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Chapter 2: Stimuli-Responsive Materials for Membrane Fabrication

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We would like to dedicate this chapter to the late Dr. Darrell Patterson, an expert on stimuli-responsive membranes and separation processes, who was meant to write this chapter. His work and devotion to the membranes field gave the authors the encouragement and motivation to write this chapter.

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2.1. Introduction

Stimuli-responsive membranes, based on “smart” polymers, have recently gained much academic interest as their separation performances can be adjusted according to changes in environmental conditions. Polymers undergo a reversible change, either physical or chemical in its properties, that is based on external stimuli and that induces a macroscopic response in the membrane. Using stimuli allows for a specific conformational transition on a microscopic level and then the stimuli-responsiveness occurs, thus amplifying these transitions into macroscopically measurable changes in membrane properties. The mutual interactions among pore structure and change in conformation, polarity, and reactivity of functional groups of the responsive polymers in the membrane bulk or its surface are the key factors that allow for the responsiveness of the membrane. These membranes can respond to external stimuli such as pH (Dai et al., 2008; Tufani et al., 2017), temperature (Park et al., 2016; Zhang et al., 2016; Kamoun et al., 2017), ionic strength (Huang et al., 2009), light (Duong et al., 2017; Kaner et al., 2017), electric (Loh et al., 1990; Ahmed et al., 2016) and magnetic fields (Wen et al., 2017), and chemical cues (Miyata et al., 2002). The most common stimuli are pH and temperature that occur spontaneously in biological systems and chemical reactions, and the more novel stimuli responsive membranes are based on an electric or magnetic field. All these responsive systems have the potential to overcome traditional membrane issues in which the pore size is defined during the fabrication process and the permeability cannot be adjusted to exploit external environmental conditions. Furthermore, membranes based on electrical polymeric systems are showing potential in water treatment, fuel cells, catalysis, and as sensors due to the possibility of combining the electrical conductivity of metals with the strength and processability of synthetic polymers (Pile et al., 2002; Reece et al., 2005). These electrically tuneable responsive membranes can be potentially used to obtain systems with controllable

transport properties and *in situ* self-cleaning mechanisms as demonstrated in recent studies (Sun et al., 2013; Lalia et al., 2015). Temperature, pH, and electrical-responsive polymers can also be introduced on pre-formed membrane supports as surface functionalities using different surface modification methods, and the resulting membrane systems are, therefore, called gating membranes (Luo et al., 2015; Liu et al., 2016).

Until now, both non-porous and porous responsive membranes have found applications in sensors, separation processes, drug delivery devices, and complex technical systems in general (Gugliuzza, 2013; Darvishmanesh et al., 2015).

In this chapter, we examine the many recent contributions to the fast growing field of stimuli-responsive membranes with specific attention to the polymer science and the material properties. The focus will be first on the progress and advances of pH and temperature-responsive systems since they have been the most researched in selective filtrations and biomaterials. Next, we will discuss electrical-responsive membranes as novel smart materials in order to provide the reader with the current state of knowledge. This chapter is meant to provide a general understanding of stimuli-responsive membranes in terms of mechanism of action and preparation methods, but more detailed reviews on the topic are available for the reader. Wandera et al. (2010) have covered in an excellent review all type of stimuli and fabrication methods, and Husson (2012) has given a detailed overview about design and fabrication of responsive membranes. Furthermore, Ahmed et al. (2016) have covered the recent developments in the application of conductive polymeric membranes to water treatment and desalination. To complement these reviews, we have presented the already established protocols for preparing pH, temperature, and electrical-responsive membranes and highlight some of features of these membranes.

The chapter is organized in three main sections: Section 2.2 is a description of materials, their basic features, and the responsive mechanism; Section 2.3 reviews fabrication methods and the latest advances are covered with specific examples. The conclusive Section 2.4 includes a discussion about future challenges for responsive membranes.

2.2. Stimuli-Responsive Materials for Membranes Systems: Basic Principles and Mechanism of Action

Temperature and pH-responsive membranes are made with macromolecular systems containing acidic or basic ionizable groups called polyelectrolytes, or soluble polymers able to undergo a phase transition at a specific temperature. Electrical-responsive membranes can be fabricated from conducting polymers that are sensitive to electrical field and electrical voltage. The responsive behavior for the three stimuli is explained in Section 2.2.1 while Sections 2.2.2, 2.2.3, and 2.2.4 will cover properties of such responsive polymers.

2.2.1. Responsive Mechanism for Stimuli Responsive Membranes

Membrane stimuli-responsive behavior can be explained based on phase transition mechanism of the membrane materials in specific controlled environments (Minko, 2006).

