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Ion-Selective Potentiometry with Plasma-Initiated Covalent Attachment of Sensing Membranes onto Inert Polymeric Substrates and Carbon Solid Contacts

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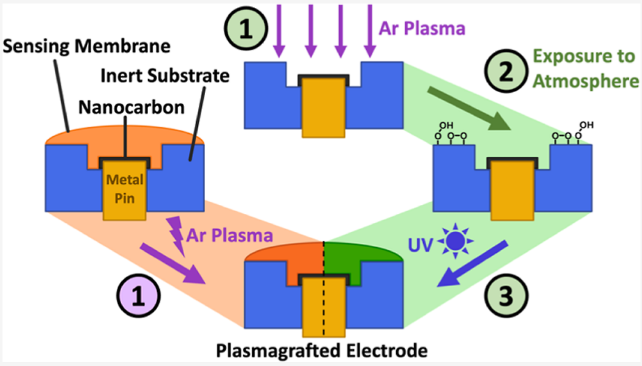
ABSTRACT: The physical delamination of the sensing membrane from underlying electrode bodies and electron conductors limits sensor lifetimes and long-term monitoring with ion-selective electrodes (ISEs). To address this problem, we developed two plasma-initiated graft polymerization methods that attach ionophore-doped polymethacrylate sensing membranes covalently to high-surface-area carbons that serve as the conducting solid contact as well as to polypropylene, poly(ethylene-*co*-tetrafluoroethylene), and polyurethane as the inert polymeric electrode body materials. The first strategy consists of depositing the precursor solution for the preparation of the sensing membranes onto the platform substrates with the solid contact carbon, followed by exposure to an argon plasma, which results in surface-grafting of the in situ polymerized sensing membrane. Using the second strategy, the polymeric platform substrate is pretreated with argon plasma and subsequently exposed to ambient oxygen, forming hydroperoxide groups on the surface. Those functionalities are then used for the initiation of photoinitiated graft polymerization of the sensing membrane. Attenuated total reflection-Fourier transform infrared spectroscopy, water contact angle measurements, and delamination tests confirm the covalent attachment of the in situ polymerized sensing membranes onto the polymeric substrates. Using membrane precursor solutions comprising, in addition to decyl methacrylate and a cross-linker, also 2-(diisopropylamino)ethyl methacrylate as a covalently attachable H^+ ionophore and tetrakis(pentafluorophenyl)borate as ionic sites, both plasma-based fabrication methods produced electrodes that responded to pH in a Nernstian fashion, with the high selectivity expected for ionophore-based ISEs.



■ INTRODUCTION

Ion-selective electrodes (ISEs) are versatile chemical sensors that are widely used to measure a range of ionic analytes in clinical settings, industrial process control, and environmental monitoring.[1−5] To meet the demands for miniaturized, wearable, and implantable sensors with long lifetimes and minimal needs for recalibration, conventional ISEs with an inner filling solution have been increasingly replaced by sensors in which the polymeric sensing membrane is directly applied to a solid contact,[6,7] such as a conducting polymer[8,9] or a high-surface-area carbon.[10−12] The lifetime of such ISEs is often limited by the leaching of plasticizers, ionophores, or ionic sites from the sensing membranes into sample solutions.[4,13] This can be addressed by covalently attaching either the ionophore or the ionic sites to a plasticizer-free polymer.[14−18] In the case of solid-contact ISEs, delamination of the sensing membrane from the electrode body and the electron conductor may pose another limitation to long sensor lifetimes. Upon extended exposure to aqueous samples and under thermal or mechanical stress, the strength of adhesion between the sensor membrane and the underlying substrate often weakens gradually, eventually resulting in the delamination of these membranes from the underlying substrates. Ion-selective membranes (ISMs) can be mechanically secured using electrode bodies that include, e.g., a screw cap,[19] but this complicates production, limits how small sensors can be built, and does not prevent effectively the formation of a water layer[20−22] between the sensing membrane and the underlying electron conductor. Similar limitations exist for plasticized poly(vinyl chloride) (PVC) membranes fused to PVC bodies, a technique that has been used for several decades to prepare ISEs with an inner filling solution and has recently also been used to encase cylindrical solid-contact electrodes.[23]

