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Review

Stimuli-responsive membranes

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ABSTRACT

Stimuli-responsive membranes change their physicochemical properties in response to changes in their environment. Stimuli-responsive membranes have been designed to respond to changes in pH, temperature, ionic strength, light, electric and magnetic fields, and chemical cues. This review covers the design of stimuli-responsive membranes and their ever-expanding range of use. It considers stimuli-responsive changes in membrane structure and surface characteristics that enable novel applications.

Contents

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1. Introduction

1.1. General overview

The rapidly increasing interest in functional materials with reversibly switchable physicochemical properties has led to significant work on the development of stimuli-responsive membranes, for which mass transfer and interfacial properties can be adjusted using external stimuli: temperature, pH, solution ionic strength, light, electric and magnetic fields, and chemical cues. Of particular interest in the development of responsive membranes is the fact that the reversible changes occur locally at a fast rate and with high selectivity. Non-porous and porous stimuli-responsive membranes have a large number of already established applications and many more potential applications where they are key components in complex technical systems such as sensors, separation processes, and drug delivery devices. Enabling reversible changes in polarity or conformation, stimuli-responsive polymers generally are considered important materials (building blocks) for developing responsive membrane systems.

In this review, we examine in detail the many recent contributions to the significantly important and fast developing field of stimuli-responsive membranes. By membrane we mean a distinct phase that separates two bulk phases. The membrane phase can be homogeneous or heterogeneous and the membrane could also be a non-porous solid (e.g. pervaporation membranes), a macroporous solid (e.g. microfiltration membranes, membrane adsorbers) or a microporous solid (e.g. ultrafiltration membranes). Focus is given to work in the last 10 years in order to provide the reader with the current state of knowledge. We consider the already established protocols for preparing stimuli-responsive membranes and highlight some of the reported applications of these membranes. The way forward for responsive membranes is explored in terms of membrane development and potential applications in various fields.

1.2. Responsive mechanisms

Building responsiveness into a membrane depends in part on whether the membrane has a porous or non-porous structure. Porous membranes generally are made responsive by grafting responsive polymer layers from the membrane external surface and, often, the pore walls. These functional polymers can be made to undergo changes in conformation in response to changes in the local environment, leading to reversible changes in the permeability and selectivity of the membranes. Non-porous membranes generally are made responsive by incorporating stimuli-responsive groups in the bulk of the membrane material. Conformational changes by these groups may lead to changes in the degree of swelling of the membrane barrier, hence triggering changes in the membrane permeability and selectivity. Of course, responsiveness in membrane systems is not limited to affecting a change in membrane barrier properties. Changes also may influence the ability of a membrane to bind and release a target compound, as needed, for example, to develop membrane adsorbers. Controlling the hydrophilic/hydrophobic behavior of a membrane surface using external stimuli can be used to reduce the level of membrane fouling and to design self-cleaning membrane surfaces.

Stimuli-responsive membranes exploit the interplay among the pore structure and changes in the conformation/polarity/reactivity of responsive polymers or functional groups in the membrane bulk or on its surfaces. Such changes in specially tailored polymer systems have been used in many systems and devices to enable applications that demand reversibly switchable material properties. It follows that novel membranes can be designed using polymers/molecules that have been shown to undergo physicochemical changes in response to environmental cues. Responsiveness is known to occur as a two step process: (i) use of stimuli to trigger specific conformational transitions on a microscopic level and (ii) amplification of these conformational transitions into macroscopically measurable changes in membrane performance properties.

Membrane stimuli-responsive properties can be explained based on phase transition mechanisms of the membrane materials (polymers) in controlled environments. Phase transitions may be induced by solvent quality, concentration or type of ions, temperature and other chemical or physical interactions. Polymer responsive mechanisms have been well explained in reviews by Luzinov et al. [1] and Minko [2]. Responsiveness generally refers to changes in polymer chain conformations. All polymers are sensitive to their immediate environments. They always respond to external stimuli to some extent by changing their conformation along the backbone, side chains, segments or end groups. Therefore, sophisticated membrane systems with responsive properties can be designed by variation of polymer chain length, chemical composition, architecture and topography. Most polymer responsive mechanisms are based on variations in surface energy, entropy of the polymers, and segmental interactions. Surface energy drives the surface responsive reorientation because, fundamentally, systems try to minimize the interfacial energy between the polymer surface and its immediate environment.

To understand the impact of solvent quality on responsiveness, it is instructive to examine how polymer chains behave in solution. The root-mean-square end-to-end distance of a polymer chain is normally expressed as,

$$\langle r^2 \rangle^{1/2} = \alpha (nC_\mathrm{N})^{1/2} l$$

where α is the chain expansion factor, which is a measure of the effect of excluded volume; n is the number of freely jointed links in a hypothetical polymer chain of equal length, l; and C_N is the characteristic ratio, which contains contributions from fixed valence angles and restricted chain rotation [3]. Another way to express the above equation is by using the unperturbed (denoted by subscript 0) root-mean-square end-to-end distance:

$$\langle r^2 \rangle^{1/2} = \alpha \langle r^2 \rangle_0^{1/2}$$

The unperturbed dimensions are those of a real polymer chain in the absence of excluded volume effects, i.e., for $\alpha = 1$. In a poor solvent ($\alpha < 1$), the dimensions of the polymer chain are smaller than those in the unperturbed state ($\alpha = 1$). While in a good solvent ($\alpha > 1$), where polymer–solvent interactions are stronger than polymer–polymer or solvent–solvent interactions, the dimensions of the polymer chain are larger than those in the unperturbed state ($\alpha = 1$). So it can be said that polymers expand in good solvents and collapse in poor solvents. An example of this behavior is expansion and collapse of poly(N-isopropylacrylamide) (PNIPAAm) in water at different temperatures. At temperatures below the lower critical solution temperature (LCST), water is a good solvent, and PNIPAAm expands. When the temperature is increased above the LCST, water becomes a poor solvent, and PNIPAAm collapses. Changes in characteristic size between good and poor solvents are normally much more pronounced for surface-confined polymer chains than for polymer chains in solution. Thus, grafting PNIPAAm chains to a membrane surface imparts a temperature-responsiveness to that membrane.

Grafting density is another parameter that affects the conformational responsiveness of polymer chains. At low chain grafting density, in the absence of strong interactions between the grafted polymer and the support surface, the response of the grafted chains to solvent quality is similar to that of the free polymer in solution. Yet, at high grafting density, the response is weaker. The explanation is that high grafting density translates to a crowded layer of already highly stretched polymer chains. At moderate grafting densities, polymers in poor solvents form clusters on the surface to avoid unfavorable interactions with the solvents. In good solvents, the polymers in this moderate grafting density region swell and form homogenous layers of stretched, tethered chains. At these moderate grafting densities, the polymer chains demonstrate a pronounced response to solvent quality.

The polymers used to prepare responsive membranes need not be neutral. Polyelectrolytes (PELs) have ionizable groups, and their interactions are determined in part by the degree of dissociation (f) of these ionizable groups. Due to their high f, strong PELs generally are insensitive to solution pH. However, at high salt concentration when the ionic strength of the solution approaches that inside the PEL, electrostatic screening results in conformational changes. Weak PELs respond to changes in external pH and ionic strength and may undergo abrupt changes in conformation in response to these external stimuli. Weakly basic PELs expand upon a decrease in pH, while weakly acidic PELs expand upon an increase in pH. At high ionic strength, weak PELs tend to collapse due to effective screening of like charges along the PEL.

Photo-chromic units (azobenzene, spiropyran, diarylethene, viologen) undergo reversible photo-isomerization reactions on absorption of light. Reversible photo-isomerism leads to switching between two states of the photo-chromic moieties, hence leading to molecular changes in group polarity, charge, color, and size. These molecular changes can be amplified into measurable macroscopic property changes. For example, membranes containing viologen groups have permeabilities that can be regulated reversibly by redox reactions. The viologen moieties have two different redox states [4]. On treatment with a reducing agent such as sodium hydrosulfite ($Na_2S_2O_4$) solution, viologens undergo reversible reduction from the dicationic state to the radical cationic state. Normally viologens in the dicationic state are highly soluble in water, but their solubility decreases in the reduced radical cation state. Therefore, in viologen grafted membranes, when the grafted viologen is in its dicationic state, the polymer chain may be expelled by the charges on the side chains and extend more in the pores leading to low permeabilities. Whereas, when the grafted viologen polymer is changed to its cationic state, the hydrophobic radical chains may be in a more entangled or collapsed state leading to higher permeabilities.

Finally, while many works cited employ one responsive mechanism, the literature contains examples of membranes modified by mixed polymers or block copolymers, where each polymer responds to a different stimulus. Mixed polymer brushes and block copolymers may impart adaptive/switching properties due to reversible microphase segregation among the different functionalities in different environmental conditions. For example, the individual polymers may change their surface energetic states upon exposure to different solvents. By imposing combinations of two or more independent stimuli, such membranes exhibit more sophisticated permeability responses than membranes modified by a single polymer type.

2. Design of responsive membranes

Increasing demand has driven the development of so-called “smart” or “intelligent” membranes that respond to external stimuli in controlled and predictable ways. In this review, we elect to call these membranes “responsive”, rather than “smart” or “intelligent”, as the latter descriptors falsely suggest that the membranes have the capacity to make decisions. Several design and production practices have been suggested, and, generally, these can be placed into two categories: (a) synthesis of stimuli-responsive materials (polymers or copolymers) and processing of these materials into membranes and (b) modification of existing membranes by various chemical/physical processes to incorporate stimuli-responsive polymers. In this section, we highlight different methods to prepare stimuli-responsive membranes.

2.1. Membrane processing

Preparation of membranes from stimuli-responsive materials has been achieved using pure stimuli-responsive polymers and copolymers or by using these polymers as components of blends or as additives during membrane formation.

2.1.1. Radiation-based methods

Radiation curing has been applied to develop stimuli-responsive membranes. In this method, a mixture of stimuli-sensitive and cross-linking monomers (and/or prepolymers) is coated on the surface of a porous film and the coated layer is cured with UV irradiation. The coating formulation may also include chemical additives for controlled release applications. A variety of monomers may be used to prepare composite membranes with permeation/release profiles that respond to changes in pH, temperature, ionic strength, etc.

2.1.2. Solvent casting

Casting solutions of mixtures containing stimuli-responsive polymers or copolymers onto flat surfaces has been used to develop composite membranes that respond to different stimuli. Membrane preparation involves dissolving stimuli-responsive polymers or copolymers in an appropriate solvent, casting the solutions obtained on flat glass plates or laboratory dishes, and allowing the solvent to evaporate. The free-standing membranes formed are dried and crosslinked by annealing them.

2.1.3. Interpenetrating polymer networks (IPNs)

Interpenetrating polymer networks (IPNs) have been used as responsive membranes. The high level of crosslinking in these membranes normally leads to responsive systems with good mechanical strength. A stimuli-responsive monomer is polymerized within a physically entangled copolymer in the presence of an initiator and a crosslinker to form the stimuli-responsive IPN membrane.

2.1.4. Phase inversion

Traditional membrane preparation techniques such as the wet phase-inversion process have been utilized to fabricate stimuli-responsive membranes, again by using stimuli-responsive polymers in the membrane formulation. Solutions containing stimuli-responsive polymers or copolymers are cast on flat surfaces and then immersed in an appropriate solvent such as water to enable membrane formation.

2.2. Surface modification using stimuli-responsive functional polymers

Successful membrane modification must satisfy two conditions: (i) preservation of the useful properties of the base membranes and (ii) introduction of functional (responsive) moieties to the membranes. Two distinct surface-selective approaches are employed for membrane functionalization. The “grafting to” approach introduces preformed, end-functionalized small molecules or large macromolecules to the membrane surface. The “grafting from” technique is a heterogeneous, surface-initiated polymerization process whereby polymer chains grow from initiator sites on the membrane surface by monomer addition from solution. Advantages and disadvantages of these two approaches have been summarized in detail elsewhere [5]. One important distinction in consideration of membrane modification by grafted polymers is that the polymer chain density achievable by the “grafting to” method depends on the chain molecular weight; whereas, grafting density and polymer molecular weight are independent design parameters in “grafting from” strategies. Grafting density is an important parameter, as it greatly affects the final performance of the membranes. High grafting density can be important to shield the underlying membrane support from fouling agents on one hand, but, on the other hand, high grafting density limits the response to external stimuli since the chains are trapped in an extended configuration. Having the ability to tailor grafting densities independently of polymer chain molecular weight provides flexibility in membrane design.

2.2.1. Surface-initiated modification (“grafting from”)

Modification by surface-initiated polymerization normally is done in two steps: the first immobilizes an initiator precursor onto the membrane surface and the second initiates polymer growth by monomer addition to the immobilized initiator sites. Numerous methods are available for grafting from modification, including photo-initiated grafting (UV and non-UV), redox-initiated grafting, plasma-initiated grafting, thermal grafting, and controlled radical grafting methods such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. In general, these grafting from methods differ by the mechanism used for radical generation.

2.2.1.1. Photo-initiated polymerization. Heterogeneous photo-initiated graft-polymerization has been used often to modify membranes with polymers that respond to changes in pH, temperature, ionic strength, light, etc. A photo-initiator such as benzophenone (BP) is coated onto the membranes by dipping them in a solution containing the photo-initiator. Polymerization from the immobilized initiator sites is carried out by soaking the membranes in monomer solutions and irradiating with UV light under an inert atmosphere. The membranes are weighed before and after polymerization to determine the degree of graft polymer modification (DG):

$$\mathrm{DG} = \frac{m_{\mathrm{gr}} - m_0}{\mathrm{m}_0} \times m_{\mathrm{sp,A}}$$

m_0 is the initial membrane mass, m_{gr} is the mass after graft modification, and $m_{\mathrm{sp,A}}$ is the specific or areal mass (mass/outer surface area).

2.2.1.2. Redox-initiated polymerization. Chemicals such as Fenton’s reagent (Fe^{2+}-H_2O_2), persulfate salts, and cerium ammonium nitrate in nitric acid are used to produce free radicals from which graft polymerization is carried out in an inert atmosphere. This method can be used to graft different stimuli-responsive polymers onto membranes leading to membranes that can respond to pH, temperature, oxidoreduction, ionic strength, light, etc.

2.2.1.3. Radiation-induced polymerization. Radiation-induced graft polymerization can be used to modify polymeric membranes with stimuli-responsive polymers to develop novel responsive membranes. In one method, membranes are immersed in aqueous solutions of the monomer with various concentrations of hydrated copper(II) sulfate, bubbled with pure nitrogen, and irradiated with ^{60}Co γ-ray radiation.

2.2.1.4. Plasma-graft-filling polymerization. Plasma-*graft*-filling polymerization has been used to modify membranes and introduce stimuli-responsiveness to them. Membranes are irradiated with argon plasma to form initiator radicals, and then polymerization is carried out from these initiator sites.

2.2.1.5. Atom transfer radical polymerization. "Grafting from" using surface-initiated atom transfer radical polymerization (ATRP) is gaining popularity to modify membrane surfaces. It provides for the controlled growth of polymer chains from the membrane surface. One use has been the modification of membranes with polymer nanolayers that respond to various external stimuli. Modification is done in two steps: immobilization of an ATRP initiator onto the membrane surface and catalyst-activated polymerization from the immobilized initiator sites.

2.2.2. "Grafting to" method

Membrane surface functionalization by grafting to modification with responsive polymers can be done by physical adsorption or chemical grafting of pre-formed polymer chains. The latter method reacts functional groups of the membrane material with a reactive group on the polymer modifier. The functional groups may be inherent to the membrane material or generated (photo)chemically. The result is a permanent immobilization of responsive macromolecules onto the membrane surface.

2.2.2.1. Physical adsorption—coating. A membrane is coated with a stimuli-responsive polymer by soaking it in a polymer solution and allowing it to dry. Annealing the coated membrane helps to strengthen the attachment of the polymer to the membrane surface. Stimuli-responsive groups (additives) can also be incorporated into the thin-film composite polymer coating that is applied to the membrane to impart switchable properties after modification.

2.2.2.2. (Photo)chemical grafting. This involves grafting pre-formed polymer chains or hydrogels onto a membrane surface. In one strategy, attaching a photo-reactive group like azidophenyl to polymer chains enables the photoimmobilization of the polymer onto the membrane surface. Immobilizing stimuli-responsive polymer hydrogels or crosslinked polymer networks onto membrane surfaces has been used as a way of modifying membranes and making them responsive to specific external stimuli.