2.2.1.1. Mechanism of pH Responsive Membranes

Membranes sensitive to pH are based on polyelectrolytes containing acidic and basic groups, which can either swell or shrink in response to a change in environmental pH caused by protonation and deprotonation of these ionizable side groups. Electrostatic interactions are one of the main factors that govern the structural change of polyelectrolytes chains, along with solvation forces and excluded volume effects (Azzaroni et al., 2007; Su et al., 2007). In particular, electrostatic repulsions and excluded volume effects support a stretched conformation in which the polymer

chains repulse each other. In difference, the minimization of electrostatic charge leads to an entropically favorable collapsed conformation.

Polyelectrolytes have also been used in the development of surfaces with switchable characteristics in the form of polymer brushes, which are assemblies of macromolecular chains tethered or grafted by one of their extremities to a surface (Rühe et al., 2004; Azzaroni et al., 2005; Minko, 2006; Das et al., 2015). In terms of mechanism of action, these brushes exploit the strong segment-segment repulsions and electrostatic interactions to switch reversibly from a collapsed to a stretched state allowing permeability control.

2.2.1.2. Mechanism of Thermo-Responsive Membranes

Thermo-responsive membranes respond to variations in the external temperature by changing accordingly their permeability, selectivity, and absorption abilities (Tang et al., 2016).

Generally, thermo-responsive membranes are dependent on the lower critical solution temperature (LCST) transition and upper critical solution temperature (UCST) transition (Figure 2.1).

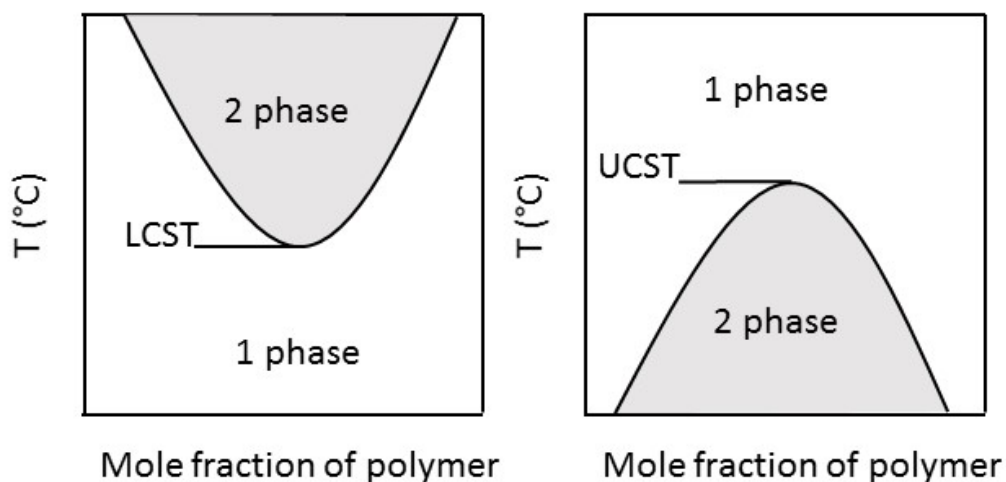


Figure 2.1: Phase diagrams for polymers exhibiting LCST behavior (left) and UCST behavior (right).

The LCST is defined as the lowest temperature of the binodal curve while the UCST is defined as

the highest temperature of the binodal curve. Polymers that undergo LCST transition in water phase separate upon increasing the temperature above their LCST, and the polymer chains collapsed in a shrunken state. For systems with UCST, an increase in temperature above the temperature of the UCST transition causes the system to merge into a single homogeneous phase and polymer chains swell. It is this shrinking and swelling behavior of the thermosensitive polymer chains that influence solute permeability by altering the pore size. The most studied temperature responsive polymer is poly(N-isopropylacrylamide) (PNIPAM), which will be reviewed in Section 2.2.3.

2.2.1.3. Mechanism of Electrical-Responsive Membranes

Electrical-responsive membranes can be either prepared by incorporating polyelectrolytes hydrogels onto membrane supports or by using conducting polymers as bulk materials and with other supporting systems.

Electrical-responsive membranes that are made from polyelectrolyte hydrogels exploit their ionizable side groups: the side groups undergo reversible contraction and expansion in response to an electric field (Haider et al., 2008). The transition between the expanded and coiled state allow the membrane pore to close and open, respectively, in response to the electrical stimulus. On the other hand, for conducting polymers the pore size actuation is triggered by changing the electrochemical state of the conducting polymer through doping (oxidation) and dedoping (reduction) (Loh et al., 1990). Doping of the conductive backbone with negative charges/anions enhance the conductivity, as dopants introduce a charge carrier into the polymer conjugated system by removing or adding electrons and relocalize them as polarons or bipolarons (part of a macromolecular chain containing two positive charges in a conjugated system). It is the polaron structure that is responsible for the transfer of the electric charge since, when an electrical potential

is applied, the polarons and bipolarons start to move along the backbone, passing through the charge (Bredas et al., 1985; Ahmed et al., 2016).

