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Responsive membranes for advanced separations

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External physico-chemical switches may modulate the performances of stimuli-responsive membranes. The switches can be turned on and off in three different ways. Sites on a membrane can interact and respond to incoming chemical agents directly. Alternatively a membrane can respond to global environmental changes such as temperature or pressure. These two mechanisms involve mass transport or mass and heat transport. The switches for field-responsive membranes, on the other hand, are external fields, where mass transport or mass and heat transport between the environment and membrane are not required. Guided by advances in modern computational methods, stimuli-responsive membranes represent a new class of advanced membranes that are finding numerous niche applications.

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Introduction

Membrane based separation processes find numerous applications in diverse areas including chemical, petrochemical, pharmaceutical, food and biotechnological industries [1]. Membrane based processes are attractive for a number of reasons. They often require lower energy input than competing processes, for example, desalination of sea water using reverse osmosis membranes [2], they are easy to scale up, for example, membrane adsorbers for bioseparations [3], they are more environmentally benign, for example, water treatment [4] or they are the only viable technology for niche applications, for example, blood oxygenation [5].

Recently there has been significant interest in developing stimuli-responsive membranes [6••,7••]. Similar to biological systems, it is not difficult to imagine transport of chemicals or energy conversion processes through synthetic materials that respond to an external stimulus. Membrane separations can be controlled through different mechanisms depending on the membrane structure (dense or porous) and the physiochemical properties of the bulk phase in contact with the membrane [8••]. Depending on whether the membrane is porous or not, response to external environment may lead to changes inside the pore structure, in the barrier surface or both [9].

Two approaches are used to fabricate stimuli-responsive membranes: first, preparing membranes from pre-synthesized stimuli-responsive polymers, copolymers, and polymer-additive mixtures; second, modifying existing membranes to incorporate stimuli-responsive polymers [7••,9]. Currently stimuli-responsive membranes are key components in advanced technologies such as sensors, protein detection kits and drug delivery devices for potential application in tissue engineering [7••,10].

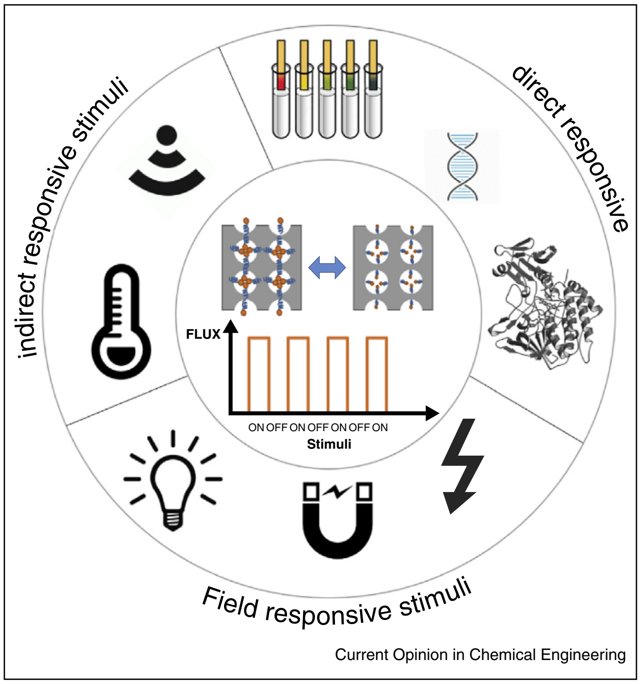
The external stimuli that modulate membrane performance may be divided into three groups (Figure 1). Direct stimulation involves a membrane in direct contact with chemical or biological cues. The cues can be relatively non-specific such as the pH or electrostatic environment or more specific such as chemical or biological agents. Indirect stimulation involves responsive sites on the membrane responding to the more general thermodynamic environment. For example, temperature responsive groups can respond to change in temperature. Pressure responsive groups can react to ultrasound. Finally field responsive membranes respond to an external electromagnetic field. Here mass transport or mass and heat transfer between membranes and cues are not required to elicit a response.

The next three sections of this article provide examples of stimuli-responsive membranes with these three modes of external stimulation. Modern computational tools are providing new insights into the design of ever more intricate stimuli-responsive membranes. Some of these methods are described next. The article closes with a discussion of probable future trends.

