymer which exhibited a higher binding affinity for silver ions than the individual calixarene monomer from which it was derived.[7] We report the syntheses of two calixarene-based copolymers with the following features: (1) the calixarene monomers are in the cone conformation, (2) the site of polymerization is located on the upper rim of the calixarene monomers and (3) the calixarene units are part of the polymer backbone.

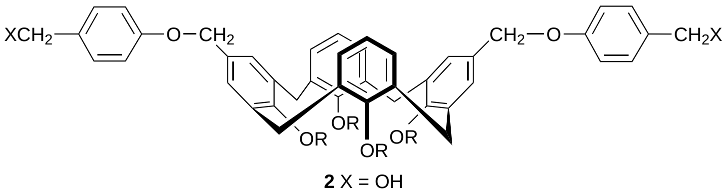
The scarcity of calixarene-based polymers is in part due to the difficulty in synthesizing rationally designed monomers. The key intermediate to both monomers, 5,17-dichloromethyl-25,26,27,28-tetraethoxyethylcalix[4]arene† **1**, was derived from the principal starting material 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene.[8] The conformationally mobile *tert*-butylcalixarene was first dealkylated at the upper rim using $AlCl_3$, then treated with 2-bromoethyl ethyl ether in the presence of sodium hydride to yield the tetraethoxyethyl calixarene which assumed the cone conformation.‡ The alkali metal binding properties of this ether-functionalized calix[4]arene were investigated by Shinkai and showed high selectivity for the sodium ion, prompting us to elaborate on its structure so that it could be incorporated into different types of polymers.[9]



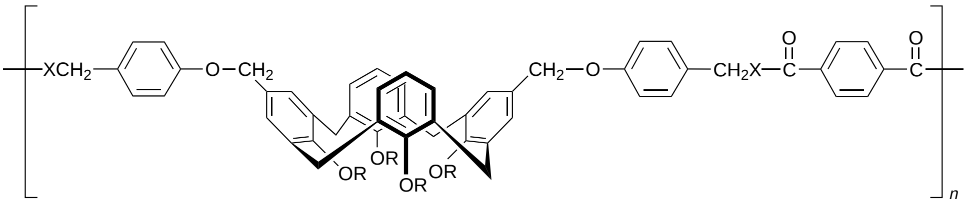
1
Cone conformation
R = CH_2CH_2OEt

The tetraethoxyethylcalixarene was selectively formylated on the upper rim by treatment with dichloromethyl methyl ether in the presence of tin(IV) chloride followed by hydrolysis of the geminal dichloride.[10] The aldehyde groups were then reduced to alcohols and the corresponding diol was transformed into the dichloride **1** by treatment with thionyl chloride. The dichloride **1** was next transformed into the two penultimate monomer compounds by reacting it with either *p*-bromo- or *p*-cyanophenol in the presence of sodium hydride to yield the corresponding dibromo and dicyano compounds which were converted into the diol monomer **2** and diamine monomer **3**, respectively. The extension of the 'arms' at the upper rim proved to be critical in the subsequent condensation copolymerization reactions because initial attempts to copolymerize various calixarene monomers with shortened 'arms' did not yield high molecular weight polymers.

Both calixarene monomers **2** and **3** were condensed with equal molar amounts of terephthaloyl chloride in dimethylacetamide. The polyester reaction was heated at 60 °C while the polyamide reaction was run at room temperature. Both copolymerization condensation reactions were allowed to react for 36 h. After that time, the solvent volume was reduced and methanol was added to the reaction mixtures to precipitate the copolymers, **4** and **5**.§ The isolated yields of the two white amorphous copolymers were 66 and 50% for the polyester **4** and polyamide **5**, respectively. The glass transition temperatures (T_g) were measured using differential scanning calorimetry and the T_g for **4** was found to be 141 °C and that of **5** was determined to be 100 °C. Due to the amorphous structure of the copolymers, no melting transitions (T_m) were observed in the thermograms.



2 X = OH
3 X = NH_2



4 X = O
5 X = NH

The thermal stabilities of each copolymer were determined by thermal gravimetric analyses (TGA) in a nitrogen atmosphere. The temperatures at which 10% weight loss occurred were 352 and 380 °C, respectively, for **4** and **5**. The inherent viscosities for the copolymers were measured using an Ostwald viscometer with chloroform as the solvent at 25 °C and were found to be 0.12 dl g^{-1} for **4** and 0.14 dl g^{-1} for **5**.[11] The fact that both copolymers were completely soluble may provide additional evidence that the copolymers are amorphous.[11*b*] The molecular weights for each copolymer were determined by size exclusion chromatography (SEC) against polystyrene standards. The eluent used in the SEC analyses was THF and the samples were run at room temperature. The chromatograms for each polymer showed only one broad signal from which the number-average molecular weights (M_n) were determined to be 29 000 Da for the polyester **4** and 52 000 Da for the polyamide **5**. Qualitatively the broadness of the signals reflects a certain degree of polydispersity. However, since no experimental determination of the weight-average molecular weight (M_w) was made, a quantitative value of the polydispersity was not obtained. Based on the step-growth nature of the copolymers *via* the condensation reactions, the polydispersity is likely to be *ca*. 2.[11*c*] Even though the signals in the ^{1}H NMR spectrum for **4** and **5** were broadened at room temperature, it was possible to discern that the calixarene moieties were still in the cone conformation. We are currently investigating the alkali metal binding properties of each copolymer in comparison with the tetraethoxyethylcalixarene previously studied in order to determine if any cooperativity is displayed.[12]

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Footnotes and References

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† IUPAC name: $1^5,3^5,5^5,7^5$-chloromethyl-$1^2,3^2,5^2,7^2$-(3-oxapentoxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane.

‡ The cone conformation is identified in the ^{1}H NMR spectra of **1**–**5** by the presence of the AX quartet (doublet of doublets) typically at 4.4 and 3.4 ppm for the diastereotopic hydrogens of the methylene carbons connecting the aromatic rings in the calixarene moieties.

§ Compounds **2**–**5** gave elemental C and H analyses that were within 0.3% of theoretical and ^{1}H and ^{13}C NMR spectra consistent with their assigned structures.

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