2.2.1.4. Mechanism of Responsive Gating Systems based on pH, Temperature, and Electrical Stimuli

Gating membranes combine the advantages of the porous nature of substrates and the smart responsive gates for advanced performance and applications. The mechanism of action can be described as follows: first, by applying the external stimulus, hydrogen bonding and charge repulsion interactions between molecules occur, which cause swelling and de-swelling of polymer chains. Therefore, the membrane pores are selectively open or closed in response to the environmental change. This open/close tuneability can be explained for gating membranes as positively responsive gating and negatively responsive gating as shown in Figure 2.2 (Liu et al., 2016). For positively responsive gating membranes, permeability increases when the stimulus appears or increases. The responsive gates undergo swelling/shrinking transition with the application of the stimulus, and consequently the membrane pores open influencing the permeability. Negatively responsive gating results in reversed properties that decrease permeability when the stimulus increases.

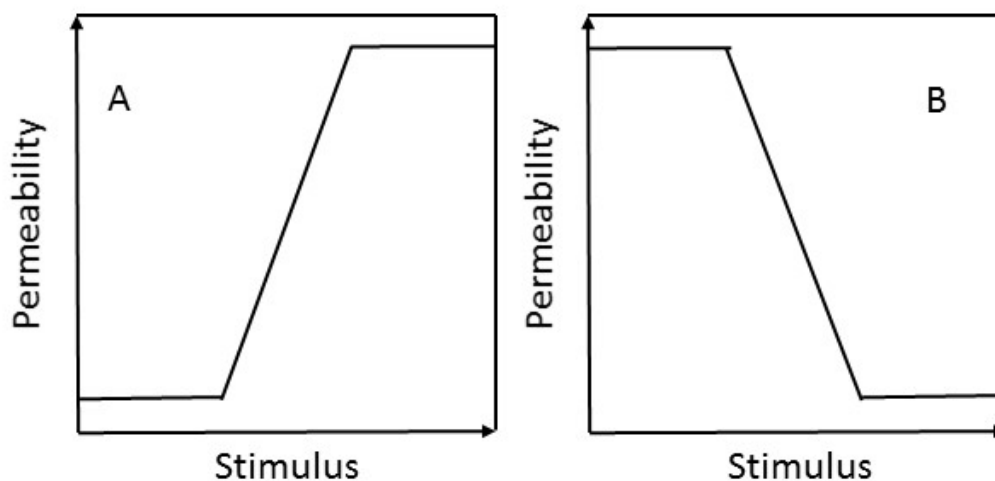


Figure 2.2: Positively (A) and negatively (B) responsive gating mechanism

For instance, thermo-responsive polymers with positively responsive gating swell at a temperature below the LCST due to hydrophilic interactions, thus the membrane pores are closed. Increasing the temperature above the LCST makes the pore open due to dominant hydrophobic interactions. On the contrary, UCST thermo-responsive polymers such as interpenetrating networks of polyacrilamide and polyacrylic acid can be used as negatively responsive gates (Chu et al., 2005). When the temperature is lower than the UCST of the polymer, the pores open due to the formation of hydrogen bonding, while increasing the temperature above the UCST can cause the polymeric network to swell because of the breakage of the hydrogen bonding, leading to pore closing.

2.2.2. Properties of pH-Responsive Polymers

For both porous and non-porous membranes, pH-responsive functional groups such as carboxyl, pyridine, imidazole, and dibutylamine groups are responsible for the conformational changes due to pH change. The carboxyl and the pyridine groups are most commonly used in the fabrication of

pH-responsive membranes (Zhao et al., 2011). Pyridine groups swell at low pH, and they are often called acid-swellaable groups or cationic groups (the same for imidazole and dibuthylamine groups) in contrast to alkali-swellaable or anionic carboxyl groups. Carboxyl groups with formula $-C(=O)OH$ or $COOH$ possess a carbonyl and an hydroxyl moiety. At low pH, carboxyl groups are protonated while at high pH they dissociate into carboxylate anions. In the first case, hydrophilic interactions dominate leading to shrinkage in volume of the polymer, while in the second the carboxyl group dissociates into carboxylate ions because of dominant hydrophobic interactions that result in a high charge density, causing the polymer to swell. Examples of pH-sensitive polymers with anionic groups are poly(carboxylic acids) as poly(acrylic acid) (PAA) or poly(methacrylic acid) (PMA) (Table 2.1). PAA possess ionizable hydrophilic properties due to the transformation between the de-ionized form of the $-COOH$ group and the ionized form of the $-COO^-$ group at pH value near a pKa of 4.7 (Hendri et al., 2001). PAA gates show negatively responsive behavior, leading to a volume shrinking of the polymeric chain at low pH, due to the formation of intermolecular hydrogen bonding between carboxylic groups (Luo et al., 2014).

