

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 carbochain 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 Willmayer with SN2 mechanism: the reaction of sulphonyl -bis(4- chlorophenyl) with two bisphenols: bisphenol A and 1,1 bis (4 hydroxyphenyl-cicloheptane) 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].

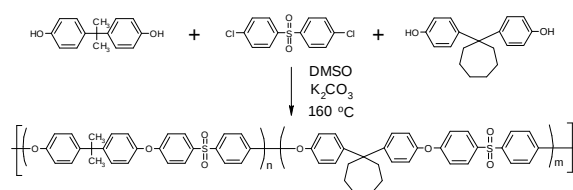


Fig. 1. The reaction for getting polysulfone.

The monomer 1,1-bis-(p-hydroxyphenyl)cycloheptane was crystallized 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.

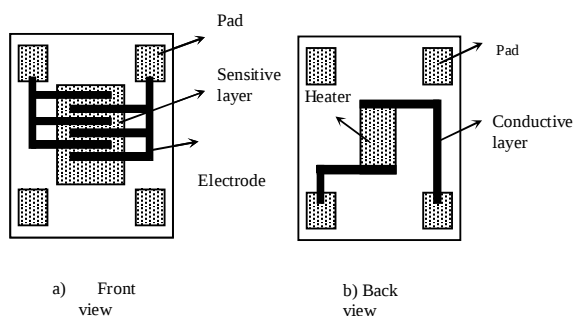


Fig. 2. The sensor configuration.

2.3 Measurement

The IR spectra of the polysulfone were recorded on a Spekord M90 Carl Zeiss Yena (Germany) spectrophotometer by using KBr pellet technique. H-NMR spectra were registered by a recorder Jeol 60 MHz NMR spectrometer at 80 °C in DMSO-d₆, CDCl₃, or (CD₃)₂CO using TMS as the internal reference. Melting and softening points were determined with a Gallenkamp hot-block melting point apparatus. The reduced viscosities of copolymer solutions (0.2 % w/v) in NMP were determined at 25 (0.1 °C) by using an Ubbelohde suspended level viscometer. Polymer solubilities were determined for eight common solvents using 0.1 g polymer in 1-2 ml solvent at room temperature. Thermogravimetric analysis (TGA) was carried out in air on F.Paulik Derivatograph at a heating rate of 12 °C/min. Differential scanning calorimetry was carried out in nitrogen on DSC 12E (Hungary) with a heating rate of 20 °C/min. Glass transition temperature (*T_g*) was taken at the inflection point on the dT versus temperature curve.

The detection testing of NO_x was performed in a concentration range of 0-1000 ppm and the voltage measurements were effected with a multimeter type UNI-TM890C.

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 C₁₉H₂₂O₂ 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 (aromatic ring). H-NMR ((CD₃)₂CO, TMS, ppm): 1.57 (s, 8H, CH₂, 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.

Color	Yield, %	Softening range, °C	Reduced viscosity, ^a dL/g
Grey-ochre	95	183-205	0.15

^aMeasured 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.

Empirical formula	Formula weight	Sulphur, %		Chlorine, %
		Calculated	Found	
(C ₃₁ H ₂₈ SO ₄) _n	(496.60) _n	6.46	7.24	0.80

The reduced viscosity value is 0.15 which is not very high, possibly due to a lower reactivity of the cardo bisphenols. The room temperature, solubility tests were performed at room temperature using eight common solvents. The results were presented in Table 3.

Table 3. The solubility of polysulfone.

Test solvent	Solubility parameter ^a , δ
Chloroform	9.21
PhCl	9.57
Cyclohexanone	9.89
1,4-Dioxane	10.01
Nitrobenzene	10.67
NMP	11.17
DMF	12.15
DMSO	13.04

^aSolubility parameter solvent in cal/cm³ after Hansen [6]

From H-NMR spectra [2], allow to calculate the practical ratio the ratio of the corresponding integrals of peaks for cycloalkylidene units versus isopropylidene biphenol 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.

Polymer	TGA temperatures (°C) for various % decomposition (<i>T₁₀</i>)					<i>T_g</i> ^a (°C)
	10	20	30	40	50	
Polysulfone	460	483	496	510	545	247

^aDSC measurements under nitrogen at a heating rate of 20°C/min, second heating cycle

3.2 NO_x detection

The sensor was exposed in NO_x atmospheres. Fig. 3 shows the characteristic voltage-concentration dependencies after 2 minutes of NO_x exposure. Figs. 4, 5 and 6 show a peculiar voltage time for the 50, 200 and 1000 ppm NO_x concentrations. It was remarked that polysulfone is very sensitive to NO_x and develops very high values of voltage 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.

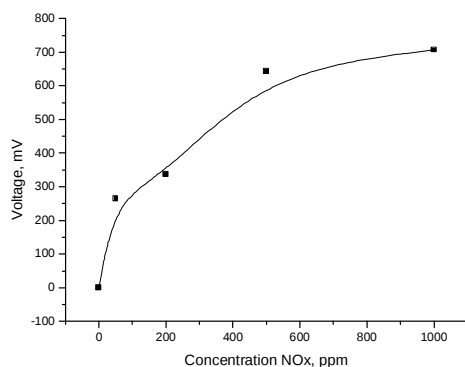


Fig. 3. The characteristic voltage-concentration for exposure to NO_x.

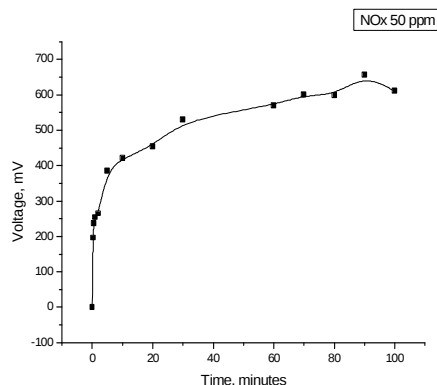


Fig. 4. The characteristic voltage- time for exposure at 50 ppm NO_x.

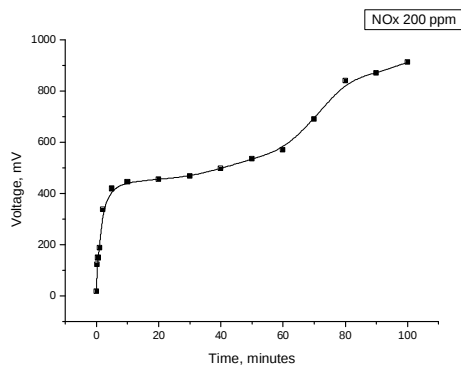


Fig. 5. The characteristic voltage-time for exposure at 200 ppm NO_x.

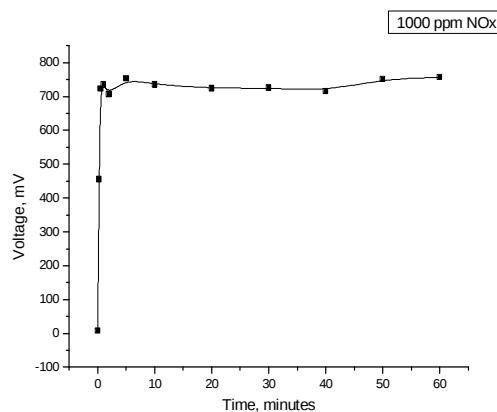


Fig. 6. The characteristic voltage-time for exposure at 1000 ppm NO_x.

4. Conclusions

The polysulfone was obtained by a polycondensation reaction Willmayer 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_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_x and up to 900 mV for 1000 ppm NO_x after 90 minutes exposure to gas, which indicates to utilize it as an electrochemical source.

References

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