Dendrimeric ion exchange materials

Alice Cherestes and Robert Engel*
Department of Chemistry and Biochemistry, Queens College of The City University of New York, Flushing, NY 11367 USA

(Received 10 February 1993; revised 28 March 1994)

New high-capacity ion exchange materials have been prepared utilizing the structural feature of dendrimeric 'balloons' or 'strings' attached to a polymer backbone. The dendrimeric regions have covalently incorporated ionic sites at the core and branch points (anion exchanging materials) or at the termini of the chains (cation exchanging materials).

(Keywords: dendrimer; comb; ion exchange)

Introduction

Recently, significant interest has developed in the preparation and investigation of dendrimers, also known as cascade molecules; these are species incorporating multidimensional elements of repetitive symmetry, which are reminiscent of the symmetry associated with fractals[1–3]. Efforts in this laboratory have been concerned particularly with the preparation and investigation of dendrimers in which multiple cationic sites are incorporated covalently into a single structural unit with attendant (loosely) associated anions[4–7]. The elaboration of such ionic dendrimeric structures along an insoluble polymeric backbone, such as a Merrifield resin, would seem to hold promise for the development of high-capacity ion exchange materials which could be suitable for use under high performance liquid chromatography (h.p.l.c.) conditions. The present preliminary report is concerned with the preparation and initial investigation of such materials.

Experimental, and results and discussion

We have earlier noted the preparation of several types of ionic dendrimer species, characterized according to their topography[6]. For example, 'balloons' are dendrimers elaborated in several directions from a core site, with a non-branching unit also bound to the core, and 'strings' are non-branching linear arrays of identical units with regularly spaced charged sites, elaborated in a stepwise manner. Materials described herein, which have been synthesized as potential ion exchangers, may be described as 'combs' wherein the 'teeth' of the comb structure are elaborated balloons ('comb bursts') or strings, and the backbone of the comb is a partially crosslinked derivatived styrene/divinylbenzene copolymer (derived from Merrifield resin).

For potential anion exchanging materials, commercially available Merrifield resin (2% crosslinked chloromethylated styrene/divinylbenzene copolymer, 200–400 mesh, ~1 meq Cl g^{-1}) was treated with a tertiary amine reagent, either triethanolamine or 1,4-diazabicyclo[2.2.2]octane (Dabco), in 1:1 CH_2Cl_2/CH_3CN at reflux for 20 h. The resultant material was filtered and washed successively with water and ethanol, and air dried. Combustion analysis (Schwarzkopf Microanalytical Laboratories) of the modified polymer indicated attachment of the incipient dendrimer at ~55% of the available sites for triethanolamine reaction and ~80% with Dabco reaction.

Elaboration of the triethanolamine 'balloon' dendrimer was accomplished with a two-step iterative procedure involving initial treatment with *p*-toluenesulfonyl chloride in pyridine, followed by heating with an excess of triethanolamine in 1:1 CH_2Cl_2/CH_3CN. This sequence was performed twice to provide a 'balloon' structure with 13 cationic (quaternary ammonium) sites for each site of substitution on the polymer backbone. A schematic representation of the resultant structure is shown in *Figure 1*. Combustion analysis of the intermediates and product of triethanolamine elaboration beyond this stage indicated that reaction at all of the available sites was incomplete; presumably some crowding occurs as each 'comb burst' is expanded along the resin backbone, which prevents complete reaction. In prior work[6] with non-polymer-bound species, complete reaction could be attained at each stage of elaboration.

