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Polymethacrylate Polymers with Appended Aluminum(III)-Tetraphenylporphyrins: Synthesis, Characterization and Evaluation as Macromolecular Ionophores for Electrochemical and Optical Fluoride Sensors

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Abstract

The synthesis and characterization of a novel polymethacrylate polymer with covalently linked Al(III)-tetraphenylporphyrin (Al(III)-TPP) groups is reported. The new polymer is examined as a potential macromolecular ionophore for the preparation of polymeric membrane-based potentiometric and optical fluoride selective sensors. To prepare the polymer, an Al(III) porphyrin monomer modified with a methacrylate functionality is synthesized, allowing insertion into a polymethacrylate block copolymer (methyl methacrylate and decyl methacrylate) backbone. The resulting polymer can then be incorporated, along with appropriate additives, into conventional plasticized poly(vinyl chloride) films for testing electrochemical and optical fluoride response properties. The covalent attachment of the Al(III)-TPP ionophore to the copolymer matrix provides potentiometric sensors that exhibit significant selectivity for fluoride ion with extended lifetimes (compared to ion-selective membrane electrodes formulated with conventional free Al(III)-TPP structure). However, quite surprisingly, the attachment of the ionophore to the polymer does not eliminate the interaction of Al(III)-TPP structures to form dimeric species within the membrane phase in the presence of fluoride ion. Such interactions are confirmed by UV/visible spectroscopy of the blended polymeric films. Use of the new polymer-Al(III)-TPP conjugates to prepare optical fluoride sensors by co-incorporating a lipophilic pH indicator (4',5'-dibromofluorescein octadecyl ester; ETH7075) is also examined and the resulting optical sensing films are shown to exhibit excellent selectivity for fluoride, with the potential for prolonged operational lifetime.

Keywords

Fluoride sensors; Aluminum(III)-porphyrins; Polymer-tetraphenylporphyrin conjugates; Dimer-monomer equilibrium

1. Introduction

The development of inexpensive fluoride sensors to potentially replace the classical single-crystal LaF₃-based ion-selective electrode (ISE) [1–4], is an area of great interest owing to the many real-world applications for such devices. Fluoride ion is added intentionally to drinking water and dental hygiene products for the purpose of reducing the frequency of dental caries,

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and fluoride levels in municipal water supplies and in these dental products need to be tightly controlled. Fluoride is also present in certain vegetables due to the use of a variety of pesticides that contain fluorine/fluoride. Further, a good fluoride sensor can be utilized as a detector for developing simple bioanalytical systems to quantitate glucose, cholesterol and a host of other clinically relevant species by employing a coupled enzymatic reaction to liberate fluoride from fluorophenol substrates via a peroxidase catalyzed reaction [5–7].

Polymeric membrane/film type electrochemical and optical ion sensors would provide an attractive alternative to the LaF_3 -based ISE. However, historically, the majority of anion-selective electrodes and optodes described in the literature are based on dissociated anion-exchangers such as lipophilic quaternary ammonium salts [8,9]. Selectivity coefficients of such membrane electrodes are related to the ability of the anion to partition from the aqueous phase into the organic phase since specific interactions between the anion-exchanger and target anions do not exist. These anion-exchanger-based electrodes are known to exhibit the so-called Hofmeister selectivity pattern (i.e., $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{HCO}_3^- > \text{F}^-$) [10] where fluoride yields the least response since it has the most negative Gibbs free energy of hydration ($\Delta G_{\text{hyd}}^{298}(\text{F}^-) = -104.3 \pm 0.7 \text{ kcal/mol}$) [11].