2.3. Gating membranes

Molecular recognition gate membranes are highly sophisticated devices. Their response is triggered by molecular recognition in macromolecular structures within the membranes. The membranes can be developed using a stimuli-responsive polymer with a receptor (e.g., crown ether) attached to it. This receptor selectively captures a specific ion or chemical in its cavity and this selective binding event leads to changes in the properties of the stimuli-responsive polymer.

Molecularly imprinted polymers (MIPs) also have been used in the fabrication of molecular-recognition gating membranes [6–15]. MIPs are synthetic materials that possess affinity and selectivity towards certain target molecules (templates) due to special recognition sites formed during the preparation of the polymer matrix. MIPs are prepared by copolymerization of functional and cross-linking monomers in the presence of the template molecule. Subsequent removal of the template molecules leaves behind receptor sites that are complementary to the template in shape and position of the functional groups. Molecular memory is introduced into the polymer, which becomes capable of selectively rebinding the template molecule. Again, this selective binding event leads to changes in the mass transfer properties of the membrane.

2.4. Summary—design of responsive membranes

Preparation of membranes from stimuli-responsive polymers, copolymers, and polymer-additive mixtures is an important approach in the design of responsive membranes. This approach enables fabrication of membranes with the desired mechanical properties, pore structure (porosity, pore size and pore-size distribution), barrier structure (symmetric versus asymmetric), and layer thickness(es). Membrane surface modification also is important in the design of responsive membranes, as the optimal required membrane surface characteristics rarely are achieved from membrane forming polymers, copolymers or polymer-additive mixtures alone. Modification imparts functionality that enhances membrane performance. By taking this approach, the useful properties of the base membrane are maintained, and responsive properties are introduced to the membrane surface. When modification is done using controlled, surface-initiated polymerization strategies such as ATRP, polymer molecular architecture can be controlled precisely, allowing fundamental studies on the role that surface architecture plays on membrane responsiveness and performance.

3. Temperature-responsive membranes

Over recent years, applications of temperature-responsive membranes as drug delivery systems, sensors, and solute separation systems have been investigated widely by many groups. PNIPAAm is among the polymers that is well known to respond to changes in temperature and has been applied broadly to develop temperature-responsive membranes. PNIPAAm is soluble in water at room temperature, but undergoes a phase separation at temperatures higher than its lower critical solution temperature (LCST), which is near 32 °C. Above 32 °C, the intrinsic affinity of PNIPAAm chains for themselves is enhanced due to thermal dissociation of water molecules from the hydrated polymer chains. Hydrophobic interactions among isopropyl groups increase, and the polymer chains associate preferentially with each other, thus precipitating from aqueous solution. Such a phase transition alters membrane structure and barrier properties.

Temperature-responsive polymers can be incorporated into the membrane bulk during membrane formation or as surface-modifying agents following membrane formation. These general strategies are described separately.

3.1. Membrane formation—temperature-responsive membranes

Temperature-responsive membranes have been prepared by solution casting of copolymers and polymer mixtures, and as interpenetrating polymer networks, core–shell microcapsules, and nanocomposites.

3.1.1. Copolymer systems

Nonaka et al. [16] and Ogata et al. [17] reported on the synthesis of temperature-responsive poly(vinyl alcohol) (PVA)-*graft*-PNIPAAm) membranes by evaporating dimethyl sulfoxide (DMSO) from a solution containing the copolymer. The copolymer was prepared by graft polymerization of NIPAAm onto PVA in DMSO using potassium peroxo-disulfate initiator. The permeation of lithium ions and methylene blue through the membranes was affected greatly by changing temperature below and above 33 °C. The swelling ratio of the membranes in water increased gradually with decreasing temperature below 40 °C, and a considerable increase in swelling occurred at the LCST. Polyethylene glycols (PEGs) with different molecular weights could be separated by size-exclusion with the membranes by changing the temperature from 34 to 45 °C.

Temperature sensitivity of membranes has been exploited in pervaporation processes to separate liquid mixtures with close boiling points. Sun and Huang [18] synthesized temperature-sensitive PVA-*graft*-PNIPAAm membranes for pervaporation of

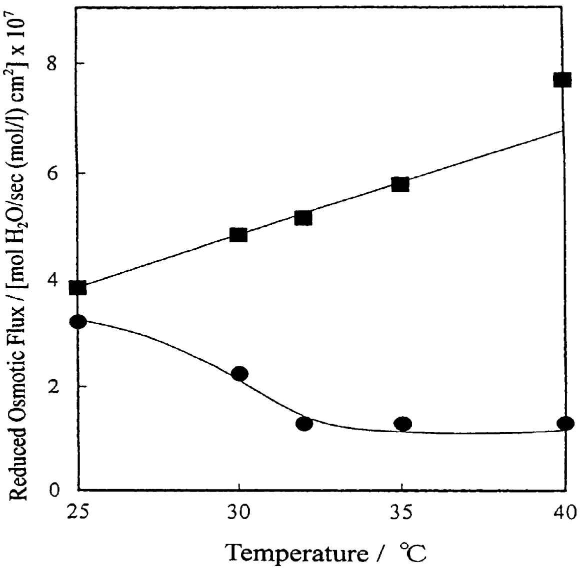

Fig. 1. Change in reduced osmotic flux through anion exchange membranes with temperature for (■) anion-exchange membrane without NIPAAm and (●) anion-exchange membrane with NIPAAm.
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ethanol-water mixtures. The membranes were prepared by grafting NIPAAm onto PVA using hydrogen peroxide-ferrous ion as initiator. A maximum in pervaporation selectivity (α_{PV}) was observed for the membranes as the operating temperature was raised from 20 to 40 °C. Maximum value of α_{PV} was observed at 30–32 °C, equal to the LCST of PNIPAAm in water, indicating that the membrane separation performance was affected greatly by the grafted PNIPAAm chains. Further evidence that the PNIPAAm was responsible for the increase in α_{PV} was given by the observation that the α_{PV} values of unmodified PVA membranes decreased monotonically as temperature increased. Also, the permeate flux increased with increasing temperature due to swelling of the polymer network and, thus, increased diffusional mobility of the permeating species.

Sata et al. [19,20] prepared temperature-responsive anion-exchange membranes by copolymerization of glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDMA), and NIPAAm using benzoyl peroxide and reaction of the epoxy groups with trimethylamine to introduce ammonium groups. The osmotic flux through anion-exchange membranes prepared without NIPAAm generally increased with increasing temperature due to swelling of the polymer matrix. However, for anion-exchange membranes containing NIPAAm, the flux decreased with increasing temperature from 25 °C due to de-swelling and showed a constant value from 32 °C until about 40 °C as shown in Fig. 1.

Ying et al. [21] prepared temperature-responsive microfiltration (MF) membranes from poly(vinylidene fluoride) (PVDF)-*graft*-PNIPAAm copolymers by phase inversion from aqueous solution at 27 °C. The copolymers were synthesized by thermally induced graft copolymerization of NIPAAm with ozone-pretreated PVDF. X-ray photoelectron spectroscopy (XPS) analyses of the membranes revealed substantial surface enrichment by NIPAAm. Increasing the concentration of NIPAAm in the copolymers yielded membranes with higher degrees of temperature-responsive swelling in aqueous solutions. The transmembrane permeability of model drugs, calcein and fluorescein isothiocyanate-dextran, in phosphate buffer solutions exhibited strong and reversible dependence on permeate temperature in the temperature range 4–55 °C, with the largest change in permeability occurring from 27 to 32 °C. The impact of temperature on the pore diameters below the LCST of PNIPAAm could be applied to the separation of macromolecules.

Yamakawa et al. [22] studied the transport properties of ions through temperature-responsive membranes prepared from a polymer mixture of PVA, PNIPAAm, and poly(VA-*co*-2-acrylamido-2-methylpropane sulfonic acid). The polymers were dissolved in DMSO and the solution was cast on glass plates and allowed to dry at 50 °C, producing free-standing membranes. The membranes were then cross-linked either physically by annealing them at 50 °C for 20 min or chemically by immersing them in an aqueous solution of glutaraldehyde, HCl and NaCl at 25 °C for 24 h. Permeation experiments in dialysis systems consisting of the membranes and mixed solutions of KCl and $CaCl_2$ showed that the permeation of Ca^{2+} through the membranes was controlled by temperature in two distinct ways: downhill transport (from high to low concentration) occurred at temperatures below the LCST of PNIPAAm, and uphill transport (from low to high concentration) occurred at temperatures above the LCST. These membranes may find use in self-regulating systems that adjust the concentration of specific solutes in response to temperature changes.

3.1.2. Interpenetrating network membranes

Several groups have developed temperature-sensitive interpenetrating network (IPN) membrane systems that have been applied in various applications. Aoki et al. [23] synthesized IPN membranes from poly(acrylic acid) (PAA) and poly(N,N-dimethylacrylamide) (PDMAAm). These IPNs showed reversible and pulsatile solute release, reflecting the “on” state at higher temperatures and the “off” state at lower temperatures. Gutowska et al. [24] prepared temperature-responsive semi-IPNs composed of PNIPAAm and linear poly(ether(urethane-urea)) (Biomer) by UV-initiated solution polymerization. The swelling ratios of the semi-IPNs decreased with increasing temperature. Muniz and Geuskens [25] studied the influence of temperature on the permeability of semi-IPNs based on cross-linked poly(acrylamide) (PAAm) with PNIPAAm chains entangled in the network. The permeability of Orange II dye through the semi-IPNs increased with increasing temperature, and a transition was observed at the LCST of PNIPAAm (32 °C). Above the LCST, the permeability increased markedly because the PNIPAAm chains collapsed.

Guilherme et al. [26] synthesized sandwich-like temperature-responsive membranes of IPN hydrogels that can be used in separation processes. NIPAAm and methylene-bis-acrylamide (MBAAm) cross-linker were co-polymerized inside previously synthesized cross-linked PAAm by UV photopolymerization using periodate as sensitizer. SEM images showed that the hydrogel membranes comprised three layers, with an internal layer fully enveloped by two external layers that had similar morphologies. The images also showed significant differences in the morphologies of the internal and external layers. Warming the hydrogel above the LCST of PNIPAAm showed that the PNIPAAm network was present mainly in the internal layer. This layer contracted, while the external layers expanded and remained highly porous. Unlike the work by Muniz and Geuskens [25], the permeability of Orange II dye through the layered membranes decreased significantly as the temperature was increased above the LCST of PNIPAAm (Fig. 2). It was observed that the permeability decreased by 52% as the temperature increased from 25 to 40 °C. This difference in performance between the two studies likely is due to differences in membrane structure. When PNIPAAm chains are well distributed throughout the IPN network, their collapse above LCST creates a more open flow structure. However, formation of a separate PNIPAAm-rich layer within the membrane structure leads to decreased flow above LCST due to collapse of that layer into a dense film.

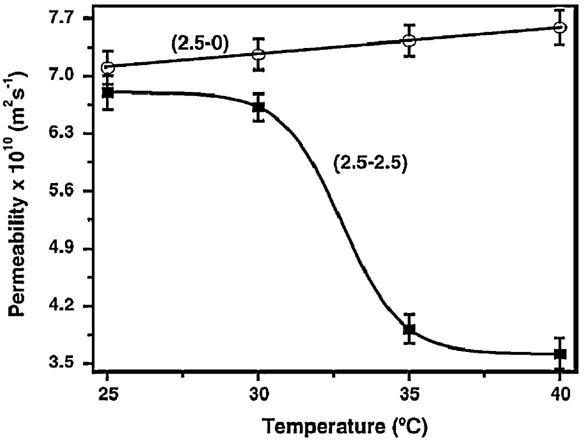

Fig. 2. Permeability of orange II dye through (2.5–2.5) sandwiched-like IPN hydrogel membranes and (2.5–0) pure PAAm hydrogel membranes as a function of temperature.
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3.1.3. Membrane microcapsules

Chu et al. [27,28] prepared temperature-responsive core–shell microcapsules with a porous outer membrane and PNIPAAm gates. Interfacial polymerization was used to prepare polyamide microcapsules, and plasma polymerization was used to graft PNIPAAm into the pores of the microcapsule walls. The PNIPAAm-grafted microcapsules showed reversible and reproducible temperature-responsive release of solute (sodium chloride or vitamin B_{12}) that had been loaded into the inner space of the microcapsules. As illustrated in Fig. 3, at low graft yields, the release rate was higher at temperatures above the LCST than at temperatures below the LCST due to pore opening controlled by the PNIPAAm gates. In contrast, at high graft yields, the release rate was lower at temperatures above the LCST than at temperatures below the LCST. At high graft yields, the pores were fully blocked and a PNIPAAm layer covered the entire capsule surface. However, the grafted PNIPAAm was still highly hydrophilic and water-soluble below LCST, and dramatically became hydrophobic and insoluble in water above LCST. Since the solutes used were water soluble, diffusion through the membranes occurred primarily within the water-filled regions in spaces delineated by polymer chains. Higher solute release rates thus occurred from PNIPAAm-grafted microcapsules at low temperatures, where the polymer film was well hydrated.

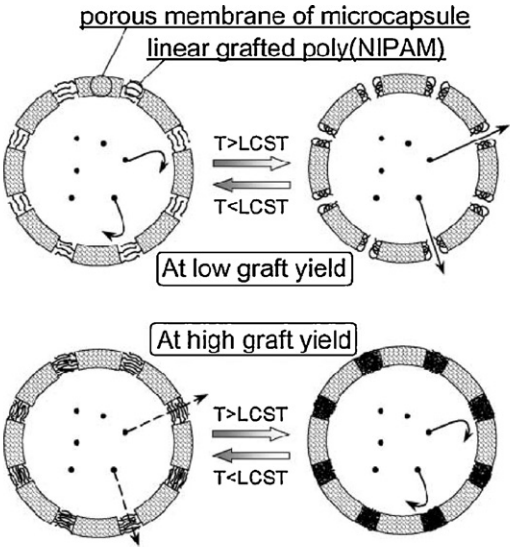

Fig. 3. A schematic illustration of the temperature-responsive release mechanism of core–shell microcapsules with a porous membrane and temperature-responsive PNIPAAm gates.
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3.1.4. Nanocomposite membranes

Csetneki et al. [29] explored the possibility of using composite gel membranes to regulate permeability in response to external temperature change. The membranes contained ordered nanochannels that acted as reversible permeability valves. The channels were designed to contain an ordered array of stimuli-responsive core–shell beads that change size in response to external stimuli. This structure was achieved by preparing magnetite (Fe_3O_4) nanoparticles within polystyrene latex using a seed polymerization process and coating the surfaces of the magnetic polystyrene (MPS) beads with PNIPAAm. NIPAAm monomer, MBAAm cross-linker and potassium persulfate initiator were mixed with the MPS at 65 °C under a nitrogen atmosphere for 30 min to form MPS-PNIPAAm beads. A uniform magnetic field was then applied to form arrays of the MPS-PNIPAAm beads, and the channel array structures were fixed in place by polymerization with PVA. Solutions of bovine serum albumin (BSA) were used to test the temperature-responsive performance of the composite membranes. With increasing solution temperature, the permeability increased. The 'on' permeation value was approximately one order of magnitude larger than the 'off' permeation value. Fig. 4 illustrates the permeation mechanism through these nanochannel containing membranes. Similar permeation patterns through the membranes were obtained for other permeating species, including methylene blue and riboflavin.

Zhou et al. [30] reported on an *in situ* method to prepare thermo-sensitive polyurethane (TSPU)/silicon dioxide (SiO_2) nanocomposite membranes by the wet inversion process for use in water vapor permeation. The water vapor permeability of the membranes depended on the size of the SiO_2 particles. When SiO_2 particles with an average diameter of 100 nm were well dispersed in the PU matrix, the nanocomposite membranes showed lower water vapor permeability at low temperatures and higher water vapor permeability at high temperature, relative to pure TSPU. At low temperatures (below the phase transition temperature of the soft segment), the nano-SiO_2 particles enhance the crystallinity of the soft segment in the polymer and this reduces the free volume available for water transport. When the SiO_2 content was higher than 5.0 wt%, the SiO_2 particles agglomerated throughout the polymer matrix, and this decreased water vapor permeation.