To that end, methods to bond sensing membranes covalently to conducting polymers and polymeric substrates

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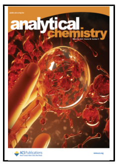

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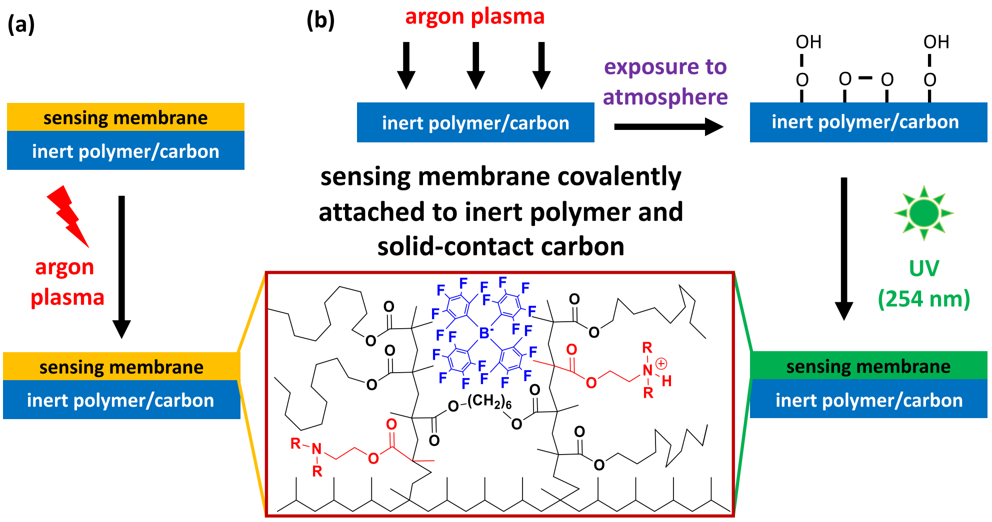

Figure 1. Plasma-based surface modification (illustrated here for a polypropylene surface): (a) deposition of sensing membrane precursors (matrix monomer, cross-linker, ionophore, and ionic sites) onto a polymeric substrate and carbon solid contact, followed by plasma-initiated graft polymerization. (b) Argon plasma generates free radicals on the surfaces of the inert polymer and carbon solid contact, which then react with oxygen to form (hydro)peroxides. This is followed by photoinitiated graft polymerization.

have been introduced.[8,24−33] In most cases, multistep processes were used, and delamination of the sensing membranes could be prevented either only from the underlying electrode bodies or from the electron conductor but not both. The latter limitation was addressed only recently by photoinitiated graft polymerization, which simultaneously attaches the sensing membrane covalently to both the inert polymeric electrode body material and the ion-to-electron transducer.[34] Thus, prepared solid-contact ISEs show good resistance to high temperatures and pressures, including autoclaving. After storage of these ISEs for 6 months in an electrolyte solution, they still showed Nernstian responses and unchanged selectivities, and the water layer test showed no evidence of a water layer formation. However, not all types of ionophores, ionic sites, and polymeric substrates are compatible with in situ photopolymerization,[35] and photopolymerization can also be a relatively slow process. Alternative methods to bond sensing membranes to the ISE platform are, therefore, still of interest.

An interesting process for this purpose is plasma-initiated polymerization, for which there has been, to date, only very limited use in ISE fabrication.[36,37] Kurosawa and co-workers prepared ion-exchanger membranes by evaporation of ammonium tetraphenylborate and plasma-polymerization onto the surface of a porous cellulose ester membrane. In this way, they prevented leakage of this ion exchanger into aqueous samples, resulting in improved sensor lifetimes. This technique is limited, though, to ionophores and ionic sites that are sufficiently volatile. Moreover, it would be difficult to control the molecular ratio of an ionophore and ionic sites in ISMs prepared this way. Because these ratios are critical for optimum ion selectivities,[38] this restricts the wider use of this technique. Plasmas have also been used previously to clean the surface of substrates prior to the application of plasticized PVC-based ISMs to solid contact,[39] but no covalent bonds between the solid contact and the sensing membrane were formed in that process.