It has been reported recently that by using certain metalloporphyrin species as ionophores (e.g., Ga(III)-porphyrins [12], Zr(IV)-porphyrins [1] or Al(III)-porphyrins [4]), it is possible to develop polymeric membrane/film based ISEs that achieve fluoride selectivity approaching that exhibited by the solid-state fluoride ISE. However, at present there are certain limitations to these sensors, such as super-Nernstian responses, long response times, short use-life and a higher than desired detection limits. These issues must be resolved before practical applications of these devices can be fully realized. Such problematic behaviors have been ascribed to the occurrence of dimer-monomer equilibria of the metalloporphyrin species within the polymeric membrane phase of the sensors when they are in contact with an aqueous test solution containing the target anion [12]. However, by taking advantage of this equilibrium process, polymeric film type optical sensors can be designed that exhibit excellent fluoride response. Indeed, it was shown recently that an aluminum(III) octaethylporphyrin (Al(III)-OEP) based fluoride optical sensor yields a detection limit even lower than that of the classical solid-state fluoride ISE but with comparable selectivity [2,3].

There are two approaches to possibly eliminate the dimer formation of metalloporphyrin ionophores, which is desired for fabrication of ideally functioning membrane electrodes. One means is to utilize picket-fence porphyrin structures as the ligand to prepare the Al(III) ionophores [4], so that dimer formation can be prevented via steric hindrance. The other approach involves covalently attaching the Al(III) porphyrins to a polymer backbone. The latter method has been studied by a number of research groups [13–16]. As reported by Qin and Bakker [17], dimer formation for a chloride ion selective In(III) porphyrin system was eliminated by modifying the metalloporphyrin with a methacrylate functionality to allow attachment within polymethacrylate polymer, and use of that polymer as a macromolecular ionophore agent in conventional PVC membranes. Herein, we report a similar effort to attach Al(III)-tetraphenyl porphyrins (Al(III)-TPP) to polymethacrylate polymers. We further examine the behavior of both potentiometric membrane electrodes and optical sensing polymeric films that are formulated with this new macromolecular ionophore. It will be shown that while excellent fluoride selectivity is maintained, and longer operational lifetimes can be achieved, the Al(III)-TPP attached to the polymethacrylate can still undergo dimer formation in the presence of fluoride ion in the bathing solution. Hence, both electrochemical and optical sensors prepared from this new material show analytical behavior quite similar to those reported for the free Al(III)-TPP ligand, but with enhanced use-life.

2. Experimental

2.1. Reagents

4-Hydroxybenzaldehyde, benzaldehyde, pyrrole, propionic acid, acetic acid, methacryloyl chloride, and triethylamine were purchased from Aldrich (Milwaukee, WI). The monomer *n*-decyl methacrylate (DMA), 99%, was obtained from Polysciences, Inc. (Warrington, PA). The monomers methyl methacrylate (MMA), 99.5% and the polymerization initiator 2,2'-azobisisobutyronitrile, 98% (AIBN), were obtained from Aldrich. Inhibitors were removed from the monomers by prior distillation. AIBN was re-crystallized from warm methanol prior to use. Potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), *o*-nitrophenyl octyl ether (NPOE), high molecular weight poly(vinyl chloride)(PVC) and ETH 7075 were purchased from Fluka (Milwaukee, WI). All salts were obtained from Aldrich and aqueous solutions of them were prepared by dissolving the appropriate sodium salts in Millipore purified water (18M Ω cm). All solvents, methylene chloride (CH₂Cl₂), methanol and tetrahydrofuran (THF) and the silica gel used for chromatography were obtained from Fisher Scientific (Pittsburgh, PA).

2.2. Syntheses of Al(III)-Porphyrin Complex

5-(4-Hydroxyphenyl)-10-15-20-triphenylporphyrin (HOTPP) was prepared as reported elsewhere [18,19]. The procedure used to synthesize the aluminum complexes Al(III)(HOTPP)Cl was analogous to that also described in the literature [20,21]. The chloro(5-(4-methacryloyloxyphenyl)-10,15,20-triphenylporphyrinato)aluminum(III) (Al(III)(MOTPP)Cl (see Fig. 1) was prepared by the procedure reported by Qin and coworkers [17]. The crude product was purified by flash chromatography on silica using CH₂Cl₂ as the solvent. Final products were characterized by mass spectrometry, yielding the desired molecular weight peak at $m/z = 755.2$.