3.2. Membrane modification—temperature-responsive membranes

As described in detail in Section 2, membrane surface modification with responsive polymers can be done by physical adsorption or chemical grafting of pre-formed polymer chains (grafting to modification) or by surface-initiated polymerization (grafting from modification). Numerous methods are available for grafting from modification, including radiation grafting (UV and non-UV), redox-initiated grafting, plasma-initiated grafting, thermal grafting, and controlled radical grafting methods such as ATRP and RAFT polymerization. Again, these grafting from methods differ by the mechanism used for radical generation.

3.2.1. Grafting to modification

Yoshida and co-workers [31–33] have studied the temperature-controlled transport properties of ion track membranes. The membranes were prepared by chemically grafting PNIPAAm hydrogel onto single/multi-pore ion track membranes of poly(ethylene terephthalate) (PET). It was discovered that, below 31 °C, the hydro-

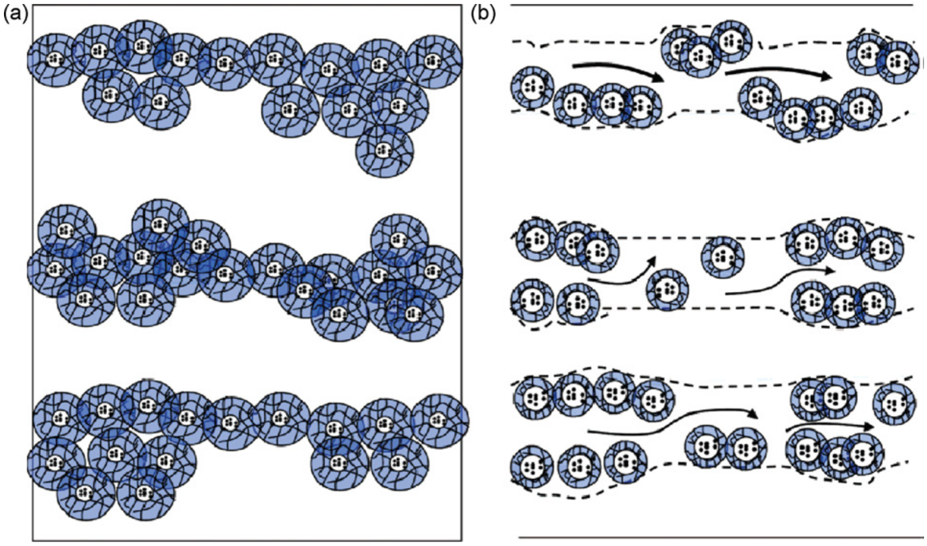

Fig. 4. Schematic representation of the permeation mechanism through the channels of MPS-PNIPAAm smart nanocomposite membranes: (a) 'off' state below LCST and (b) 'on' state above LCST.
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gel took up water rapidly, which led to enormous swelling and pore blocking. The opening and closing of pores was cycled repeatedly many times over long periods by varying the temperature above and below 31 °C [31]. The mass flow of various molecules with molecular weights ranging from 18 to 69,000 g/mol through the membranes could be controlled thermally, and the degree of control increased with increasing molecular weight of the permeating molecule [32]. The permeation rates of orange G, methylene blue and BSA through the membranes were controlled thermally, with the BSA permeation rate in the membrane with open pores being 35 times higher than that in the membrane with closed pores [33].

Park et al. [34] investigated the permeation rate of water and tryptophan through porous polycarbonate (PC) membranes that had been modified with immobilized PNIPAAm. Photoimmobilization was carried out by attaching a photoreactive azidophenyl group onto the PNIPAAm and casting it on the porous membranes. When small amounts of polymer were immobilized, the membrane pores were covered only partially, yielding porous membranes. When large amounts of polymer were immobilized on the membranes, the pores were covered completely, yielding non-porous membranes. Water permeation through the modified porous membranes changed at different temperatures; higher flux rates were observed above the LCST of PNIPAAm as the polymer chains contracted and the pores opened. Water permeation through the modified non-porous membranes was not observed at any temperature. Tryptophan permeation through the modified porous membranes decreased below the LCST of PNIPAAm; whereas, that through the modified non-porous membranes increased below the LCST. This result was attributed to the fact that the non-porous (gel like) membranes swell below the LCST, thereby enhancing the rate of diffusion of tryptophan and collapsed (densified) above the LCST, reducing the rate of diffusion.

3.2.2. *UV photografting*

Peng and Cheng [35] investigated the effect of grafting yields on the temperature-responsive permeability of porous PNIPAAm-g-PE membranes. The membranes were prepared by grafting PNIPAAm onto porous PE MF membranes by UV irradiation. They observed that temperature changes affected diffusional permeation in two distinct ways depending on the grafting yield: permeability of vitamin B_{12} increased with increasing temperature in low graft yield membranes and decreased with increasing temperature in high graft yield membranes. For low graft yield membranes, permeability was controlled by pore-grafted PNIPAAm, and the expanded conformation of the grafted polymer below the LCST gave rise to reduced effective pore size in comparison with the collapsed state above LCST. As the grafting yield increased, polymer filled the pores and also formed a confluent layer of grafted polymer at the membrane–solution interface. In higher graft yield membranes, permeability was controlled by this polymer surface layer. With increasing temperature, the layer densified and became more resistant to diffusion, resulting in decreased permeability.

Liang et al. [36] developed temperature-sensitive membranes by grafting PNIPAAm on the surface of hydrophilic polypropylene (PP) MF membranes by UV photopolymerization. The membranes showed reversible separation behavior by changing the external temperature. Below the LCST of PNIPAAm, the separation properties were characteristic of ultrafiltration (UF) membranes, while, above its LCST, they were characteristic of MF membranes. With changes in temperature, there was reversible swelling and shrinking of the PNIPAAm modifying layer, which caused the membrane pores to shrink or expand. The flux through the membranes varied from 1200 to 10,000 $\mathrm{L\,m^{-2}\,h^{-1}}$ for temperature changes from 22 °C to 40 °C. It was discovered that for solutions of dextran with molecular weights between 6.3 kDa and 2000 kDa, a marked change in separation performance occurred by adjusting the temperature.

Yang and Yang [37] developed temperature-responsive membranes regulated by pore-covering polymer brushes by photografting NIPAAm onto PET MF track membranes with BP as initiator. ATR-FTIR and SEM confirmed that the PNIPAAm brushes were grafted only on the membrane surfaces but not inside the pores. The modified membranes responded to changes in temperature. Pore sizes and water flux varied as the PNIPAAm brushes swelled and collapsed with temperature variation.

Wu et al. [38] used rapid 'bulk' surface photopolymerization to modify nylon MF membranes with poly(N,N-diethylacrylamide) (PDEAAm), using BP as an initiator. ATR-FTIR spectra confirmed the successful grafting of PDEAAm on the membrane surfaces. The water flow rate through the membranes increased sharply with increasing temperature within the range 30–35 °C, near the LCST of PDEAAm. Changes in surface morphology were observed with changes in temperature, as shown by the AFM images in Fig. 5.

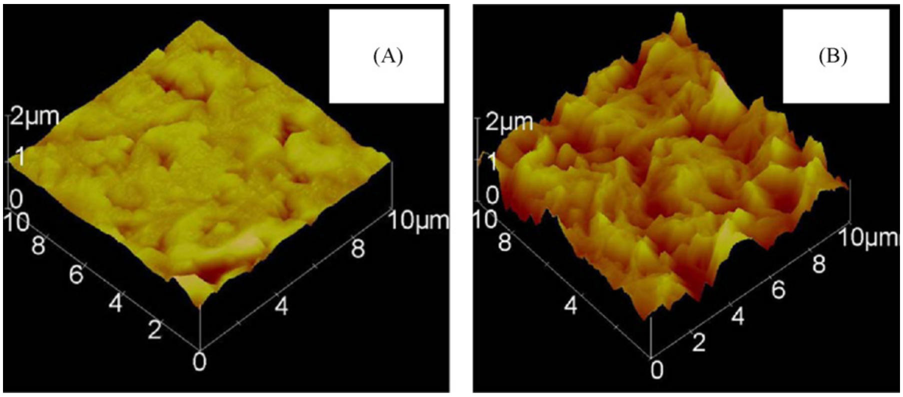

Fig. 5. AFM images of dried PDEAAm modified nylon membranes: (A) above the LCST and (B) below the LCST. Reproduced with permission from [38]; Copyright (2006) Elsevier.

The PDEAAm chains expanded below the LCST of PDEAAm and collapsed onto the membrane surface above the LCST.

Vertommen et al. [39] demonstrated the reversible on/off-switching of BSA permeation through temperature-responsive composite membranes. The membranes were prepared by UV-photografting of PNIPAAm onto PET MF membranes using BP as the photoinitiator and N,N′-methylenebisacrylamide (MBAAm) as the crosslinking agent. They observed that above the LCST of the PNIPAAm hydrogel (on-state), the collapsed grafted layer appears to only partially cover the membrane pores, allowing BSA permeation through the uncovered pores. Provided the grafting density is high enough, the swollen PNIPAAm covers the membrane pores completely below LCST (off-state) thus preventing BSA permeation. Negligible permeation was measured in the off-state. The authors proposed an on-demand release mechanism that is based on switching the membrane surface coverage, rather than the effective pore size, as discovered earlier by Peng and Cheng [35].

3.2.3. Radiation curing

Kaetsu et al. [40,41] found that responsive membranes for drug permeation and release could be obtained by coating a mixture of stimuli-sensitive monomers and UV curable cross-linkable prepolymers on the surfaces of porous films and drug-containing films and curing the coating with UV irradiation. The porous membranes were prepared by irradiating polymeric films such as PET and PC and etching them with ion beams. Mixtures of an electrolyte monomer (AA), a crosslinker such as tetraethyleneglycol dimethacrylate, and a UV curable prepolymer were then coated on the surface of the porous membranes by spraying or dipping. The coated membranes were irradiated with UV light. For immobilization of enzymes, aqueous solutions of the enzymes were added to the coating mixture. Membranes were coated with the enzyme solution and cured similarly by irradiation. Fig. 6 shows how both the drug permeation and drug release membranes were used.

Nakayama et al. [42] developed membranes for pH- and temperature-responsive drug release by coating and radiation curing of polymer–drug composite films with PEL (AA) or NIPAAm (NIPAAm)-containing mixtures. Fig. 7 shows how the membranes were prepared and how they were applied as stimuli-responsive systems. Mixtures of a matrix monomer such as 2-hydroxyethyl methacrylate (HEMA) and a model drug such as methylene blue were cast into molds consisting of two reinforced glass plates and polymerized by UV irradiation into drug containing membranes. The membranes were then coated by dipping or spraying them with stimuli-responsive hydrogels obtained from NIPAAm or AA, a crosslinker such as PEGDMA and a UV curable cross-linking prepolymer. Finally, the coated membranes were placed on a conveyer and irradiated continuously with UV light.

Lequieu et al. [43] developed PET track-etched membranes with thermo-adjustable porosity and separation properties by surface photochemical immobilization of poly(N-vinylcaprolactam) (PVCL). Photo-reactive azidophenyl was first incorporated into the PVCL chains, and then the chains were cast on PET membranes followed by irradiation with UV light. The water permeation through the modified membranes increased drastically when the cloud point (T_{cp}) (27 °C) of the grafted PVCL chains was reached. Below T_{cp}, the immobilized polymer chains are in a swollen state, which decreases the average effective pore diameter. Above T_{cp}, the polymer chains collapse, resulting in more open pores and increased water permeability. The permeability of a mixture of dextran molecules also was affected strongly by the temperature. Grafted PVCL chains act as valves, regulating the barrier properties of the membranes with changes in temperature.

Geismann et al. [44] reported on the photograft copolymerization of a temperature-responsive monomer (NIPAAm) from PET track-etched membranes. In order to facilitate surface-selective grafting, two variations of the photoinitiator precoating were selected: adsorption of BP to unmodified PET surfaces (with moderate surface carboxyl density) and adsorption of BP carboxylic acid to aminated PET surface, prepared as described previously. Utilizing the acid–base complexation to enhance adsorption of photoinitiator to the membrane surface led to higher graft copolymerization efficiencies. Highly pronounced changes in permeability as a function of temperature were measured for membranes modified with PNIPAAm.

3.2.4. Radiation-induced grafting (non-UV)

Shtanko et al. [45] prepared track-etched membranes with controllable permeability by the radiation-induced graft polymerization of NIPAAm onto PET and PP track-etched membranes. AFM topography images of pristine PP membranes showed a smooth surface with pore diameters of about 900 nm; while the images of the modified membranes in water at room temperature showed a swollen polymer structure on the surface, and the pore diameters had dropped to about 300 nm. On warming the water to 50 °C, the polymer structure collapsed, and the modified membrane pore diameters increased to about 600 nm. The changes in pore sizes with temperature also affected water permeability through the membranes. Flux through the modified membranes increased as the temperature increased with the most significant increase between 32 and 34 °C, consistent with the LCST of PNIPAAm.

Shtanko et al. [46] investigated the properties of polymeric track-etched membranes modified by grafting poly(2-methyl-5-vinylpyridine) (PMVP) and PNIPAAm. PET membranes were modified by radiation-induced graft polymerization of MVP and NIPAAm to create hydrophilic and temperature-responsive copoly-

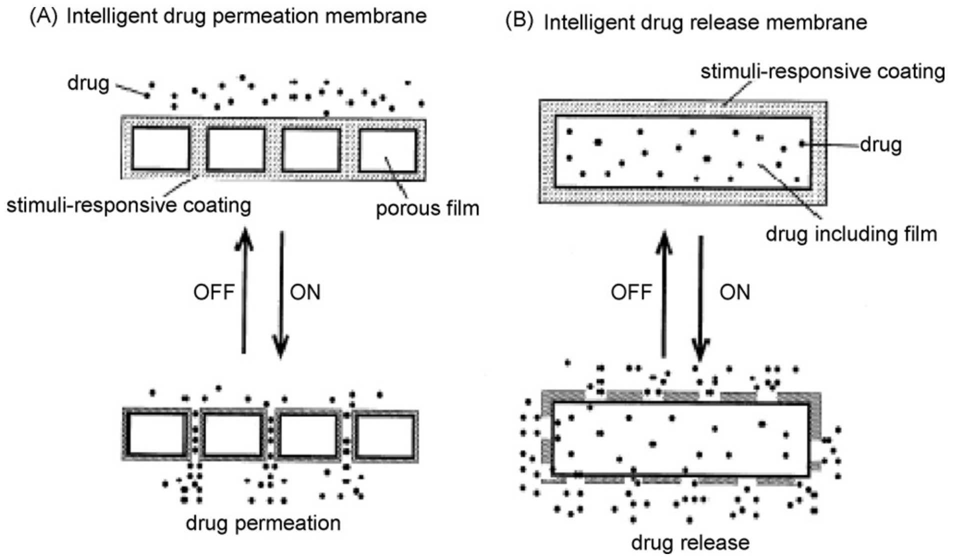

Fig. 6. Application mechanisms of drug permeation and drug release using "intelligent" membranes.
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mers on the membrane surfaces. Conductometric measurements showed that the conductivity across the modified membranes increased substantially in the temperature range 32–34 °C on heating and decreased drastically in the same temperature range on cooling. Water filtration through the modified membranes revealed a substantial increase in permeability on warming to temperatures between 30 and 34 °C, indicating that the pore sizes of these membranes could be controlled by changing temperature. This conclusion was supported by AFM and SEM images of the membrane surfaces at different temperatures.

Lin et al. [47] prepared temperature-responsive membranes by ^{60}Co γ-ray radiation-induced grafting of NIPAAm onto brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) membranes. The water flux of these BPPO-*g*-PNIPAAm membranes changed instantly upon changes in environmental temperature, and changes were most pronounced at 32 °C, the LCST of PNIPAAm. They later prepared positively charged, temperature-responsive membranes by quaternary amination of the BPPO-*g*-PNIPAAm membranes [48]. The amination process was carried out by immersing the BPPO-*g*-PNIPAAm membranes in triethylamine solution. Residual bromine atoms on the BPPO membranes reacted with triethylamine [$(C_2H_5)_3N$] to form $-(C_2H_5)_3N^+Br^-$ groups on the membrane surface. The permeability coefficients of the ionic model drug, sodium salicylate, through the membranes at different temperatures increased markedly after amination. The authors concluded that the temperature sensitivity of the membranes was enhanced by amination.

