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Electrospun nanofibers and spin coated films prepared from side-chain copolymers with chemically bounded platinum (II) porphyrin moieties for oxygen sensing and pressure sensitive paints

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ABSTRACT

Pressure sensitive paints (PSP) containing oxygen probes were primarily used to measure air pressure. In this perspective, a polymerizable methacrylate-derived tetraphenylporphinato platinum(II) (PtTPP-MA) monomer was copolymerized with acrylic/vinyl monomers to produce four different copolymers. Octafluoropentyl methacrylate (OCFPM) and pentafluorophenyl acrylate (PFPA) were used as fluorinated monomers. Methyl methacrylate (MMA) and styrene (S) were used as non-fluorinated monomers. The structures and physical properties of the polymers were confirmed by ^{1}H NMR, ^{19}F NMR, GPC, and DSC. Experimental conditions were optimized to get fine nanofibers. Pressure sensing electrospun membranes and spin coated films were fabricated. Nanofibers showed fast response and good sensitivity towards gaseous oxygen. The influence of types of substrate and polymer natures on response time, oxygen sensitivity, and pressure responses were deliberated. Among our synthesized copolymers, poly(PS-*co*-PFPA-*co*-OCFPM-*co*-PtTPPMA) (Polymer **P3**) showed fast response time and good pressure sensitivity both as spin coated films and nanofibers.

1. Introduction

Among functional coating, pressure sensitive paint (PSP) is an astonishing technology to measure air pressure on substrate. Basically, PSP is an optochemical oxygen sensor which consists simply of a luminescence dye and polymer support. It works on the mechanism of luminescence quenching. Changes in luminescence intensities or in excitation lifetimes of oxygen probes embedded in a polymer support are correlated with oxygen concentration [1], which was first described by Stern and Volmer [2]. Optochemical sensors offer considerable advantages over conventional sensors in various fields such as polarographic oxygen electrodes. Oxygen electrode measured oxygen with a reference electrode. For example L. Nei and R.G Compton fabricated galvanic oxygen sensor based on Ni-Cu alloy. On exposer, electrode senses the molecular oxygen via O_2 reduction mechanism [3]. Many improvements have been achieved in electrochemical oxygen sensors and are being used as biosensors. In this regards, C-C Wu et al. constructed oxygen sensing chip from amino group modified polydimethylsiloxane (PDMS) to track the respiration activities of adhering cells [4]. In addition, platinum (II) porphyrins based electrodes are also used for the better performance of fuel cell technology due to electrocatalytic reduction mechanism of molecular oxygen [5,6]. Optical oxygen sensors are widely used as compared to electrochemical oxygen sensors. In Clark type oxygen sensing system, continuous oxygen monitoring is possible but it cannot provide oxygen distribution or pressure map over the target object. Moreover continuous consumption of oxygen of platinum electrode leads towards false results. CO_2 and halothane interferes and disturbs the oxygen measurements. Different from the electrodes, optochemical sensors work on fluorescence and/or phosphorescence quenching mechanism. Due to reversible photoluminescence quenching properties, optochemical sensors provide continuous and remote control access to oxygen measurements [7].

In addition, thickness of sensing layer plays a critical role. For example: thick sensing layer showed slow response. However, thin sensing layer showed low luminescence intensity which raised signal to noise ratio issue. Moreover the response of these sensing layers to oxygen is limited to time required for diffusion. Therefore, variety of sensing layers such as nanoparticles and thin films were employed for

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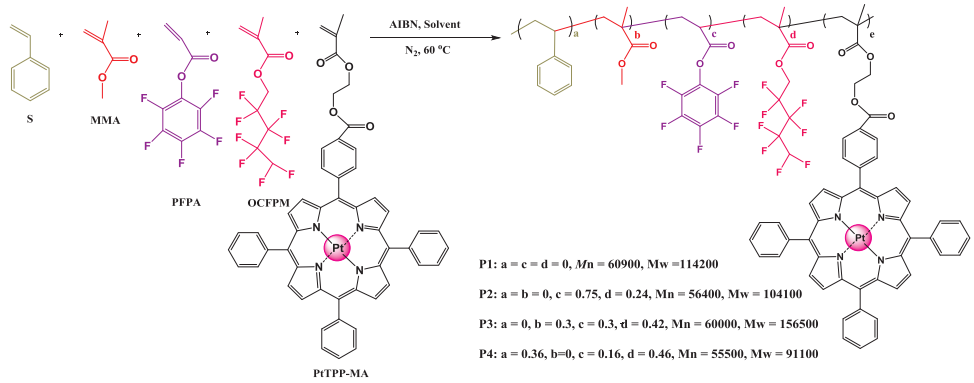

Scheme 1. Synthesis of copolymers **P1** – **P4** containing PtTPP moieties as the pendent groups via conventional free radical polymerization.