2.3. Synthesis and Characterization of Polymeric Ionophore

The methacrylate copolymer was synthesized via a thermally initiated free radical solution polymerization. Five wt % of the Al(III)(MOTPP)Cl (50 mg) species, 0.78 g of MMA, and 0.20 g of DMA were dissolved in anhydrous ethyl acetate. The solution was purged with nitrogen for 30 min before 6 mg of AIBN was added. The homogeneous solution was stirred at a temperature of 90 °C and the reaction was maintained for 18 h. After this time, the solvent was evaporated and the polymer was re-dissolved in 2 mL of THF. Aliquots of polymer solution were added dropwise to 100 mL of methanol under vigorous stirring. The precipitate was collected and washed thoroughly with methanol to ensure the complete removal of any free porphyrin. The polymer was then dried under vacuum.

2.4. ISE membrane Formulation and EMF Measurements

The ISE membranes used for potentiometric measurements consisted of 1 wt% (20 wt% of copolymer) of the macromolecular Al(III) porphyrin ionophore and various quantities of anionic additive salt (KTFPB), 66 wt% NPOE of NPOE plasticizer, and 33 wt% PVC. All components (total mass 200 mg) were dissolved in 2–3 mL of freshly distilled THF and the cocktails were poured into a 25 mm-id glass ring affixed to a glass microscope slide. The solvent was allowed to evaporate overnight, yielding a transparent colored film. Disks with 8 mm diameter were cut from the parent membrane and mounted in electrode bodies (Oesch Sensor Technology, Sargans, Switzerland). An internal filling solution composed of 0.01 M NaCl or 0.01 M NaCl and 0.01 M NaF was used. These same solutions were also employed as conditioning solutions for the ISE prior to fluoride calibration measurements. The sample buffer employed in this study was 0.05 M glycine, adjusted to pH 3.0 with phosphoric acid (gly/phos buffer). All analyte solutions were prepared from sodium salts of various anions

dissolved in the buffer. Since at pH=3.0, ca. 60% of all fluoride present in solution is protonated (HF) and is not detected by the electrode, all calibration curves were plotted by using total fluoride concentrations in the test buffer solution (i.e., $[F^-] + [HF]$), instead of free activity of fluoride. Data presented in the figures were normalized in order to make the starting EMF values of all electrodes equal to zero.

2.5. Optical Measurements

The optical sensing films either have exactly the same composition as the ISE membranes or contained 25.8 mmol/kg (40 wt% copolymer) ionophore, 100 mol% ETH7075, plasticizer NPOE, and PVC (2:1 mass ratio). All the components (total mass 100 mg) were dissolved in distilled THF to give a 2 mL cocktail. Then the films were made by a spin-coating device (model SCS-G3-8 obtained from Cookson Electronics; Providence, RI) on a square-shaped quartz plate of 35 mm in length. The rotation speed is 600 rpm, while 100 μ L of the polymer film cocktail was injected onto the rotating glass plate each time to spin for 5 sec. The films were dried in air before using and were stored in the dark when they were not used. For future optical measurements, the quartz plate coated with the deposited film was mounted in a custom-built spectrophotometer flow cell similar to that described elsewhere [22]. The flow cell was mounted into a Perkin-Elmer double-beam UV-visible spectrophotometer (model Lambda 35; Boston, MA). The 0.05M gly/phos buffer (pH = 3) was allowed to flow for 30 min at a flow rate of 1.4 mL/min to precondition the films, using a Gilson Minipuls-3 peristaltic pump (Middleton, WI). The response of the optical sensing film toward different anions was recorded by adding respective aliquots of the test solution to a stirred reservoir containing 50 mL of buffer. The resulting buffered salt solution was pumped through the cell and recirculated into the buffer reservoir. The spectra of the films were recorded in the range between 360 nm to 630 nm when equilibrium was reached. To correct for the background absorbance, the absorbance measured at 630 nm was subtracted from the absorbance values at the wavelengths of interest. Total fluoride ion concentration was used instead of fluoride activity in all experiments.

