Use of the polysulfone polymer in NO$_x$ detection

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The sensor with polysulfone sensitive layer was made by thick film technology. An alumina substrate 6 x 6 x 0.5 mm was used. On substrate was screen-printed an interdigitated electrode array, using Au ink and heat treated at 950 °C for 1 h. The sensor contains the pads of Pd-Ag conductive ink and the conductive layer of Ag ink. The sensitive polysulfone layer dissolved in chloroform was deposited by spin coating on the substrate over electrode. The structure of polysulfone was characterized by IR, H-NMR, viscometry, elemental analysis, X-ray and thermogravimetric measurements. 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. The characteristic voltage-concentration and voltage-time were presented.

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1. Introduction

Among the heat-resistance polymers, aromatic polyethers are of great interest. They are known for their high resistance to heat and chemical attack, good mechanical and dielectric properties and facile processability [1,2]. Several polysulfones with different phenylene bridge groups in the bisphenol monomer, i.e., other than the isopropylidene unit of the familiar PSF were synthesized and examined. The properties of polymers are largely determined by their chemical structure. It has been reported that heat stability is considerably increased when the polymer molecule contains cyclic side groups whose one of the atoms belongs to the main polymer chain. Polymers of this type are cardo polymers.[3]. The introduction of cardo groups in different hetero- and carbonchain polymers leads simultaneously to an increase in both heat resistance and solubility of polymers. This aspect is of particular importance for aromatic polymers with rigid chains [3]. It was shown that the presence of cardo groups in the polymer increased the softening point of aromatic polysulfone. In this study we tested polysulfone material in NO$_x$ detection using a device made by thick layer technology.

2. Experimental

2.1 Synthesis of polysulfone

The polysulfone was obtained by a polycondensation reaction Willmsayer with SN2 mechanism: the reaction of sulphonyl –bis(4- chlorophenyl ) with two bisphenols: bisphenol A and 1,1 bis (4-hydroxyphenyl)cycloheptane) in molar ratio 2/1/1. This synthesis was carried out in solvent consisting of dimethylsulfoxide DMSO/ chlorobenzene in the presence of anhydrous potassium carbonate for the eliminating the azeotropic water. The polymer was precipitated in water. Then, it was rinsed with water. Then, the prepared material was cleaned in methanol. Finally, the polymer was dried at 80 °C for 24 hours. The preparation route of polysulfone is shown in Fig. 1.

The most common bisphenol synthesis is the condensation of a ketone with excess of phenol in the presence of an acidic condensing agent [4]. In this paper, the cardo bisphenol was synthesized according to the reported earlier [5].

![Fig. 1. The reaction for getting polysulfone.](image)

The monomer 1,1-bis-(p-hydroxyphenyl)cycloheptane was crystalized from ethanol, mp 189-194 °C.

2.2 The preparation of the sensor

Fig. 2 a,b shows the behaviour of sensor. An alumina plate 6x6x0.5 mm was used. On one of this plate was screen-printed an interdigitated electrode array using Au ink and heat treated at 950 °C for 1h. A thick resistive layer was pasted on the other side of the same plate and the layer was heated of 850 °C for 1 h. The sensitive layer obtained by dissolving polysulfone in chloroform was deposited on the plate with provided electrode by spin coating method. The sensor contains the pads of Pd-Ag conductive ink and the conductive layer of Ag ink heat was previously treated at 750 °C for 30 minutes.
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3. Results and discussion

3.1. The polymer characterization

The structural characterization of 1,1-bis-(p-hydroxyphenyl)cycloheptane is characterized by the:
- elemental analysis for C₁₅H₂₀O₂ calculated (％): C, 80.81; H, 7.85; found (％): C, 79.95; H, 7.92; IR analysis on KBr (cm⁻¹): 3100-3600 (OH); 2945, 2880 (CH₂), 1610,1600, 1595, 1515, 1445 (C=C, aromatic); 1250 (C-O); 826, 830 (aromaticing ring). H-NMR ((CD₃)₂CO, TMS, ppm): 1.57 (s, 8H, CH₃), β + γ (cycloheptane); 6.52 (d, 4H, ortho to OH); 7.00 (d, 4H, ortho to quaternary carbon) [2].

The properties of the polymer are listed in Table 1.

Table 1. The properties of polysulfone.

<table>
<thead>
<tr>
<th>Color</th>
<th>Yield, %</th>
<th>Softening range, °C</th>
<th>Reduced viscosity, dL/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grey-shine</td>
<td>95</td>
<td>183-205</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Measured in NMP at a concentration of 0.2 g/dL at 25 °C.

Data of the elemental analysis presented in Table 2 show a good agreement between calculated and found values.

Table 2. Elemental analysis of polysulfone.

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>Formula weight</th>
<th>Sulphur, %</th>
<th>Chlorine, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₁₅H₂₀SO₂)ₖ</td>
<td>(496.60)ₖ</td>
<td>6.46</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.24</td>
<td></td>
</tr>
</tbody>
</table>

From H-NMR spectra [2], allow to calculate the practical ratio the ratio of the corresponding integrals of peaks for cycloalkyldiene units versus isopyrolidene bipheno A (bis A) units.

The thermal stability of polymer in air was checked by thermogravimetric analysis (TGA). The temperature at which 10% weight loss occurred (T₁₀) was considered as a useful parameter to characterize the thermal stability of the polymer. As can be seen from Table 4 what T₁₀ values of homopolymer are ranged between 460 and 545 °C.

Table 4. Thermal properties of polysulfone.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>TGA temperatures (°C) for various % decomposition (Tₙ)</th>
<th>T₁₀ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysulfone</td>
<td>460 483 496 510 545</td>
<td>247</td>
</tr>
</tbody>
</table>

DSC measurements under nitrogen at a heating rate of 20 °C/min, second heating cycle.
3.2 NO\textsubscript{x} detection

The sensor was exposed in NO\textsubscript{x} atmospheres. Fig. 3 shows the characteristic voltage-concentration dependencies after 2 minutes of NO\textsubscript{x} exposure. Figs. 4, 5 and 6 show a peculiar voltage time for the 50, 200 and 1000 ppm NO\textsubscript{x} concentrations. It was remarked that polysulfone is very sensitive to NO\textsubscript{x} and develops very high values of voltage in the range 0-700 mV over the first seconds after exposure to NO\textsubscript{x}. These voltage values allow to consider the polysulfones as electrical microsources.

![Fig. 3. The characteristic voltage-concentration for exposure to NO\textsubscript{x}.](image)

![Fig. 4. The characteristic voltage-time for exposure at 50 ppm NO\textsubscript{x}.](image)

![Fig. 5. The characteristic voltage-time for exposure at 200 ppm NO\textsubscript{x}.](image)

![Fig. 6. The characteristic voltage-time for exposure at 1000 ppm NO\textsubscript{x}.](image)

4. Conclusions

The polysulfone was obtained by a polycondensation reaction Willmsayer with SN2 mechanism by the reaction of sulphonyl-bis(4-chlorophenyl) with two bisphenols a 1,1 bis (4-hydroxyphenyl-cicloheptane) in molar ratio 2/1/1. The sensor was prepared by thick film technology and was exposed in NO\textsubscript{x} atmospheres in 0-1000 ranges, where have been developed very high voltages in the range of 0-700 mV for 2 minutes exposure to NO\textsubscript{x} and up to 900 mV for 1000 ppm NO\textsubscript{x} after 90 minutes exposure to gas, which indicates to utilize it as an electrochemical source.

References


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