We report herein two plasma-based grafting methods (see Figure 1) for the simultaneous attachment of ISE membranes to inert polymeric electrode body materials that are more readily controllable than the method by Kurosawa and co-workers.[36,37] We used polypropylene, poly(ethylene-*co*-tetrafluoroethylene), and polyurethane as representative polymers because they are widely used in industry and have good mechanical, temperature, and chemical resistance suitable for industrial-grade sensor bodies. Our first method is based on one step only; the precursor components of the sensing membrane are deposited onto a polymeric platform substrate with a carbon-solid contact and then exposed to an argon plasma, resulting in graft-polymerization of the sensing membrane to the substrate.[40−43] The second method is a hybrid method; it comprises three steps but avoids exposure of the sensing membrane precursors to a plasma. The polymeric substrates with the carbon solid contacts are pretreated with argon plasma and subsequently exposed to oxygen or the ambient atmosphere, resulting in the formation of hydroperoxide and peroxide functional groups on the surface of the polymer.[44−48] This is followed by photoinitiated graft polymerization.[49−52] This work adds to the methods that can be used to chemically bond ISE membranes to electrode bodies and electron conductors. It will facilitate the selection of a grafting method that, in a specific case, is most compatible with the desired type of sensing components, electrode body polymer, and electron conductor.

■ EXPERIMENTAL SECTION

Reagents, Materials, and Instrumentation. Nanographite powder (GS-4827) was purchased from the Graphite Store (Northbrook, IL, USA). It consists of graphite platelets (particle size distribution from 0.10 to 10 μm) and exhibits a Brunauer−Emmett−Teller surface area of 165 m^2/g.[52] Plasma-initiated graft polymerization and plasma treatments were performed using a Vision 320 RIE plasma chamber with a 13.56 MHz radio frequency (RF) generator from Plasma-Therm (Saint Petersburg, FL, USA).

Preparation of Precursor Solutions for Plasma Grafting of pH Sensing Membranes. Precursor solutions were prepared by mixing 91.3 wt % decyl methacrylate, 1.4 wt % 1,6-hexanediol dimethacrylate, 3.9 wt % potassium tetrakis(pentafluorophenyl)borate, and the covalently attachable ionophore 2-(diisopropylamino)ethyl methacrylate[17,34] (300

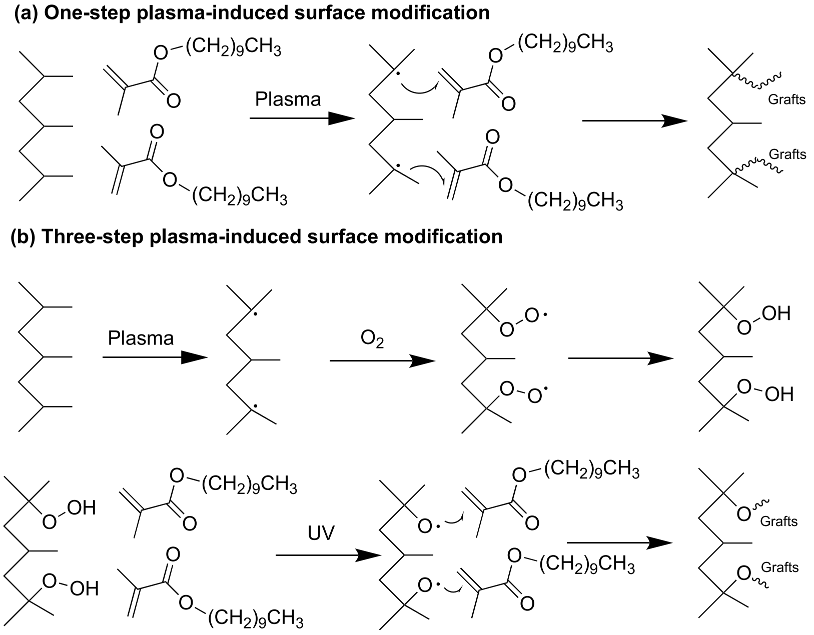

Figure 2. Schematic of (a) one- and (b) three-step plasma-initiated graft polymerization of sensing membranes shown here for a polypropylene substrate.

mol % with respect to the ionic sites, which corresponds to 3.4 wt % of all membrane components). No solvent was used.