Direct stimulation by chemical or biological cues

Three examples of direct stimulation: pH responsive, salt ion responsive and biological responsive systems are described. These systems represent increasing degrees of specificity.

Figure 1



The external stimuli that modulate membrane performance divided into three groups.

pH-responsive

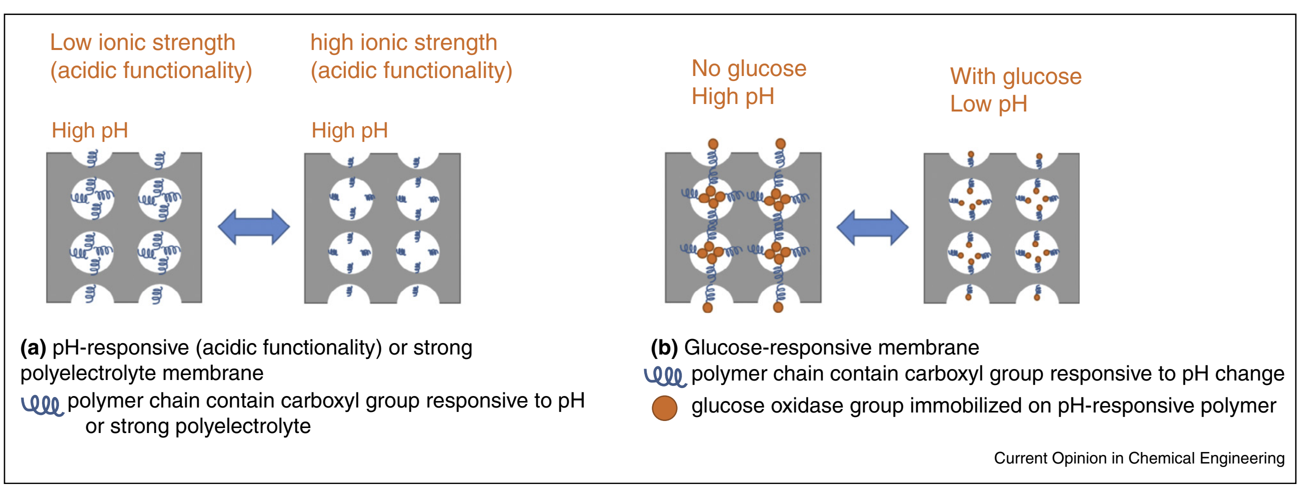
In response to pH changes, these membranes show reversible structural and conformational changes leading to reversible pore size or permeability/selectivity change. Potential applications of these membranes include controlled drug release, self-cleaning membranes, size and charge selective membranes, and membranes as sensors [11•,12•]. Typically, pH-responsive polymer brushes or cross-linked polymer gels are grafted on the pore walls or barrier surfaces of the membrane that could trigger changes in membrane permeability and/or selectivity in response to pH change. pH-responsive groups such as carboxyl, pyridine, imidazole, and dibutylamine can influence the adsorption (fouling) properties and function as a membrane adsorber [6••].

A carboxyl group (e.g. acrylic acid) at pH below its pK_a, is protonated leading to decreased hydration. The polymer network swells when the pH exceeds its pK_a as the carboxylic acid groups become deprotonated and repel each other (Figure 2a). Membrane pore size can be continuously adjusted by changing pH [13–18] regulating membrane separation performance. Pyridine groups on the other hand, are protonated, positively charged and swell at low pH [19,20]. In a recent study, Himstedt *et al.* grafted polyacrylic acid chains from the surface of commercial nanofiltration membranes. The switch between swollen and collapsed conformation was reversible by changing solution pH [21,22•]. These pH-responsive nanofiltration membranes demonstrate interesting selectivity for glucose/sucrose separations.

Salt ion responsive

Solution ionic strength affects the degree of swelling observed for pH responsive membranes. For example, in a high ionic strength solution, deprotonated polyacrylic acid chains swell much less due to charge screening by salt ions present in solution. All pH responsive membranes also respond to ionic strength. Moreover, polymers used to prepare these responsive membranes do not need to be neutral. Polyelectrolytes are polymers containing multiple ionizable groups. Strong acid or base groups (e.g. quaternary amines) are generally insensitive to pH. However at high salt concentration, when the ionic strength of

Figure 2



Mechanism of stimuli response for **(a)** pH-responsive (acidic functionality) or strong polyelectrolyte membrane and **(b)** glucose-responsive membrane.