1. Introduction

Polymers offer a lot of advantages for sensor technologies: they are relatively low cost materials, their fabrication techniques are quite simple (there is no need for special clean-room and/or high temperature processes), they can be deposited on various types of substrates and the wide choice of their molecular structure and the possibility to build in side-chains, charged or neutral particles, and even grains of specific behaviour into the bulk material or on its surface region, enables films to be produced with various physical and chemical properties including also sensing behaviour.

Active sensing polymers are used in sheet or film form as an integral part of inorganic solid-state devices. The latter ones are fabricated using monolithic semiconductor processing, processing of ceramics and glasses or thin and thick film technologies. The deposition and patterning of microsensor polymer films include the following processes[1]:

(1) Spinning or casting and subsequent photolithography of photosensitive and non-photosensitive polymers.

(2) Screen printing or its modified versions and subsequent cross-linking (UV, IR or heat annealing) of polymers.

(3) Electrochemical polymerisation: conducting and semiconducting polymers can be synthesised and deposited on to a conductive surface part of a given substrate from monomer solutions by electrochemical polymerisation. The advantage of this method is the precise flow control and rate of film deposition by varying the potential of the working electrode in the system.

(4) Vacuum deposition processes are also possible methods of obtaining thin polymer films which have high density, thermal stability and insolubility in organic solvents, acids and alkalis. The layers can be grown by:

* vacuum pyrolysis which consists of a sublimation, a pyrolysis and a deposition-polymerisation process;
* vacuum polymerisation stimulated by electron bombardment;
* vacuum polymerisation initiated by ultraviolet irradiation;
* vacuum evaporation using a resistance-heated solid polymer
source and more effectively using an electron beam;
• RF sputtering of polymer targets in a plasma composed of polymer fragments and with argon added to the plasma;
• plasma or glow discharge polymerisation of monomer gases or vapours;
(5) other techniques, such as Langmuir-Blodgett method, gamma-irradiation, etc.

2. Sensor structures with sensing polymers

The typical device structures, that can be used to measure the changes in the properties of polymer films, can be categorised into the following groups[1]:
• impedance type sensors follow the sensing phenomena with capacitance and/or with resistance changes.
• semiconductor device based types are more complicated; the sensing effect can change the most important characteristics and/or parameter of the devices, for example shift the diode characteristics, alter the threshold voltage of a field effect transistor (FET), etc.
• resonant sensors, the shift of the resonance frequency can be measured as a function of the quantity to be measured due to the changes of mass or to changes in wave propagation properties. According to the types of the waves, they can be grouped into bulk acoustic, surface acoustic and flexural plate wave (BAW, SAW, FPW) devices.
• electrochemical cells are widely used in chemical sensors; the electrode potential, the cell current and/or the cell resistance can be measured as a function of the analyte, which is in close contact with the sensing polymer film; thus, potentiometric, amperometric, and conductimetric devices can be distinguished.
• calorimetric sensors are based on the measurement of a temperature changes caused by physical or chemical process effects from the environment.
• fibre optic sensors represent a new generation of sensors; they are based on the changes of the light propagation, absorption, and/or emission properties in the sensing polymer films and give an optical output signal. The possible structures are: optrode-style, core-based, coating-based, interferometric, and other type fibre-optic sensors.

3. Sensing effects in polymers

Sensing effects are those physical and chemical phenomena that are the bases of the sensors’ operation, i.e. provide an electrical or optical signal as a function of the quantity to be measured. It is a difficult task to give a proper categorisation of the sensing effects due to the wide variety of material structures and physical/chemical interaction phenomena that can be used to fabricate sensors based on sensing polymer films.

The sensing effects in polymers can be described using the following grouping of materials: dielectrics, conductive or other composites, electrolytes, electroconducting conjugated polymers, sorbent materials, ion-exchange membranes, permselective membranes, membranes with specific recognition sites, optically sensitive polymers.

3.1. Dielectrics

These are insulating materials, which means they theoretically do not contain movable electrical charges. However, the gravity centres of electrically charged particles can be shifted under certain conditions. The dielectric behaviour can be described by two important physical parameters: one is the permittivity which describes the “polarisability” in electric fields, and the other is the vector of spontaneous polarisation which exists without electric fields.