One-Step Plasma Grafting of Cross-Linked Poly(decyl methacrylate) Membranes. Polypropylene sheets and poly(ethylene-*co*-tetrafluoroethylene) films were cut into 2.5 × 2.5 cm^2 squares, which were then washed with 10 mL of acetone and dried in a stream of nitrogen for 5 min. A total of 30 μL of plasma grafting precursor solution containing decyl methacrylate, cross-linker, ionophore, and ionic sites was drop-cast onto these substrates, which were then placed into the plasma chamber. The membranes were grafted to polypropylene and poly(ethylene-*co*tetrafluoroethylene) substrates by plasma treatment over 180−600 s with a chamber pressure of 10−13 Pa, an argon flow of 9 sccm (standard cubic centimeter per minute), and an RF power of 40−100 W (for details, see Table 2). The modified sheets were then immersed in acetone to remove unreacted monomers and washed with 10 mL of deionized water.

Three-Step Plasma Grafting of Cross-Linked Poly(decyl methacrylate) Membranes. Polypropylene and poly(ethylene-*co*-tetrafluoroethylene) substrates were first treated with an argon plasma with a gas flow rate of 9 sccm and an RF generator power of 40 W. Subsequently, the plasma treated polymer substrates were exposed to ambient oxygen to permit the formation of surface peroxides and hydroperoxides. A total of 30 μL of plasma grafting precursor solution was drop-cast onto each of the substrates, which were then placed into a well-sealed box covered by a UV-transparent quartz glass plate, followed by flushing of the box with argon for 10 min. The membranes were then grafted to the functionalized substrates by UV irradiation (peak output 254 nm) over 20 min, followed by drying at room temperature in air for 1 h.

Potentiometry. Electrodes for potentiometric studies were prepared as described above, except the sensing membranes were grafted onto custom electrode bodies with a gold-coated stainless steel pin as the electrical contact, using nanographite as the solid-contact material. The design of the electrode bodies was reported previously.[34] However, the inert body material used here was Hei-Cast 8550 (H&K, Tokyo, Japan), which is a vacuum-casting polyurethane material for the manufacture of polyethylene and polypropylene prototypes and is prepared by mixing and curing of two components comprising a polyol and 4,4′-diphenylmethane diisocyanate. The deposition conditions used for the electrodes were 40 W and 10 Pa for 300 s unless described otherwise. Selectivity coefficients against Na^+, K^+, and Li^+ were measured using the fixed interference method.[53]

For further experimental details, see the Supporting Information.

■ RESULTS AND DISCUSSION

The first strategy that was used in this work to form ISMs that were covalently attached to underlying substrates included the deposition of a membrane precursor solution comprising 2-(diisopropylamino)ethyl methacrylate as a covalently attachable ionophore, tetrakis(pentafluorophenyl)borate to provide for mobile ionic sites, decyl methacrylate as the monomer to form the bulk of the membrane matrix, and 1,6-hexanediol dimethacrylate as a cross-linker onto the substrate with the carbon solid contact, followed by subjection to an argon plasma (see Figure 2a). When the substrate coated with the film of membrane precursor solution is exposed to the plasma, this leads to the formation of radicals, which subsequently initiate the polymerization of the decyl methacrylate. This results in the grafting of polymer chains through covalent bonds onto the underlying substrates. Simultaneously, the polymerization reaction also covalently attaches the ionophore to the growing poly(decyl methacrylate) (PDMA) chains. In the case of substrates such as polypropylene, poly(ethylene-*co*-tetrafluoroethylene), and urethane, the grafting reaction includes the abstraction of hydrogen atoms from the substrates as the critical step for surface attachment (see Figure 2).[54−56]

ATR-FTIR spectra confirm for both polypropylene and poly(ethylene-*co*-tetrafluoroethylene) that the plasma-initiated surface grafting results in the formation of a PDMA film, as can be seen from the intense C═O stretch vibration band for the ester group of poly(decyl methacrylate) (PDMA) (see Figure S1).[57]

Table 1 shows advancing and receding contact angles of H_2O on unmodified and PDMA-modified polypropylene and poly(ethylene-*co*-tetrafluoroethylene) substrates. The plasma-initiated graft polymerization of decyl methacrylate and cross-linker on the surfaces of polypropylene and poly(ethylene-*co*-tetrafluoroethylene) decreased the water contact angle by 40 and 33°, respectively, as expected for the increase in surface polarity as a result of the PDMA modification.