3. Results and Discussion

3.1 Polymethacrylate with Covalently Linked Al(III)TPP

The copolymer with covalently linked Al(III)TPP ionophore (see Fig. 1) was characterized by $^1\text{H-NMR}$, where low intensity resonances from protons on the porphyrin phenyl rings were observed due to the presence of a nearby quadruple nuclei (Al(III)). Therefore, to determine the amount of Al(III) porphyrin complex in the copolymer, UV-Visible spectroscopy was employed. Based on using pure Al(III)TPP as a standard, the concentration of the grafted aluminum porphyrin on the polymer backbone was estimated to be 64.7 mmol/kg. The molecular weight of the copolymer was determined by gel permeation chromatography with stabilized THF as the carrier solvent and polystyrene as a standard. The respective peak, number and weight molecular averages were determined as $M_p = 29,411$, $M_n = 20,919$, and $M_w = 42,214$. Moreover, the amount of Al(III) porphyrin attached could be changed by altering the ratio of starting monomers. Reduced amounts of Al(III)(MOTPP)Cl results in a lower value of attached Al(III) porphyrin, which possibly will increase the distance between two Al(III) porphyrin molecules in the polymer chain.

3.2. Potentiometric Response Characteristics of ISEs Formulated with Covalently Attached Al(III)TPP

Although Al(III)OEP has been used as a highly selective fluoride ionophore in optical sensing films [2,3], when free Al(III) porphyrins (including Al(III)TPP) have been utilized in polymer membranes for potentiometric sensing of fluoride, the response toward fluoride was found to be quite slow and also super-Nernstian with slopes greater than -100 mV/decade [4]. The

undesirable behavior of such ISE membranes was attributed to the dimer-monomer equilibrium within the polymeric film when the film contacts with fluoride ion [4]. It was anticipated here that use of the new macromolecular ionophore would overcome these problems. Initial efforts to prepare films directly with only the new copolymer with covalently linked Al(III)TPP species yielded brittle membranes that did not have adequate mechanical properties to be used to construct ion selective electrodes.

Therefore, the new methacrylate copolymer with covalently attached Al(III)TPP was mixed with appropriate amounts of KTFPB, PVC and NPOE to yield a dark purple transparent film. Preliminary testing suggested that optimal potentiometric fluoride selectivity and response can be achieved by adding 50 mol% KTFPB (relative to Al(III)TPP content in the copolymer) to the membrane formulation (data for other KTFPB levels not shown here.). Indeed, potentiometric response and selectivity of a PVC/NPOE membrane containing 20 wt% methacrylate copolymer with the covalently attached Al(III) porphyrin and 50 mol% of KTFPB were tested using two different internal filling solutions (with and without fluoride added). Membrane electrodes with 10 mM NaCl only as the inner filling solution (and conditioned in this solution as well) display near-Nernstian fluoride response (-62.0 mV/decade in range of 10^{-4} – 10^{-2} M total fluoride) (see Fig. 2) and maintain a high degree of potentiometric selectivity toward fluoride ion. Only salicylate is a significant interference, with a potentiometric selectivity of the membrane for fluoride relative to salicylate, $K^{\text{pot}}_{\text{F/Sal}} = 0.1$. In contrast, membrane electrodes with fluoride added to the inner solution (at 0.01 M) and preconditioned in this solution and then washed thoroughly with test buffer, display a sub-Nernstian fluoride response (-33.2 mV/decade) in the range of 10^{-5} M – 10^{-2} M (data not shown here). Such behavior is quite similar to membrane electrodes formulated with free Al(III) porphyrins (Al(III)OEP or Al(III)TPP) as ionophores as reported previously [4] where it was found that employing fluoride within the internal solution decreases the observed slope value of the fluoride calibration curve. Such behavior in the presence of high fluoride may indicate a dimer-monomer equilibrium when the membranes are in prolonged contact with fluoride ion [4]. Indeed, it has been suggested previously that Al(III) porphyrins can interact with fluoride ion and potentially form dimeric species in which one or two fluoride ions are bridging ligands [2–4]. Further examination of the sensing membranes used in this work by UV/visible absorption spectroscopy could confirm whether such chemistry is occurring in the films that are also formulated with the new polymethacrylate copolymer possessing the immobilized Al(III)TPP species.

