AROMATIC POLYSULFONES USED IN SENSOR APPLICATIONS

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Abstract. Aromatic poly(ether sulfone)s are a family of amorphous thermoplastics that possess unique high performance properties as engineering materials: high strength, the highest service temperature of all melt-processable thermoplastics, low creep, good electrical characteristics, transparency, self-extinguishing properties and resistance to greases, many solvents and chemicals. They may be processed by extrusion and injection molding. Since the chemical and physical properties of polymers may be tailored by the chemist for particular needs, they gained importance in the construction of sensor devices. The knowledge of new materials, such as polysulfone allows to expand the possibilities of constructing potentiometric and amperometric sensors. Recently polysulfones have been used in the fabrication of sensors in various fields such as: humidity sensor, gas sensors, biosensors, immobilization of enzyme, enzyme membrane reactor, etc.

1. INTRODUCTION

Aromatic poly(ether sulfone)s are a family of amorphous thermoplastics that possess unique high performance properties as engineering materials, proved by their continuous commercialization since 1965 [1-3]. From the chemical point of view these polymers are characterized by aryl groups linked by sulfonyl ($-SO_2-$) and ether (O) groups.

Synthetic routes to poly(arylene ether sulfone)s were discovered independently in three laboratories: the 3M Corporation, the Union Carbide Corporation, and the plastics division of ICI. Two main routes have been reported, either a polysulfonylation process, which is a classical electrophilic aromatic substitution, or a polyether synthesis, which is a nucleophilic substitution of activated aromatic dihalides. Analyzing the diversity of chemical structures encountered for these polymers, one can select some basic types: *polysulfone* (PSF), *poly(ether-sulfone)* (PES) and *poly(phenyl-sulfone)* (PPSF). Examples of common polysulfones are given in Table 1.
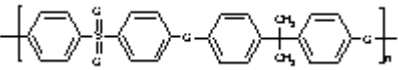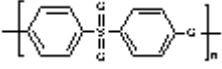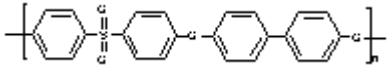
All these aromatic polysulfones (PSF) are characterized by high strength, the highest service temperature of all melt-processable thermoplastics, low creep, good electrical characteristics, transparency, self-extinguishing properties and resistance to greases, many solvents and chemicals. They may be processed by extrusion and injection molding. The presence of aromatic structural elements and sulfone groups are responsible for the resistance to heat and oxidation, while the ether and isopropylidene groups contribute to some chain flexibility.

Polysulfones are used in the manufacture of medical equipment (nebulizers and dialysis components), appliances (coffeemakers, humidifiers, and microwave ovens), automobile parts (steering column lock switches, relay insulators, and pistons), and electronic equipment (television components and capacitor film) [1]. Also polysulfones has been widely used in last years in the field of sensors. The function of a sensor is to provide information about the physical, chemical and biological environment. The principle of a solid-state sensor de-

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Table 1. Data for the first commercial aromatic polysulfones.

Trade name, abbreviation, starting of production and producer	Chemical structure
Udel, (PSF), 1965, Union Carbide Corp.	
Victrex, (PES), 1972, ICI America Inc.	
Radel, (PPSF), 1976, Union Carbide Corp. *RadelR,* 1990, Amoco Corp.	

vice is based on the electrical response to the chemical environment and the electrical properties are influenced by the presence of gas phase or liquid phase species. Such a change in electrical properties is used to detect the chemical species. Since the chemical and physical properties of the polymers may be tailored by the chemist for particular needs, they gained importance in the construction of sensor devices. The knowledge of new materials, such as polysulfone allows to expand the possibilities of constructing potentiometric and amperometric sensors [4].

The first polysulfone membranes were studied during in the 1960s as an alternative to cellulosic membranes in separation processes, due to the high resistance in extreme pH conditions as well as good thermal stability of the polysulfone [5].

Furthermore, polysulfone is soluble in chloroform and dimethylformamide, and membranes are easily prepared by conventional phase inversion technique. Its porosity allows it to be used in micro-, ultrafiltration and reverse osmosis processes as well as in the development of composite membranes to facilitate transport [6].

