

Synthesis and receptor properties of calix[4]arene–bisphenol-A copolymers

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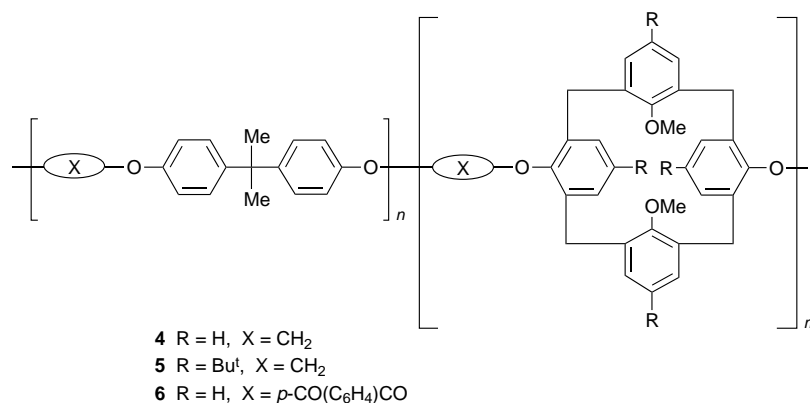
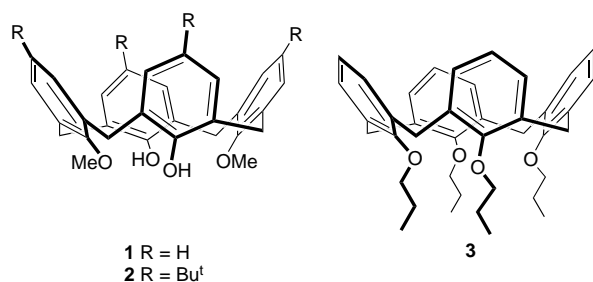
The synthesis of 1,3-dimethyl calix[4]arene–bisphenol-A copolyethers and copolyesters with variable amounts of the macrocycle in the chain is described; the receptor ability of the copolyethers **4 toward silver(i) ions was one hundred-fold that of calix[4]arene tetrapropyl ether **3**.**

Compared with the considerable interest during recent years in the use of calixarene monomers as platforms for the construction of supramolecular receptor assemblies,¹ there are few studies on calixarene-containing polymers, most of which exhibit the macrocycle moiety as an appendage of the polymer chain.² This issue has been addressed in recent reports. One of these describes the synthesis and the cation receptor properties of low molecular weight calixcrown telomers with different chain backbones such as ether, ester, amide and siloxane;³ a second deals with the synthesis of oligomers by ruthenium-catalysed metathesis of alkenyl substituted calixarenes;⁴ and the third describes the optical properties produced by the incorporation of an upper-rim derivatized calix[4]arene in a water-soluble antenna polyacrylate.⁵ It thus appears that calixarene insertion in a polymer chain may give rise to new materials where the intrinsic properties of the macrocycle are enhanced and efficiently exploited. Among the broad range of applications of calixarene-based polymers, one can foresee their use as sensors for chemical and biochemical species,⁶ as substrates for the construction of membranes for selective transport of ions,⁷ and as antioxidant additives of other polymeric materials.⁸ We report here the first synthesis of high molecular weight copolyethers and copolyesters incorporating 1,3-(dis-

tal)calix[4]arene and bisphenol-A moieties in the chains in different ratios and describe preliminary studies of the receptor properties of these materials.⁹

A mixture of 1,3-dimethyl calix[4]arene **1**, bisphenol-A and NaH in a minimum amount of anhydrous THF was stirred at room temperature for 0.5 h, then concentrated. The suspension of the sodium salts in toluene was treated with tetrabutylammonium hydrogensulfate and dibromomethane (10 equiv.) at 60–80 °C for 16 h to give the copolyether **4** (50–60% yield) after reprecipitation from a large volume of acidified methanol. The M_w of this material ranged between 15 000 and 24 000 (determined by GPC analysis referenced to polystyrene standards) depending on the reaction temperature and the amount of the phase transfer reagent (40–80 mol%), and the polydispersity (M_w/M_n) was between 4 and 8. ¹H NMR analysis revealed that the calixarene content in the polymer chains varied depending on the phenolic monomers ratio. Typically a 0.5 : 1 molar ratio of **1** and bisphenol-A led to a copolyether containing 25% of **1** with respect to bisphenol-A whereas a 1 : 1 ratio gave 50% content.† Higher ratios (2 : 1 up to 10 : 1) did not increase the calixarene content but produced a substantial decrease in yield of the isolated material (20%). Copolyether **5** (M_w 10 000, ca. 60% yield) was prepared from 1,3-dimethyl *p*-*tert*-butylcalix[4]arene **2** by the same procedure. This calixarene proved to be less reactive than **1** in the copolymerization process, thus resulting in low incorporation in the polymer chains to a 20% maximum content. Copolyethers **4** and **5** were semicrystalline materials with a melting temperature range of 210–250 °C and were soluble in chloroform and toluene at room temperature. These copolyethers showed glass transition temperatures between 80 and 120 °C depending on the molecular weight. They showed rather complex ¹H NMR spectra both at low (–40 °C) and high temperatures (120 °C) indicating that the calixarene units exist in numerous statistical conformations, each one being determined by its adaptability to the complex arrangement of the polymer chains in solution.

