A Hydrogen Ion-Selective Sensor Based on Non-Plasticised Methacrylic-acrylic Membranes

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Abstract: A methacrylic-acrylic polymer was synthesised for use as a non-plasticised membrane for hydrogen ion-selective sensor incorporating tridodecylamine as an ionophore. The copolymer consisted of methyl methacrylate and n-butyl acrylate monomers in a ratio of 2:8. Characterisation of the copolymer using FTNMR demonstrated that the amount of each monomer incorporated during solution polymerisation was found to be similar to the amount used in the feed before polymerisation. The glass transition temperature of the copolymer determined by differential scanning calorimetry was -30.9 ºC. Potentiometric measurements conducted showed a linear pH response range of 4.3 – 9.6 with the response slope of 56.7 mV/decade. The selectivity of the sensors towards hydrogen ions was similar to other plasticiser based membrane electrodes and the logarithmic selectivity coefficients for discrimination against interference cations is close to –9.7. However, the incorporation of a lipophilic anion as membrane additive is essential in ensuring optimum performance of the hydrogen ion sensor.

Key words: Hydrogen ion sensor, Methacrylic-acrylic membrane, Lipophilic anion, Non-plasticised

Introduction

There is no doubt that glass electrode is the most commonly used device for pH measurements but this is not always acceptable as an implantable sensor for continuous and *in vivo* monitoring in clinical medicine. The use of polymeric membrane based pH sensors to replace glass electrode not only benefits modern medicine but it also allows microfabrication of such sensors for implant applications[1]

Electrodes based on plasticised PVC membranes coupled with proton-selective ionophores, e.g. tridodecylamine have been reported[2]. However, the use of plasticiser in PVC membrane based electrodes were later found to be the main cause of thrombocity when used as implantable sensors[3,4]. Many polymer membranes that require less plasticisers compared with PVC were studied as sensing membrane for pH, e.g. polyurethane (Tecoflex) and silicon rubber[5,6]. To ensure that biocompatibility of the sensor is achieved, these membranes were further coated with antithrombogenic substances such as tridodecylmethylammonium heparinate complex or poly(ethylene oxide) [6,7].

An obvious solution to the problem of non-biocompatibility caused by plasticiser is to eliminate the use of plasticiser altogether. This has been attempted with polymer matrix such as sol-gel[8] and also methacrylic-acrylic copolymers [9-14]. In this work, we have synthesised a methacrylic-acrylic copolymer and employed it as a non-plasticised membrane for hydrogen ion-selective sensor application. The performance of the sensor with this type of polymeric membrane is reported here.

Experimental

Materials: Various chemicals used in the research were: Methyl methacrylate (MMA), n-butyl acrylate (nBA), potassium tetrakis(4-chlorophenyl) borate (KTClPB), lithium acetate dehydrate, tris(hydroxymethyl) aminomethane (Tris), hydrogen ionophore (tridodecylamine), chlorides of potassium, sodium, lithium, ammonium, calcium and magnesium (all are analytical grade) were from Fluka, benzoyl peroxide was from Merck, petroleum ether 60-80°C fraction from Fisher and dichloromethane from Baker. Standard solutions were prepared with doubly deionised water.

Preparation of methacrylic-acrylic polymers: Procedure for the synthesis of the copolymer of methyl methacrylate (MMA) and n-butyl acrylate (nBA) as reported before [11,13]. The polymerisation was accomplished by adding 2.44 g of MMA and 3.06 g nBA and 0.001 g of benzoyl peroxide as initiator to 5 mL of dry benzene. The mixture was degassed with nitrogen for 10 min before heated for 6 hours at 100°C. The product, i.e. copolymer MB28 was then isolated by precipitation with petroleum ether. The clear, elastic but tacky copolymer was air dried for several days before used as ion sensor membrane material.