Table 1. Contact Angles of H_2O on Unmodified Substrates as Well as on PDMA Membranes Attached to Inert Substrates Modified with the One-Step Plasma-Initiated Method[a]

type of substrate	advancing contact angle (deg)		receding contact angle (deg)	
	substrate unmodified	PDMA attached	substrate unmodified	PDMA attached
polypropylene	113 ± 2	73 ± 4	112 ± 2	72 ± 2
poly(ethylene-*co*-tetrafluoroethylene)	106 ± 2	75 ± 2	107 ± 3	73 ± 2

[a] Corresponding advancing and receding contact angles (values shown for 15 μL drop volumes; see Table S1 for further details) are identical within error, confirming that the measured values are not affected by hysteresis, as it could be introduced, e.g., by surface roughness.

The grafting degrees, membrane thicknesses, and efficiency of the plasma-initiated graft polymerization can be optimized by controlling the flow rate and pressure of the plasma gas as well as the RF power.[40,58] These parameters were calculated as follows:[34]

$$\text{grafting degree} = (W_1 - W_0)/(A)$$

$$d = (W_1 - W_0)/(AD_M)$$

$$\text{grafting efficiency} = (W_1 - W_0)/(W_2)$$

where W_0 is the weight of the unmodified polymer sheet, W_1 is the weight of the polymer sheet with the covalently attached PDMA film or ISM, A is the surface area, d is the thickness of the covalently attached PDMA film, D_M is the density of decyl methacrylate, and W_2 is the weight increase of the substrate as expected assuming inclusion of all components of the membrane precursor solution into the grafted PDMA films.

As Table 2 shows, graft polymerization efficiencies as high as 66% were achieved with only a little optimization. A plasma treatment time of 180 s was too short for efficient graft polymerization, but no significant difference in grafting efficiencies was seen between plasma exposures for 300 and 600 s. Notably, moderate increases in RF power and gas pressure decreased polymerization efficiency.

The second strategy used in this work for the covalent attachment of sensing membranes to underlying substrates utilized the argon plasma only to activate the inert polymer surfaces and the carbon solid contacts, which were then exposed to atmospheric oxygen to induce the formation of surface hydroperoxides and peroxides by reaction with molecular oxygen (see Figure 2b).[54] Upon deposition of membrane precursor solution onto these surface-modified substrates and UV irradiation at 254 nm,[59] the surface-confined peroxide species decompose into alkoxy and peroxy radicals,[52,60] initiating graft polymerization. We note that a broad band was seen in the infrared (IR) spectrum at around 3300 cm^{-1} after the plasma-pretreated polymer sheets were exposed to the ambient atmosphere (see Figure S2), which is likely due to a combination of hydrogen-bonded −OOH groups and water adsorbed onto the substrates, which become hydrophilic as a result of the surface functionalization.[44] After the photoinitiated polymerization, the IR spectra again confirm the formation of PDMA, as evidenced by the intense C═O stretch vibration.

