



# Photochemical attachment of polyelectrolyte membrane to electrode substrate and their humidity-sensitive properties

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## ABSTRACT

New cinnamate group-containing copolymers for a humidity-sensitive polyelectrolyte were prepared by copolymerization of [2-[(methacryloyloxy)ethyl]dimethyl]propyl ammonium bromide (MEPAB), methyl methacrylate (MMA) and 2-(cinnamyloxy)ethyl methacrylate (CEMA). They were self-crosslinkable terpolymers composed of different contents of MEPAB/MMA/CEMA = 70/27/3, 70/25/5, 70/23/7 and 70/20/10. Pretreatment of the alumina substrate with 3-(triethoxysilyl)propyl cinnamate (TESPC) containing silane-coupling agent was performed to attach the humidity-sensitive membrane to the substrate through covalent bonds. The sensors were irradiated with UV light, causing the electronically excited cinnamate molecules to form a crosslinking reaction via the  $[2\pi + 2\pi]$  addition. The impedance ranged from  $10^7$  to  $10^3 \Omega$  between 20 and 95%RH, which was required for a humidity sensor operating at ambient humidity. Water durability, hysteresis, response time and long-term stability at high temperature and humidity were also measured and estimated.

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## 1. Introduction

Various methods for preparing polyelectrolyte have been attempted to improve the performance of a high humidity sensor [1]. Crosslinking [2–10] and copolymerization with hydrophobic monomer [11–15] have been frequently employed for the preparation of water-durable polymer membrane. The modification of humidity-sensitive monomer with hydrophobic group is a promising method for changing impedance characteristics as well as water durability [16–18]. An interpenetrating polymer network (IPN) [19–21] and hybridization of sensing material to electrode substrate using trialkoxysilyl compound [22–26] are another methods of preparing water-resistive humidity sensors.

The covalent attachment of ultra-thin films of organic/inorganic hybrid materials to a solid substrate is often desirable in order to enhance the stability of the films against solvents and displacement reagents (e.g., water for hydrophilic surface). As a consequence of this need, numerous organic/inorganic hybrid protocols have been developed [27–30]. The most common procedures use silane-coupling agents that are suitable for binding to the inorganic surface and organic polymer. New silane-coupling agent such as (3-triethoxysilyl)propyl cinnamate having both the cinnamate group, which acts as a photodimerizable function and an alkoxy-silyl group that react with silica or alumina. Treatment with these agents could

form covalent bonding to improve the adhesion between incompatible inorganic surface and organic polymers through covalent bonds [31–34].

Photopolymerization technology has drawn significant attention in recent years for industrial applications in regards of coating of various materials, adhesives, printing inks, photoresists and biomaterials [35–38]. This technology is based on the use of a self-crosslinkable polymer, containing a photoinitiator system suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species in order to convert a polymer into a crosslinked network [39]. We have been interested in the synthesis of a new family of photo-curable polyelectrolyte in which the polyelectrolyte chains are simply crosslinked by irradiation of UV light after fabrication of the self-crosslinkable humidity-sensitive membrane on the aluminum electrode [40].

Conventional negative-working photoresists based on poly(vinyl cinnamate) (PVCi) and its derivatives have played a leading role in the scientific development of photopolymers [41]. The photofunctionality of PVCi arises from photodimerization that leads to insolubilization due to the formation of crosslinks. In addition to these unique properties, the ability of the cinnamate group to undergo rapid photodimerization without the addition of a photoinitiator is critically important in the present investigation [42].

This paper describes the use of the photodimerizable silane-coupling agent, its immobilization on an alumina electrode surface, and the subsequent attachment of photo-curable polyelectrolyte by irradiation of UV light of dip-coating layers of this copoly-

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mer on cinnamate-modified surface. Copoly(MEPAB/MMA/CEMA) was chosen because it represents example of self-curable and attachable polyelectrolyte to the substrate cinnamate group, and therefore, demonstrates the water-durable humidity sensor system.