Polarisation can be changed by mechanical stress or by temperature variation; the former is called piezoelectric, while the latter pyroelectric effect. A classical piezo/pyroelectric polymer example is the stretched and poled polyvinylidene fluoride (PVDF) and its copolymer, polyvinylidene fluoride – trifluoroethylene, (PVDF-TrFE). These materials have a wide application in the field of mechanical (pressure, acceleration, vibration and tactile sensors etc.)[2], acoustic[3], and infra-red radiation sensors[4]. New types of piezoelectric composites have also been developed recently that consist of piezoelectric ceramic (PZT) powder and a polymer matrix[24].
Dielectrics with high spontaneous polarisation, called electrets, can also be used in capacitive acoustic sensors (condenser microphones). Electron-beam poled polytetrafluoroethylene (PTFE) and polyfluoroethylene propylene, (PFEP) can be mentioned as the best polymer electrets[3].

Permittivity changes may also be detected in a lot of polymeric materials, due to the absorption of molecules with high dipole moments[5], or to the swelling[6], even when sorbing non-polar molecules. Swelling is a pure geometrical effect which can be detected by capacitance changes[6]. Polyimides are widely used in humidity sensors[5], and heteropolysiloxanes with various organic side-chains can be sensitised for different gas components[6].

3.2. Conducting polymer composites
These materials contain an electrically insulating polymer matrix loaded with a conductive filler. The concept of percolation can be used to understand the change in resistivity as a function of filler concentration in composites. It describes the conduction with the presence of electrically conducting paths between two filler particles. The number of these paths will be dramatically destroyed below the critical volume fraction of filler. All environmental effects that can change the volume fraction of the filler, such as temperature change due to the thermal extension mismatch, deformation due to the elasticity coefficient differences, and polymer swelling due to the sorption of vapours or humidity, will cause a change in resistivity[7].

The often used filler materials are metals (Cu, Pd, Au, Pt), carbon black and semiconducting metal-oxides (V₂O₅, TiO, etc.). The most important polymers that can be used as matrices are: polyethylene, polyimides, polyesters, poly(vinyl acetate) (PVAc), PTFE, polyurethane, poly(vinyl alcohol) (PVA), epoxies, acrylics, e.g. polymethyl methacrylate (PMMA), etc. They have been used in PTC thermistors[7], piezoresistive pressure[8], tactile, humidity and gas sensors with success[7].

3.3. Polymer electrolytes and polyelectrolytes
A group of organic polymers having constituent ionic monomer or inorganic salt exhibit ionic conductivity; thus they are called polymer electrolytes and polyelectrolytes, respectively. Their ionic conductivity can be modulated by several parameters of the environment, which is the basis of their application possibilities in sensors. In sensitive electrolyte films, an increase in the conductivity can be generated by increasing the number of ionic carriers by the addition of ions from the environment, the degree of dissociation in the polymer electrolyte, and the mobility of ionic carriers based on a modification of the density and energy levels of trapping and/or hopping sites or on a change of the ionic carriers’ effective size and mass[9-11]. Ion conductive polymers can be widely used in electrochemical cells with different electrodes and measuring methods as solid electrolytes for the detection of various gas or ionic components respectively. Nafion\textsuperscript{10} (Du Pont), polyhydroxyethyl methacrylate (PHEMA), and its copolymers can be mentioned as examples. Alkali salt-polyether complexes, such as polypropylene oxide (PPO) and polyethylene oxide (PEO) typically with LiClO₄, LiCl, LiCF₃SO₃, LiSCN[9,11], polystyrene sulphonate, and quaternized polyvinyl pyridine (PVPy)[10] have successfully been used in impedance type or semiconductor based humidity sensors.