Table 2. Plasma-Initiated Grafting of Poly(decyl methacrylate) onto Polypropylene Substrates Using the One-Step Process: Grafting Degrees, Membrane Thicknesses, and Grafting Efficiencies Were Calculated from the Differences in Weight (as Determined upon Drying to Constant Weight) Prior to and after Plasma Grafting

plasma parameters	grafting degree (mg/cm^2)	thickness, d (μm)	grafting efficiency
40 W, 10 Pa, 180 s	polymerization failed	polymerization failed	polymerization failed
40 W, 10 Pa, 300 s	6.44 ± 2.04	74 ± 23	66% ± 21%
40 W, 10 Pa, 600 s	5.39 ± 0.66	62 ± 8	55% ± 7%
100 W, 10 Pa, 300 s	2.58 ± 0.48	30 ± 5	26% ± 4%
40 W, 13 Pa, 300 s	2.61 ± 0.27	30 ± 3	27% ± 3%

This surface functionalization was also confirmed by contact angle measurements. Table 3 shows that upon plasma treatment and air exposure, contact angles of polypropylene and poly(ethylene-*co*-tetrafluoroethylene) substrates decreased from 113 and 107° to 64 and 68°, respectively. This is consistent with a more hydrophilic surface with (hydro)-peroxide groups,[57,61] as also suggested by the IR spectra. Upon PDMA-modification, the contact angles increased again, as was also observed for the PDMA-modified substrates prepared with the one-step method. Notably, the contact angles of the thus obtained PDMA films do not depend on the type of the underlying polymer substrate, and they do not differ when either the one- or three-step method is used. Moreover, the advancing and receding contact angles are within error identical, all factors that are consistent with films that cover the entire substrate evenly.

To demonstrate the mechanical robustness of the PDMA modification of polypropylene, poly(ethylene-*co*-tetrafluoroethylene), and polyurethane substrates, peeling tests were performed along with control experiments in which covalent attachment of the PDMA membrane was not expected. Likewise, to demonstrate covalent attachment to carbon-solid contacts, analogous experiments were also performed with glassy carbon substrates. This type of substrate was chosen because peeling tests require a flat surface and are, therefore, not feasible with the nanographite that was used to prepare ISEs (see below). Glassy carbon has a fullerene-related structure with extensive sp^2 bonding, which makes it very similar to nanographite.[62]

Notably, choosing a control experiment with conditions very similar to those of the one-step plasma-initiated surface grafting was not straightforward because leaving out the plasma or using a monomer without a C═C double bond would have not only prevented grafting to the underlying surface but also precluded the polymerization of the matrix

Table 3. Contact Angles of H_2O on Unmodified Substrates, as Well as PDMA Membranes Attached to Substrates Modified with the Three-Step Grafting Method (Values Shown for 15 μL Drop Volumes; See Table S4 for Further Details)

	advancing contact angle (deg)			receding contact angle (deg)		
type of substrate	substrate not modified	after plasma and air exposure	PDMA attached	substrate not modified	after plasma and air exposure	PDMA attached
polypropylene	113 ± 2	64 ± 2	77 ± 2	112 ± 2	64 ± 1	75 ± 3
poly(ethylene-*co*-tetrafluoroethylene)	106 ± 2	68 ± 2	72 ± 3	107 ± 3	68 ± 1	75 ± 3

monomer. Indeed, variation of only one method parameter that could have been used to prevent surface grafting while still permitting polymerization in the plasma chamber was not possible. Therefore, the closest control samples for peeling tests were obtained by photoinitiated polymerization of PDMA-based membranes on polypropylene and poly(ethylene-*co*-tetrafluoroethylene) substrates using a precursor solution that contained the same decyl methacrylate, cross-linker, ionophore, and ionic site concentrations as for the plasma-initiated surface grafting and, in addition, the photoinitiator 2,2-dimethoxy-2-phenylacetophenone. However, unlike photoinitiated surface grafting,[34] no surface activation was performed prior to the photopolymerization. Details of this type of photopolymerization were reported previously.[17] The reasoning with regard to control experiments for the three-step plasma grafting method is very similar. When the first step of this procedure, i.e., the plasma exposure of the polymer substrates, is left out, there are no peroxide and hydroperoxide O−O bonds to cleave in step 2, making not only surface grafting impossible but also preventing polymerization of decyl methacrylate. We conclude that the control experiments most suitable for the three-step plasma grafting method are indeed the same as for the one-step plasma grafting method.