Pyridine group is a basic heterocyclic compound with formula C_5H_4N ; its structure is similar to a benzene ring but one of the carbons is replaced by a nitrogen atom. At low pH, the nitrogen of the pyridine group is protonated causing internal charge repulsion that leads to an expansion of the dimension of the polymer. Higher pH values reduce the charge repulsion between the less ionized protonated pyridine groups while the polymer-polymer interactions increase, leading to a decrease in the overall hydrodynamic diameter of the polymer. The most common example of a pyridine-containing polymer is poly(vinyl pyridine) (PVP) with a pKa in solution of 3.5 (Tantavichet et al., 2001). Typical examples of polyelectrolytes containing cationic functional groups are poly(N,N-dialkylaminoethyl methacrylates), poly(L-lisine) (PLL), poly(ethylenimine) (PEI), and chitosan

(CS).

A wide range of polyelectrolytes can be used to impart pH responsiveness by exploiting protonation/deprotonation of their ionizable side chains. Some of them, such as chitosan and PMA, have a good biocompatibility and are preferred for biological applications (Jayakumar et al., 2011; Dupré de Baubigny et al., 2017) while other examples have also found application as ion exchange membranes for desalination and in separations (Wei et al., 2009; Zou et al., 2010).

2.2.3. Properties of Thermo-responsive Polymers

Thermo-responsive polymers have garnered a lot of interest in the last three decades since temperature variations can be applied and controlled externally in a non-invasive manner. Thermo-responsive membranes are specifically attractive where the chemical modification of the feed solution is either not practicable or unwanted. As mentioned before, PNIPAM (Figure 2.3) is one of the most common thermos-responsive polymers and has been applied broadly to develop thermo-responsive membranes. This polymer is soluble in water at room temperature with the key advantage of reversible phase transition at the LCST around 32°C (Table 2.1) (Schild, 1992). When the environmental temperature is lower than the LCST, the amide groups of PNIPAM can bind to water molecules by hydrogen-bonding interactions and the polymer chains swell, reaching a hydrophilic state. However, above 32°C, the PNIPAM is in a shrunken, hydrophobic state, due to thermal dissociation of water molecules from the polymer chains that now associate preferentially with each other, thus precipitating (Chu et al., 2011). Membrane structure and barrier properties are altered by such phase transition.

Poly(N-vinylcaprolactam) (PVCL) is another thermo-responsive polymer (Figure 2.3 and Table 2.1) that has been reported to possess similar characteristics to PNIPAM, such as biocompatibility and a LCST around 31°C (Vihola et al., 2005). PVCL has been less researched, but like PNIPAM

it does not degrade to low molecular weight cytotoxic products, making both of them good candidates for biotechnological application.

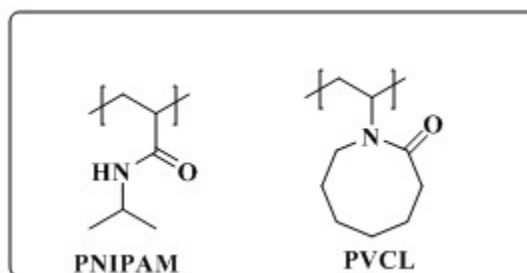


Figure 2.3: Examples of common temperature responsive polymers.

Thermo-responsive polymers with UCST behavior in water are less common and generally based on polybetaines, which are zwitterionic polymers with a positive and a negative charge in every repeat unit (Kudaibergenov et al., 2006).

A recent example is reported in Section 2.3.2 where the latest progress in fabrication of thermo-responsive membranes as thermo-responsive hydrogels, copolymeric systems, and responsive gates are covered.

2.2.4. Properties of Electrical-responsive Polymers

Generally, electrical-responsive polymers are intrinsically conducting polymers with a characteristic conjugated molecular structure (alternating double-bond system with planar conformation) of the polymer chain where the π -electrons are delocalized over the polymer backbone. The p-orbitals in the series of π -bonds overlap each other, and the electrons freely move between atoms (Ahmed et al., 2016). Representative conducting structures include polyaniline (PANI), polypyrrole (PPy), polyacetylene and polythiophene. Among these, PANI and PPy are widely investigated in membrane fabrication and tissue engineering for their interesting properties such as chemical stability and good processability (Balint et al., 2014). These macromolecular

conjugated structures become conductive after doping. Polyaniline has a promising future because of its ease of synthesis, low cost monomer, tunable properties, and better stability compared to other conducting polymers (Bhadra et al., 2009). The main structure of PANI is an alternation of single and double bonds (Figure 2.4(A) and Table 2.1).

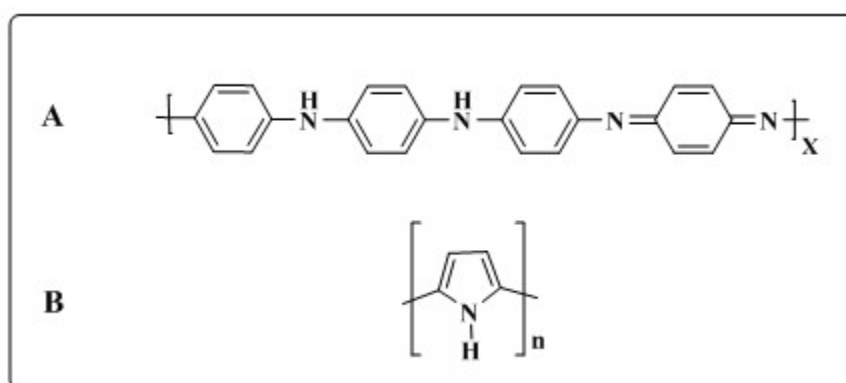


Figure 2.4: Schematic representation of polyaniline (A) and polypyrrole (B) main chain structure.

