First approach to the use of liquid crystal elastomers for chemical sensors

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Abstract

Liquid crystalline thin films elastomers that are able to bind pesticides have been developed. The synthesis involves grafting mesogen and crosslinkable groups on a polysiloxane chain in the presence of a template molecule. The molecular imprinted material is obtained after thin film deposition, UV crosslinking and washing. Experiments of readsorption of pesticide are presented. Development of a multisensor platform based on thermal and capacitive sensors is described and tests of deposition of the polymer film are presented.
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1. Introduction

The molecular imprinting technique is a valuable method for preparing materials able to mimic the molecular recognition phenomena present in living systems. These are synthesized by polymerizing and crosslinking monomers in interaction with a chosen template. After removal of this by washing steps, the material presents specific cavities that are complementary in shape and size to the template (Scheme 1). Most drawbacks of this method have been linked to the need for a large amount of crosslinking agent (usually around 80–90%) to restrict distortion phenomena of the polymer backbone. In order to overcome this problem, we have recently developed new molecular imprinted polymers (MIPs) using liquid crystal elastomers [1]. Owing to the physical crosslinking of the mesogens, low chemical crosslinking (below 15%) has been found sufficient to induce recognition properties by the MIP. In this first approach, the synthesized materials were quite thick membranes (0.6 mm) without any control of the thickness. In our continuing studies on this subject, we wish to report in this article a first approach to use these liquid crystalline MIPs in chemical sensors. This implied the elaboration of thin films having a controlled thickness and the design of suitable sensor platform. In this study, the chosen template is diazinon, an organophosphorus pesticide. Although numerous methods for the detection of such species have been proposed, only few are both sensitive and simple to carry out. The need for sensors that would be small, very sensitive and selective to the desired pesticide is still high. The molecular imprinting method has already been applied in the field of sensors using different types of detection [2]: weighing with a quartz crystal microbalance (QCM), capacitance or conductance measurements, fluorescence or other spectroscopic methods. There are several examples of solid phase extraction of insecticides based on MIPs in which the material is aimed at preconcentrating the insecticide to be characterized by chromatography [2–5]. Concerning MIP-based sensors, several studies have reported the detection of organophosphate pesticides [6–10]. The limit of detection was in some cases as low as 7 ppt. However, very often, these materials lack selectivity between closely related molecules. This communication represents the first step towards new MIP-based sensors that are controllable by an external stimulus. Furthermore, developments in the field of silicon micro

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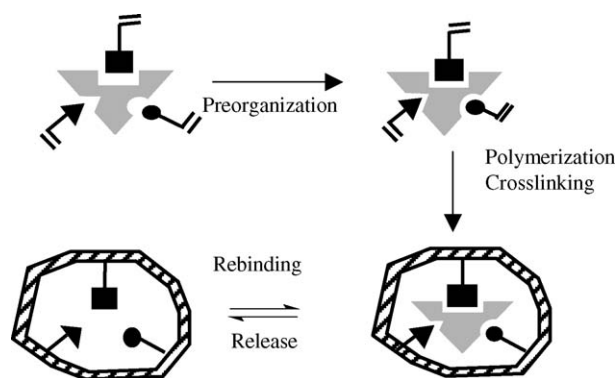
Scheme 1. Molecular imprinting technique.

fabrication techniques offer advanced technologies to improve the domain of sensors applications.

2. Experimental

2.1. Materials

Solvents were dried over CaH_2, distilled, and degassed before use when necessary. 4-Methoxy-4'-(3-butenyloxy)phenyl benzoate was synthesized as previously described [11]. Polyhydrogenomethylsiloxane ($\overline{DP_n} = 80$) (ABCR), diazinon (AB7 Industries) and dichlorodicyclopentadienyl-platinum II (Strem) were used as received.

2.2. Characterizations

^{1}H NMR spectra were recorded on a Bruker AC 250 spectrometer at 250.13 MHz. ^{13}C and ^{29}Si NMR spectra were recorded on a multinucleus Bruker DPX400 spectrometer, respectively, at 100.61 and 99.36 MHz. IR spectra were carried out on a Perkin-Elmer FTIR 1760X spectrometer. HPLC was performed on a column from Waters XTerra RP 18 (eluent acetonitrile/water 80/20, flowrate 1 mL min^{-1}).