For the peeling tests, substrates modified by plasma-based grafting of PDMA membranes, as well as the control substrates prepared with photoinitiated graft polymerization, were immersed in phosphate buffer (pH = 7.1) for 7 days. The purpose of this waiting period was to allow for ample time during which a water layer at the interface of the PDMA and the underlying surface could form if the modified substrates were prone to water layer formation at all. After those 7 days, all polymer membranes could be removed with little effort from substrates to which they were not covalently attached. However, PDMA membranes covalently attached to the underlying substrates by both the one- and three-step methods of plasma-based graft polymerization could not be detached from the underlying substrates. Forceful attempts to remove the PDMA membranes from the underlying polymer substrates using metal tweezers resulted in scratch marks on the PDMA surface but failed to delaminate the membranes by breaking the bond between the PDMA and the substrate (see Figures 3 and S3). This is consistent with the successful covalent attachment of membranes to the underlying inert polymer and glassy carbon substrates.

Most importantly, electrodes fabricated with both the one- and three-step plasma-based graft polymerization methods exhibited the theoretically expected Nernstian response to pH (see Table 4). For both polymerization methods, exposure of the membrane components to the plasma did not affect the response slope, and the selectivity over metal ions was very high, as expected for an ISE membrane doped with a trialkylamine ionophore. Interestingly, the low pH end of the Nernstian response range was at a slightly higher pH than for UV-photografted membranes. Indeed, the interpretation of the upper detection limit is complicated by the observation of a narrow super-Nernstian response region preceding Donnan failure[19,63−65] (see Figure S4), a phenomenon that we are further investigating. The slightly lower cation selectivities of the ISE membranes prepared with the plasma-based methods as compared to those of the UV-photografted membranes cannot be readily explained by the magnitude of the ionophore complex stability. This may be related to the extent of polymerization, which is not exhaustive (see Table 2) and could affect the ratio of ionophore and ionic sites in the final sensing membranes. The same effect might also explain the somewhat larger potential drift for the one-step plasma polymerization (Figure S6). While the selectivities and drift reported here appear satisfactory for many applications, it will be interesting to see in future work whether optimization of the plasma polymerization conditions will provide further improvements in device characteristics.

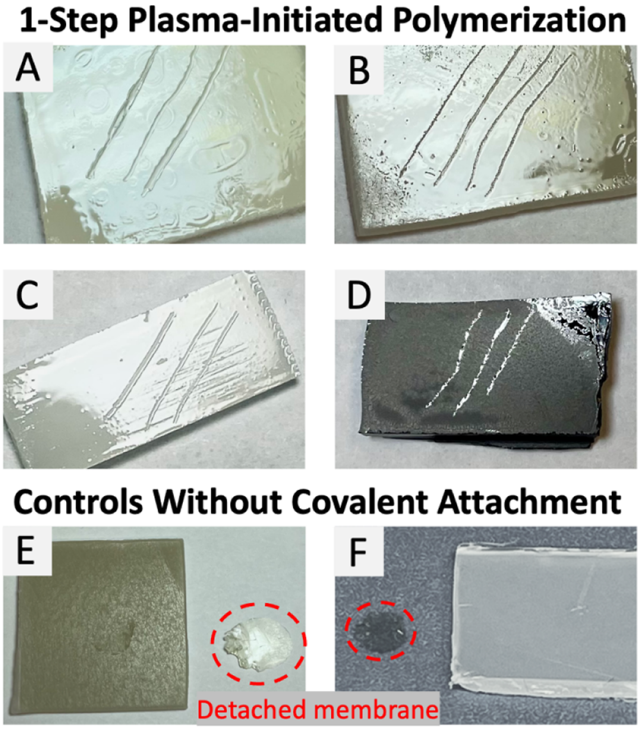

Figure 3. PDMA membranes fabricated by one-step plasma-initiated graft polymerization on polypropylene (A), poly(ethylene-*co*-tetrafluoroethylene) (B), polyurethane (C), and glassy carbon (D) substrates after storage for 7 days in buffer solution, followed by forceful attempts of removal with tweezers: PDMA membranes could be damaged with scratches but did not delaminate from the substrate surface. Control experiments with UV-polymerized PDMA membranes on unmodified poly(ethylene-*co*-tetrafluoroethylene) (E) and unmodified polypropylene (F) show that the membranes can be fully removed from the substrates.