Fig. 3 illustrates the UV-Vis spectra of a polymer film prepared using the exactly same composition as the membrane employed in the potentiometric measurements reported in Fig. 2. The film was initially equilibrated in 0.05M gly/phos buffer (pH 3.0) and the Soret absorbance band was observed at 421 nm (dashed line in Fig. 3). After the film was equilibrated with solutions containing increasing concentrations of fluoride by using a flow cell system to pump the solution over the film [2,3], the absorbance at 421 nm decreases with a concomitant appearance and increase of a new band at 404 nm. Previous studies have attributed such a hypsochromic shift in the Soret band to formation of a dimeric metalloporphyrins in polymer phase (compared to monomers). The spectral data shown in Fig. 3 therefore clearly indicates the likely formation of a fluoride-bridged dimeric species between Al(III)TPP species covalently linked to the polymethacrylate polymer with about 33% of the initial monomeric Al(III)TPP species dimerized at a fluoride level of 0.1 M. Such fluoride induced dimer formation was also shown recently to occur within polymeric films formulated with free Sc(III)-porphyrins as ionophores, and an X-ray structure of the bis-fluoro bridge Sc(III)-porphyrin dimer was obtained to support the occurrence of this process [23]. The observation of dimer formation for the polymer linked Al(III)TPP species is somewhat surprising since similar polymers with covalently linked In(III)TPP were found previously not to form hydroxide ion bridged dimers when used to prepare chloride ion-selective sensing membranes [17]. One

possible explanation may be a more favorable conditional equilibrium constant for fluoride induced dimer formation in the case of the Al(III)/TPP species vs. the dimer formation constant for In(III)/TPP with hydroxide when examined under relatively low pH conditions (pH 5.5) [17]. Since in the case of the In(III) porphyrins, hydroxide dimers are broken to monomers by the addition of low levels of chloride to the bathing solution, the binding constant for dimer formation at pH 5.5 is probably not as strong as the formation constant for forming bis-fluoro bridged dimers as one increases fluoride ion in the bathing solution. In addition, since multiple Al(III)/TPP structures exist on a single polymeric chain, it is possible that a cooperative type of stacking between porphyrins on adjacent chains is possible, further increasing the apparent equilibrium constant for fluoride bridging induced dimer formation for the polymer with the Al(III)/TPP structure attached.

Although the covalent attachment method cannot eliminate the dimer formation completely, it gives the ISE membrane a longer operational lifetime. Compared with free Al(III) porphyrins Al(III)/TPP, Al(III)/OEP and Al(III) picket fence porphyrin [4], the slope of fluoride calibration curve of the covalently attached Al(III) porphyrin system did not change dramatically over two weeks (22:10) (see Fig. 4), although a decrease could be observed with a longer time period (one month). Furthermore, no phase separation of copolymer with covalently linked Al(III)/TPP species and the PVC was observed. Membranes having the same composition as employed for potentiometric measurements were immersed in 0.01 M NaCl as well as 0.01 M NaCl and NaF buffer solutions (pH = 3.0 phosphate/glycine) for one week. Microscopic examination of such membranes revealed no obvious phase separation or clear islands of different polymeric materials within the membranes.