Polysulfone is a porous polymer that provides a suitable environment to embed some hydrophilic components like solvent mediators and ionophores. In addition, it is possible to modify the concentration of ionophores in the membrane and also the chemical nature of the solvent in order to optimize membrane composition. Moreover, it is easy and fast to prepare electrodes based on polysulfone membranes. Therefore, polysulfone is an attractive structural material to be studied in the field of potentiometric sensors. Polysulfone allows the design of tailored membranes due to its high compatibility with a large number of ionophores and organic and biological compounds.

Recently polysulfones have been used in the fabrication a wide range of sensors, including: humidity sensors, gas sensors and biosensors.

2. HUMIDITY SENSOR

Humidity sensors are useful for the detection of the relative humidity (RH) in various environments. These sensors attracted a lot of attention in the medical and industrial fields. The measurement and control of humidity are important in many areas, including industry (paper, food, electronic), domestic environment (air conditioner), medical (respiratory equipment), etc. The operating principle of a humidity sensor is based on the modification of the materials property, usually electrical conductivity, in moisture conditions. Polymer-polymer composites and modified polymers with hydrophilic properties have been used in humidity sensor devices. Chemical modification of hydrophobic polymers was done in view to generate ionic groups and to obtain a material sensitive to humidity [4].

Recently, it was demonstrated the successful use of polysulfone in humidity sensors [7]. Polysulfone has a good electrical performance (as insulator) and durability in severe conditions: high temperatures, chemical and biological environments, radiation. For the first time the sulfonated polysulfone (SPSF) humidity-sensitive materials was investigated. The preliminary results show that SPSF with a certain degree of sulfonation is an excellent humidity-sensitive material. Its characteristics are as follows: (1) good humidity sensitivity and good humidity-sensitive linearity at humidities of more than 30% RH; (2) quick response (the response time is 5 s in adsorption); (3) good chemical stability and good water-resistance; (4) simple structure and low cost.

T. Kuroiwa et al. have been fabricated a capacitive-type relative-humidity sensor utilizing a thin polysulfone (PSF) sensing material to achieve reproducible relative-humidity measurements with long-term stability even in hot and humidity conditions [8]. The schematic structure of a humidity
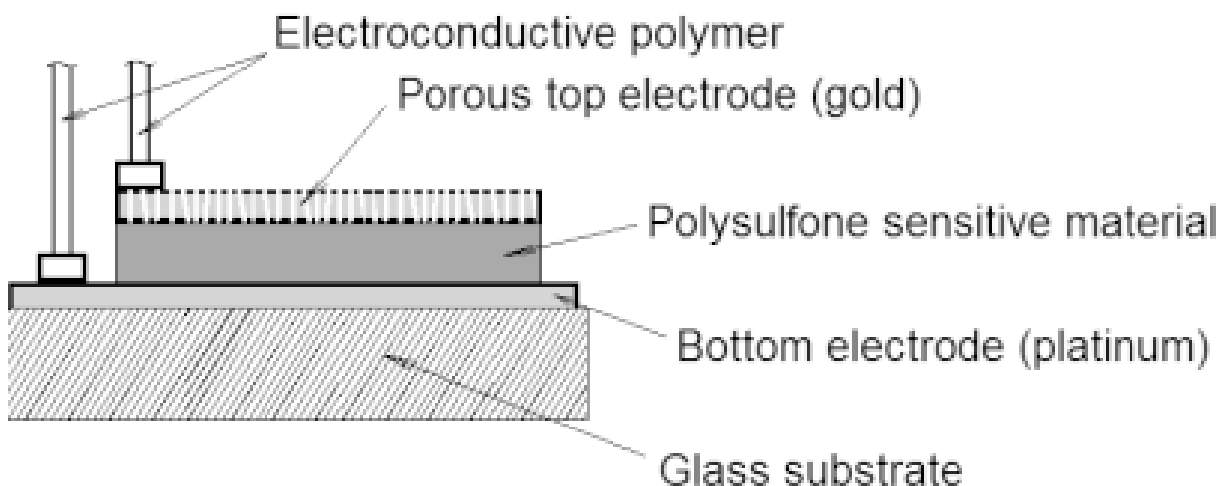
Fig. 1. Schematic setup of a humidity sensor.

sensor using polysulfone as sensitive material is depicted in Fig. 1.