3.4. Electroconductive conjugated polymers
Electroconductive conjugated polymers (ECPs) exhibit intrinsic electronic conductivity. Their structure contains a one-dimensional organic backbone based on the alternation of single and double bonds, which enables a superorbital to be formed for electronic conduction. Polyacetylene, polyaromatic and polyheterocyclic chains can provide such a structure. Macroscopic conduction through these polymers takes place by charge hopping both along the polymer chains and also between the macromolecules that make up individual fibres and between the fibres themselves. However, in the neutral (undoped) state these materials are only semiconducting. The electronic conductivity appears when the material is doped, i.e. when electrons or holes are injected into the superorbital. For reasons of electroneutrality, counter ions called dopants are simultaneously inserted into the polymer matrix. They are generally synthesised by electrochemical polymerisation[12].
One of the increasingly studied subjects in connection with ECPs is their application in sensors, mainly in electrochemical sensors. This is due to their key property that they are remarkable transduction matrices sensitive to gases, vapours, ions and biomolecular systems, resulting in a straightforward conductance, impedance or redox potential change “via” the modulation of their doping level. Polyacetylene, polyaniline, polythiophene, and polypyrrole (PPy) are the most widely used materials. Their technology allows the possibility of building up polymers with controlled amount and type of entrapped ionophores including neutral ionic carriers or even enzymes, and also membranes with controlled size pores, when using the doping-dedoping technique. These materials have great possibilities in the detection of any type of analytes (gases, ions, enzyme substrates, liquids, etc.)[12]. Especially, ionically stabilised poly-N-methylpyrrole films with galvanostatically immobilised enzymes have gained attention in biosensor applications for detecting glucose, uric acid and cholesterol[25]. Polyaniline and polypyrrole have successfully been applied in multicomponent gas sensing. Their advantages over inorganic gas sensor materials are their high selectivity and the ability to operate at ambient temperatures, without the necessity of heating[26].

3.5. Polymer sorbent coatings
These materials can sorb molecules from their surroundings. The term is used here only in those material/sensor systems in which simply the mass change due to the sorption can cause a transduction effect[13]. Two types of sorption can be distinguished. Adsorption is the collection of a species on a surface. In adsorption, adsorbed species go on to dissolve into the bulk of the material. Absorption is dependent on the strengths of various fundamental interactions between the absorbed species and the sorbent material. In sensor applications, bulk absorption can collect more vapour into a sensor surface than surface adsorption, thus offering higher sensitivity. In addition, sensors based on absorption have greater resistance to surface contamination effects that can degrade the performance of sensors relying entirely on surface adsorption for their selectivity. A great variety of polymers could be mentioned here. Polysiloxanes and polyetherurethanes utilise the selective bulk absorption of molecules[14].

3.6. Polymers with molecular recognition sites
Supramolecular compounds like calixarenes or högbergarenes are bound generally to polymeric surfaces and utilise the incorporation of molecules in molecular cages as the sensing effect[15]. Experimental and theoretical work on polymeric and supramolecular compounds indicates these approaches to design highly selective chemical sensors. These are based on different transducer principles to monitor the change of physical-chemical properties of the selective layer upon interactions with molecules to be detected in air and water. In particular, changes of mass, temperature, capacitance, and thickness may be monitored using resonator, calorimetric, impedance, or fibre-optic type sensors, each of them providing specific advantages and disadvantages in practical applications.

Since supramolecular chemistry aims at the preparation of molecules with specific binding sites inside their “cavities”, even very complicated supramolecular recognition structures may be available in the future. In addition, techniques for the preparation of self-organized layers with a well-defined “architecture” have been developed. This will make it possible to design completely new highly specific chemical sensors which exclusively utilise very fast adsorption processes between recognition sites at the surface of these monolayers and the molecules to be detected[15].

3.7. Polymeric permselective membranes
Polymeric permselective membranes can be applied to the separation of different gaseous and liquid-state constituents, which can be used not only in industrial and medical cleaning processes but in analytical chemistry and also in the field of sensors[16]. A few examples from the practical utilisation are as follows:

- gas-separation membranes in gas sensors to improve their selectivity to certain gas constituents;
- ion-separation membranes in ion selective electrodes and ISFETs to improve their selectivity to certain ion type;
separation of dissolved gas components from solvents to measure the partial pressure of dissolved gases;
• diffusion membranes in amperometric electrochemical cells.

A few selected examples are as follows: polyethylene, PTFE, PFEP, cellulose acetate, silicone rubber, polyvinyl chloride (PVC), polydimethylsiloxane (PDMS), etc.

