European Polymer Journal 56 (2014) 140–158

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

New elastomeric polymethylsiloxane membranes bearing cationic exchanging sites for anionic dyestuffs sensors

Hassen Touzi [a], Yves Chevalier [b,*], Rafik Kalfat [c], Nicole Jaffrezic-Renault [d]

[a] Laboratoire des Interfaces et Matériaux Avancés, Faculté des Sciences de Monastir, Université de Monastir, 5000 Monastir, Tunisia
[b] Laboratoire d'Automatique et de Génie des Procédés, UMR 5007 CNRS, Université Lyon 1, 43 bd 11 Novembre, 69622 Villeurbanne, France
[c] Laboratoire des Méthodes et Techniques d'Analyse, INRAP, BioTechpôle Sidi-Thabet, 2020 Sidi-Thabet, Tunisia
[d] Institut des Sciences Analytiques, UMR CNRS 5180, Université Lyon 1, 43 bd 11 Novembre, 69622 Villeurbanne, France

ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form 9 April 2014
Accepted 14 April 2014
Available online 26 April 2014

Keywords:
Anionic dyestuffs
Polymethylsiloxane
Anion-exchange
Impedance spectroscopy

ABSTRACT

Novel anion exchanging materials based on functional polymethylsiloxane elastomers have been prepared and used as sensitive membranes of electrochemical sensors made of SiO_2/Si heterostructures coated with thin films of functional polymer. Their synthesis and their use in electrolyte/insulator/semiconductor (EIS) electrochemical devices are reported. The anion exchanging materials are cationic cross-linked polymers based on either poly(methylhydrosiloxane) (PMHS) or poly(methylhydrosiloxane-*co*-dimethylsiloxane) copolymer (PMHS-*co*-PDMS 50/50). Their synthesis has been carried out in two stages. A brominated derivative was firstly prepared by hydrosilylation reaction of undecenyl bromide with Si—H bonds of various polymethylsiloxane in the presence of Karstedt's catalyst. The kinetics of the hydrosilylation reaction was investigated. The second stage is based on the formation of quaternary ammonium ($—^+N(CH_2—CH_3)_3$), pyridinium ($—^+NC_5H_5$) and phosphonium ($—^+P(C_6H_5)_3$) groups by quaternarization reactions to brominated polymers. Full characterizations of the materials by IR, liquid ^1H and ^{13}C NMR and solid ^{29}Si NMR spectroscopy are given. The sensitivity of EIS devices to different anionic dyestuffs species have been assessed for Acid Blue 25 (AB25), Acid Blue 74 (AB74) and Acid Yellow 99 (AY99) in aqueous solution. The shifts of flat band potential and the variations of capacitance in inversion mode were extracted from the impedance measurements as a function of the concentration of anionic dyestuffs species in solution. The electrical parameters of the EIS devices came from a non-specific adsorption of organic dyes and anion exchange phenomena that showed specificity with respect to the type of anion exchanging group. The membranes bearing pyridinium or phosphonium groups gave a Nernstian response towards anionic dyestuffs AB25 and AY99.

1. Introduction

Residual dyestuffs are present in many industrial effluents, such those of textile and leather tanning; their toxic character is a major concern regarding human health and environment. Their removal from wastewaters rely on several techniques and processes such as chemical precipitation [1,2], photodegradation [3,4], electrochemical degradation [5] and ion exchange [6,7]. Such processes are necessarily associated with appropriate analyses of the residual dyestuff concentration before and after the purification process of wastewaters. The measurement of dyestuffs concentrations is generally performed in an analytical laboratory by means of various methods such as capillary electrophoresis in aqueous and non-aqueous

* Corresponding author. Tel.: +33 472431877.
E-mail address: chevalier@lagep.univ-lyon1.fr (Y. Chevalier).

http://dx.doi.org/10.1016/j.eurpolymj.2014.04.010
0014-3057/

media [8–10], thin-layer chromatography [11], HPLC [12–14], UV [15–17], fluorescence [18], mass spectrometry [19,20] and electrochemical detection [21–23]. It would be advantageous to replace such methods requiring sample collection and transfer to the analysis laboratory by in line measurements using chemical sensors. The development of chemical sensors sensitive to anionic dyestuff requires the design of sensitive membranes based on anion exchange materials. The same anion exchange materials may also be useful for the wastewater treatment by ion exchange. The present work is aimed at the design of such materials and their evaluation for the determination of anionic dyestuff concentration using electrochemical measurements.