Copolymer characterisations: Fourier Transform Nuclear Magnetic Resonance (FTNMR) of the copolymer was taken with JNM-LA400 FTNMR, JEOL (a 400 MHz NMR instrument). A sample of the copolymer was dissolved in deuteriated chloroform and the proton chemical shifts from 0-12ppm were recorded.

The glass transition temperature (T_g) of the copolymer was measured with a Mettler Toledo Differential Scanning Calorimeter (DSC), model DSC 822^e, scanned at a rate of 10°C/min from -50 to 50°C. The T_g was then determined from DSC thermogram.

Fabrication of hydrogen ion sensors: For the fabrication of hydrogen ion sensors, 0.05 g of the MB28 copolymer was mixed with the required amount of ionophore and potassium tetrakis-chlorophenyl borate (KTClPB) as shown in Table 1. The mixture was then dissolved in 1 mL of dichloromethane and 15 µL of this mixture was drop coated onto the tip of a Ag/AgCl electrode (Clark Instruments) and dried at room temperature for 24 h before potentiometric measurements were carried out with these electrodes.

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Table 1. The membrane composition of hydrogen ion sensors
prepared from MB28 polymeric membranes.

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Sensor	Hydrogen Ionophore (g) (mol)	KTClPB (g) (mol % relative to ionophore)
E1	0.007 (1.34×10^{-5})	NIL
E2	0.007 (1.34×10^{-5})	0.0012 (17.1)
E4	NIL	0.0012

Evaluation of the response of hydrogen ion sensors: The response of the sensor to hydrogen ions was tested with a double junction Ag/AgCl electrode (Orion) as reference electrode. The internal reference solution was 0.1 M TrisHCl (pH=7) whilst 1 M lithium acetate as the bridge electrolyte[15]. Both the reference electrode and sensor were connected to an Orion ion meter where the difference in the potential of the cell (electromotive force, EMF) (mV) was recorded when a stable value was reached.

All sensors were examined with 0.05 M TrisHCl buffer solutions of pHs between 2 –10 and the pH value of each buffer solution was measured with a Ecomet pH electrode before use. The interference of various cations, e.g. potassium, sodium, lithium, ammonium, calcium and magnesium on the sensors was evaluated using the mixed solution method[16]. The hydrogen ion response of each sensor was also evaluated in the presence of a fixed concentration (0.1 M or 1 M) of the interfering cations. The EMF response of the test cell was then plotted against the logarithmic concentration of the test solutions according to the Nernst Equation.

Results and Discussion

Composition and characteristics of methacrylic-actaylic polymers

The composition of the copolymers synthesised can be determined from their proton FTNMR spectra. The characteristic chemical shift of the nBA and MMA monomers remain the same even though after incorporation into the polymer network[13]. For nBA the characteristic chemical shift is at 1.4 ppm ($- CH_2 -$ proton) whilst for MMA, 3.6 ppm ($-COCH_3 -$ proton). Because of that, the FTNMR spectrum can be used to determine the composition of MMA and nBA in the polymer. After the monomer peak is identified, the fraction of the monomer in the copolymer may be calculated by using the peak intensity (I) according to Equation (1) below [17].

$$F_{nBA} = \frac{\frac{1}{2}I(-CH_2)_{nBA}}{\frac{1}{2}I(-CH_2)_{nBA} + \frac{1}{3}I(-OCH_3)_{MMA}} \tag{1}$$

For copolymer MB28, the monomer composition that calculated based on proton FTNMR spectra was closely resembled to the monomer compositions used in the feed before polymerisation (Table 2). Although the reactivity of the monomer MMA, r_1 is approximately four times higher than that of nBA, r_2[18], the large amount of nBA in the feed dominated the polymerisation reaction. Hence, the

composition of the copolymer produced was higher in nBA then MMA. The yield of the copolymer after purification was 74 %.

Table 2. The monomer and copolymer composition of MB28.