3.2.5. *Plasma-initiated grafting*

Choi et al. [49] developed a temperature-responsive membrane for separations based on solute hydrophobicity. The membranes were prepared by grafting PNIPAAm onto porous PP films using plasma polymerization. Water flux at 14 °C was lower by a factor of 6 compared to the flux at 39 °C, and changes in flux were rapid, occurring within 60 s of the temperature change. Non-ionic surfactant NP-10 was adsorbed on the pore surfaces at 39 °C and desorbed at 14 °C. Solutions containing hydrophobic and hydrophilic solutes were supplied continuously to the feed side, while changing the membrane temperature. It was observed (as shown in Fig. 8) that above PNIPAAm LCST, only the hydrophobic solutes were adsorbed onto the membranes, while the hydrophilic solutes permeated through the pores. By changing the temperature to below PNIPAAm LCST, the adsorbed hydrophobic solutes desorbed from the membranes. Thus, with stepwise temperature change below and above

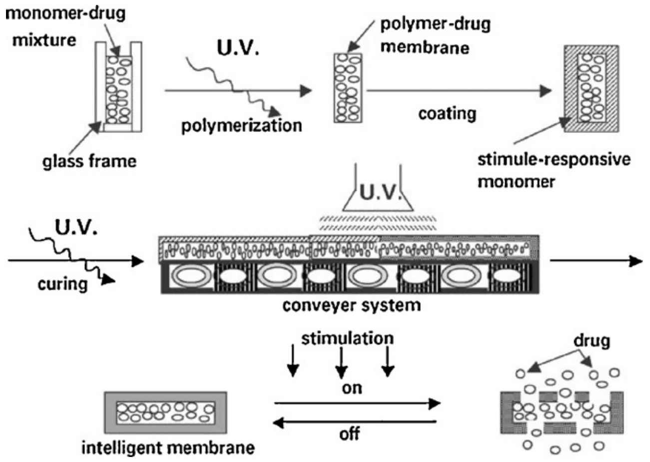

Fig. 7. Preparation and use of "intelligent" membranes developed by radiation curing.
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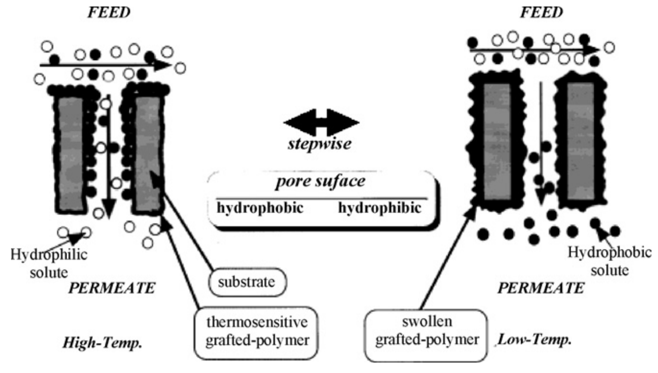

Fig. 8. Schematic representation of a separation system consisting of a temperature-responsive gel membrane.
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LCST, specific solutes could be concentrated and purified on the permeate side.

Liang et al. [50] prepared temperature-sensitive PP membranes by grafting PNIPAAm on PP MF membranes using plasma polymerization. The modified membranes exhibited a hydrophilic surface with a contact angle of 40° at 20 °C and a hydrophobic surface with a contact angle of 90° at 40 °C. When the temperature was changed from 20 to 40 °C, with a constant applied transmembrane pressure of 1.38×10^6 Pa (13.6 atm), the water flux through unmodified membranes remained constant at about 700 kg/m^2 h, while the flux through modified membranes changed from 22 to 500 kg/m^2 h. Collapse of PNIPAAm chains at the LCST was responsible for the flux increase.

Huang et al. [51] prepared temperature-sensitive membranes by grafting PNIPAAm on microporous PE membranes by plasma-induced graft polymerization. Scanning electron microscopy was used to show that the grafted PNIPAAm chains had different configurations around the LCST. X-ray photoelectron spectroscopy data indicated that the polar amide groups of the grafted PNIPAAm were present at the outer surface when the chains were in a swollen state and were enveloped by non-polar PE chains when in a collapsed state. The authors trapped the polymer configuration by freeze drying (below LCST) or hot drying (above LCST) the membranes prior to XPS analysis. The water flux through the PNIPAAm grafted membranes showed strong temperature responsiveness, and the grafted chains acted like chemical valves that would regulate the membrane pore radii by changing the temperature.

Kim et al. [52] investigated the rate of water permeation through temperature-responsive PP membranes grafted with NIPAAm by plasma polymerization. The graft polymerization of PNIPAAm onto the PP membranes was performed after the formation of radicals on the PP membranes by irradiation with argon plasma. SEM images showed morphologic changes in the PP-*g*-PNIPAAm membranes at 25 °C in water. The membranes appeared swollen compared to base PP membranes. The water permeability of these membranes showed sensitivity to temperature. Below the LCST of PNIPAAm, the PP-*g*-PNIPAAm membranes had higher permeabilities than the unmodified PP membranes. This result was attributed to the addition of hydrophilic groups to the hydrophobic PP substrate membranes by grafting. Below LCST, the grafting of hydrophilic PNIPAAm onto the hydrophobic PP membranes led to an increase in permeability due to enhancement of the membranes' hydrophilic properties. However, unlike prior studies mentioned earlier in this section, the permeabilities gradually *decreased* with increasing temperature. The authors offer the following argument for the decrease in permeability: above LCST, the PNIPAAm chains became hydrophobic due to dissociation of ordered water molecules surrounding hydrophobic N-isopropyl groups. An alternative explanation may be that the polymerization resulted in a confluent surface layer of PNIPAAm. Below LCST, this hydrophilic layer improves membrane wettability and improves permeability. Above LCST, this layer densifies and reduces permeability.

In a subsequent study [53], PP-*g*-PNIPAAm membranes were used to design cell-separation systems. The membranes were loaded with adsorbed monoclonal antibodies that bind specifically to surfaces of target cells. It was predicted that, above LCST of PNIPAAm, the PP-*g*-PNIPAAm membranes coated with monoclonal antibodies would specifically capture cell types having certain receptors on their surfaces and then release the captured cells below the LCST. Membranes were soaked in solutions of fluorescein-conjugated goat antibody at 37 °C, and a fluorescence signal was observed on the membrane surfaces. After the membranes were soaked in phosphate buffered saline solutions at 4 °C, the fluorescence signal on the membrane surfaces was low. This verified that the antibody adsorbed onto the membrane at 37 °C and desorbed almost completed at 4 °C. PP-*g*-PNIPAAm membranes containing CD80 monoclonal antibodies preferentially captured CD80 transfected cells at 37 °C compared with membranes lacking antibodies or having CD86 antibodies, demonstrating selective antibody adhesion to the desired target cell.

Xie et al. [54] investigated the temperature response of membranes fabricated by adding hydrophilic or hydrophobic monomers into NIPAAm monomer solution during membrane preparation. Plasma polymerization was used to graft PNIPAAm, poly(NIPAAm-*co*-AAm), and poly(NIPAAm-*co*-butyl methacrylate(BMA)) as functional gates on porous PVDF or Nylon-6 (N_6) membranes. Water flux measurements were used to infer LCST values for the copolymer systems. LCST values were assigned as the inflection points in flux versus temperature plots. From these measurements, the LCST was found to increase linearly with increasing molar percentage of the hydrophilic monomer (AAm) in the NIPAAm solution and decrease linearly with increasing molar percentage of the hydrophobic monomer (BMA) in the NIPAAm solution. The response temperature for the P(NIPAAm-*co*-AAm)-*g*-PVDF membranes increased to 40 °C when 7 mol% of AAm was added into the NIPAAm solution, and that of the P(NIPAAm-*co*-BMA)-*g*-N_6 membranes decreased to 18 °C when 10 mol% of BMA was added to the NIPAAm solution. This study provides guidance on the design and fabrication of temperature-responsive gating membranes with the desired temperature responses for various applications.

Lue et al. [55] reported on the successful modification of PC membranes by grafting PNIPAAm chains using argon plasma treatment. Drug permeability through these membranes changed markedly at 34 °C, and the on-off permeability ratios of 4-acetamidolphenol and ranitidine HCl were 11 and 14, respectively.

Xie et al. [56] prepared temperature-dependent, molecular recognition membranes comprising poly(NIPAAm-*co*-GMA/β-cyclodextrin (CD))-*g*-PET) by the combination of plasma polymerization and chemical reaction. The membranes were prepared by a two-step process. Firstly, the NIPAAm and GMA comonomers were grafted on the surface and into the pores of the PET track-etched membranes by plasma polymerization. In a second step, CD moieties were reacted with epoxy groups of the grafted copolymer chains. The P(NIPAAm-*co*-GMA/CD)-*g*-PET membranes exhibited temperature-responsive water contact angle. When the temperature was increased from 25 to 45 °C, the contact angle of the modified membranes increased from 65 to 80°; whereas, the contact angle for the unmodified PET membranes decreased from 85 to 77°. During dynamic adsorption experiments, the guest molecule, 8-anilino-1-napthalenesulfonic acid ammonium salt (ANS), adsorbed onto the modified membranes at low temperature (25 °C) and desorbed at high temperature (40 °C) with good repeatability. There were no significant temperature-dependent adsorption characteristics either for membranes without CDs [P(NIPAAm-*co*-GMA)-*g*-PET] or for membranes without PNIPAAm chains [PGMA/CD-*g*-PET]. Thus, the authors attribute temperature-dependent adsorption of guest molecules to both the configuration change of P(NIPAAm-*co*-GMA) grafted chains and the molecular recognition of CD towards ANS. Because these membranes yielded temperature-dependent adsorption of guest molecules, they may find application in temperature-controlled affinity separations.

3.2.6. *Controlled radical grafting*

The temperature responsiveness of PNIPAAm was exploited to achieve actively controlled thermo-responsive, size-selective transport by grafting PNIPAAm brushes from gold-coated nanocapillary array membranes using ATRP [57]. A smooth Au layer on the track-etched PC membrane surfaces was prepared by thermal evaporation of ∼50 nm Au on the exterior surfaces. An initiator-terminated disulfide $(BrC(CH)_2COO(CH_2)_{11}S)_2$ was self-assembled on the gold surfaces. PNIPAAm brushes with thicknesses between 10 and 30 nm were grafted from the Au surfaces by surface-initiated ATRP. Molecular transport through the membranes was investigated by fluorescence measurements using fluorescein isothiocyanate-labeled dextrans ranging from 4.4 to 282 kDa. Membranes had variable pore diameters as a result of different PNIPAAm thicknesses grafted. It was observed that manipulating the temperature of the membranes below and above the LCST of PNIPAAm caused large, size-dependent changes in the transport rates. It also was noted that a combination of highly uniform PNIPAAm brushes and monodispersed pore size was critical to have highly reproducible switching behavior.

Lue et al. [58] immobilized cross-linked PNIPAAm polymer networks into microporous track-etched PC films to create temperature-responsive composite membranes for controlled drug release. These membranes exhibited rapid and reversible responses to temperature changes, resulting in on-off drug permeation. The on-off ratios for water and for model drugs, 4-acetamidophenol and ranitidine HCl were as high as 26, 11, and 20, respectively.

Nystrom and co-workers [59] grafted PNIPAAm on polysulfone (PS) membranes that had been treated with corona discharge. They observed that despite the apparent low grafting densities observed from SEM images, the effect of grafting PNIPAAm on water permeability and solute retention was clear. The permeabilities and retentions of PEG and dextran were influenced by temperature for the modified membranes but not significantly for the unmodified membranes, and changes were greatest around the LCST of PNIPAAm. A higher permeability and lower retention were measured at temperatures above the LCST where it is known that the membranes have larger pores due to collapse of the grafted PNIPAAm. They also reported that grafting PNIPAAm on PS increased the hydrophilicity of the membranes below the LCST of PNIPAAm, as determined by contact angle measurements.

Alem et al. [60] reported on the temperature-responsive behavior of PNIPAAm brushes grafted in the nanopores of track-etched membranes. The membranes were prepared by water-accelerated, surface-initiated polymerization of NIPAAm from the nanopore walls of PET membranes. Base membranes had two different pore sizes: 80 nm (small pores) and 330 nm (large pores). Modification was done by ATRP and standard free radical polymerization. The authors observed two permeation control mechanisms depending on the membrane pore size. For the large pore membranes, expanded PNIPAAm chains at $T < \mathrm{LCST}$ resulted in reduced effective pore size and, hence, lower permeabilities than for the collapsed chains at $T > \mathrm{LCST}$. For the small pore membranes, the PNIPAAm layers at the membrane surface were the controlling factor for permeation. Expanded chains meant greater degrees of hydration in the surface layer and, therefore, higher permeabilities than for the collapsed chains, which yielded a dense surface film.

Fan et al. [61] developed a class of temperature-responsive membranes by immobilizing PNIPAAm or P(NIPAAm-*co*-AA) (2 mol% AA) on the surface and inside the pores of hydrophilized PVDF membranes. Doxycycline HCl permeability through the PVDF-*g*-P(NIPAAm-*co*-AA) membranes at 33 °C almost doubled compared to that at 32 °C. The authors demonstrated using *in vitro* studies with mouse skin mounted beneath the membranes that the doxycycline HCl release would be switched on and off at the LCST of PNIPAAm. It was observed that at 32 °C there was no release through the skin after 24 h, while at 33 °C, 30 μg/cm^2 of doxycycline HCl accumulated in the receiving reservoir after passing through the skin. Permeability values for the ‘on state’ were similar to those measured for unmodified PVDF/mouse skin composite. The authors envision that these membranes may find application as transdermal controlled-release systems for treating fever symptoms, where variations in skin temperature may occur.

Surface-initiated ATRP has been used to synthesize temperature-responsive PNIPAAm layers on chemically inert microporous PP membranes [62]. Hydroxyl groups were first introduced on the inert membrane surfaces by the UV-induced graft polymerization of 2-hydroxyl methacrylate. ATRP initiators were then immobilized through the reaction between the tethered hydroxyl groups and 2-bromoisobutyryl bromide, an initiator group for the ATRP of NIPAAm from the membrane surface. Modified membranes showed significant changes in time-dependent water contact angles at different temperatures with the critical temperature observed between 30 and 35 °C. The authors reported that the water flux values of the modified membranes declined with decreasing temperature and the temperature-responsive changes in flux were reversible. They attributed the temperature-responsive changes to the changes in membrane pore size caused by the conformational changes of the grafted PNIPAAm chains.

Li et al. [63] fabricated a series of temperature-responsive gating membranes by grafting PNIPAAm chains in the pores of anodic aluminum oxide (AAO) porous MF membranes using ATRP. They report using ATRP to control the PNIPAAm chain length and chain density. They observed from the diffusional permeability of vitamin B_{12} through the membranes below and above the LCST of PNIPAAm that both the chain length and graft density were key factors for obtaining PNIPAAm-grafted membranes with the desired temperature-responsive gating characteristics, and they suggest that the influence of grafting length was more significant than that of the grafting density. The grafted PNIPAAm chains showed reversible and reproducible temperature-responsive behavior in the AAO membrane pores.

3.2.7. Ion-gating, temperature-responsive membranes

Yamaguchi et al. [64–70] reported on temperature-responsive ion-gating membranes comprising a copolymer of NIPAAm and benzo[18]-crown-6-acrylamide (BCAm) grafted onto the surface of porous PE films by plasma-graft polymerization. The BCAm receptor allows for ion-specific sensing by the copolymer. These membranes spontaneously open and close their pores by means of swelling and shrinking of the grafted copolymer in response to specific ions in solution as shown in Fig. 9. PNIPAAm has a well known LCST; but it was observed that when the BCAm receptor captured a specific ion, the LCST shifted (Fig. 10). As shown in Fig. 11, the temperature-dependent permeability of aqueous Ca^{2+} solution was equivalent to that for pure water. However, the permeability of aqueous Ba^{2+} solution was effectively zero for temperatures well below and above the LCST of pure PNIPAAm. It was noted that Ba^{2+} has a high stability constant when bound by the crown ether; hence, the LCST of the poly(NIPAAm-*co*-BCAm) shifted to a higher temperature. The gel remained swollen at all temperatures studied, and, thus, the pores remained closed and impermeable.