A capacitive parallel flat is formed on a glass substrate with a layer of polysulfone placed between two electrodes: one lower from platinum and one higher from a thin gold film permeable to water (Fig. 1). On the side openings are attached porous filters which allow a rapid response to changes in moisture and protect against smoke. Electrical contacts of the two electrodes are provided by conductive polymer enclosures with metal filling. The sensor showed a good initial performance with 0.5% U (% R.H) hysteresis and 0.1 ± 0.1% U °C^{-1} temperature coefficient of capacitance along with good stability with less than +3% U shift after 1000 h of exposure to 40 °C, 90% U conditions [8].

3. GAS SENSOR

The emission of gaseous pollutants such as sulfuroxide, nitrogen oxide and toxic gases from related industries has become a serious environmental concern. Sensors are needed to detect and measure the concentration of such gaseous pollutants. In fact analytical gas sensors offer a promising and inexpensive solution to problems related to hazardous gases in the environment. Conducting polymers showed promising applications for sensing gases having acid–base or oxidizing characteristics. Polymers with active functional groups and screen-printed electrodes (SPEs) are also used to detect such gases [9-16].

Among the heat-resistance polymers, aromatic polyethers are of great interest due to their high resistance to heat and chemical attack, good me-

chanical and dielectric properties and facile processability [17]. Recently, we have reported the fabrication and characterization of a gas sensor for NO$_x$ detection, by thick layer technology [18]. In this study a cardo polysulfone was used as a sensitive layer to construct the gas sensor. The polysulfone was obtained by a Williamson polycondensation reaction, with a SN2 mechanism, by the reaction of sulphonyl–bis(4-chlorophenyl) with two bisphenols: bisphenol A and 1,1-bis(4-hydroxyphenyl)-cycloheptane in a 2/1/1 molar ratio. The structure of polysulfone is depicted in Fig. 2.

The sensitive polysulfone layer dissolved in chloroform was deposed by spin coating on the substrate over electrode. The device was tested in NO$_x$ atmospheres in the concentration range of 0-1000 ppm. The obtained results were situated in the range of voltage values exceeding 300 mV. It was remarked that polysulfone is very sensitive to NO$_x$ allowing voltages in the range 0-700 mV over the first seconds after exposure to NO$_x$. These voltage values allow to consider the polysulfones as electrical microsources.

4. BIOSENSOR

A biosensor may be considered as a combination of a bioreceptor, biological component, and a transducer. The main effect of a biosensor is to transform a biological event into an electrical signal. Biosensors found extensive applications in medical diagnostics, environmental pollution control for measuring toxic gases in the atmosphere and toxic soluble compounds in river water. These pollutants
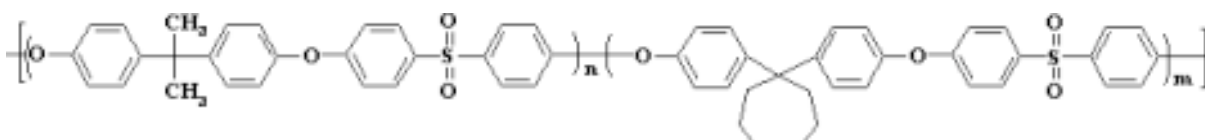
Fig. 2. Structural representation of polysulfones used as a sensitive layer.

include heavy metals, nitrates, nitrites, herbicides, pesticides, polychlorinated biphenyls, polyaromatic hydrocarbons, trichloroethylene, etc. Pollutant sensitive biocomponents have been used with a variety of detection modes for quantitative estimation of the pollutants. The estimation of organic compounds concentration is very important for the control of food manufacturing process and evaluation of food quality. Online analysis of raw materials and products is also necessary in industrial fermentation processes. The use of enzyme sensors can help the direct measurement of such compounds, including organic pollutants for environmental control [19].