Monomer	Composition from feed (mol fraction)	Composition from FTNMR (mol fraction)
MMA	0.20	0.30
nBA	0.80	0.70

The MB28 copolymer has a soft but elastic physical characteristic. This is in agreement with the glass transition temperatures (T_g) of –30.9 ^{o}C obtained from DSC study. For a functional hydrogen ion sensor, the ionophore tridodecylamine must be 'active' after entrapped in a polymer matrix. The ability of the ionophore to selectively detect the presence hydrogen ions depends on the complexation processes that occurring at the membrane-solution interface[19]. It is generally known that for a ionophore to be active, the matrix materials must be highly flexible to allow movement of the ionophore for conformation changes during ion complexation processes[20]. For the methacrylic-acrylic types of copolymers, it has been established that the very low T_g, i.e. below -20°C is essential for the functioning of the ionophore without resort to incorporation of a plasticiser to reduce the T_g[13]. Therefore, the copolymer MB28 has satisfied the requirement of a non-plasticised membrane for ion sensor as the copolymer demonstrated T_g value well below that of –20 °C.

Response of hydrogen ion sensor and effects of KTClPB

For a non-plasticised methacrylic-acrylic membrane containing only the tridodecylamine ionophore, no clear response to changes in pH was observed (Fig. 1, sensor E1). However, if the hydrogen ionophore is added together with 17.1 mole percent of a lipophilic salt, KTClPB, the sensor (E2) gave satisfactory response slope and selectivity towards hydrogen ions in the absence of interference cations (Fig. 2). A good response was also obtained even in the presence of 0.1M of sodium ions (Fig. 1).

The lipophilic anions or anionic sites play an important role in inducing good response of an ion sensor. Lipophilic anionic sites in ion sensor membrane is beneficial in lowering the electrical membrane resistance, reduce the activation barrier for the cation-exchange reaction at the membrane/solution interface, improve response time and also selectivity towards the primary ions[21]. The absence of anionic sites in the methacrylic-acrylic type of membranes have been known and was considered as one of the factor affecting the performance of ion sensors based on these polymer membranes[14]. Thus incorporation of anionic sites such as KTClPB is essential for a functional ion sensor based on methacrylic-acrylic membranes. Nevertheless, a membrane containing only KTClPB will also response to cations, including hydrogen ions in a sub-Nerntian manner, e.g. sensor E3 (Table 2) with a small linear response range. But unlike the hydrogen ionophore, cationic response from KTClPB is not selective. The hydrogen ion sensor E2 although also contained KTClPB but the response is not attributed to the lipophilic anion but the hydrogen ionophore. This is confirmed by the response of E2 in the presence of 0.1 M Ca^{2+} or Mg^{2+} ions where the slope remained near to the

theoretical value of 59.6 mV/decade for a single charge ion instead of 29.8 mV/decade for a doubly charge ion (Table 2).
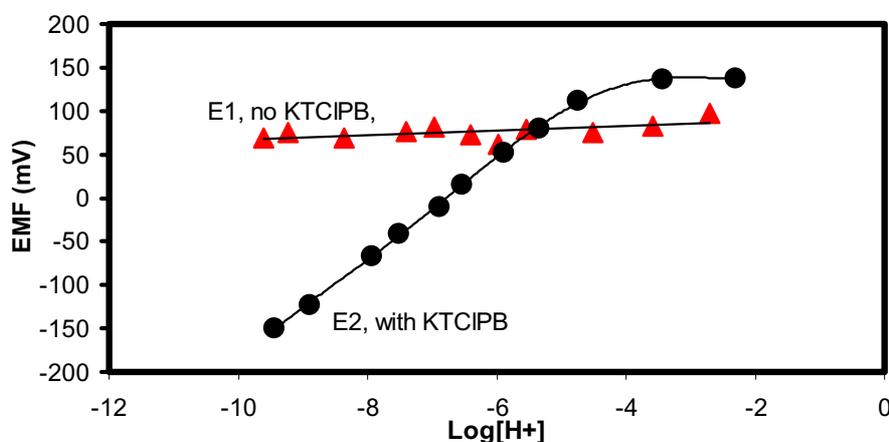