Ito et al. [65] reported that solution flux through molecular recognition ion-gating membranes changed selectively in response to ions Ba^{2+}, Pb^{2+}, Sr^{2+} and K^+ independent of coexisting ions such as Ca^{2+}, Na^+, and Li^+. It was observed that the order of the complexation constants of the crown ether receptor and therefore the order of the width of the LCST shift in the NIPAAm/BCAm copolymer was $Pb^{2+} > Ba^{2+} > Sr^{2+} > K^+ > Li^+ \approx Na^+ \approx Ca^{2+}$. The membranes also changed pore sizes between 5 and 27 nm with Ba^{2+} concentration changes from 0 to 0.014 M, and the pore size changes occurred uniformly in all pores. They also later showed the osmotic pressure control function of these gating membranes (Ito and Yamaguchi [66]). Molecular recognition ion-gating membranes captured Ba^{2+} and generated osmotic pressure in response to Ba^{2+}. A dextran concentration gradient was used to control the critical concentration and the duration time of the osmosis response.

Okajima et al. [68] developed regenerable cell culture membrane systems from porous PE membranes grafted with a copolymer of NIPAAm/BCAm in which the cell culture substrate on the membrane surfaces detected cell death and selectively

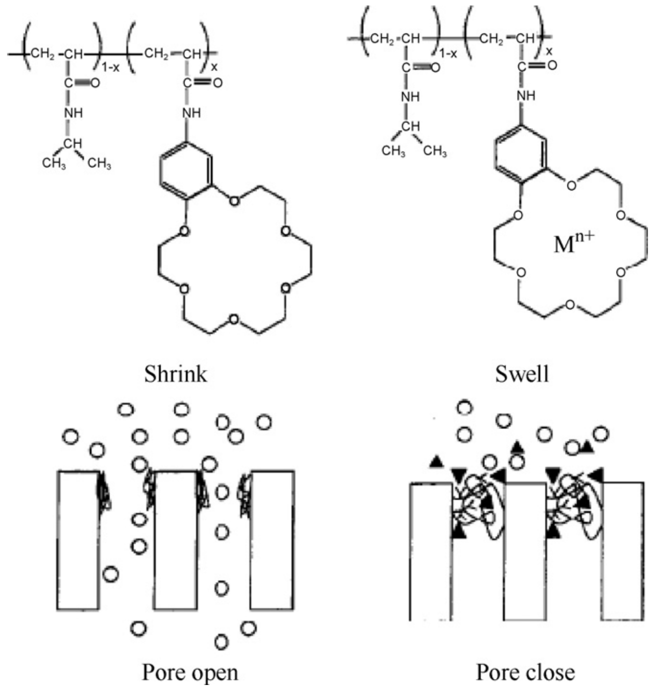

Fig. 9. Schematic representation of a molecular recognition ion-gating membrane prepared from NIPAAm/BCAm copolymer. The membrane senses a specific ion, M^{n+} with its crown ether receptor and closes its pores rapidly.
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released the dead cells. In these systems, BCAm was used as the detector to recognize cellular signals from the dead cells, while NIPAAm was used as the actuator to release the dead cells. NIPAAm/BCAm copolymer responded to potassium ions and changed from hydrophobic to hydrophilic at the culture temperature at 37 °C. Living cells concentrate potassium ions internally and when they die, the potassium ions are released. The polymer surface recognized the ions released by the dead cells, NIPAAm hydrated and the dead cells were detached selectively from the membrane surfaces. Once the dead cells were detached, the polymer returned to the dehydrated state and the surface was repopulated by the proliferation of the surrounding living cells.

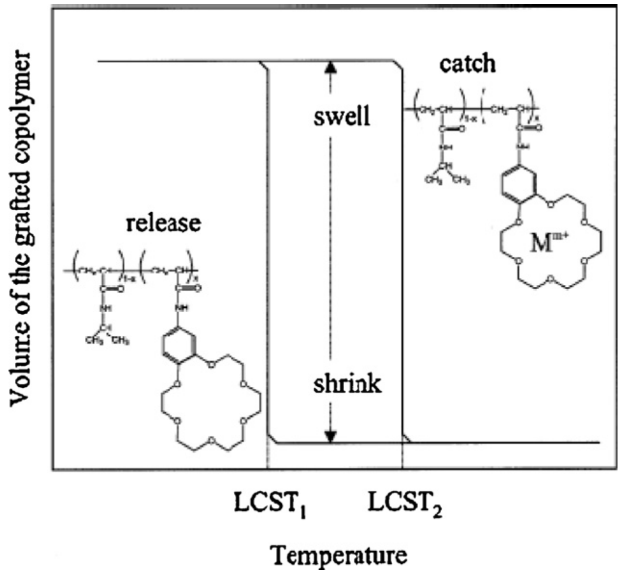

Fig. 10. Illustration of the volume change of the NIPAAm/BCAm copolymer. On capturing a specific ion, the copolymer changes its LCST from $LCST_1$ to $LCST_2$ therefore the copolymer swells and shrinks in response to the presence of M^{m+} between $LCST_1$ and $LCST_2$.
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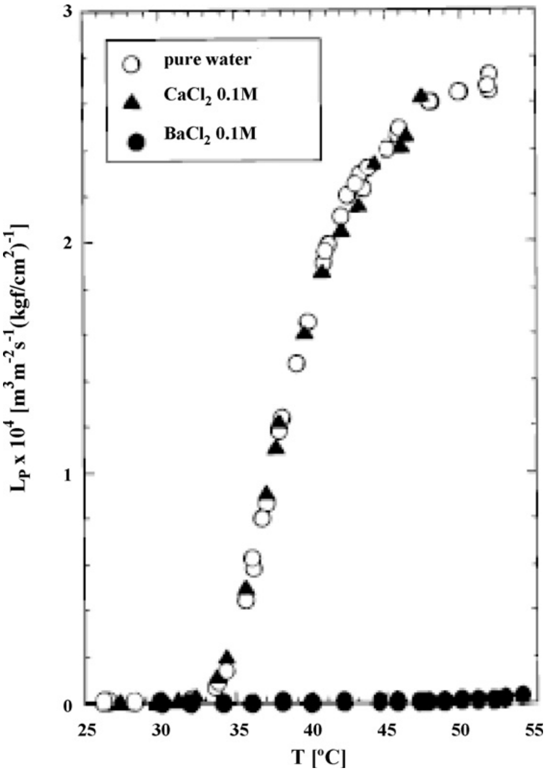

Fig. 11. Temperature dependence of the solution permeability coefficient for water containing different ions through PE-*g*-NIPAAm/BCAm membranes.
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3.3. Summary—temperature-responsive membranes

This section has considered membranes whose properties can be controlled by changes in temperature. Temperature-responsive membranes can be categorized by how responsiveness is introduced to the membrane: incorporation of responsive groups in the bulk or on the surface. Membranes with bulk responsiveness to temperature show decrease in barrier properties above LCST due the fact that the entire polymer layer (membrane structure) collapses into a dense film. On the other hand, porous membranes with surface modifier layers generally show the reverse trend, as their pores open when the polymer layer collapses. Non-porous membranes or porous membranes where the surface modifier layer covers the external membrane surface behave like membranes with bulk responsiveness. The behavior of IPN systems depends on the type of system: non-hydrogel-based IPNs behave more like surface-modified membranes, while IPN hydrogels act more like bulk responsive membranes.

4. pH- and ionic strength-responsive membranes

Numerous research studies have been devoted to the fabrication of membranes with variable barrier properties, specifically membranes whose pore or mesh sizes change controllably in response to changes in pH. These membranes are of interest in applications such as controlled release of chemicals and drugs, flow regulation, sensors, self-cleaning surfaces, size and charge selective filtration

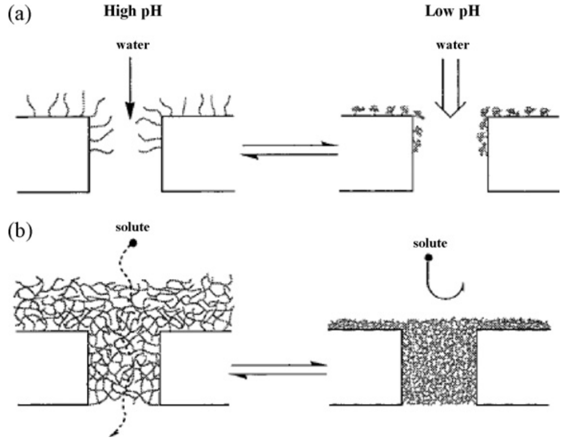

Fig. 12. Permeation mechanism through; (a) PAA-grafted porous filters and (b) PAA-based hydrogels.
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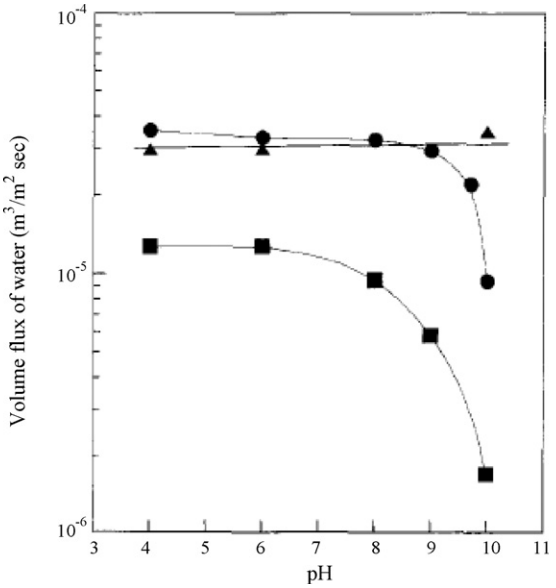

Fig. 13. Water flux at various pHs under applied pressure of 760 mm H_2O through (▲) PAN, (●) P(AN-co-AA) copolymer, and (■) P(AN-co-MAA) copolymer membranes.
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and fractionation. A widely used approach in the fabrication of pH-sensitive membranes is the surface modification of existing membranes with a layer(s) of pH-sensitive polymer chains/brushes or pH-sensitive, cross-linked polymer gels. pH-sensitive membranes also have been fabricated by other methods, including immersion precipitation of graft copolymers with pH-sensitive side chains and PEL layer-by-layer assembly. Generally speaking, pH responsiveness occurs by the structural rearrangement of PELs that occurs upon protonation/deprotonation of ionizable side groups. As an example, Fig. 12 shows the permeation mechanism through (a) a pH-responsive polymer (PAA)-grafted porous filter and (b) a PAA-based hydrogel. Under high pH conditions, deprotonation of PAA reduces the pore size to decrease water permeation in (a) and leads to swelling to enhance solute permeation in (b). Under low pH conditions, protonation of PAA increases the pore size to increase water permeation in (a) and leads to deswelling to reduce solute permeation in (b). This section is devoted to work being done to fabricate these membranes and their applications in various fields. The structure and behavior of the PELs used to impart pH responsiveness also depend on solution ionic strength. Thus, we also consider the effect of solution ionic strength on membrane pore size, surface characteristics, and performance.

4.1. Membrane formation—pH-responsive membranes

Bulk pH-responsive membranes have been prepared by solution casting of copolymers and polymer mixtures, and as interpenetrating polymer networks and micro/nanocomposites.

4.1.1. Copolymer systems

Tamada et al. [71] prepared hydrolyzed pH-sensitive track-etched membranes from copolymer films of *N*-methacryloyl-L-alanine methyl ester and diethyleneglycol-bis-allylcarbonate in two steps. In the first “rigorous” etch step, copolymer films were ion-irradiated in 6 M NaOH solution at 60 °C to obtain virtually cylindrical pores of 4 μm diameter. During the second “soft” etch step, the resulting filter membranes were hydrolyzed with 1 M NaOH solution to create surface layers of varying thicknesses, which were responsive to pH. The pH responsive swelling ratio, $S\,(=(M-M_0)/M_0)$, was obtained from measurements of membrane mass in swollen state (M) and mass in the dry state (M_0). The membranes showed steep increases in their swelling ratios by more than two orders of magnitude in moving from pH 3 to pH 5. The pore diameters of the membranes showed pH response, with pore diameters of 3.7 μm in solutions of pH 3 and completely closed pores at pH 5.

Oak et al. [72] reported on the preparation of pH-sensitive UF membranes from poly(acrylonitrile (AN)-*co*-AA) and poly(AN-*co*-methacrylic acid (MAA)) by phase inversion in dimethylsulfoxide/water medium. Water permeation through the membranes was examined at different pH, as shown in Fig. 13. When the pH of the permeate was varied from acid to alkaline conditions, the flux through the P(AN-*co*-AA) and P(AN-*co*-MAA) membranes decreased slightly until pH 8 and then decreased significantly in the pH 8–10 region. It was also observed that the flux through P(AN-*co*-MAA) membranes began to change gradually at pH 6, while the flux through P(AN-*co*-AA) membranes began to change in the range of pH 9–9.5. The flux through PAN only membranes remained almost constant at 3×10^{-5} m^3/m^2 s. Molecular weight cut-off data obtained by dextran permeation studies at pH 4, 6, and 10 showed that the pore size of the membranes decreased significantly under alkaline conditions.

Neoh and co-workers [73] synthesized a new graft copolymer by modification of ozone pretreated PVDF using thermally induced graft copolymerization with AA in *N*-methyl-2-pyrrolidone (NMP) solution. The PAA-*g*-PVDF copolymers were used to fabricate MF membranes by phase inversion. The authors argue that, in contrast to membrane modification post-casting, molecular modification of PVDF with PAA pre-casting helps to better control the final membrane pore size and pore-size distribution, and it also helps to minimize disparity in graft concentrations/chemical compositions of the membrane surface and the surfaces of the pores. The rate of permeation of aqueous solutions through the membranes increased with decrease in solution pH from 6 to 1, with the most drastic increases observed between pH 2 and 4. This reversible change in permeation rate was attributed to the changes in the conformation of AA polymer chains on the surface of the membrane. At high pH, the chains adopt a highly extended conformation arising from strong interaction with water and electrostatic repulsion among the negatively charged side groups. At low pH, the chains have a collapsed conformation; hence, the steric obstruction of the membrane pores is reduced substantially. Therefore, PAA-*g*-PVDF copolymer can be used to fabricate MF membranes with well-controlled pore sizes, uniform surface composition, and pH-sensitive properties.

Mayes and co-workers [74] examined membranes with pH-responsive characteristics fabricated in a single step by self-organizing blends of PVDF and amphiphilic comb copolymers having a PVDF backbone and PMAA side chains using immersion precipitation. The PVDF-*g*-PMAA membranes exhibited rapid and reversible pH-dependent flux variations of over an order of magnitude as the feed solution pH was varied between 2 and 8. AFM measurements confirmed that the flux variations obtained were due to pH-sensitive conformational changes of the surface-localized PMAA side chains of the graft copolymer.

Ying et al. [75] reported preparing pH- and temperature-responsive MF membranes from blends of PAA-*g*-PVDF copolymer and PNIPAAm in NMP solution by phase inversion in water at 25 °C. The blend membranes exhibited strong and reversible pH- and temperature-dependent permeability to aqueous solutions, with the most drastic changes in permeability observed at permeate pH between 2 and 4 and temperature around 32 °C, the LCST of PNIPAAm.

Zhai et al. [76] reported on the synthesis and characterization of PVDF with 2-vinylpyridine (2VP) and 4-vinylpyridine (4VP) polymer side chains from the thermally initiated graft polymerization of 2VP and 4VP from PVDF that had been pre-activated by ozone treatment. MF membranes were fabricated from the P2VP-*g*-PVDF and P4VP-*g*-PVDF copolymers with different degrees of grafting by phase inversion in water at 25 °C. The flux of aqueous solutions through the P2VP-*g*-PVDF MF membranes exhibited strong dependence on solution pH from pH 1 to 6 arising from protonation/deprotonation of the pyridine groups of the grafted polymer chains. Being sterically less hindered from protonation, P4VP-*g*-PVDF MF membranes were more sensitive to changes in permeate pH than the P2VP-*g*-PVDF MF membranes.

Liu and Lu [77] synthesized PS-*graft*-poly(*tert*-butyl acrylate) (PS-*g*-PtBA) membranes by immersion of microscope slides into solutions of PS-*g*-PtBA in NMP and propionic acid (PA). PS-*g*-PAA membranes were then prepared by soaking the PS-*g*-PtBA membranes in trifluoroacetic and formic acid to hydrolyze the *tert*-butyl acrylate groups of PtBA. PS-*graft*-poly(sodium acrylate) (PS-*g*-PSA) membranes were obtained by soaking the PS-*g*-PAA membranes in NaOH solution. The water flux through PS-*g*-PtBA membranes was independent of pH because the membrane contained no pH-responsive PELs. The water flux was significantly higher in the PS-*g*-PAA membranes (lower pH) than in the PS-*g*-PSA membranes (higher pH) because of the conformational changes associated with PAA chains described earlier.