## 2. Experimental

### 2.1. Chemicals and instrument

[2-[(Methacryloyloxy)ethyl]dimethyl]propyl ammonium bromide (MEPAB) was synthesized by quaternization reaction of 2-(*N,N*-dimethylamino)ethyl methacrylate with propyl bromide. 2-(Cinnamyloxy)ethyl methacrylate (CEMA) was prepared by the method previously reported [43]. Methyl methacrylate (MMA, Aldrich Chem. Co.), allyl cinnamate, triethoxyhydrosilane and azobisisobutyronitrile (AIBN, Aldrich Chem. Co.) were used as received. 2-Methoxyethanol was dried with calcium hydride and sodium metal and purified by distillation. Dimethylsulfoxide (DMSO) was purified by distillation under reduced pressure after drying by refluxing a mixture of DMSO and benzene using Dean-Stark separator.  $^1\text{H}$  NMR spectra were recorded on a Varian Gemini-2000 spectrometer performed at 200 MHz. FT-IR spectra were taken on a Bio-Rad Model MX-3000 spectrometer. Elemental analyses were performed using a CE Instrument (EA1110). Impedance versus relative humidity characteristics of the sensors were measured using a thermostatic humidity chamber (The humidity and temperature controller (Jeio Tech Korea, Model: TM-NFM-L; 20–95%RH) was used for the measurement of relative humidity at constant temperature.). The atmosphere in the chamber and its water content can be controlled by two flowmeters, one for dry air and the other for humid air. The two separated fluxes are mixed in a mixing chamber. The temperature was controlled in the range from  $-40$  to  $150^\circ\text{C}$  with an accuracy of  $\pm 0.5^\circ\text{C}$  and the humidity was controlled over 20–95%RH within  $\pm 2\%$ RH.

The impedance was measured with an LCR meter (Model EDC-1635,  $0.1\ \Omega$  to  $20\ \text{M}\Omega$ ). UV exposure of the humidity-sensitive membrane was performed using a commercial bench-top high power UV curing system (Hg, MTL 1000 W, 1 kW (80 W/CM), Sei Myung Vactron Co. Ltd.).

#### 2.1.1. Synthesis of (3-triethoxysilyl)propyl cinnamate (TESPC)

Allyl cinnamate (2 g) and triethoxyhydrosilane (2 g) was dissolved in freshly distilled THF (20 mL). Pt/C (20 mg, 10% Pt) was added and the mixture was maintained  $60^\circ\text{C}$  for 5 h. The catalyst was removed by filtration. The solvent was removed under vacuum and the excess triethoxyhydrosilane was vacuum distilled yielding the desired product TESPC as oil. FT-IR ( $\text{cm}^{-1}$ ): 3057, 3025, 2940, 2876, 1730, 1680, 1651, 1620, 1230–1100, and 1086.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm): 7.24–7.72 (m, 5H,  $\text{Ph}-\text{CH}=\text{CH}-$ ), 5.64–6.68 (m, 2H,  $\text{Ph}-\text{CH}=\text{CH}-$ ), 4.19 (t, 2H,  $\text{Ph}-\text{O}-\text{CH}_2\text{CH}_2-$ ), 3.83 (m, 6H, 3  $\text{Si}-\text{O}-\text{CH}_2-$ ), 1.60 (m, 2H,  $-\text{O}-\text{CH}_2-\text{CH}_2\text{CH}_2-$ ), 1.21 (s, 9H, 3  $-\text{Si}-\text{CH}_2\text{CH}_3$ ), 0.58 (t, 2H,  $-\text{CH}_2-\text{Si}-\text{O}-$ ).

#### 2.1.2. Immobilization of TESPC on alumina surfaces

The silane-coupling agent TESPC was immobilized on the alumina surface of sensor electrode at room temperature from methanol solutions using HCl as catalyst. The sensor chips were rinsed in 0.1N NaOH and 0.1N HCl for 3 h and washed with distilled water before use. The alumina substrates were pretreated with cinnamate-containing silane-coupling reagent. A solution of HCl (1 wt%) and TESPC (2 wt%) in methanol/water ( $v/v = 95/5$ ) was spread on substrates, and the substrates were dried at  $130^\circ\text{C}$  for 1 h.

