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Formation of ionic polymers by the alkylation of polyethyleneimine with tetra-chloromethyl and mono-bromopropyl substituted calix[4]arenes

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An insoluble cross-linked polymer has been obtained by functionalization of polyethyleneimine. The functionalization reaction has been carried out by treating a 50% aqueous solution of polyethyleneimine with 5,11,17,23-tetrachloromethyl-25,26,27, 28-tetrahydroxycalix[4]arene. The cross-linking takes place by alkylation of the amine nitrogens of different polymer chains by the chloromethyl groups on the upper rim of the calixarene. A soluble functionalized polymer with a single chemical link between each calix[4]arene and the polymer has been prepared by treating polyethyleneimine with 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene. The reaction involves alkylation of the polyethyleneimine nitrogen of the polymer by the bromopropyl group on the upper rim of the calix[4]arene.

INTRODUCTION

The calixarenes are phenolic metacyclophanes that can be used to selectively occlude organic molecules and metal ions based on their size and shape.[2] The growing interest in calixarene chemistry comes from their conformational properties, in addition to the ease with which chemical modifications can be made to both their upper and lower rims. The phenolic groups of the upper rim are particularly amenable to synthetic modification, and functional groups as ketones,[3] esters,[3,4] ethers,[5] amides,[6] and carboxylates[7] can be assembled at this rim. The resulting molecular assemblies have been used for the selective binding of inorganic ions such as Na^+,[8] Ca^{2+},[9] and UO_2^{2+},[10] and the products used for effecting the separation of these particular ions from solution.

A relatively new development in calixarene chemistry is their immobilization on polymeric supports. For certain applications such as the separation of heavy metal ions from aqueous media, it is advantageous for these calixarene-impregnated polymers to be available in an insoluble form. This goal is relatively easy to achieve since insoluble materials can be obtained by cross-linking the calixarene to the polymer *via* several attachment points. Since reactions leading to the chemical modification of calixarenes usually lead to functionalization at multiple sites, precursor calixarenes for such uses are readily available. Several examples of such cross-linked calixarene modified polymers are reported in the literature. An example by Harris *et al.* involves the synthesis of silicone bound calixarenes where the attachment is *via* multiple ester functionalities between the polymer and the calixarene.[11] A further cross-linked calixarene modified polymer has been prepared by Shinkai *et al.* from treating polyethyleneimine with a chloro-sulfonated calixarene.[12] These insoluble modified polymers have been used by Shinkai *et al.* for the extraction of uranium ion from seawater.[13]

Recently Harris *et al.* have reported the synthesis of a new calixarene bearing a single methacrylate functionality that is potentially suitable for using as a reagent to give living polymers and copolymers. Attempted homopolymerization of this compound, however, yielded an oligomer that had only approximately six calixarene units in the chain.[14] For our particular applications in radiopharmacy or electrokinetics we desire that the calixarene-impregnated polymer be soluble in aqueous media, and be attached by strong covalent bonds. In this paper we report a synthetic approach to using the water soluble polyethyleneimine polymer as support for calixarenes. This polymer was chosen because it has a chain of secondary amines that can potentially be alkylated by

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reaction with an alkyl halide to give a strong covalent carbon-nitrogen bond between the polymer and the calixarene. By using a calixarene with haloalkyl substituents at each position on the upper rim, a cross-linked functionalized polymer can be obtained that is insoluble in all solvents. By contrast, when a calixarene with a single haloalkyl substituent on the upper rim is employed, a calixarene functionalized polymer can potentially be obtained that is soluble in pure organic or in aqueous organic solvents.

EXPERIMENTAL SECTION

All compounds used were of reagent purity and used as supplied. Polyethyleneimine (50% by weight in water with an average molecular weight in the 50,000–60,000 range) was purchased from Aldrich. The compounds 5-allyl-25,26,27,28-tetrahydroxycalix-[4]arene and 5,11,17,23-tetrachloromethyl-25,26,27,28-tetrahydroxycalix[4]arene were prepared according to the literature procedures.[15,16] 5-(3-Bromopropyl)-25,26,27,28-tetrahydroxy calix[4]arene was prepared according to the procedure described in the immediately preceding paper.[17] Infrared spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer. ^{1}H NMR spectra were obtained on a GE Omega 400 NMR spectrometer. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. The thermogravimetric analysis was obtained on a Seiko SSC 5200 TGA/DTA instrument under an air atmosphere. The sample was heated at a rate of 1 degree per minute over the temperature range of 25–300°C.