Minko and co-workers [78–80] reported on a method for fabricating responsive polymer gel membranes. They prepared thin-film membranes with two-dimensionally arranged submicron pores whose size could be varied by changing the pH of aqueous medium. Solutions containing P2VP that had been partially quaternized with 1,4-diiodobutane (qP2VP) and additional unreacted 1,4-diodobutane were used for the formation and deposition of the membranes on flat smooth surfaces (ideally silicon wafers). P2VP is a weak cation PEL; its cross-linked gel demonstrates pH-dependent swelling properties. The membrane solution was spin-coated onto a solid substrate in a controlled humidity environment since the presence of water vapor was found to be a necessary condition for pore formation. This method yielded membranes with regular pore structures. Reversible contraction of the membrane pores was observed when the membranes were subjected to aqueous acid solutions, and this behavior was attributed to the swelling of the P2VP gel. It was reported that these membranes changed their pore sizes by the swelling and shrinking of the entire membrane volume. The swelling and shrinking of the entire membrane volume allows regulation of pore size over a broad range, from completely closed pores to large open pores (pore diameter of 0.3 μm). Thus, the same membrane could be used for filtration of both small and large molecules provided that the pH conditions used for filtration are compatible with the filtration media. These thin-film membranes could be transferred easily onto the surfaces of porous or non-porous commercial supports to produce composite membranes with pH-controllable barrier properties.

Gopishetty et al. [81] reported preparing multi-responsive membranes from biopolymers (alginates) suitable for biomedical applications. These membranes have a wide range of properties and functions that mimic natural skin. Most of the membrane functions could be tuned by proper selection of pH, especially in the range of interest for biological systems. The membranes were biocompatible and biodegradable. Membranes with thicknesses between 100 and 200 nm were prepared by salt-induced phase separation of sodium alginate and gelatin and cross-linked by divalent calcium cations. This synthesis procedure allowed for regulation of the average effective membrane pore sizes from 200 nm to 1 μm. Sodium alginate is a naturally derived polysaccharide consisting of (1–4) linked β-D-mannuronic acid units and α-L-guluronic acid units. It forms a gel in the presence of divalent cations such as calcium. The membranes were prepared by spin-coating or dip-casting on smooth flat surfaces such as silicon wafers or glass slides. The membranes were then transferred and chemically attached onto porous or non-porous supports. The bio-PEL membranes swelled in response to external pH changes, leading to pore shrinkage and changes in the membrane barrier properties. The reversible swelling allowed for the pH-dependent pore size regulation from completely closed pores to fully opened pores. The pores were fully opened at pH > 5 and completely closed at pH < 4. The pore sizes also were dependent on the ionic strength of solutions; an increase in ionic strength screened electrostatic interactions and decreased the degree of swelling, thus opening up the pores.

Neoh and co-workers [82] reported on the controlled grafting of poly[2-(N,N-dimethylamino)ethyl methacrylate] (PDMAEMA) side chains from PVDF by VDF-initiated ATRP of DMAEMA. The PVDF-*g*-PDMAEMA copolymers were then cast into pH- and temperature-responsive MF membranes by phase inversion in deionized water. The permeability of aqueous solutions through the membranes exhibited reversible dependence on both temperature and pH as shown in Fig. 14. The permeability increased with increase in pH from 3 to 11 and in permeate temperature from 30 to 70 °C. These changes were attributed to the changes in conformation of the grafted PDMAEMA brushes on the membranes. At pH below 7, PDMAEMA chains adopt a more extended conformation due to protonation of amino groups resulting in a reduction in the effective pore size and thus the permeation rate. At high pH, PDMAEMA chains are more compact (collapsed conformation), resulting in opening of the pores and thus an increased permeation rate. At permeate temperatures below the LCST of PDMAEMA (50 °C), the polymer chains are hydrophilic and have an extended conformation hence leading to a reduction in the effective pore size. While at temperatures above the LCST, the chains are less hydrophilic, resulting in opening of the membrane pores and an increased permeation rate.

4.1.2. Interpenetrating network systems

Gudeman and Peppas [83,84] prepared pH-sensitive membranes with varying degrees of crosslinking from IPNs of PVA and PAA. The membranes were characterized and tested for permeation of a wide range of solutes. Changes in pH from 3 to 6 increased the membrane mass swelling ratio, accompanied by up to 86% increases in the mesh sizes. The swelling ratio also increased with a decrease in the ionic strength of the swelling medium. Membranes with loosely crosslinked structures were observed to swell and de-swell more quickly than densely crosslinked membranes.

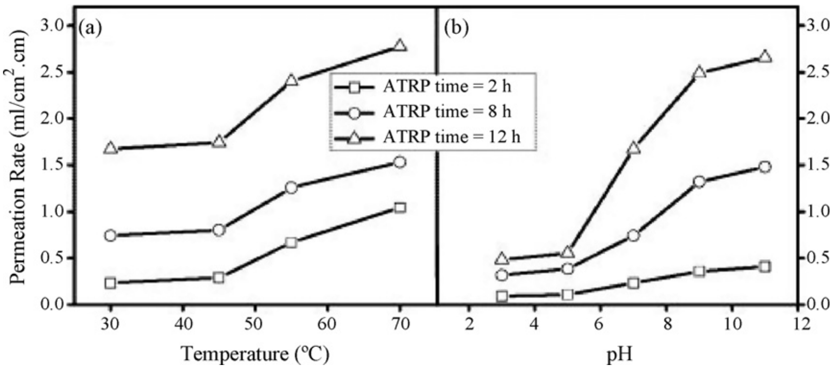


Fig. 14. Temperature and pH dependent permeability of aqueous solutions of (a) pH 7 and (b) 30 °C through PVDF-*g*-PDMAEMA MF membranes for 2, 8, and 12 h of ATRP. Reproduced with permission from [82]; Copyright (2008) American Chemical Society.

Permeation studies demonstrated that for ionizable solutes such as L-tryptophan and urea, the diffusion coefficient was smaller at pH 3 than at 6. Transport of neutral molecules depended more on the solute size.

Park et al. [85] describe organic–inorganic IPN membranes prepared using tetraorthosilicate (TEOS) as the inorganic material and chitosan as an organic compound. Chitosan ((1 → 4)-2-amino-2-deoxy-β-D-glucan) is charged positively and swells in acidic medium and shrinks in basic solution because of ionization of its amino groups. When incorporated in the TEOS IPN, chitosan imparts the membranes with pH sensitivity. Equilibrium swelling studies showed that the membranes swelled at pH 2.5 and shrunk at pH 7.5 regardless of TEOS–chitosan ratio. The swelling behavior was completely reversible. Also, drug permeability within the membranes changed immediately as environmental pH conditions were altered. Permeation studies showed that an increase in pH from 2.5 to 7.5 increased the rate of drug permeation regardless of TEOS–chitosan ratio, while decreases in pH resulted in low permeation rates (Fig. 15). These membranes have potential use as drug carriers and as a bioseparation platform.

Turner and Cheng [86] studied the pH responsiveness of PDMS/PMAA IPN membranes. PMDS/PMAA IPNs were prepared from 70:30 mass ratios on a dry basis using a monomer immersion technique. It was observed that the membranes retained the pH responsiveness of PMAA. Equilibrium hydration (mass fraction of water in the swollen membranes) decreased significantly with decreasing pH. Equilibrium hydration was determined gravimetrically to be between 0.77 and 0.9 at pH 7 and between 0.42 and 0.5 at pH 3, which corresponds to average hydration values of 0.93 and 0.74 of the PMAA component, respectively. The pH-dependent hydration of the PMAA regions resulted in pH-dependent morphologies in the IPN membranes, and the fraction of hydrophilic solute-accessible regions decreased as pH decreased. Vitamin B_{12} diffusivity through the IPN membranes was found to be 1.7×10^{-7} cm^2/s at pH 7 and below detection at pH 3, consistent with the observed pH dependent morphology.

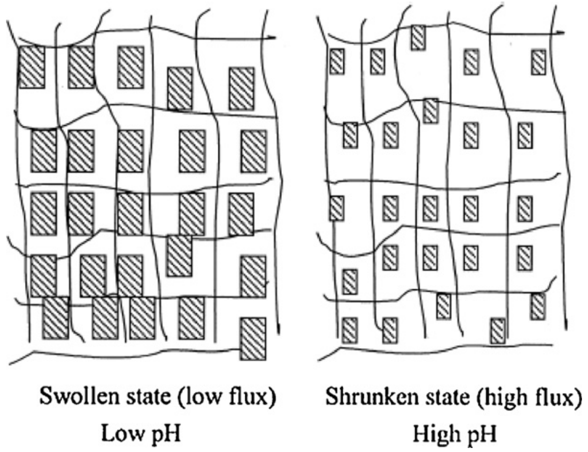


Fig. 15. pH responsive mechanism of TEOS–chitosan IPN hybrid membranes. Reproduced with permission from [85]; Copyright (2001) Elsevier.

4.1.3. *Micro/nanocomposites*

Turner and Cheng [87] developed composite-heterogeneous PEL gel (composite-PG) membranes consisting of PMAA gel particles dispersed within mechanically stronger, hydrophobic, elastic poly(dimethyl siloxane) (PDMS) networks and evaluated them as pH-responsive membranes. The PMAA gel particles remained responsive within the membranes allowing for external pH control of the membrane hydration and, hence, local diffusivity. The membranes with 17% and 22% PMAA gel particles showed little change in permeability in response to pH change, despite increased hydration of the gel particles in these membranes with increasing pH. This result was attributed to the low gel mole fraction of these membranes resulting in little or no particle connectivity despite increases in particle hydration. However, membranes with 28% and 33% PMAA gel particle loading showed 10-fold and 40-fold increases in permeability for caffeine and vitamin B_{12}, respectively, when the pH was changed from 3 to 7.

Zhang and Wu [88] investigated the temperature- and pH-responsive permeability of various peptides, proteins, and vitamin B_{12} through composite membranes containing dispersed poly(NIPAAm-*co*-MAA) nanoparticles. The polymeric membranes were developed by dispersing the nanoparticles in a hydrophobic polymer (ethylcellulose). Permeability of the solutes across the membranes increased with increasing temperature but decreased with increasing pH. The temperature and pH sensitivity of the composite membranes was determined by the composition of the nanoparticles. Nanoparticles with higher percentages of NIPAAm imparted greater temperature sensitivity, while those with higher percentages of MAA imparted greater pH sensitivity to the membranes. Therefore, the membranes could be tailored for a specific application by selecting appropriate nanoparticle composition.

4.2. *Membrane modification—pH-responsive membranes*

4.2.1. *Grafting to modification*

Ito et al. [89] designed nanometer pore-size, pH-responsive membranes by self-assembly of ionizable polypeptide brushes on gold-coated, commercial track-etched porous PC membranes. The membranes were coated with platinum and then with gold and were thereafter immersed in an aqueous solution of lyophilized poly(L-glutamic acid) (PLGA) for 24 h. Water permeation through the membranes was investigated, and it was observed that the water permeation through the unmodified membranes was independent of pH, while that through the modified membranes was dependent on pH, with high permeation at low pH and low permeation at near neutral pH. At low pH, PLGA chains are protonated and folded forming α-helical structures that lie on the surface. At high pH, they are deprotonated forming extended random structures that extend into the solution. These conformational changes affect the porosity of the membrane leading to the observed pH-dependent water permeability. The observed inflection point of the water permeation rate was at pH 4.5–5, which is the same as the isoelectric point of PLGA (4.58).

Zhang and Ito [90] self-assembled chains of PAA conjugated with cysteamines (PAA-SH) on gold-coated nanoporous membranes to produce membranes whose water permeability was pH controlled. Porous PC membranes with an average pore diameter of 200 nm were coated with gold up to a thickness of 50 nm and then exposed to an aqueous solution of PAA-SH at different pH values and ionic strength concentrations for 24 h. The modified membranes were rinsed with water until the pH of the rinse liquid became neutral. Transport through the modified membranes was investigated. The rate of water transport through the bare membrane was independent of pH; whereas, the transport through the modified membranes could be regulated reversibly by variation in pH and ionic strength. High permeability was observed at low pH, low permeability was observed at neutral pH, and an increase in ionic strength increased the permeability at high pH. At high pH, permeability was strongly dependent on ionic strength but the effect was limited at low pH. At high ionic strength, water permeability became less sensitive to changes in pH and this was attributed to the high ionic strength shielding deprotonated polymer segments from electrostatic repulsion. Filtration of solutions of ionic (oligodeoxyribonucleotide) and non-ionic PEG polymers through the modified membranes showed that pH-responsive permeability depended on the molecular weight of the solutes.

Hollman and Bhattacharyya [91] investigated the influence of covalently attached PLGA on the performance characteristics of microporous cellulosic supports. They determined the effect of polypeptide on water transport through the functionalized supports. The helix–coil transitions of the PLGA affected the permeability in a reversible fashion upon variations in solution pH. Synthesis of the functionalized cellulose membranes involved two steps, aldehyde derivatization followed by PLGA attachment. PLGA attachment was carried out by permeating aqueous PLGA solutions through the cellulosic supports at pH 9.2–9.8. Functionalization involved the reaction between the terminal amine group present on the PLGA with the aldehyde group present in the cellulosic support. The functionalized membranes displayed marked decreases in water flux at high pH and increased water fluxes at low pH due to the extended random-coil formation and helix formation of the PLGA chains, respectively.

Nakayama et al. [92] prepared stimuli-responsive nicotine release biomembranes by applying coating and radiation curing. Ng et al. [93] employed the same technique to synthesize pH-responsive membranes using PHEMA membranes coated with a single pH-sensitive coating, PAA, for the controlled release of model drugs with a wide range of molar masses. They later used variable pH-sensitive polyampholyte coatings comprising copolymers of AA/2-(diethylamino)ethyl methacrylate (DEAEMA) with varying monomeric compositions to develop photo-cured, pH-responsive, drug-incorporated membranes [94].

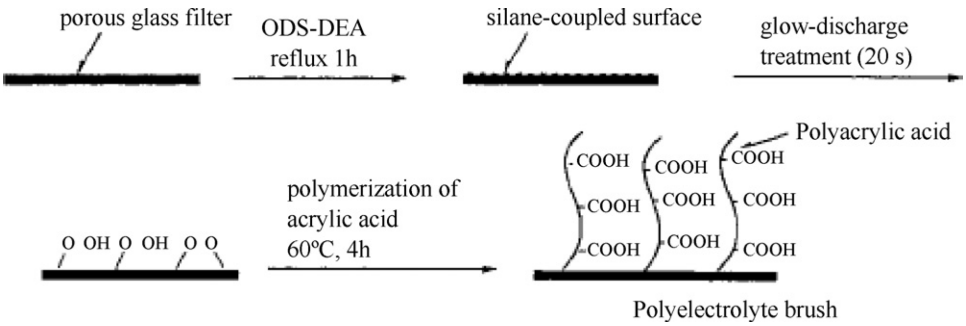
4.2.2. Grafting from modification

Imanishi and co-workers [95] investigated the pH-dependent changes of the pore sizes of PAA grafted, straight-pore PC membranes. Peroxide groups were generated on the surface of the PC membranes by glow discharge, and the membranes were then heated in aqueous solutions of AA to initiate the graft polymerization. Water permeability of the modified membranes increased sharply in pH regions below 4, representing an expansion of pores. However, very high grafting densities or very long grafted chains restricted the mobility of the PAA chains and the pore size became pH-independent.

Ito et al. [96] developed a membrane device that controlled the rate of water permeation according to pH and ionic strength by thermally initiated surface grafting of vinyl, carboxylic acid containing monomers from a straight-pore membrane. AA, MAA, and ethacrylic acid (EAA) were used as the functional monomers. The rate of water permeation through the modified membranes changed reversibly with changes in solution pH. The pH response of the water permeability also was controlled by changing the grafting density and the polymer layer thickness. Membranes modified with poly(carboxylic acid) of a high degree of polymerization grafted in low densities produced the most sensitive pH response. The most drastic change of water permeability occurred at pH 3.0, 4.0, and 6.8 for membranes modified with PAA, PMAA and PEAA, respectively. These pH differences reflect different pK_a values of the grafted polymer chains: PAA, 4.8; PMAA, 6.2; PEAA, 7.2. Water permeation also was affected by the ionic strength of the aqueous solution.