Treatment of the mixture of the sodium salts of **1** (0.5 equiv.) and bisphenol-A (1 equiv.) with terephthaloyl chloride (1 equiv.) under the above conditions (toluene, Bu₄NHSO₄, 60 °C, 16 h) gave, after a similar purification, the copolyester **6** in 66% yield. The soluble fraction of the recovered material (ca. 20% in CHCl₃ at room temperature) showed a M_w of ca. 21 000 (GPC



analysis). The calixarene content appeared to be 24% from its ^1H NMR spectrum. This content increased to 50% in the copolymer obtained under the same conditions but starting from a 1:1 ratio of the phenolic monomers.† Both polymers were soluble only in 1,1,2,2-tetrachloroethane at 120 °C.

The Ag^+ binding properties of the calixarene containing copolyether **4** were compared with those of the known¹⁰ calix[4]arene tetrapropyl ether **3** using the picrate extraction procedure¹¹ originally described by Cram and coworkers.¹² Recent work by Ikeda *et al.*¹³ has demonstrated that Ag^+ is bound to cone and partial-cone calixarenes by π -donor participation of the phenyl rings. Results of two-phase extraction measurements with **4** at 50% calixarene content showed linear correlations between the calixarene concentration and the picrate exchange between the aqueous and organic phase (Fig. 1). We noted also that the extraction by the calixarene in the copolymer is about one hundred-fold that of the tetrapropoxy derivative **3**.§ The involvement of the calixarene in the picrate extraction was proved by the same efficiency shown by a two-fold more concentrated solution of the copolyether **4** at 25% calixarene content.¶ Finally, the decreased concentration of Ag^+ in the aqueous layer was confirmed by atomic absorption spectroscopy.

The more pronounced extraction of Ag^+ by the calixarene moiety in the copolyether **4** than in the compound **3** suggests that in the former there are more units of the macrocycle with the required conformation for cation- π -interaction. Unfortunately the complexity of the NMR spectra of the polymeric materials did not allow more detailed study. The binding properties of the copolyester **6** could not be studied because of its low solubility in organic solvents at room temperature.

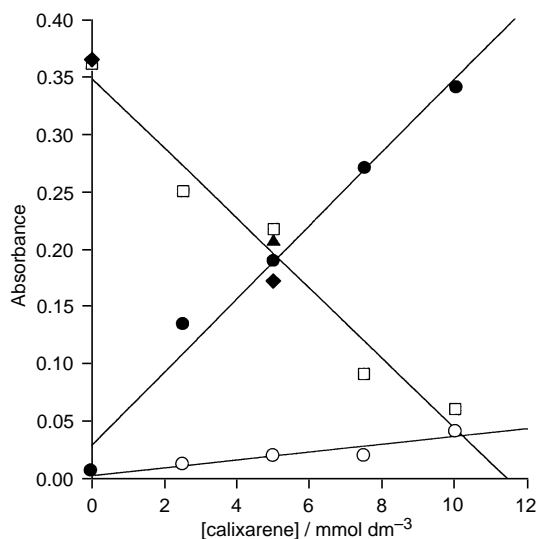


Fig. 1 Absorbance changes of: (a) aqueous solution of AgNO_3 (10^{-2} M) and picric acid (2.38×10^{-3} M) extracted with the CHCl_3 solutions of **4** with (□) 50% and (◆) 25% calixarene content; (b) the corresponding CHCl_3 solutions of **4** with (●) 50% and (▲) 25% calixarene content; (c) CH_2Cl_2 solution of compound **3** (○) after extraction of the above aqueous solution ($\lambda = 356$ nm)

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Footnotes

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† Selected data for copolyether **4** (from a 1:1 ratio of the phenolic monomers); ^1H NMR (300 MHz, CDCl_3 , 20 °C): δ 7.13 and 6.96 (2 d, 8 H, $J = 9.0$ Hz, 2 Ar of bisphenol-A), 6.55–6.29 (m, 12 H, 4 Ar of calixarene), 5.58 (s, 4 H, 2 OCH_2O), 4.55–2.80 (m, 14 H, 4 ArCH_2Ar , 2 OCH_3), 1.61 (s, 6 H, 2 CH_3).

‡ Selected data for copolyester **6** (from a 1:1 ratio of the phenolic monomers); ^1H NMR (300 MHz, CDCl_3 , 20 °C): δ 8.30 (s, 8 H, 2 $p\text{-COOC}_6\text{H}_4\text{CO}$), 7.32 and 7.15 (2 d, 8 H, $J = 9.0$ Hz, 2 Ar of bisphenol-A), 6.80–6.20 (m, 12 H, 4 Ar of calixarene), 4.20–2.80 (m, 14 H, 4 ArCH_2Ar , 2 OCH_3), 1.72 (s, 6 H, 2 CH_3).

§ Copolyethers **4** are not soluble in CH_2Cl_2 , therefore their binding properties were evaluated using CHCl_3 as a solvent.

¶ Polyethers not incorporating calixarene units (*i.e.* **4** where $m = 0$) did not display any complexation of silver(i) cations.

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