Immobilization of 5-(3-bromopropyl)-25,26,27,28-tetrahydroxy calix[4]arene on polyethyleneimine

A solution of 5-(3-bromopropyl)-25,26,27,28-tetrahydroxy calix[4]arene (1.354 g, 2.48 mmol) in tetrahydrofuran (20 ml) was added dropwise to a stirred solution containing polyethyleneimine (3.716 g of a 50% solution in water) in water (10 ml). After the first few drops were added the solution turned cloudy, but further addition of the calixarene solution resulted in the formation of a clear brown solution. This solution was stirred for 5 h at room temperature. The reaction mixture was then shaken two times with 500 ml aliquots of a mixed acetone: petroleum ether (1:4) solution. The aqueous tetrahydrofuran layer was heated at 80°C under reduced pressure to yield a constant weight residue. This brown solid was collected. Yield 3.062 g (95%). Anal. Found: C, 61.2; H, 9.29; Br, 6.40; N, 19.9%. IR (KBr pellet): 2333 cm^{-1} and 2351 cm^{-1} $\nu(R_3\overset{+}{N}-H)$. The TGA gives $T_{\text{glass}} =$ 75.5°C (after extrapolation) and $T_{\text{decomp}} = 231.3$°C with the loss of 3.5% water until 93.8°C, and an additional 3.6% until 231.3°C.

Immobilization of 5,11,17,23-tetrachloromethyl-25,26,27,28-tetrahydroxycalix[4]arene on polyethyleneimine

A solution of 5,11,17,23-tetrachloromethyl-25,26,27,28-tetrahydroxycalix[4]arene (1.37 g, 2.22 mmol) in tetrahydrofuran (60 ml) was added dropwise to a stirred solution polyethyleneimine (9.84 g of a 50% solution in water) in water (100 ml). A precipitate was immediately formed. The mixture was stirred for 2 h at ambient temperature and then poured into acetone (500 ml). The precipitate was filtered and then washed with acetone (2 × 50 ml). The yellow solid polymer was dried to constant weight at 60°C under reduced pressure. Yield 4.77 g (76%). Anal. Found: C, 56.7; H, 9.34; Cl, 3.8; N, 22.5%. The calixarene impregnated polymer was insoluble in water and common organic solvents.

RESULTS AND DISCUSSION

Preparation of insoluble cross-linked polymers

Polyethyleneimine is a useful polymer for functionalization studies because it can be readily obtained in water soluble form, and it also has evenly spaced amine functional groups along the chain that can be used to introduce chemical modifications. Our synthetic approach to functionalizing the polymer is to introduce a haloalkyl substituent onto the calixarene, and to then use this group as an alkylating agent for the amine groups that are spaced along the polyethyleneimine chain. Such a route is shown schematically in Figure 1. By changing the relative stoichiometric ratio of the calixarene and the polyethyleneimine that is present in the solution, it is possible to quantitatively vary the loading of the calixarene that is bound onto the polymer chain up to the saturation limit of the polymer where all the amine groups are alkylated. For the preparation of insoluble cross-linked calixarene impregnated polymers it is possible to use the known compounds 5,11,17,23-tetrachloromethyl-25,26,27,28-tetrahydroxy calix[4]arene, which has a chloromethyl substituent bound to each of the *para* positions of the upper rim. This compound can be readily prepared by treating an unsubstituted calix[4]arene with *n*-octyl chloromethyl ether.[16]

When a solution of 5,11,17,23-tetrachloromethyl-25,26,27,28-tetrahydroxycalix[4]arene in THF is added dropwise to an aqueous solution of polyethyleneimine,

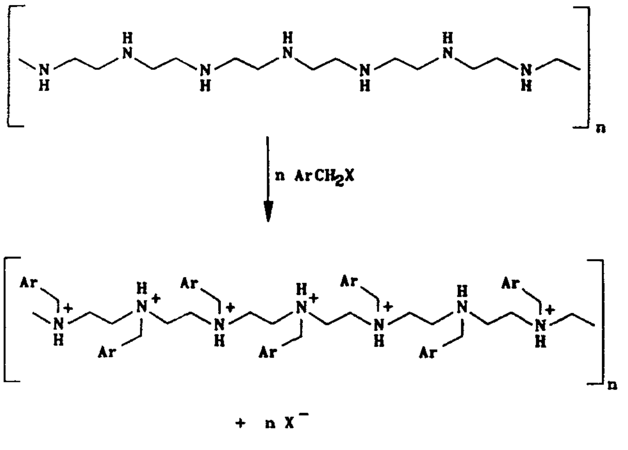
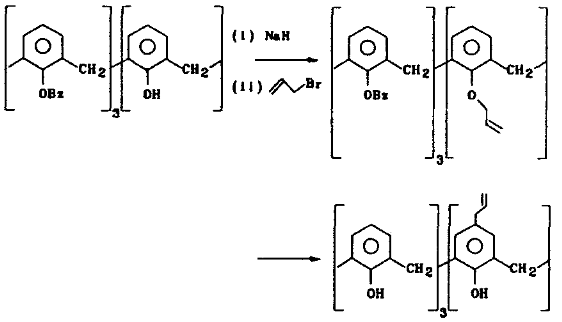