Mika et al. [97] successfully synthesized composite membranes made of MF substrates and pore-filling PELs by UV-induced grafting of 4VP from PE and PP MF membranes. They showed by simple changes in pH that the barrier properties of these membranes changed reversibly from that characteristic of MF to that characteristic of reverse osmosis. At low pH values, the pyridine nitrogen atoms in P4VP are protonated to form positively charged pyridinium groups. The charged polymer has an extended chain conformation due to electrostatic repulsion, which effectively fills the pores. The flux through the membranes decreased by three to four orders of magnitude in moving from high pH to low pH. This very large change in flux occurred over a very narrow range of pH of the contacting solution, and the changes were found to be reversible.

Ulbricht and co-workers have used photoinitiated graft polymerization to develop different types of stimuli-responsive membranes. Ulbricht [98] reported using photoinitiated graft polymerization to modify commercial nylon (Ny) and PP MF membranes with PAA. A photoinitiator, BP was coated onto the membranes by dipping them in a solution of BP in methanol. Polymerization from the initiator sites was done by soaking the membranes in AA solutions and irradiating with UV light under a nitrogen atmosphere. pH-dependent swelling (at $\mathrm{pH} > \mathrm{p}K_{\mathrm{a,\,PAA}}$) or shrinking (at $\mathrm{pH} < \mathrm{p}K_{\mathrm{a,\,PAA}}$) of the grafted PAA resulted in variable membrane thickness and permeability. Ulbricht and Yang [99] developed pH-responsive membranes by photoinitiated, surface-selective graft copolymerization of PAA from PP membranes coated with photoinitiator (BP). Coating of BP onto the membranes was carried using either an adsorption method or an entrapment method, which involved pre-swelling the PP membranes in heptane. Copolymerizations of AA with AAm and the cross-linker monomer methylene bisacrylamide (MBAA) also were carried out. Compared to the BP adsorption method, the BP entrapping method yielded lower grafting density with longer PAA chains at the same degree of modification, and this was attributed to the somewhat lower amounts of immobilized BP and fewer side reactions via non-selective photoinitiated cross-linking of grafted chains by dissolved BP. The PAA-*co*-AAm brush layers showed larger degrees of swelling/de-swelling as a function of pH change compared to the PAA brush layers. Geismann and Ulbricht [100] functionalized PET track-etched membranes with PAA. The membranes were first carboxylated by immersing them in a reaction mixture of potas-



Scheme 1. Surface modification of a porous glass filter by grafting PEL (PAA) polymer brushes to create a pH-dependent system.
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sium permanganate and sulfuric acid at room temperature and treating them with hydrochloric acid. The carboxylated membranes were aminated by immersing them in solutions of diisopropylcarbodiimide and N-hydroxybenzotriazole at room temperature and then subsequently reacting with tetraethylenepentamine. Initiator functionalization was done by immersing the membranes in solutions of charged BP derivatives. Finally, PAA was grafted from the initiator sites by photopolymerization.

Park et al. [101] reported grafting PEL brushes of PAA from porous glass filters in order to construct new solvent-tolerant, pH-dependent systems for control of liquid permeation. The porous glass filter was treated with octadecyldimethyl(*N*,*N*-diethyl amino)silane and subjected to glow-discharge treatment to facilitate thermally initiated graft polymerization of the PAA as shown in Scheme 1. Water permeation through a glass filter treated only by glow-discharge was independent of pH, while water permeation through glass filters modified with grafted PAA was controlled reversibly by pH change. The permeation rate was high under low pH conditions and low under high pH conditions. At low pH, protonated PAA chains collapse, thereby opening the pores of the filters. At high pH, negatively charged PAA chains extend to fill in the pores. The permeability change was rapid, changing within 2 min of pH change. This rapid response was explained by direct contact of each PAA brush chain with water. The permeation of a water/acetone mixture through the PAA-modified glass filter was also pH dependent; although, in moving from water to the water/acetone mixture, the inflection point of permeation shifted to a higher pH, which was attributed to a decrease in the apparent acid dissociation constant resulting from a decrease in the dielectric constant of the solvent.

Ito et al. [102,103] used AFM to study the effect of grafting a pH-sensitive polymer, PMAA, on porous membranes in aqueous solutions. Peroxide groups were generated on the surfaces of porous PC membranes by glow discharge, and the membranes were then heated in an aqueous solution of MAA to initiate graft polymerization. AFM images showed that the pore sizes of the modified membranes differed depending on the pH. At pH 2 the grafted chains were protonated and contracted, opening the pores, while at pH 7 the chains were fully solvated and extended, thus reducing the average effective pore size of the membrane. The rate of water permeation through the modified membranes was less than that of the unmodified membranes because of reduced pore sizes due to pore filling by the grafted polymer chains. Water permeation through the modified membranes also reflected the effect pH on the pore sizes; modified membranes had high water permeability at low pH and low permeability at neutral pH.

Ito et al. [104] graft polymerized benzyl L-glutamate *N*-carboxyanhydride onto porous poly(tetrafluoroethylene) membranes, and the modified membranes were used to study the effect of pH and ionic strength on permeation rate. The membranes were first treated by glow-discharge in the presence of ammonia in order to produce amino groups on the surface to facilitate graft polymerization. After thermal graft polymerization, the poly(γ-benzyl L-glutamate) (PBLG) chains were hydrolyzed to yield PLGA chains. Fig. 16 shows the pH dependence of water permeation for aminated, PBLG-grafted, and PLGA-grafted membranes. The permeation rate of PBLG-grafted membranes was significantly lower than aminated membranes and both were independent of pH. The permeation rate of PLGA-grafted membranes was strongly pH dependent, with the permeation rate nearly equal to that of PBLG-grafted membranes at low pH and dramatically lower at pH values above 5.5. Permeation rates were reversible. The grafting density also affected the pH-dependent water permeation. The difference in permeation rates between low and high pH regions decreasing with increasing grafting density. At high pH, the permeation rate was nearly independent of grafting density; however, at low pH, membranes with lower grafting densities showed higher permeation rates. At high pH, permeability was strongly dependent on ionic strength; however, the effect was minimal at low pH. As the ionic strength was increased, the permeability became less sensitive to changes in pH. This result was explained by the fact that at high pH, randomly coiled PLG chains extended to close the pores; while at low pH, the chains formed collapsed structures, thus opening the pores.

Iwata et al. [105] grafted PAA on PC membranes and used AFM to show that the surface topography of the modified membranes in solvents varied with pH. Polymer chains were grafted covalently from peroxide initiator sites on the membrane surfaces introduced by exposure to low temperature plasma. From AFM images of the modified membranes, pores were observed clearly at pH 3.5 since

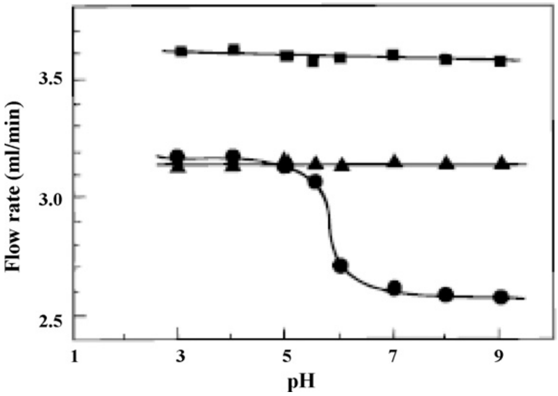

Fig. 16. pH responsive water permeation through (■) aminated, (▲) PBLG-grafted, and (●) PLG-grafted porous membranes.
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the PAA chains collapsed onto the membrane surfaces at low pH. The images changed drastically at pH near the pK_a of PAA (pH 5.2), with the pores being fully covered with solvated PAA chains, indicating conformational changes in the grafted chains. Permeation experiments also showed that the filtration rates were nearly independent of pH in the range 5–7, but, at pH near the pK_a of PAA, the filtration rate increased sharply with decreasing pH. The authors discovered that at high grafting densities and high degrees of polymerization, mobility of the PAA chains was restricted, and the effective pore sizes became pH-independent. They also reported in subsequent work [106] that the filtration rate through porous PC membranes modified with PAA was 28 times higher at pH 2.4 than at pH 5.4. AFM images also showed that the PAA grafted layer thickness was several tens of nanometers at pH 2.6 and increased to 20–430 nm at pH 7.6 depending on the grafting density. This result was again attributed to the grafted chains collapsing onto the pore walls at acidic pH values, and chain hydration and swelling at neutral and alkaline pH values.

Peng and Cheng [107] studied the pH-responsiveness of PE-*g*-PMAA membranes. Graft yields were calculated as $(W_g - W_u)/W_u$ where W_u and W_g were the dry weights of the ungrafted and grafted membranes, respectively. Membranes with a wide range of graft yields were prepared by photo-grafting PMAA on porous PE membranes by UV irradiation. The pH-dependent permeability of the modified membranes was studied as a function of the graft yield. Two types of permeability response were observed depending on the graft yield. At low graft yields, the membranes showed porous membrane responsive behavior, that is, the collapse of the grafted polymer would leave the membrane pores open compared with expansion of the grafted polymer. At high graft yields, the membranes became hydrogel-like, showing lower permeability in the collapsed state. Generally, it was observed that membrane permeability changed reversibly in response to solution pH alternation between pH 2 and pH 7.4.

Wang et al. [108] prepared pH-responsive membranes by grafting AA from porous PP membranes using supercritical (SC) CO_2 as a solvent. The monomer and the initiator, benzyl peroxide, were impregnated into the PP substrate with the aid of SC CO_2 and PAA chains were then grafted from the microporous PP substrate by thermal initiation. The water permeation of the unmodified membrane was nearly independent of pH, while the water permeation of the modified membranes decreased dramatically as the pH was increased from 3 to 6 because of conformation changes in PAA.

Yang and Yang [109] reported on the synthesis of full/open pH-valves based on pore covering of PET track-etched membranes with grafted P4VP. Grafting degree (DG) was calculated as $100(m - m_0)/m_0$, where m_0 and m were the masses of the nascent and grafted membranes, respectively. DG was adjusted by changing the irradiation time during photografting. The membranes had thin grafted layers that were confined to the membrane external surfaces, rather than inside the pores. Solution fluxes of the modified membranes were close to zero in acidic conditions (closed state) and were restored to those of the unmodified membranes in neutral conditions (open state). Fluxes in acidic conditions (closed) greatly decreased with DG with even a low DG of 0.3% leading to sharp declines in fluxes. Yet fluxes in neutral conditions (open) remained nearly the same as those of the blank membranes; even by increasing the DG to 2.5%, 90% of the blank membrane flux was still retained. Therefore, a very low DG was enough to make the membranes exhibit the valve effect. The ratio of the fluxes in neutral to acidic conditions increased from 20 to 150 when the DG increased from 0.3% to 2.5%.

Wang et al. [110] reported on the use of redox graft pore-filling polymerization to prepare pH-responsive phenolphthalein poly(ether sulfone) (PES-C) membranes. The porous membranes were prepared from PES-C dissolved in DMSO using the classic phase inversion method. Then MAA was grafted from the membranes by redox-graft pore filling polymerization. ATR-FTIR spectra confirmed that PMAA was grafted from the PES-C porous membranes. In hydraulic and diffusional permeability experiments using vitamin B_{12} and KCl as solutes, the graft modified PES-C membranes showed marked, rapid and reversible pH-dependent variations.

Hu and Dickson [111] developed PVDF-PAA pore-filled pH-sensitive membranes by *in situ* thermally initiated cross-linking polymerization of AA inside hydrophobic PVDF microporous membranes. The incorporation of the pH-sensitive PAA changed the membrane performance significantly. The neutral PVDF membranes are converted to charged membranes and their ion-exchange capacity increases with mass gain. The membranes exhibited rapid and reversible responses in their fluxes as the permeation pH was switched between 2.5 and 7.4. Between pH 3.5 and 5.5, the membranes demonstrated a pH-valve as the carboxyl groups change from neutral to negatively charged, with the corresponding changes in chain configuration.

4.3. *Ionic strength-responsive membranes*

Neoh and co-workers [112] used thermally induced graft copolymerization to graft a zwitterionic monomer, N,N′-dimethyl-(methylmetharcyloyl ethyl) ammonium propanesulfonate (DMAPS) on ozone-treated PVDF in a mixed solvent of NMP and DMSO. MF membranes were prepared from DMSO solutions of the copolymers by phase inversion in aqueous media of different ionic strength and temperature. Due to the interaction of the grafted zwitterionic DMAPS chains with the aqueous electrolyte during phase inversion, the mean pore size of the membranes increased with increasing ionic strength of the casting bath. Due to the anti-PEL effect, the permeability of aqueous solutions through the membranes exhibited a dependence on ionic strength, and the flow rate was observed to decrease as the ionic strength of the permeate increased.

Singh et al. [113] demonstrated a method of preparing high capacity membrane adsorbers by growing surface-tethered, charged polymer nanolayers from the surfaces of regenerated cellulose membranes. Surface-initiated ATRP was used to graft cation-exchanger, PAA. Membrane permeabilities were measured using two different buffers, buffer A (a phosphate buffer) and buffer B (a high salt concentration buffer consisting of 1 M NaCl in phosphate buffer). Overall, the permeabilities decreased with increasing ATRP modification time. The PAA-modified membranes showed a strong salt effect; permeabilities were markedly higher for buffer B. This result was attributed to the fact that at this high added salt concentration, the charged polymer layer thickness is lower than it would be in a solution of lower ionic strength due to screening of the like charges on the chains, which strongly reduces Coulombic repulsion between the individual chain segments.

Shi et al. [114] synthesized a zwitterionic polymer-modified PES, bearing quaternized amine groups and sulfonate groups. The polymer was cast into flat sheet UF membranes by phase inversion in pure water or aqueous NaCl solutions in the coagulation bath. The membranes exhibited distinct ionic strength-dependent flux due to the inherent zwitterionic characteristics. The permeate flux of the membranes varied dramatically by changing the ionic strength of the coagulation bath.

Ghosh and co-workers [115] developed biocompatible environment-responsive membranes by modifying commercial microporous PVDF membrane supports with a salt-responsive hydrogel composed of poly-N-vinyl-lactams and bisacrylamide cross-linker via *in situ* thermal polymerization. At low NaCl concentrations, the polymer chains were fully extended, hence closing the membrane pores and leading to low permeability and low

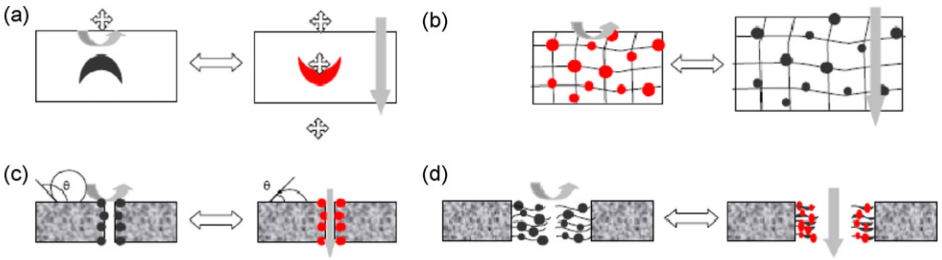

Fig. 17. Photo-stimulated reversible changes of barrier properties of membranes with photo-chromic units: (a) switching between non-binding and binding state for non-porous carrier membrane, (b) switching mesh-size for non-porous polymer hydrogel, (c) switching wettability for micro- or meso-porous polymeric membrane, (d) switching grafted polymer chain conformation for macroporous polymeric membrane.
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protein transmission through the membranes. While at high NaCl concentrations, the polymer chains were collapsed, leading to fully open pores and thus higher permeability and higher protein transmission through the membranes.

4.4. Summary—pH- and ionic strength-responsive membranes

In this section, we examined work being done to fabricate membranes that respond to pH and their applications in various fields. Generally PELs are used to impart pH responsiveness due to protonation/deprotonation of ionizable side groups. PEL behavior also depends on solution ionic strength, as illustrated by examples showing the effect of solution ionic strength on membrane pore size, surface characteristics, and performance. Membrane responsiveness due to changes in pH depends on how PELs are incorporated. For porous membranes with PELs grafted from pore surfaces, adjusting pH to ionize the polymer reduces the pore size due to swelling of the modifier layer. For PEL hydrogels, adjusting the pH to ionize the polymer leads to swelling, which enhances solute permeation.