2.2.1. 4-(10-Undecenyloxy)benzophenone
Ten grams of 4-hydroxybenzophenone (50.4 mmol), 8.6 g of 10-undecenylalcohol (50.5 mmol) and 13.2 g of triphenylphosphine (50.4 mmol) were dissolved in 100 mL of THF. A solution of 8.8 g of diethylazodicarboxylate (50.5 mmol) in 50 mL of THF was slowly added at 10 °C. The resulting solution was stirred during one night at ambient temperature. The solution was concentrated and 50 mL of cyclohexane/ethylacetate 20/5 (v/v) was added to precipitate triphenylphosphineoxide and diethyloxycarbonyl hydrazine. The product was recrystallized twice from cyclohexane. Yield: 9.0 g (51%). ^{1}H NMR: 1.2–1.6 (m, 12H, CH$_2$); 1.8 (m, 2H, CH_2–CH$_2$–O); 2.04 (m, CH_2–CH=CH$_2$); 4.0 (t ^3J = 6.6 Hz, CH$_2$=O); 4.95 (m, 2H, CH$_2$=); 5.8 (m, 1H, CH=); 6.95 (d ^3J = 8.8 Hz, 2H, o-aromatics); 7.4–7.9 (m, 7H, aromatics). ^{13}C NMR: 195.6 (C=O); 162.9 (C$_{Ar}$–O); 139.2 (CH=); 138.4, 132.6, 131.8, 130.0, 129.9, 128.2 (aromatics); 114.2 (=CH$_2$ and C$_{Ar}$); 68.3 (CH$_2$–O); 33.8 (CH$_2$=); 28.9–29.5 (CH$_2$); 26.0 (CH_2–CH$_2$–CH$_2$–O). IR (KBr pellet) $\bar{\nu}$ (cm^{-1}): 3080 w (aromatic and vinylic CH stretching), 2921, 2850 str (aliphatic CH stretching), 1640 str (CO stretching), 1603 str (C=C), 1291, 1308 m, 1255 str (Ar–O), 1175, 1149, 1018, 911, 847, 795, 739 m, 692 str (aromatics). EI mass spectrum (relative intensity): 350 (51) M$^+$, 198 (46) M$^+$ − undecadiene, 121 (80), 105 (38), 77 (29) phenyl, 55 (79), 41 (100) propenyl. High resolution MS ESI: th. 351.2324 (M + H$^+$); exp. 351.2425.

2.3. Hydrosilylation reaction

Polymethylhydrogenosiloxane (1.3 mmol of SiH groups), 1.36 mmol 4-methoxy-4'-(3-butenyloxy)phenyl benzoate (105 mol% relative to the polymer units), 0.067 mmol 4-undecenyloxybenzophenone (5 mol%) and 0.13 mmol of diazinon (10 mol%) were mixed with 3 mL of degassed toluene under argon atmosphere. To this solution was added about 2.5 μmol of $C_{10}H_{12}Cl_2Pt$ in 0.5 mL of degassed toluene. The resulting mixture was stirred for 65 h at 70 °C under argon atmosphere. Toluene was evaporated and the resulting polymer was kept in the dark until use in films. ^{1}H NMR: 0.23 (br s, Me−Si); 0.6–0.8 (m, −Si−CH$_2$−); 1.0–2.0 (m, CH$_2$); 3.8–4.0 (3 br s, CH$_2$−O and Me−O); 6.8–7.4 (m, aromatics); 7.5–7.9 (m, benzophenone aromatics); 8.0–8.3 (mesogen aromatics). ^{13}C NMR: 165.5, 164.2 (C$_{Ar}$−O); 157.1 (C$_{Ar}$−O); 144.7 (C$_{Ar}$−OCO); 138.4, 132.5, 130.8, 129.4, 128.6, 126.4, 125.7, 122.9, 115.5, 115.3, 114.1(aromatics); 69.4, 68.2 (CH$_2$−O); 55.7 (MeO−); 33.2, 20.0, 17.8 (CH$_2$); 0.3 (Me−Si). ^{29}Si NMR: −22.5 (O−Si−O).

2.4. Films of polymer

The polymers were spread on substrate with 25 or 70 μm thickness spacers in the isotropic state (75 °C). Films of about 2 cm^2 surface area were obtained. The layers were then irradiated at 50 °C during 40 min with a Xenon lamp equipped with a high pass filter at 335 nm, in order to crosslink the polymer through the reaction of benzophenone.

2.5. Microfabrication process

Sensors were performed on 100 mm silicon wafers. The process consisted in 12 leading stages with six photolithographic masks:

1- Low pressure chemical vapor deposition (LPCVD) of silicon oxide (SiO$_2$) and of silicon nitride (SiN$_x$) films. The total thickness of the layer was 1.4 μm.
2- Deposition (LPCVD) of a doped polysilicon layer (e: 0.5 μm).
3- Photolithography (Mask 1) and chemical etching to pattern the polysilicon layer.
4- Passivation with a plasma enhanced chemical vapor deposition (PECVD) SiO$_2$ layer (e: 0.1 μm).
5- Photolithography (Mask 2) and chemical etching of the SiO$_2$ layer in order to open electrical contacts with the polysilicon layer.