Figure 1. The response of hydrogen ion sensor of non-plasticised methacrylic-acrylic membrane to various concentrations of hydrogen ion (0.05 M TrisHCl buffer) in 0.1 M sodium ion. E1: membrane contained only a hydrogen ionophore, E2: Membrane contained both hydrogen ionophore and the lipophilic salt, KTClPB.
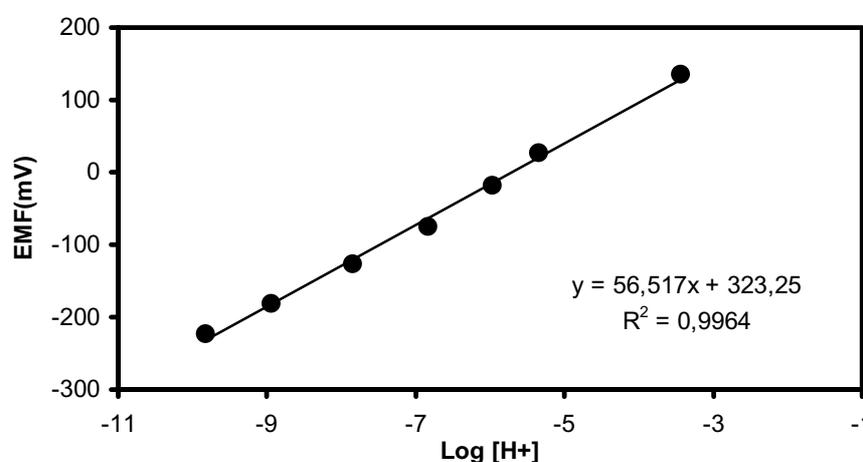

Figure 2. The potentiometric response of sensor E2 with a non-plasticised methacrylic-acrylic membrane containing hydrogen ionophore and KTClPB.

The slope of sensor E2 as shown in Fig 2 is 56.7 mV/decade and very close to the theoretical Nernstian value. The linear pH response range was large and ranged from pH 3.4 to 9.8. In terms of selectivity towards other interfering cations, the logarithmic selectivity coefficients calculated from fixed interference studies (0.1 M interference cations) and based on the lowest hydrogen ion concentration were estimated to range from –9.15 to –9.73 (Table 2). Hence, the presence of 0.1 M of some common interference cations did not exert large effect on the response slope and values between

55.8 to 56.9 mV/decade were obtained. However, the linear range is slightly diminished to a pH range of 5.23 to 9.56 (Table 2, Figure 3).
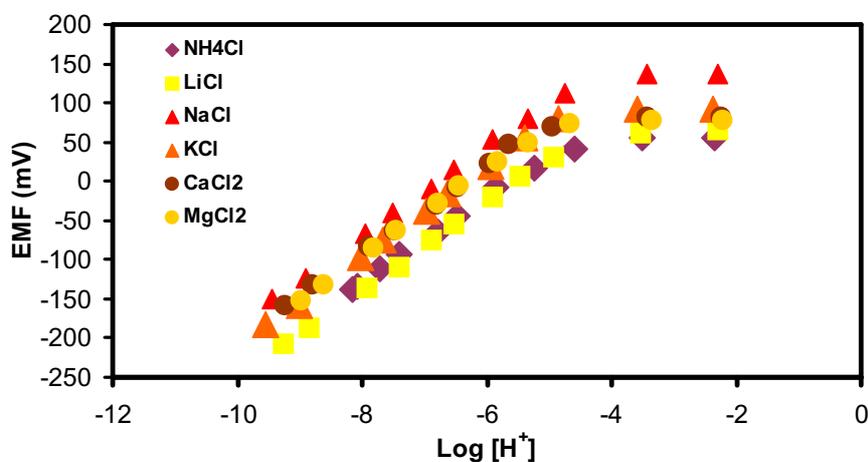

Figure 3. The presence of 0.1 M of various cations in the solution did not interfere with the pH response of electrode E2 (From Figure 3).