Its electrochemical stability depends on the pH conditions and the counterion of the Brönsted acid used as dopant (Negi et al., 2002).

Polypyrrole has a tight and rigid structure consisting of the repetition of a five-member ring with the formula $\text{C}_4\text{H}_4\text{NH}$ (Figure 2.4(B) and Table 2.1). The polymer possesses a good stability in air and water, as well as good conductivity (Wang et al., 2001). However the polymer is difficult to further process into membranes because of its insolubility and infusible processing nature, therefore deposition of the conductive layer on a support is often employed for membrane preparation.

In addition, composite membranes have been developed from polyelectrolytes or soluble polymers and polymer-carbon nanotubes (CNT) composites. Carbon nanotubes are allotropes of carbon with a cylindrical structure and walls formed by graphene sheets with nanoscale diameters. CNTs membranes can be prepared as composites or self-supported systems; however, the latter tend to

have irregular pores and limited control over the pore size. Moreover, potential leakage due to CNTs not being chemically bonded is reported as a drawback for these systems (Ahmed et al., 2016). Recent examples of the fabrication of composites carbon nanotube polymeric membranes will be reported in Section 2.3.4.

Table 2.1: Common pH, temperature, and electrical-responsive polymers and their properties.

Stimulus	Common materials		
pH		pKa	General properties
	Poly(acrylic acid) (PAA_	~4.7	Reversible conformational transition around pH 5 is driven by carboxylic groups (Swift et al., 2016).
	Poly(methacrylic acid)	~5.5	Ionizable hydrophilic polymer. At pH value lower than 5.5, COOH are not ionized and the polymer is in its collapsed state. Increasing the pH value, the charged COO ⁻ groups repel each other, leading to polymer swelling (Zhang et al., 2000).
	Poly(2-(dimethylamino)ethyl methacrylate)	7.3-7.5	Water-soluble polymer sensitive to both temperature and pH changes (Fournier et al., 2007).
	Poly(vinylpyridine)	3.5-4.5	Based on basic and cheap monomers. pKa depends on measurement method (Zhao et al., 2011).
	Chitosan	6.5	Abundant natural polymer, common in the fabrication of drug delivery systems (Park et al., 2001; Sinha et al., 2004) and membranes in combination with other functional materials to form polymer blends or composites (Pandis et al., 2014).
Temperature	Poly(N-isopropylacrylamide) (PNIPAm)	LCST	LCST lies between body and room temperature. Non-biodegradable and limited in vivo biocompatibility. High glass transition temperature (140-150°C) limits its processability (Van Durme et al., 2004; Aguilar et al., 2014)
		32	
	Poly(N-vinylcaprolactam)	31	High biocompatibility and low toxicity Soluble in both polar and non-polar solvents (Cortez-Lemus et al., 2016)

Electrical Field/ Electrical voltage	Polyelectrolytes		Poly(acrylic acid) (PAA) with Poly(vinyl alcohol) (PVA) hydrogels is the most common combination (Wandera et al., 2010)
	Polyaniline (PANI)	Conductivity (S/cm)	
		10	Good stability and processability (Bhadra et al., 2009). Cheap monomer and easy synthesis (Negi et al., 2002).
Polypyrrole (PPy)	100	Chemical stability and good processability (Bhadra et al., 2009). Good in vivo and in vitro biocompatibility (Balint et al., 2014).	

2.3. Fabrication of pH, Temperature, and Electrical-Responsive Membranes

Stimuli responsive membranes can be designed and fabricated with various styles and using three basic preparation approaches.

The responsive systems can be developed by (i) pre-synthesizing the polymers or copolymers and then processing these into membranes, (ii) involving *in-situ* polymerization to form membrane films or interpenetrating polymer networks, and (iii) chemical or physical modification of either the membrane surface or the membrane pores with stimuli responsive units, which has been widely employed for the preparation of smart gating membranes (Liu et al., 2016). Generally, modification imparts functionality that enhances membrane performance, maintaining the useful properties of the base membrane and introducing responsive sites on its surface.

2.3.1. Preparation Methods for Stimuli-responsive Membranes

In order to prepare membranes from stimuli-responsive polymers and copolymers, these materials can be used either as pure single phase systems, as components of blends, or as additives during membrane formation. During the fabrication of stimuli responsive membrane systems, classic

techniques such as solvent casting and phase inversion are generally employed (Ren et al., 2011) while surface modification can be performed to obtain membranes with responsive gates. A brief introduction to these techniques is given below.