3.8. Polymeric ion-selective membranes

The properties of ion-selective polymeric, mainly plasticized PVC membranes, as used in ion selective electrodes, are well-known. Ion selective electrodes based on plasticized PVC in which a neutral carrier, such as valinomycin (an ionophore) is dissolved, are now widely used[17]. The role of an ionophore is to bond (i.e. form a complex) with the ion being sensed, known as the primary ion, rather than to any other similar ions within the material of the membrane. This ion is known as the ion to which the ionophore is selective. Ionophores are in most cases small molecules. However, they must be lipophilic so that they remain in the polymer phase and do not enter their contacting aqueous phases to any significant extent. Various ion-selective potentiometric sensors (ion-selective electrodes and ISFETs) have already been developed based on plasticized PVC membranes with different ionophores[18]. The greatest problem of the ISFET sensors is the reliable binding of polymer films to the SiO₂ surface. The best results have been found with polysiloxane membranes, or when applying PHEMA hydrogel intermediate film between membranes and device surfaces[19].

3.9. Optically sensitive polymers

Sensing effects based on optical behaviour are the colorimetric, fluor- and luminescence effects and light refraction/propagation changes. Polymer materials (for instance polymethyl methacrylate (PMMA)) are widely used in fibre optic sensors as optical waveguides or claddings. However, polymer materials alone are generally not active sensing materials in the sense that their optical parameters cannot be influenced by the environment. Therefore, fibre optic sensors generally use composite polymers, in which an optoactive sensing material is entrapped into the polymer matrix.

Colorimetric changes can be followed by absorption, or reflection spectra changes, or in more simple cases when using a monochromatic light source, by absorbance or reflectance value changes[20]. Polymer composites (e.g. PMMA, PHEMA, PTFE, cellulose, Naftion®, PVC, polyacrylamide, polyvinyl pyrrolidone, etc.) with various indicator dyes can be widely used in chemical sensors including ion-, gas, humidity or enzyme sensors[20,21]. Other types of optodes utilize not only the colorimetric changes but the fluorescence quenching of the indicator dyes as well. Here the excited light is used for detection[21]. Another approach is based on the measurement of the resultant catalysed light emission luminescence effect[22].

It is also possible to build up sensor elements that are based on the light refraction changes and/or interferometry[23]. The optical pathlength in a given medium is determined by the refractive index and the geometric pathlength. The changes of both parameters result in a change in the phase shift, which can be detected by interferometry. Based on the same effects, in optical waveguides the waveguide effective refractive index or transmission effectiveness variation can also be measured by the refractive index change of the cladding. By this means, film materials that could not be applied before may be used for fibre optic or optical integrated chemical sensors. For example, the addition of indicators such as dyes or fluorescence materials to the film is not necessary. The physical-chemical changes take place with the direct participation of the sensing polymer material. Polysiloxane polymers seem to present these properties and can be used successfully in chemical-sensor applications. The refractive index of the polymeric film and/or cladding varies with the permittivity when the vapour to be detected is absorbed in it. Another often used method is to detect small thickness changes of a transparent layer using optical reflection mode interferometry, which can also be used in fibre-optic sensors. Polydimethylsiloxane (PDMS) was examined in several studies and seems to be a good candidate for applications in sensors. It shows both swelling and refractive index shift when exposed to organic solvent vapours[23].
4. Summary

Polymers have gained an extremely wide application in the field of sensor technology in the last decade. Their effect can be compared to that of silicon in microsensors. The various sensors applying sensing polymers can be used for the measurement of quantities as follows: temperature, mechanical quantities (touch switch devices, deformation sensors, tactile sensors, pressure sensors, accelerometers, vibrometers, etc.), acoustic quantities (microphones, ultrasonic sensors, hydrophones, etc.), infra-red radiation, relative humidity, gas, and ion-concentrations, in special sensors for medicine and biology (enzyme and immunosensors) and in other fields (liquid component sensors, material identification, etc.). More recently the application of polymers even in microactuators has gained a considerable attention with the application of piezopolymers and low friction materials. A summary of the possible sensing effects, materials, optional additives and sensor applications is given in Table I. Conventional abbreviations are used for the polymer names (see[1] for more details), while Table II summarizes the status of each application field giving also the advantages and disadvantages when comparing them with inorganic sensing films. The most important future prospects of polymers in sensor technology, where they have no real

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competitors on an inorganic basis, are in the field of robotic tactile and infra-red sensor arrays, the highly selective chemical sensors, as well as biosensors.

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