Ion exchange is the microscopic phenomenon involved in most analytical devices aimed at measuring the concentration of ionic species in solution [24–26]. Ion exchanging materials are required for that purpose, either as the membrane separating two compartments containing the analyte and a reference solution in conventional ion-sensitive electrodes (ISE), or as thin films deposited at the surface of a transducer in chemical sensor applications [27,28]. In the later case, the ion exchange phenomenon taking place at the close vicinity of the transducer surface gives rise to an electrical or optical signal that is detected, amplified and converted into the concentration of analyte. In most instances, the electrochemical methods rely on measurements of the variation of either surface potential or electrical conductivity [29,30].

Such principles have been applied in our recent works dealing with the chemical sensing of anions by means of anion exchange inside a polymeric membrane (thin film) deposited at the surface of Si/SiO_2 electrodes [31,32]. In particular, measurements of the impedance of an electrolyte/insulator/semiconductor (EIS) heterostructure as a function of applied polarization provided two parameters that appeared quite sensitive to anion concentrations in the solution. Firstly, the capacitance of the polymer coating where the anion exchange was taking place was depending on several parameters such as the dielectric constant and thickness of the membrane. This was depending on ion exchange because the type of anion inside the membrane influences both the polarizability of the material and its swelling by water. Secondly, the variation of the flat band potential with respect to the anion concentration was identical to the variation of the electrical potential drop inside the polymer membrane and in the ionic double layer at the membrane–solution interface [33]. Measurements of the flat band potential in such heterostructures incorporating semiconducting silicon are an easy way to investigate the surface potential in the presence of an ionic double layer. This type of impedance measurement itself can be used for the design of chemical sensors since it is sensitive to the concentration and type of anion [34]. Ion-sensitive field-effect transistor (ISFET) is an alternative technology which is working on the basis of similar principles (variation of surface potential) [35]. ISFETs can be miniaturized as robust devices used for in line measurements; their manufacture involves a rather complex technology however. Impedance measurements are readily available tools for investigating and evaluating different ion exchanging membranes that could be used for the sensitization of ISFET's in a subsequently development stage.

Lastly, investigations of ion exchange phenomena, especially their specificity, are also of prime importance at the academic level because of their implication in so many fields of technological applications and life sciences [36]. Specific effects in ion exchange phenomena are often discussed with regards to the Hofmeister lyotropic series [37]. The Hofmeister series offers an interesting framework as this empirical rule appears of quite a general bearing [37–39]. Such a rule has been applied in particular to the case of conventional membrane-based ion-sensitive electrodes [40,41] because the underlying electrochemical phenomena involve ion transfer into the membrane, ion adsorption to the membrane/electrolyte surfaces and ion accumulation or depletion inside the electrical diffuse double layer. However the Hofmeister series does not provide a universal rationale for ion-sensitive electrodes since the reverse Hofmeister effect (anti-Hofmeister selectivity) has been observed in several instances [42,43]. Whether direct or reverse Hofmeister series are followed, the different ions sort in the same order. This issue has been addressed by looking carefully to the several elementary physicochemical phenomena included in the global framework known as Hofmeister series [44].

The thin films used as sensitive layers must be stable and strongly immobilized at the surface of the transducer. Polysiloxane materials are suitable candidates because of their several interesting properties, e.g. excellent heat resistance, low toxicity, biocompatibility, poor wettability, low surface tension, outstanding electrical isolating properties [45,46]. Organic functionalization of poly(methylhydrosiloxane) (PMHS) allows a fine tuning of physical and chemical properties of the resulting polysiloxanes [47]. Appropriate substitution on the polysiloxane backbone affords various materials such as cross-linked materials [48] conductive [49] and electroluminescent [50] polymers, non-linear optical materials [51], liquid crystalline ionomers [52], polymeric surfactants [53], and drug delivery systems [54]. The functionalization of linear polysiloxane is often performed by means of hydrosilylation and dehydrocoupling of Si—H bonds of a precursor poly(methylhydrosiloxane) [55,56] using platinum catalyst (especially Karstedt's catalyst [57,58]).

The present work deals with the elaboration of elastomeric polymethylsiloxane membranes bearing cationic functionalities working as anion exchanging groups. It is required that the cationic polymethylsiloxane is not soluble in water and adheres at the surface of the transducer made of silica. The elaboration of such a membrane consists in two stages: firstly, the synthesis of cationic elastomers; and secondly, the deposition of a thin film. The elaboration of a cationic silicone polymer starts from poly(methylhydrosiloxane) (PMHS) or the poly(methylhydrosiloxane)-*co*-poly(dimethylsiloxane) copolymer (PMHS-*co*-PDMS 50/50). The synthesis has been designed such that the deposited film of the non water-soluble polymer could be chemically grafted on silica and cross-linked *in situ* at the surface of the transducer. The synthesis and characterization of functional polymers bearing either quaternary ammonium, pyridinium of phosphonium