4.1. Enzyme sensor

An enzyme sensor may be considered as the combination of a transducer and a thin enzymatic layer, which normally measures the concentration of a substrate. The enzymatic reaction transforms the substrate into a reaction product detectable by a transducer. The sensitive surface of the transducer remains in contact with an enzymatic layer, and it is assumed that there is no mass transfer across this interface. The external surface of the enzymatic layer is kept immersed into a solution containing the substrate under study. The substrate migrates towards the interior of the layer and is converted into reaction products when it reacts with the immobilized enzyme [20].

Different strategies are followed for the immobilization of molecular recognition agent in sensor devices particularly in biosensors. Polymers are the most suitable materials to immobilize the enzyme, the sensing component, and hence to increase the sensor stability. Polysulfone is a porous polymer widely used as a support material for composites and ultrafiltration membranes [21]. It displays good chemical and thermal stability, excellent film-forming ability and provides a hydrophobic environment similar to that of membrane-bound enzymes in vivo [22]. The hydrophobicity could be a disadvantage as it allows non-specific adsorptions (i.e. electrode

fouling), but this can be alleviated by the addition of redox-mediators, since they increase the hydrophilicity of the membrane.

Recently polysulfone has been used for the immobilisation of enzymes [23,24] including glutamate dehydrogenase in ammonium biosensors [25].

Polysulfones membranes was use to design an enzyme membrane reactor for the continuous hydrolysis of penicillin G. For the reactor containing native penicillin acylase, a thermally treated polysulfone membrane of 10,000 Da nominal cut-off was selected, whereas in the case of the reactor containing stabilized enzyme, an untreated polysulfone membrane with the same cut-off parameter is preferable. Both enzyme preparations were stable during that period. The expected conversion of penicillin G was estimated on the basis of a kinetic equation. Good agreement between the calculated and the measured data was obtained; however, comparison of the enzyme stability at 37 °C shows that penicillin acylase mixed with poly(ethyleneimine) is several times more stable than the native enzyme. The membrane reactor with penicillin acylase stabilized by poly(ethyleneimine) seems to be very promising as far as industry applications are concerned [23].

L. Giorno et al. have been investigate the conversion of fumaric acid into L-malic acid by fumarase immobilized in a membrane reactor made by asymmetric capillary polysulfone membranes. The stability of the immobilized enzyme was very good, showing no activity decay during more than 2 weeks of continuous operation [24].

Recently, B. Prieto-Simón et al. used polysulfone membranes as new materials for the development of compact dehydrogenase-based biosensors. Composite films were prepared by mixing polysulfone with graphite and were deposited on epoxy-graphite composite electrodes. Redox mediators were successfully immobilized in the composite film leading to highly reproducible biosensors, without leakage of the immobilized species. This results in a more reliable analytical

system as, at the same time, problems of electrode fouling related to the detection of the coenzyme nicotinamide adenine dinucleotide (NADH) on which is based the amperometric detection of dehydrogenase-based biosensors are avoided. Several procedures to immobilize enzymes in these membranes were demonstrated. Glutamate dehydrogenase (GlDH) was immobilized as an example of dehydrogenase enzyme, in this case for the development of an ammonium biosensor. High sensitivity, good selectivity, wide linear ranges and short response times were obtained for the optimized sensors and biosensors [25].

Moreover, a method to produce disposable biosensors by casting these composite membranes on disposable screen-printed electrodes was study, exploiting the simplicity of the fabrication procedure of polysulfone–composite films. B. Prieto-Simón et al., investigated two strategies for immobilisation of lactate dehydrogenase (LDH), cofactor NAD⁺ and redox mediator onto two transducers, screen-printed electrodes (SPE's) and graphite–epoxy composite electrodes. The first strategy was to use sol–gel matrices. Sol–gels have emerged as attractive materials for the encapsulation of enzymes and other organic species [26], including the development of SPE's [27]. When used in the construction of SPE's, it is essential that the sol–gel matrix is printable, matures without cracking and retains components, such as mediators. The second strategy was based on the use of polysulfone–graphite composite films incorporating a mediator. Polysulfone was used to retain LDH onto epoxy–graphite composite electrodes, as well as SPE's. It has been demonstrated that both sol–gel and polysulfone matrices can be used to construct amperometric lactate biosensors based on lactate dehydrogenase. Electrodes based on a LDH-Meldola's Blue(MB)-polysulfone–graphite composite covered with a polyamide layer were able to detect lactate at -0.100V, thus avoiding electrochemical interference, with a sensitivity of 80 mA/M and an R.S.D. of 2%. Finally, the performance of the LDH-MB polysulfone- composite film-based SPE's in a flow system was studied. Short response times were obtained ($t < 30$ s). Furthermore, repeatability and reproducibility values were notably improved, especially when working with electrodes covered with a polyamide layer prepared with *N*-(2-aminoethyl)-piperazine [28].