2.3.1.1. Solvent Casting

The solvent casting process involves dissolving stimuli-responsive polymers or copolymers in an appropriate solvent and casting the obtained solution on a flat surface. The solvent is then allowed to evaporate, and membranes are dried and cross-linked by annealing them (Wandera et al., 2010; Husson, 2012). Solvent casting is normally used with robust polymers and generates relatively thick membranes.

2.3.1.2. Phase Inversion

The phase inversion technique is the most popular preparation method, not only for classic polymeric membranes but also for stimuli-responsive membrane systems. A solution of stimuli-responsive polymers and copolymers is cast on a flat surface and then immersed in a non-solvent coagulant bath to enable membrane formation. Phase inversion generally produces much thinner membranes with less diffusive resistance compared to solvent casting.

2.3.1.3. Membrane Surface Modification

In this method, membrane surfaces are modified following two distinctive surface-selective approaches: the “grafting to” approach and the “grafting from” approach (Minko, 2008; Wandera et al., 2010). The first approach introduces end-functionalized polymer chains on the membrane surface, whereas in the “grafting from” approach, the grafting reaction proceeds by polymerization from the surface and polymer chains grow from initiator sites by monomer addition from solution. The final result is the formation of a polymer brush layer on the membrane surface that, in the case of stimuli sensitive membranes, introduce sensitive functionalities. Comparing the above two

approaches, the “grafting from” is a more promising method in the synthesis of polymer brushes with a high grafting density because of the limitation of immobilization of polymer “grafting to” approach (Zhao et al., 2000).

The “grafting from” modification is done using methods that differ from the mechanism used for radical generation. The initiator can be a photo-initiator or a redox species as in the photo-initiated polymerization and redox-initiated polymerization case, or the reaction can be induced by a radiation. Plasma-graft-filling and atom transfer radical polymerization represent two additional approaches.

The surface modification of a membrane by the “grafting to” method is carried out by physical adsorption or chemical grafting. Physical adsorption involves coating the membranes with a stimuli-responsive polymer; alternatively, stimuli-responsive additives can be incorporated into a thin film polymer composite coating that will be placed on the membranes. The modification of membranes by chemical grafting results in immobilization of responsive macromolecules onto the membrane surface by reaction with membrane functional groups, or photo-generated on it, and a reactive group of the additive polymer.

Surface modified membranes can also be designed as membranes with grafted stimuli responsive surface or membranes with porous substrates and stimuli-responsive gates (Husson, 2012; Liu et al., 2016). The first type of membranes is prepared by grafting or coating responsive materials onto the substrate membrane surface, using chemical or physical methods. The substrates provide mechanical strength, and the grafted chains possess freely mobile ends that respond quickly to environmental stimuli. The second type are prepared by grafting functional macromolecules either onto the external membrane surface or both the external surface and the inside surface of pores. The grafted chains in the membrane pores have freely mobile ends, and their length and density

can be controlled to adjust the pore switching characteristic (Zhao et al., 2000).

2.3.1.4. In Situ Polymerization of Responsive Membranes: Preparation of Interpenetrating Polymer Networks IPNs

Interpenetrating polymer networks (IPNs) are a class of high performance multicomponent polymer material that have been used as responsive membranes. IPNs comprise two or more miscible polymers whose networks are at least partially interlaced on a molecular scale but are not covalently bonded to each other and cannot be separated unless their chemical bonds are broken (Sperling, 1981). The stimuli-responsive IPN system is formed by polymerizing a stimuli-sensitive monomer within a physically entangled copolymer in the presence of an initiator and a cross-linker (Wandera et al., 2010; Husson, 2012). Chain interpenetration does not involve chemical bonding; therefore, the two networks may retain their own properties while combined together, and each network responds to stimuli in an independent manner. Membranes prepared by IPNs possess synergistic effects by sharing the properties of both the polymers. A disadvantage associated with the use of the IPN is that sometimes the polymers are interpenetrated to such an extent that it becomes less responsive.

Each of the above mentioned methods have their advantages and disadvantages. By choosing the appropriate fabrication approach based on the stimuli-responsive polymer, copolymer, and polymer-additive mixture, membranes with desired mechanical properties, pore structure (porosity, pore size and pore-size distribution), barrier structure (symmetric versus asymmetric), and layer thickness(es) can be prepared.

2.3.2. Formation of pH-Responsive Membranes

In terms of configuration, pH-sensitive membranes can be fabricated as flat sheet membrane and hollow-fiber membranes, and in both cases the pH sensitive polymers are either incorporated in

the membrane matrix to prepare blended membranes or coated on the membrane surface (Zhao et al., 2011).