#### 2.1.3. Representative preparation of self-crosslinkable humidity-sensitive copolymers

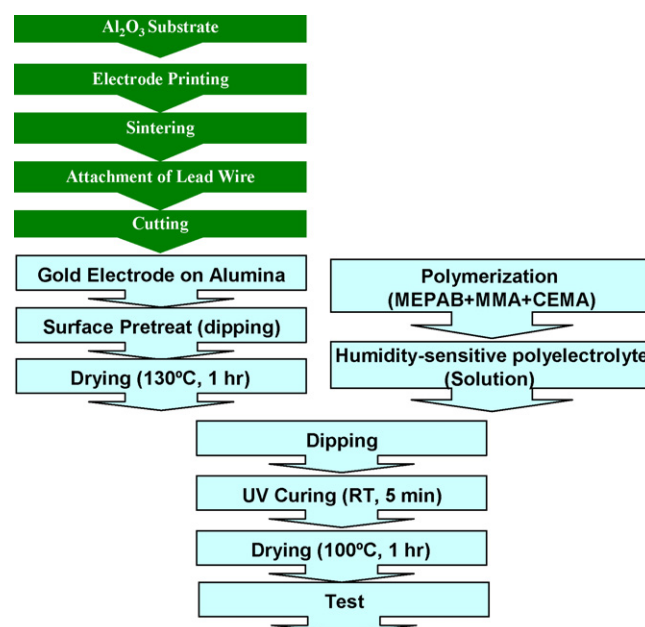
A mixture of the humidity-sensitive monomer MEPAB (19.74 g, 70 mmol), comonomer MMA (2.00 g, 20 mmol), CEMA (2.60 g, 10 mmol) and AIBN (0.09 g, 0.56 mmol), dissolved in anhydrous 2-methoxyethanol (100 g), was placed in a glass ampoule. The solution was degassed by freeze–thaw method. The sealed glass ampoule was heated at  $65^\circ\text{C}$  and maintained for 24 h. The polymerized mixture was precipitated into a large amount of anhydrous ethyl ether. The product was purified by dissolution in dry 2-methoxyethanol followed by reprecipitation in *n*-hexane. The copolymers were dried under vacuum at  $50^\circ\text{C}$  for 12 h. Other copolymer polyelectrolytes with different contents of comonomers were prepared by similar procedures, as described above.

#### 2.1.4. Fabrication of humidity-sensitive membrane

The copolymer (0.65 g) was dissolved in anhydrous DMSO (5.0 g) at room temperature. The mixture was fabricated on the alumina electrode by dipping. The photochemical crosslinking reaction of the sensor chips was induced by irradiating UV light for 5 min at room temperature. Then, the sensor chips were then heated at  $60^\circ\text{C}$  for 2 h and subsequently at  $100^\circ\text{C}$  for 1 h. Other humidity sensors with different contents of comonomers were prepared by the similar procedures described above. The full process for the humidity sensor electrode setup was illustrated in Scheme 1.

#### 2.1.5. Measurements of impedance characteristics

Impedance versus relative humidity characteristics of the sensor were measured for an absorption process, at 20%RH  $\rightarrow$  95%RH, and for a desorption process, at 95%RH  $\rightarrow$  20%RH at 1 V, 1 kHz and  $25^\circ\text{C}$ . Response time was determined over saturated salt solution of  $\text{KNO}_3$  for 94%RH and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  for 33%RH at its equilibrium state. The sensor was immersed in water for 5, 24, 240 and 720 h and then dried in air. The durability of the humidity sensor in water was tested. The long-term stability at high temperature and high humidity was evaluated at 80 and 90%RH at  $80^\circ\text{C}$ .



Scheme 1.

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