Figure 1

the cross-linked copolymer formed by reaction between the two compounds immediately precipitates. This solid polymeric material is insoluble in water and in all organic solvents. The presence of four chloromethyl groups on the calix[4]arene leads to the possibility that multiple alkylation by the substituted calixarene can occur on amine functional groups on different polyethyleneimine molecules. Such multiple alkylation across different polyethyleneimine chains results in the formation of insoluble cross-linked calixarene-functionalized polymers. The insolubility of this new material in aqueous and organic solvents suggests that such cross-linking has occurred. The chlorine: nitrogen ratio in the microanalytical data correlates with a polymeric material that contains one molecule of the calixarene bound to sixty monomer units of polyethyleneimine.

Preparation of soluble single-linked polymers

If a soluble calixarene-functionalized polymer is desired it is necessary to avoid the formation of a cross-linked product, and to therefore use a calixarene that will lead to the formation of only a single chemical link between each attached calixarene and the polyethyleneimine chain. Our approach to binding the calixarene to the polymer *via* a single linkage attachment is to use as precursor a calixarene that has a single allyl group bonded to the upper rim. Such a compound is 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene with sodium hydride and then allyl bromide to give first 25-allyloxy-26,27,28-tribenzoyloxycalix[4]arene. This intermediate can then be converted to the final product by carrying out a Claisen rearrangement, followed by hydrolysis of this rearranged product (equation 1).[12]



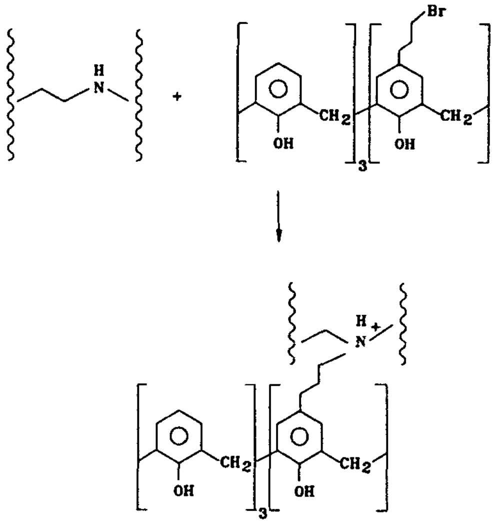
(1)

Our attempts to obtain a copolymer of 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene with either methacrylic acid in DMF solvent using ammonium persulfate initiator, or maleic anhydride in DMF solvent using dibenzoyl peroxide as initiator, proved unsuccessful. The soluble materials obtained by polymerizing these monomers with differing ratio of added 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene contained insignificant quantities of the calixarene incorporated.

Attachment to polyethyleneimine

An alternative approach to the synthesis of calixarene-modified polymers with the calixarene bound to the polymer by a single chemical linkage can involve an alkylation reaction whereby a single haloalkyl group on the calixarene can be used for its attachment to amine-containing polymers. We have therefore converted 5-allyl-25,26,27,28-tetrahydroxycalix[4]arene into 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene by the anti-Markownikov addition of hydrogen bromide, as described in the preceding paper.[17]

This compound 5-(3-bromopropyl)-25,26,27,28-tetrahydroxycalix[4]arene with a 3-bromopropyl substituent on only one of the *para* positions of the upper rim reacts with polyethyleneimine to give a soluble polymer with the amine nitrogens alkylated by the 3-propyl group of the calix[4]arene (equation 2). Even



(2)

at low loadings of the calix[4]arene we have been unable to synthesize a modified polymer that is soluble in water, but even at relatively high loadings of the calix[4]arene we can obtain modified polymer samples that are soluble in aqueous THF. These polymer samples, after drying to constant weight, show bands in the infrared spectrum at 2333 cm^{-1} and 2351 cm^{-1} that are characteristic of a quaternary amine functionality of the type $R_3\overset{+}{N}H$. The bromine: nitrogen ratio in the microanalytical data correlates with a polymeric material that contains one molecule of the calix[4]arene bound to eighteen monomer units of polyethyleneimine.

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