investigated for tuning the sensing responses, sensitivity and response time as well as for different applications such as intracellular measurement [8] and microfluidic devices [9,10], etc. In the similar sense, modification of PSP sensing layers by using nanofibers can also be performed in order to avoid the above mentioned drawbacks of conventional sensing layers. Recently, electrospun nanofibers have been employed for oxygen sensing in medical field due to their biocompatibility, cell adhesion properties and 3D mimic extracellular matrix properties [11,12]. Furthermore, electrospun nanofiber films were also used to sense gaseous oxygen [13]. The electrospinnings technique was first introduced by J.F Cooley in 1902. Later on, it was being employed in medical applications due to unique properties of fibrous membranes [14,15]. In electrospinnings process, high voltage is applied between the sample (capillary) and substrate (collector). Due to high voltage, a strong pull is developed between polymer sample drop and collector. Consequently, high pull due to surface charges converts the drops into jet and finally into textile like fibers with diameters ranging from micro- to nano- level with large surface area [16]. Excellent properties of nanofibers such as high porosity, large surface area and unique accessibility of gases diffusion make the oxygen sensors response ultrafast. For example, C. Wolf et al. fabricated polystyrene (PS) nanofibers via electrospinnings to immobilize platinum-tetra(pentafluorophenyl)porphyrin (PtTFPP). The resultant nanofibers showed fast response (t_{90} ≈ 40 ms from deoxygenated condition to oxygenated condition) [17]. In another study, Ir(III) complex doped PS nanofibers exhibited even shorter response time (t_{95} ≈ 8 s) [13]. For PSP, a polymer support should have excellent oxygen permeability, probe solubility, and long term compatibility with the probes. Low solubility, migration and aggregation of probes lead toward non-linear Stern Volmer response. Various polymers such as silicone [18,19], acrylic polymers [20,21], PS [13,22] and cellulosic polymers [23,24] were used as host matrix in PSP applications. For example K.H Lo et al. used methyltriethoxysilane as host matrix for PtTFPP and tris-bathophenanthroline ruthenium II (Ru (II)) oxygen probes. During pressure sensitivity test in wind tunnels, the emission intensity ratio of paint was decreased with wind tunnel runs that might be due to the removal of oxygen probes from host matrix or deactivation of oxygen probes [25]. To overcome these issues, Nishide et al. chemically attached oxygen probes with a polymer. They synthesized poly(3-trimethylsilyl-1-propyne) with pendent tetraphenylporphinato platinum(II) (PtTPP) probe. The spatial distribution of PtTPP was improved and it showed large oxygen diffusion. However, it was not found favorable for wind tunnel applications [26]. Among various conventional polymer matrices, polymers which have good oxygen permeability such as PS were employed for PSP development. Considering the unique features of PS, K. Koren et al. used various derivatives of PS and did a fine tuning for sensors' sensitivity. For example, poly(4-tert-butylstyrene) was suitable when high sensitivity with low oxygen level was required, while poly(2,6-dichlorostyrene) was favorable for high oxygen concentrations [27]. Similarly, fluoro-substituted acrylic polymers also showed excellent oxygen permeability and sensitivity. In this context, M. Obata et al. synthesized copolymer of PtTPP methacrylate monomer (PtTPP-MA) with isobutyl methacrylate and 2,2,2-trifluoroethyl methacrylate and resultant polymer showed linear Stern Volmer response [28,29]. Considering all of the aspects regarding the nature of sensing layers and the species of polymers involved, we herein synthesized a series of copolymers with chemically immobilized 5,10,15,20-tetraphenylporphinato platinum(II) monomer (PtTPP-MA) (Scheme 1). Methyl methacrylate (MMA), octafluoropentyl methacrylate (OCFPM), pentafluorophenyl acrylate (PFPA) and PS were copolymerized with PtTPP-MA in different combinations to give poly(MMA-*co*-PtTPPMA) (**P1**), poly(PFPA-*co*-OCFPM-*co*-PtTPPMA) (**P2**), poly(PS-*co*-PFPA-*co*-OCFPM-*co*-PtTPPMA) (**P3**) and poly(MMA-*co*-PFPA-*co*-OCFPM-*co*-PtTPPMA) (**P4**). The preparation of electrospun nanofibers by using these polymers will be investigated. The oxygen and pressure responses of these fibers and their corresponding spin-coated films will be elucidated to explore their effects in terms of oxygen sensitivity along with response time.

2. Experimental

2.1. Materials and methods

PtTPP-MA was synthesized according to the method reported in previous publication [29]. MMA, OCFPM and PFPA were purchased from J&K Scientific, respectively and used without further purifications. Styrene (S) was purified by distillation under vacuum at 70 °C. All of the solvents and other chemicals were of analytical grade and used as they were received. For spin coating, quartz glasses were used as substrates. Glasses were cut with 1.3 cm × 1.3 cm dimension so that they can fit well in quartz cuvettes for phosphorescence measurements and oxygen titrations. Nitrogen and oxygen gas mixtures were used to saturate the environment to adjust the oxygen partial pressure for oxygen responses measurements. The gas mixtures were precisely controlled with a custom-built, in-line, digital gas flow controller. Molecular weights were determined by using a Waters 1515 GPC system (Waters, Milford, MA) coupled with a RI detector.

2.2. Synthesis of copolymers

Copolymers were synthesized by traditional radical polymerization. For the synthesis of copolymer P1, MMA (0.606 g, 6 mmol), PtTPP-MA (8.6 mg, 6.2×10^{-3} mmol) and AIBN (3.68 mg, 0.6%W/W to total monomers) were added in polymerization tube. 1.4 mL of dried toluene was added to dissolve the monomers and initiator. The resultant mixture solution was degassed by freeze pump thaw thrice. Then the reaction mixture was heated at 60 °C continuously for 24 h. After the completion of reaction, excess of the solvent was removed under vacuum and the resultant polymer was obtained after precipitating the