Table 4. Upper Detection Limit, Selectivities, and Stabilities of ISEs with PDMA Sensing Membranes Prepared with 2-(Diisopropylamino)ethyl Methacrylate as the Ionophore, along with Data for an Ionophore-Free Ion-Exchanger PDMA ISE, Reported as Means along with Standard Deviations

	three-step plasma grafting[a]	one-step plasma grafting[b]	UV-photografting (no ionophore)[64]	UV-photografting
slope	−57.2 ± 0.5	−57.8 ± 0.1	−50.3 ± 1.2	−58.5 ± 1.2
electrical resistance	331 ± 216 MΩ	91 ± 35 MΩ	n.a	38.4 ± 3.2 MΩ
$\log K^{\text{pot}}_{\text{H,Li}}$	−9.5 ± 0.1	−9.4 ± 0.1	−0.5 ± 0.1	−10.7 ± 0.1
$\log K^{\text{pot}}_{\text{H,Na}}$	−9.1 ± 0.1	−9.1 ± 0.1	−0.3 ± 0.1	−10.4 ± 0.3
$\log K^{\text{pot}}_{\text{H,K}}$	−8.4 ± 0.1	−8.3 ± 0.1	+0.4 ± 0.1	−9.8 ± 0.3
upper detection limit[c]	2.6	2.5	n.a	1.4
long-term drift[d]	31 ± 15 μV/h	−5 ± 206 μV/h	n.a	7 μV/h

[a] $n = 3$. [b] $n = 2$. [c] Determined using 10 mM sodium phosphate buffer by adjusting the pH with 1.0 M HCl. To exclude a short super-Nernstian region, the upper detection limit was defined by the pH at which the electrode potential deviated by 5 mV from the linear response.[64] [d] Determined from continuous potential measurements over 141 h.

Water layer tests performed after conditioning the electrodes for 5 days in a buffer solution of pH 7 confirmed that water layers were not formed (see Figure S5), which further supports the covalent attachment of the sensing membrane to the electrode bodies and carbon-solid contact.

CONCLUSIONS

While plasma-initiated graft polymerization has been used to improve the adhesion of polymeric films to underlying substrates for a wide variety of other applications,[66,67] previous use of the plasma technique for the fabrication of ISE membranes has been very limited. For the work reported here, two plasma-based grafting techniques were used, i.e., direct plasma-initiated graft polymerization of ISE membranes onto inert polymeric substrates and surface functionalization using a plasma treatment, followed by photoinitiated graft polymerization. Both methods directly attach cross-linked decyl methacrylate-based membranes onto inert surfaces, resulting in PDMA membranes that could not be delaminated from the underlying inert polymer substrates and the glassy carbon that was used as a representative carbon-solid contact. In this work, we demonstrated this using 2-(diisopropylamino)ethyl methacrylate as a covalently attachable H^+ ionophore, as trialkylamines are well-known to provide for high H^+ selectivities.[68−70] However, by using different ionophores (covalently attachable or not), we expect that plasma-based graft polymerization can be easily adapted to prepare ISEs for the detection of various other ions.

These plasma-based graft polymerization methods broaden the options for the direct attachment of ISMs to underlying substrates and high-surface-area carbons to prevent the delamination of sensing membranes. In particular, the one-step plasma-initiated polymerization method enables the use of ionophores and ionic sites that are unsuitable for photopolymerization because of their UV absorbance. In our hands, the fabrication of electrodes by plasma-initiated graft polymerization was less time-consuming than when photoinitiated graft polymerization was used, but further work will be required to assess whether that is still true in more industry-like settings in which these processes are fully optimized.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.4c00204.

Further experimental details, contact angles and IR spectra of polymer substrates, unmodified as well as modified with PDMA membranes, photographs of membranes prepared with three-step plasma-induced grafting polymerization, and EMF response curves (PDF)

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Author Contributions

[†] K.R.C. and M.L.H. contributed equally to this work.

Notes

The authors declare no competing financial interest.
K.R.C., P.B., and the University of Minnesota have a U.S. patent application related to this technology and will be entitled to standard royalties should licensing revenue be generated.

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