Examination of the ion exchange capabilities of these materials indicated that chloride ion could be exchanged

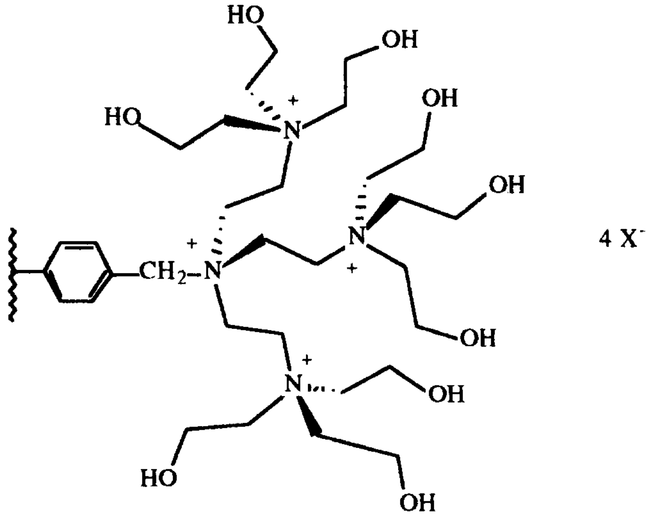

Figure 1 Schematic representation of the 'balloon' structure

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* To whom correspondence should be addressed

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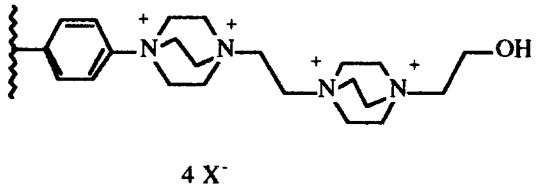

Figure 2 Schematic representation of the 'string' structure

with a variety of other monovalent anions (fluoride, bromide, iodide, chloroacetate, toluenesulfonate, but not acetate) as well as divalent anions (sulfate). Using the spectrophotometric characteristics of the picrylsulfonate anion, a capacity for exchange of anions of 9.3 meq g^{-1} was measured for the second generation triethanolamine material, in complete agreement with the determination of attachment at 55% of the potentially available sites of the backbone and their complete elaboration through a second generation dendrimeric structure. Further elaboration (with incomplete reaction) yielded material with an exchange capacity of 13–14 meq g^{-1} as measured by the picrylsulfonic acid method and n.m.r. evaluation of chloroacetate ion exchange.

Preliminary molecular modelling efforts[8] concerned with the cationic dendrimers indicate the anions to be located preferentially near the surface of the cascade rather than intercolated between the arms near the cationic sites. The steric interactions in the interior of the cascade are too great to allow significant intercolation.

Using Dabco as the unit attached to the resin, 'string' structures were elaborated as the 'teeth' of the comb. This was accomplished by the three-step iterative procedure involving initial reaction with 2-chloroethanol in CH_3CN, followed by tosylation in pyridine and continued reaction with an excess of Dabco. This sequence was performed twice to provide a 'string' structure bearing five cationic sites on each 'string'. A schematic representation of the resultant structure is shown in *Figure 2*. This material again exhibited the ability to undergo rapid exchange of chloride for other monovalent anions, and exchange of picrylsulfonate anion was used to determine a capacity of 3.9 meq g^{-1}, again in accord with the complete elaboration of the 'string' and an initial 80% reaction of sites along the parent polymer.

Both of these types of materials exhibit particle size of ~200 mesh as generated in the reaction systems, and their swelling characteristics are being investigated for suitability in h.p.l.c. applications.

In addition, 'balloon' species have been elaborated on the Merrifield resin backbone using a sequence of reactions which generate hydrocarbon dendrimeric arms with carboxylate anionic termini. The preparation involves three repetitions of the following sequence of reactions: (1) treatment with sodiodiethylmalonate to displace the benzylic halide; (2) reduction with lithium borohydride to generate free hydroxyl groups at the dendrimeric termini; (3) tosylation with tosyl chloride in pyridine. Upon completion of the third tosylation an additional displacement with sodiodiethylmalonate is performed, followed by acidic hydrolysis of the ester linkages. It should be noted that reaction for the elaboration of the successive generations of this material proceeded less efficiently than did those for the construction of the anion exchanger materials. Presumably there is significant steric hindrance for the incorporation of successive generations of dendrimer when the species is attached to a polymer backbone. The resultant 'comb burst' species has been demonstrated to serve as a high-capacity weak cation exchanger, rapidly exchanging sodium, potassium and silver ions. The swelling characteristics and h.p.l.c. capabilities of this material are currently being investigated.

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