Ammonium biosensors were developed using glutamate dehydrogenase (GlDH) enzyme incorporated into polysulfone composite films placed onto SPEs. This enzyme can be incorporated in the films during the phase inversion process that causes the precipitation of the polysulfone. These biosensors showed a linear correlation for the evaluated ammonium concentrations ranging from 5×10^{-5} to 2×10^{-2} M under the working conditions described. The sensitivity to ammonium obtained for these biosensors in a flow system was 15 μAM^{-1} and the sensitivity R.S.D. was 1.9% ($n = 5$ consecutive calibration curves), corresponding to the operational stability. In addition, the storage stability was evaluated, proving that these biosensors can be stored at 4 °C at least for 1 month, showing a lost of sensitivity of 4%, being negligible as it is comparable to the sensitivity R.S.D. for different electrodes of the same sheet. Finally, the response time ($t_{95\%}$) for sample volumes of 100 μL was lower than 30 s, followed by a short recovery time, allowing an analysis time of 1 min. These results prove the usefulness of these biosensors for determining ammonium in flow, being able to be changed each day for a new electrode stored at 4 °C [29].

4.2. Immunosensor

Immunological sensors (or immunosensors) are based on the recognition involved in the coupling of an antigen with an antibody, with immunoagents immobilized in a polymer matrix such as PVC, polyacrylamide gel, etc. Either an immobilized antigen detects an antibody, or an immobilized antibody detects an antigen. Due to the interaction between an antibody and an antigen, a variation in electric charge, mass or optical properties, is detected directly with a variety of transducers [16].

Electrochemical immunosensors, which combine specific immunoreactions with electrochemical transduction, have attracted growing attention in recent years due to its quick and sensitive immunological response. Polysulfone is an attractive membranous immunomaterial carrier because of its high thermal, chemical and biological stability. Polysulfone has been widely used in last years for different applications in chemistry and in sensors field. Polysulfone can act not only as a membrane but also as reservoir for immunological materials.

S. S. Oróñez et al., reported a new and simple immobilization technique for preparing effective graphite–PSF composites based electrochemical sensors and biosensors. The main novelty of this research is the integration of the immunologic material to a transducer into a polymeric material using an inversion phase technique. Small amount of antibody was immobilized into the surface from a diluted aqueous solution. This is and advantage

comparing with rigid biocomposites [30] since the biological material is not needed to be in solid phase and the immunoreagent consuming is much lower. The biological material is incorporated during the inversion phase process, meanwhile PSF precipitates since the non-solvent (H_2O) displaces the organic solvent (DMF). The main interest about PSF is that it allows the agglutination of a conductive material (graphite), a recognition element (RIgG) and a redox mediator, if it's needed, to form a conductor immunocomposite. To construct the sensor, a conductor membrane was deposited on the surface of working graphite–epoxy composite (GEC) electrode. This sensor was based on the competitive assay between free and labeled anti-RIgG for the available binding sites of immobilized rabbit IgG (RIgG). The immunological reaction was detected using an enzymatic-labeling procedure (HRP enzyme) (antirabbit IgG peroxidase) combined with the amperometric detection using H_2O_2 as substrate and hydroquinone as mediator. This sensor shows stability during a week and a good reproducibility [31].