Often, blended membranes are prepared from mixtures of copolymers and polymers. Poly(vinylidene fluoride) (PVDF) is a recurrent material in membrane fabrication, with excellent thermal and good chemical stability (Prest Jr et al., 1975), and has gained popularity in the fabrication of blended pH-responsive membranes. Functional modification of PVDF is necessary in order to overcome its hydrophobic properties, which make it easily fouled. A large number of the pH-responsive membranes reported in literature in the last 10 years are based on a PVDF matrix blended with amphiphilic copolymers that possess functional and hydrophilic segments able to improve membrane's properties. A PVDF-g-PMMA copolymer blended with PVDF has been reported (Yang et al., 2017) in the preparation of a pH-responsive membrane. The key point of the synthesis method was blending the base polymer (PVDF) with its derivatives and tailoring the membrane casting conditions (Liu et al., 2013). The same copolymer blended with PVDF has been used to produce a series of novel pH-sensitive microfiltration membranes via ultraviolet irradiation-induced atom transfer radical polymerization (Hua et al., 2014). This "grafting from" approach provides the control growth of the polymer chains from the membrane surface.

Furthermore, microfiltration membranes with excellent pH-sensitivity and pH-reversible behavior based on PVDF blended with a functional ter-polymer have been reported (Ju et al., 2014). Poly(methyl methacrylate-2-hydroxyethyl methacrylate-acrylic acid) (PMMA-HEMA-AA) is a combination of hydroxyethyl methacrylate, a neutral monomer with hydroxyl groups, and poly(acrylic acid), the most commonly used pH responsive polymer, and it has been synthesized by free radical solution polymerization and blended with PVDF via the phase separation process. The resulting blended membrane showed changes in the permeation rate in response to the changes

in the pH due to the switching between stretched and collapsed states in the PAA-modified membrane that altered the apparent size of the micropores.

Novel pH-sensitive membranes have also been prepared exploiting surface segregation method by blending pH-sensitive amphiphilic copolymers with PES (Su et al., 2015). Surface segregation is presented as a facile and simple *in-situ* method to add pH responsive segments on the membrane surface. The copolymer system, made of Pluronic F127 and PMMA segments, PMMA_n-F127-PMMA_n, is synthesized by free radical polymerization and used as surface segregation additive during the membrane formation process.

2.3.3. Formation of Thermo-responsive Membranes

Preparation protocols of temperature-responsive membranes involve the use of copolymers and hydrogels as common materials as well as the functionalization of existing membranes to develop responsive gating systems (Xie et al., 2007). Polymeric groups can be grafted on the external membrane surface or both the membrane surface and inside the pores; hydrogels and micro- or nanospheres, not only polymeric chains, can also be used as responsive groups (Chu et al., 2011; Liu et al., 2016).

Very recently, pore-filling *N*-isopropylacrylamide (NIPAM) polymer hydrogels have been grafted onto track-etched polycarbonate (PC) membranes by plasma-induced graft copolymerization. The PC-g-PNIPAM membrane shows thermo-responsive gating characteristics dependent on the pore size change, since the swelling and de-swelling of the cross-linked PNIPAAm hydrogels in the temperature range of its LCST are responsible for the switching on and off of the pores (Wang et al., 2010).

Membranes with nanoscale pores are fabricated by attaching a layer of poly(ethylene glycol methyl ether methacrylate)-*b*-polystyrene-*b*-poly(ethylene glycol methyl ether methacrylate) (PMENMA-

b-PS-b-PMENMA) to a PVDF macroporous supporting layer. The water flux increase at a temperature higher than the LCST suggests that the pore size is temperature controllable. This polymer possesses oligo(ethylene glycol) side chains where the number of ethylene glycol units affects the LCST, providing a means of tuning the thermo-responsivity (Tang et al., 2016).

Another recent example reports that a membrane constructed by grafting a UCST polymer, such as poly(sulfobetaine), onto graphene oxide sheets, can exhibit changes in ion permeability in a non-aqueous electrolyte (Shen et al., 2014). The attractive interactions between zwitterions that form hydrophobic aggregates on the membrane are disrupted above the UCST, causing the polymer chains to uncoil and expose the zwitterions to the electrolyte. The ionic permeability is potentially influenced and lowered by the obstruction of the dissolved polymer chains.

2.3.4. Membranes with both pH and Temperature Responsive Behavior

Numerous membranes that are both pH- and thermo-responsive have been reported in literature. These systems can be synthesized following the same methods already explained. A lot of work has been done to combine pH and temperature sensitivities into a single membrane by copolymerizing two monomers or forming IPNs. Very recently, interpenetrating membranes composed of poly(N-isopropylacrylamide) thermo-sensitive polymer and hyaluronan pH-sensitive polymer have been reported. PNIPAM-HA hydrogels membranes display increased swelling/deswelling based on HA content and both temperature and pH response (Kamoun et al., 2017).

Membranes based on hydrogels of interpenetrating polymeric network have been fabricated from different combination of temperature sensitive and pH-responsive polymers, such as PNIPAM/PMMA (Zhang et al., 2000), PNIPAM/PAAm (Hebeish et al., 2015), and β -cyclodextrin copolymerized with 2-methylacrylic acid and N,N'-methylene diacrylamide (Yang et al., 2016).

