Chapter 15

POLYMERS FOR OPTICAL SENSORS

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1. WHY POLYMERS FOR OPTICAL SENSORS?

Polymer materials are frequently used matrices for the indicator chemistry in optical sensors. This is necessary for several reasons: first, the indicator has to be immobilized to an optical waveguide or an optical fibre which is then brought into contact with the analyte solution. If one would pour an aqueous solution of the indicator dye directly into the sample solution, e.g. into a bioreactor, then the whole sample solution would be contaminated.

Next, the indicator dye needs a solvent to interact with the analyte. Pure crystalline indicator dyes might react at the surface but not all indicator would react due to hindered diffusion. Therefore, the indicator is dissolved in a polymer which allows free diffusion of the analyte to and from the indicator molecule.

The polymer has the function to retain the indicator in place so that no leaching into e.g. aqueous sample solution occurs. This can be achieved by covalently immobilizing the dye to the matrix but also by simply dissolving a hydrophobic and water-insoluble dye in a hydrophobic polymer.

The polymer can also be used to tailor the selectivity and sensitivity of the optical sensor due to enrichment of the analyte by the polymer material. Furthermore, the polymer may the permeable for gases but not by ions again inducing selectivity for certain analytes. Finally, the polymer can provide optical isolation against ambient light and thus prevent bleaching and light interference.
2. REQUIREMENTS FOR SENSOR POLYMERS

Polymer materials have to fulfil various requirements to enable optical sensing. First of all, the indicator dye and all additives have to dissolve well in the polymer (and must not be washed out). The analyte also has to be soluble in the polymer and must be able to diffuse fast into the polymer and within the polymer. The polymer material has to be chemically and physically stable in order to achieve good operational lifetime and shelf-life (important for practical applications). Furthermore, no crystallisation/migration/reorientation of the indicator chemistry in the polymer must occur. This can happen even after weeks or months if indicator solubility is not as high as expected. The polymer must be stable even at elevated temperatures (e.g. to be resistant to steam heat sterilization). It should be stable against ambient light, chemicals (acids, bases, oxidants) and it should be non-toxic and biocompatible (especially when used in clinical and biochemical applications). The polymer should not have any intrinsic colour/luminescence, and it should be optically transparent in the spectral range where measurements are being performed. Finally, the material should have good mechanical stability.

3. TYPES OF POLYMERS USED IN OPTICAL SENSING

3.1 Lipophilic Polymers and Plasticizers

Polymers that have a high glass transition temperature \((T_g)\) are brittle. They require plasticizers to make them flexible. Furthermore, the high density/rigidity of the polymer chains (without plasticizers) hinders diffusion of ions and gases in the polymer matrix. Therefore, a plasticizer content of up to 66% is required for the preparation of sensor layers. While poly(vinyl chloride) is soluble in tetrahydrofuran and cyclopentanone, polymers such as poly(methyl methacrylate), polystyrene and poly(vinyl acetate) are also soluble in ethyl acetate, ethylmethyl ketone, or dichloromethane (Table 1). The advantage of plasticized polymers is that their polarity and lipophilicity (and thus selectivity and sensitivity) can be tailored by using different plasticizers with different physical properties. High \(\varepsilon\) values indicates strong polarity while high \(\log P\) values indicates high lipophilicity’ (Tables 2 and 3). A significant disadvantage is that plasticizers may leach out into sample solution or may evaporate on storage. If toxic they must not be used for clinical diagnostics. Immobilization of the indicator chemistry is usually performed by dissolving hydrophobic dyes and ligands in hydrophobic polymers.