Recently were reported electrochemical biosensors based on polysulfone membrane encapsulating multiwall carbon nanotubes and immunoreagents layered on disposable screenprinted electrodes. The fabricated carbon nanotube/polysulfone (CNT/PSF) strips combine the attractive advantages of carbon nanotube materials, polysulfone matrix and disposable screen-printed electrodes. Such thick-film carbon nanotubes/polysulfone sensors have a well defined performance, are mechanically stable, and exhibit high electrochemical activity [32-34]. These membrane is printed by serigraphy onto an electrode built on a polycarbonate sheet. Rabbit IgG is used as model antibody being easily labelled with enzymes. HRP is a very used enzyme for immunological analysis as label, being an easy and cheap reagent. Direct and competitive immunoassays are carried out and the electrochemical response of HRP is followed by the addition of hydrogen peroxide to the solution. This biosensor was based on the competitive assay between free and labelled anti-RIgG for the available binding sites of immobilized rabbit IgG (RIgG). The detection limit for competitive assay was determined to be 1.66 µg/ml [35].

The application of new polymeric matrices as ion-sensitive membranes has given possibilities for fabrication techniques for ion-selective electrodes (ISEs). Although a limited number of polymeric materials are used in conventional ISEs, the large choice of different ionophores that can be embedded into the polymer matrix provides the possibility of building up many different electrode types. The main material used as polymer matrix in ISEs is polyvinyl chloride (PVC) [36]. Alternative polymeric membranes such as silicon rubber, epoxy polyurethanes and modified PVC [37] have been tested and found to improve adherence to solid state devices or to reduce adsorption of macromolecules from analytical samples, but PVC is still the most used polymer in ISE membranes. The knowledge of new materials, such as polysulfone allows to expand the possibilities of constructing potentiometric and amperometric sensors. Recently it was proved that polysulfone can be useful as a potentiometric electrode membrane and nitrate-selective electrode. Furthermore, polysulfone has a great advantage over PVC, in that its capacity to embed biological material extends the field of potentiometric biosensors. A nitrate-ISE is chosen as a model electrode to study the efficiency of polysulfone as a polymer matrix of the membrane. Tetra-octyl ammonium nitrate is used as ionophore and 2-nitrophenyl octyl ether as plasticizer. The new electrode is more selective to nitrate than to another anions studied and its performance is in the same ranges as those of commercially available electrodes. There is a great advantage of a newly developed PSF electrode towards NO_3^- detection in complex matrices. The electrode can be used over a wide pH range (2.5–12) which makes it useful for measurements in different types of samples. The electrode showed good response characteristics (sensitivity, stability and lifetime) and a slope between 45 and 60 mV/decade (depending on the calibration medium and membrane composition) [38-39].

A. G. Bellavista et al., have constructed potentiometric Ag^+ selective biosensors by using metalloproteins, in particular metallothioneins (MTs), as ionophores embedded into a polysulfone matrix. The phase inversion procedure used for the construction of the membrane requires small amounts of protein that ensure its low cost in case of non-commercial proteins that have to be recombinantly synthesized or obtained from their native sources. Among other advantages, this immobilization procedure maintains the protein practically intact throughout the process as it always remains in an aqueous media and at controlled pH. It is also noticeable that by this procedure the amount of required protein is greatly reduced, as it remains mainly bound to the outer membrane layers. Furthermore, polysulfone not only provides a

suitable environment to embed hydrophilic components but also hydrophobic ones, too [40-42].

5. CONCLUSIONS

Due to their unique high performance properties as engineering materials, aromatic polysulfones distinguished in a large variety of applications as sensors, such as:
- humidity sensor exhibited by sulfonated polysulfone;
- gas sensor (NO_x) with very fast response time, realized by using a spin coating polysulfone film, containing cardo moieties;
- enzymatic system comprising both enzyme immobilization and enzyme membrane reactor;
- biosensors: 1) detection of Ag^+, by mixing a polysulfone matrix with metalloproteins; 2) detection of ammonium, by mixing a PSF composite film with glutamate dehydrogenase enzyme; 3) detection and retention of lactate dehydrogenase by mixing a PSF matrix with graphite and deposition of such a system onto a composite electrode made from epoxy-graphite; 4) electrochemical biosensor based on encapsulation of multiwall carbon nanotubes into a polysulfone membrane. All these interesting practical applications of aromatic polysulfones proved and encouraged the research interest in this respect.

ACKNOLEDGEMENTS

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