Table 2. The performance of hydrogen ion sensors with
non-plasticised MB28 methacrylic-acrylic membranes.

Cations (M^{Z+})	E2 Slope (mV/decade) (0.1 M cations)	E2 Linear range (- log [H^+]) (0.1 M cations)	E2 **Estimated selectivity coefficient ($\log K_{H\text{-}M}^{pot}$)	E2 Slope (mV/decade) (1.0 M cations)	E2 Linear range (-log [H^+]) (1.0 M cations)	E3 Slope (mV/decade)	E3 Linear range (-log [M^{Z+}])
NH_4^+	56.3	5.23–8.15	< -9.15	33.6	4.88–7.05	51.5	1.0 – 3.0
Li^+	56.7	5.47–9.26	< -9.26	42.5	4.31–7.15	50.7	1.0 – 3.0
Na^+	56.6	5.35–9.44	< -9.44	36.2	4.23–7.18	51.3	1.0 – 3.0
K^+	56.9	5.39–9.56	< -9.56	39.7	4.44–7.26	51.5	1.0 – 4.0
Ca^{2+}	55.8	5.65–9.23	< -9.73	40.9	4.56–7.32	28.1	1.0 – 4.0
Mg^{2+}	56.8	5.33–8.98	< -9.48	32.6	4.35–7.07	32.6	1.0 – 4.0

** Calculated by using fixed interference method based on the lowest concentration of hydrogen ion used in each solution containing 0.1 M of interference cation.

Although the sensor contained a membrane that was not plasticised, its analytical performance is very close to the performance of other plasticised membranes for pH sensors reported in the literature (Table 3). This non-plasticised based membrane sensor for hydrogen ion also showed constant response after been kept unused for three months where the response slopes only varied from 56.0 to 56.6 mV/decade and the linear range remained at pH 4.3 to 9.6.

Table 3. Comparison of performance of non-plasticised membrane
pH sensor with plasticised membrane pH selective electrodes.

	Methacrylic-acrylic (Solid state sensor)[+]	**PVC (ion-selective electrode)**[(22)]	**PVC (solid state sensor)**[(23)]	**Tecoflex (ion-selective electrode)**[(7)]
Plasticiser	None	DOS*	DOS	DOS
Slope (mV/decade)	56.7	57.8	58.0	58.6
Selectivity coefficient, $\log K_{\text{H-M}}^{\text{pot}}$ **(0.1 M cations)**				
Na^+	< -9.44	-10.4 **	-11.9	-9.1
K^+	< -9.56	-9.8**	-10.8	-9.3
Ca^{2+}	< -9.73	-11.1**		-9.1

* DOS: Dioctyl sebacate   ** 1.0 M cations   + This work

When the concentrations of the interference cations were increased to 10 folds, the slopes of the hydrogen ion response reduced to 33-45 mV/decade (Table 2) indicating deterioration of sensor performance. There is also a decrease in the linear response range of the sensor but this occurred at low hydrogen ion concentrations. The sub-Nernstian behaviour of a cation selective sensor is normally caused by permeation of anions[(24)], especially if the sample activities are low compared to the anion activities. In this study, when the interference cation concentration was increased, the anion concentration was also increased, therefore anion permeation might account for the reduction in response slopes. This anion permeation behaviour can be removed by the introduction of lipophilic anion such as KTClPB into the membrane. For sensor E2, the low level of KTClPB incoporated into the methacrylic-acrylic membrane is probably insufficient to hinder anion permeation, particularly when the sample anions are high.

Conclusion

This study has shown that non-plasticised based methacrylic-acrylic polymer membrane can be used successfully as membrane for hydrogen ion-selective sensor. The use of a lipophilic anion as membrane additive is essential for good analytical performance of the sensor. Both the slope and selectivity of the sensor is comparable to similar sensors employing plasticiser based polymeric membranes.

Acknowledgement

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Sample Availability: Available from the authors.