2.3.5. Formation of Electro-Responsive Membranes

Electro-responsive membranes for different purposes are prepared from polymer composites, generally conducting polymers, or PELs, and from polymer composites incorporating conducting fillers (e.g., carbon nanotube). In general these materials can be used as surface coatings or bulk materials during the fabrication process.

Recently, the fabrication of a nanoporous membrane based on PPy doped with dodecylbenzenesulfonate has been reported. The conducting polymer is electro-polymerized on an anodized aluminium oxide membrane with a regular pore size that is then electrically actuated by changing the electrochemical state of PPy. (Jeon et al., 2011).

However, conducting polymers are often not soluble in common solvents and are difficult to cast; therefore, the deposition of conductive layers on porous supports is an extensively employed technique. Examples include PVDF/PANI blends (Wang et al., 2002), sulfonated poly(phenylsulfone) SPPSU (Dyck et al., 2002), and a mixture of poly(carbonate)-poly(pyrrole) (Hacarlioglu et al., 2003).

Recent examples also report preparation of flexible conductive bacterial cellulose/ polypyrrole membranes via *in situ* chemical synthesis of PPy nanoparticles on the surface of cellulose nanofibrils (Tang et al., 2015) and polypyrrole/polyacrylonitrile (PPy/PAN) conducting electroactive polymer membranes for potential electro-separation of synthetic azodyes from simulated wastewaters (Karimi et al., 2014). Electrically conductive polymeric membranes have been fabricated using carboxylated multiwalled nanotubes and poly(vinyl alcohol) (PVA) active layers. These composite membranes exhibit high electrical conductivity, high permeate flux, and a hydrophilic surface (de Lannoy et al., 2012).

PVA has also been employed to fabricate robust and permeable PVA-CNT-COOH thin films via

sequential deposition and the cross-linking method. The thin films have been coated onto ultrafiltration supports and present potential for application in reducing fouling of UF treatment process (Dudchenko et al., 2014).

A CNT-PVDF mesh has been placed as a layer on a PES UF membrane in order to create a system able to capacitively-reduce negatively-charged organic matter fouling (Zhang et al., 2014).

2.4. Conclusion and Future Directions

As seen from the above discussion, developing stimuli-responsive membranes with easy-to-tailor properties has extensively driven research in many fields. At present, pH and temperature responsive systems are widely investigated for the possibility of developing controlled drug delivery systems as well as chemical and bioseparations. These systems are based on polyelectrolytes and soluble polymers that undergo a reversible change in their properties that allows control of membrane performance. Electro-responsive membranes are fabricated from conducting polymers that possess a characteristic conjugated structure in which electrons can move freely. Changing the electrochemical states of these conducting polymers leads to changing their membrane pore size accordingly. The membranes from the above mentioned polymer systems can be prepared from the desired stimuli-responsive polymer materials exploiting classic fabrication methods such as solvent casting and phase inversion, or alternatively by *in-situ* polymerization to form IPNs. In addition, surface modification of a pre-formed membrane can be performed using a “grafting to” or a “grafting from” approach. In general, phase inversion produces thinner membranes with less diffusive resistance compared to solvent casting, and IPNs can be less responsive due to the strong interactions among the polymeric chains. Depending on the required pore topology, barrier structure, and mechanical properties, each of these methods can be chosen to fabricate the stimuli-responsive membranes.

Considering the current state of art, there are a number of opportunities in design and synthesis of stimuli-responsive membranes, but the main challenges that remain are large scale production of membrane responsive systems as well as the development of smart membranes adaptable to different environments. Future efforts should focus first on implementing robust stimuli-responsive systems with long-term stable performance in large scale applications by investigating easily up-scalable fabrication processes. In addition, the next generation stimuli-responsive membranes should be able to mimic natural systems with flexible and adaptable properties. For pH- and thermo-responsive membranes, their potential application in the biomedical field is often prevented by biocompatibility and cytotoxicity limitations of the systems, which need to be carefully tested. Similarly, the downside for electrical-responsive membranes is the limited processability of conducting polymers that makes them difficult to cast, and hence the preparation of reliable and robust systems with controllable properties is challenging.

Potential applications of stimuli-responsive membranes range from advanced separations to drug delivery and tissue engineering. In particular, electrical-responsive membranes can be designed as self-cleaning systems to prevent fouling by removing the unwanted layer and to extend the overall membrane performance. Another innovative application is the development of electro-catalytic systems, where electrical-responsive membrane can be coupled with chemical reactions to catalyze the reaction and separate the desired products or reactants. Furthermore, stimuli-responsive systems can be employed to regulate the transport and release of chemicals in biological systems where pH and temperature fluctuations normally occur. They can also be used as scaffolding to artificially grow cells and tissues exploiting the electrical stimulation triggered by conducting polymers.

Finally, membranes with switchable or responsive physiochemical properties have strong potential

to improve many technological fields.

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