3.3. Optical Response Characteristics of Membranes Formulated with Covalently Attached Al(III) Porphyrin Together with ETH7075

As mentioned above, optical fluoride sensors that take advantage of the dimer-monomer equilibrium between Al(III)/OEP have been reported in literature [13,14]. The optical sensing film uses the principles of anion/proton co-extraction chemistry to achieve an optical response. The lipophilic pH chromoionophore translates the binding of the fluoride ion to the Al(III) porphyrin as an optical signal, allowing optical measurement at a higher wavelength range than for the porphyrin species itself. In addition, there is evidence to suggest that the pH chromoionophore can also interact with certain porphyrins via a π - π interaction, potentially weakening the dimer formation constant to a point where reversibility in dimer formation is possible [3]. When a buffer solution (0.05 M gly/phos, pH 3.0) without fluoride flows over the film, the deprotonated form of the indicator dye (C^-) ($\lambda_{\max}=530$ nm) is the predominant absorbance band observed in the wavelength range of 450–550 nm. As fluoride is added to the buffer, the deprotonated form of the indicator decreases, and the protonated form (CH) increases in absorbance ($\lambda_{\max}=470$ nm).

A film with the new methacrylate copolymer possessing covalently attached Al(III) porphyrin and 100% mole of ETH-7075 relative to the Al(III)/TPP species present in the polymer phase exhibits very good selectivity toward fluoride ion in such an optical sensing configuration (see Fig. 5). Selectivity is similar to that observed with the electrochemical sensor described above. The response is reversible and the detection limit (ca. 10 μ M) is comparable with previous studies with free Al(III)/TPP as ionophore for optical fluoride measurements (data not shown here), but not as good when free Al(III)/OEP is employed to fabricate optical sensors for fluoride (0.1 μ M) [2]. While we observe the expected absorbance change in the deprotonated form of the chromoionophore, a change in the Soret band absorbance of Al(III) porphyrin could also be observed which indicates some dimer formation during the process; however, the dimer formation in this material is not as strong as the dimer formation in the Al(III)/OEP system [2,3].

4. Conclusion

A methacrylate copolymer with covalently attached Al(III) porphyrin has been synthesized and characterized. Although a portion of the Al(III) porphyrins appended to the structure still forms dimeric species in the presence of fluoride, electrochemical measurements toward fluoride ion show one advantage of this macromolecular type ionophore in providing electrodes with a longer operational lifetime (vs. sensors fabricated with free Al(III)TPP). When used in an optical sensor configuration, the sensing films prepared with the newly synthesized material yield comparable fluoride responses to those obtained with the corresponding free Al(III)TPPP species.

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Al(MOTPP)Cl

Covalently attached ionophore

Fig. 1.
Structure of Al(MOTPP)Cl and the methacrylate copolymer with covalently attached Al(III) porphyrin.

Fig. 2. Potentiometric anion response for electrodes containing 20 wt% methacrylate copolymer with covalently attached Al(III) porphyrin and 50 mol% KTFPB (relative to Al(III) porphyrin) in PVC/NPOE membrane; (●) F⁻, (■) SCN⁻, (□) ClO₄⁻, (×) Br⁻, (□) NO₃⁻, (□) Cl⁻, (□) Sal⁻. Response obtained in pH = 3.0 gly/phos buffer. Internal solution: 0.01 M NaCl in pH = 3.0 gly/phos buffer.

Fig. 3. UV/visible spectra of a membrane containing methacrylate copolymer with covalently attached Al(III) porphyrin and 50 mol% KTFPB (relative to Al(III) porphyrin) upon increasing the bathing concentration of fluoride. (---) initial spectrum equilibrated in gly/phos buffer, pH 3.0. Concentration of fluoride increased from zero to 100 mM, increasing 10 fold each spectrum.

Fig. 4. Response of membrane electrodes containing 20% methacrylate copolymer with covalently attached Al(III) porphyrin and 50 mol% KTFPB (relative to Al(III) porphyrin) toward fluoride ion as a function of time; ($\square$) the first day, ($\blacksquare$) after one week, ($\blacktriangle$) after two weeks.

Fig. 5. Optical response at 535 nm (background absorbance subtracted) of methacrylate copolymer with covalently attached Al(III) porphyrin in PVC/NPOE film containing 100 mol% ETH7075 toward different anions; (●) F⁻, (■) SCN⁻, (□) ClO₄⁻, (×) Br⁻, (□) NO₃⁻, (□) Cl⁻, (□) Sal⁻. Response obtained in pH = 3.0 gly/phos buffer.