5. Photo-responsive membranes

In this section, we consider work done to develop membranes that respond to photo-irradiation. Focus is given to the use of photo-stimulation to induce reversible changes in membrane barrier properties and functions. Reversible changes in physicochemical properties due to photo-irradiation generally are caused by isomerization of photo-chromic units in the polymer used to prepare the membrane or its surface coating. Structural changes in the photo-chromic groups lead to changes in the macroscopic properties of porous and non-porous membranes, including wettability, charge, and mass transport as shown in Fig. 17.

5.1. Photo-chromism

Photo-stimulation of membrane barrier properties is attractive because photo-excitation can be imparted in a highly selective and rapid way without causing any additional changes to the system chemical potential [116]. Of course, as an external stimulus, photo-irradiation does require that the membrane housing is optically transparent.

The interest in creating photo-responsive membranes has led to the incorporation of photo-chromic molecules in membrane polymer formulations. Fig. 18 shows photo-chromic units (azobenzene, spiropyran, diarylethene, viologen) that have been investigated most often in the development of photo-responsive membranes. Photo-chromic molecules can, after absorption of light, undergo reversible photo-isomerization reactions. Reversible photo-isomerization (photo-chromism) switches a chromophoric moiety between two or more states. Associated molecular changes include group polarity, charge, color and size. Such molecular changes lead to observed responses, i.e., changes in macroscopic properties.

Membranes containing photo-chromic units undergo reversible photo-stimulated changes in their barrier functions (Fig. 17). Carrier membranes can be switched reversibly from a non-binding to a binding state for a given chemical functionality by alternating photo-irradiation. Reversible changes in non-porous polymer hydrogel membranes occur as the mesh size of the hydrogel is switched by the photo-irradiation. Microporous membranes (pore diameter, $d_p \leq 2$ nm) with photo-chromic units undergo changes in surface wettability by switching photo-irradiation. Macroporous membranes ($d_p = 50$–500 nm) undergo reversible changes in their properties, for example permeability, due to switching of grafted polymer chain conformation in the membrane pores caused by different photo-irradiation. These and other examples are highlighted below. As there are fewer examples of photo-responsive membranes, we elect to highlight some of the early work in addition to recent examples.

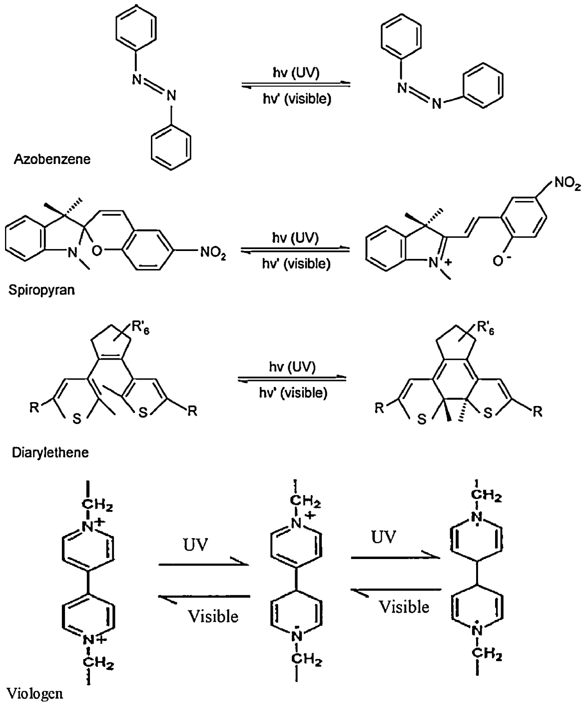

Fig. 18. Four groups of photo-chromic polymer conjugates and their reversible photo-reactions.
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5.2. Membrane formation—photo-responsive membranes

By preparing membranes from monomers or polymers containing photo-chromic groups, various groups have shown that photo-irradiation can be used to reversibly switch the barrier properties of these membranes, and this concept has been utilized to tailor the membranes for certain applications.

Anzai et al. [117] reported that ion permeabilities through poly(vinyl chloride) (PVC) membranes containing azobenzene-modified crown ethers could be facilitated by UV irradiation. They investigated the photo-controlled permeation of alkali cations through PVC/crown ether membranes. Before irradiation, the permeation selectivities of the membranes for the cations were $K^+ > Rb^+ > Na^+ > Cs^+$. On irradiation, the permeation rate of the K^+ ion was accelerated; whereas, the permeation rates of the other cations were little affected. Therefore, they showed that the selective acceleration of K^+ ion permeation through the membranes was possible using light energy as a driving force.

Ishihara et al. [118,119] showed that protein permeabilities through membranes of PHEMA containing azobenzene side groups could be regulated reversibly by photo-irradiation. Here again, changes were associated with contraction of the swollen membrane caused by photo-induced polarity changes in the azobenzene moieties. Amphiphilic azoaromatic polymer membranes from PHEMA and *p*-phenylazobenzoyl chloride in a DMF/pyridine mixture were prepared, and the effects of photo-irradiation on their swelling behavior were investigated [118]. The swelling degree of a membrane in water in the dark decreased on UV irradiation. On exposure to visible light, the degree of swelling recovered to the original level. The degree of swelling decreased with an increase in the mole fraction of the azobenzene moieties in the dark and under UV irradiation. Permeation profiles of various molecular weight proteins through the amphiphilic azoaromatic membranes showed that, in the dark, permeation of insulin, lysozyme, and chymotrypsin occurred and the amount of permeated proteins increased with time until a plateau value was reached, which indicated that equilibrium had been established between the protein feed solution and the phosphate buffer receiving solution [119]. However, permeation of albumin was not observed, and this was attributed to the relatively large hydrodynamic size of this protein. When the membranes were photo-irradiated, the permeation of every protein decreased significantly, and it was observed that lysozyme and chymotrypsin, which have larger hydrodynamic sizes than insulin, did not permeate through the membranes. The degree of swelling of the membrane is an important factor for protein permeability through hydrated hydrophilic membranes. On UV irradiation, the degree of swelling of the membranes decreased from 0.20 to 0.12, and, therefore, the decrease in permeability of proteins on UV irradiation was attributed to the decrease in the degree of swelling (lower mesh size). These results showed that azoaromatic polymeric membranes could be applied to continuous purification processes of proteins to remove low-molecular weight compounds from mixtures obtained by ultrafiltration.

Kinoshita et al. [120] and Sato et al. [121] prepared photo-responsive polypeptide membranes by casting chloroform solution of PLGA with azobenzene groups in the polymer side chains (azo-modified PLGA). The membrane functions were photo-controlled by *cis*–*trans* isomerization in the side-chain azobenzene groups. The azobenzene side chains in the solid membrane exhibited *trans* to *cis* photo-isomerization under UV light irradiation, which was reversed completely in the dark. The water content of the membranes increased on UV light irradiation due to a polarity change of the azobenzene moieties. This increase in hydration of the membranes resulted in the acceleration of acid dissociation of the L-glutamic acid moieties; hence, the potential across the membrane increased by UV irradiation, indicating an increase in the negative charge of the membranes. The cross-membrane conductance also changed on UV irradiation, depending on the potassium chloride concentration in the bulk solution. This conductance change was attributed to the enhanced diffusivity of ions and accelerated acid dissociation due to increased membrane water content. The photo-induced changes in the membrane potential and permeability were reversible.

Anzai et al. [122] reported improved photo-induced membrane potential across PVC membranes doped with photo-sensitive crown ether having lipophilic side chains. Photo-irradiation-induced potential changes of 10–20 mV were observed across the PVC membranes doped with photo-sensitive lipophilic crown ether, *p*-[3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)phenylazo] hexadecyloxybenzene. The highly improved photo-responsiveness of the membrane was attributed to the lipophilic nature of the crown ether. The photo-response was stable and reproducible in the presence of alkali-metal chlorides.

Aoyama et al. [123] reported on the development of a membrane from a novel polyvinyl/polypeptide graft copolymer composed of a photo-responsive copolypeptide branch with β-*p*-phenylazobenzyl L-aspartate and β-benzyl L-aspartate attached to a poly(butyl methacrylate) backbone. This membrane exhibited a photo-induced permeability change that was attributed to the conformational change of the peptide chains in the membrane on photo-irradiation. Permeation rates of mandelic acid and other polar and non-polar substances such as N-((benzyloxy)carbonyl)-D,L-alanine, acetone, and biphenyl across the membrane immersed in trimethyl phosphate were increased by UV irradiation and suppressed on irradiation with visible light. It was observed that there was inversion of the helix sense of the polypeptide chains in the membrane from left- to right-handed with UV irradiation and reversal on irradiation with visible light.

Yashima et al. [124] studied the photo-controlled chiral recognition of [4-(phenylazo)phenyl]carbamoylated cellulose and amylose membranes. With chiral ability, these membranes were used for enantioselective adsorption of several neutral racemates at various degrees of photo-irradiation. Since membranes prepared by casting THF solutions of the polysaccharide derivatives ([4-(phenylazo)phenyl]carbamoylated cellulose and amylose) were brittle, PTFE membrane filters were used as supports. Solutions of the polysaccharide derivatives in THF were cast on the PTFE membranes and allowed to dry on glass plates under a nitrogen atmosphere at room temperature. Chiral recognition in these membranes was controlled by photo-irradiation, and the enantioselective adsorption of several racemates on the membranes was reversibly changed via photoisomerization.

Darkow et al. [125] synthesized poly[acrylonitrile-*co*-butadiene-*co*-styrene-*co*-2-(ethenyl)phenyl-5-phenyl-2H-tetrazole] (PABSV) containing a photosensitive moiety. This polymer was used to develop photo-responsive membranes by dissolving it in THF, filtering the solution, casting it on glass plates and allowing the solvent to evaporate at ambient temperature overnight. PABSV membranes of 14–17 μm thickness were obtained. These membranes were photo-modified by equilibrating them with methanolic reagent solutions and then irradiating them with UV light to produce highly reactive nitrilimine groups on the membrane surfaces. Nitrilimine reacts quickly and specifically with a variety of nucleophiles, electrophiles as well as acetylenic and olefinic compounds and their homologues. Photochemically induced functionalization enhanced the permselectivity of the PABSV membranes towards benzene in a cyclohexane/benzene mixture during pervaporation.

Viologen compounds such as 1,1′-dimethyl-4,4′-bipyridinium dichloride are reduced to monocation radicals and then bi-radicals by irradiation with UV light. Ageishi et al. [126] prepared cross-linked membranes containing viologen moieties. Electron transfer through these membranes proceeded smoothly by electron diffusion among the viologen moieties. Sata [127] and Sata and Matsusaki [128] prepared anion-exchange membranes with viologen moieties by reaction of a film of chloromethylated PS and 4,4′-bipyridine. When light from a xenon lamp was irradiated on the membrane swollen in ethylene glycol, FTIR spectra showed new absorbance peaks at 406 and 615 nm, which were assigned to the formation of monocation radicals. These peaks decreased on further irradiation, which was attributed to the formation of bi-radicals. A photo-voltage of 82 mV and a photo-current of 410 nA at a 200 kΩ load resistance were generated from the membrane upon photo-irradiation. The 4,4′-bipyridine moieties in the membrane were reduced by photo-irradiation to generate the photo-voltage, but, with increasing irradiation, the photo-voltage decreased slightly due to an increase in the reduced form of the 4,4′-bipyridine in the membrane.

The same group investigated the transport properties of membranes containing viologen moieties as anion-exchange groups in the presence or absence of photo-irradiation [129]. Anion-exchange membranes containing viologen moieties were prepared by the reaction of copolymers of chloromethylstyrene and divinylbenzene with 4,4′-bipyridine. FTIR spectra of the membranes in pure water and various salt solutions indicated that the viologen moieties were reduced by photo-irradiation to form radical monocations and bi-radicals. The transport numbers (measure of the fraction of the total current carried by given ions in an electrolyte) of various anions relative to those of chloride ions were measured with and without photo-irradiation. Upon photo-irradiation, the transport numbers of sulfate, bromide, nitrate, and fluoride ions decreased relative to those of chloride ions. However, on removal of photo-irradiation, the transport properties of these anions through the membranes became the same as before photo-irradiation. Therefore, the transport properties of these anion-exchange membranes were changed reversibly by photo-irradiation. It was concluded that the decrease in the transport numbers of the various anions relative to chloride ions was due to a sieving effect because of the shrinkage of the polymer network upon irradiation. The decrease in the pore size of the membranes upon photo-irradiation was confirmed by the decrease in the permeability of a neutral molecule (urea).

Kodzwa et al. [130] prepared photo-responsive, ion-selective membranes from PAAm hydrogels containing bis-[4-(dimethylamino)phenyl]methyl leucohydroxide (TPMLH). An increase in flux was observed for the methyl orange anion on UV irradiation, attributed to the photo-induced generation of fixed cationic charges in the membranes. The observed change in permeate flux resulted from photoionization of only 10% of the TPMLH groups in the membrane. Therefore, a more dramatic change would be expected if more of the groups could be ionized. TPMLH also can be ionized by lowering the pH of the aqueous phase, and, at pH 4, essentially 100% of the TPMLH groups are ionized without UV irradiation. The observed flux of methyl orange at pH 4 was six times higher than that of a non-irradiated membrane at pH 10, and four times that of the irradiated system. However, the flux of neutral 4-dimethylamino pyridine in both systems was essentially unchanged by UV irradiation.

Sata et al. [131] prepared three different ion-permeable membranes: membranes with azobenzene moieties, membranes with both *p*-aminobenzene and benzyl trimethylammonium salt moieties and membranes with only benzyl trimethylammonium salt moieties. They studied their transport properties in electro-dialysis with and without photo-irradiation. Water content, ion-exchange capacity and electrical resistance of the membranes having azobenzene moieties and those having both azobenzene and benzyl trimethylammonium salt moieties changed with UV irradiation due to changes in the polarities of the azobenzene moieties and changes in the pore size of the membrane. No change in transport properties was observed for the membranes which only had benzyl trimethylammonium salt moieties. Changes in pore size with UV irradiation were confirmed by measurement of permeability of urea (neutral molecule). On UV irradiation, the transport numbers of sulfate, bromide, fluoride and nitrate relative to chloride ions increased in the membranes with azobenzene moieties only due to the conversion of the *trans* form of the azobenzene moiety into a more polar *cis* form, which caused the water content and pore size of the membrane to increase, and decreased in the membranes with both azobenzene and benzyl trimethylammonium salt moieties because the pore size and water content of the membranes decreased. The transport numbers of sulfate ions relative to chloride ions changed reversibly with sequential irradiation of UV light and visible light.

Minoura et al. [132] reported on the development of molecularly imprinted polymeric membranes containing azobenzene chromophores, and they studied how light affected their performance properties. The imprinted, photosensitive membranes were prepared by using *p*-phenylazoacrylanilide (PhAAAn) as the photosensitive functional monomer, dansylamide (DA) as the template, and mixtures of EGDMA and tetraethylene glycol diacrylate (TEGDA) as crosslinkers. The affinity of the DA specific recognition sites within the MIP membranes could be changed reversibly by illumination with UV and visible light. Imprinted, photo-responsive membranes have potential for extractive separations and assays of chemical and biological compounds.

Kimura et al. [133] reported on the synthesis of vinyl polymers carrying crowned spirobenzopyran moieties as side chains. They called these crowned spirobenzopyran vinyl polymers. The electrically neutral form of the crowned spirobenzopyran side chains can bind alkali metal ions with their crown ether moieties, while the spirobenzopyran moieties isomerize photo-chemically to the corresponding merocyanine form. The zwitterionic merocyanine form binds metal ions with higher affinity than the crown ether ring by interactions of their phenolate anions with the metal ions. Therefore, photo-isomerization improves the metal–ion binding affinity of the vinyl polymer. This principle was extended to develop PVC membranes with malachite green derivatives carrying a bis(monoaza-15-crown-5) moiety [134]. The membranes were prepared by pouring a mixture of PVC, bis(2-ethylhexyl)sebacate, and THF onto a flat petri dish, allowing the solution to evaporate, removing the membranes from the dish, and conditioning them by soaking them in alkali metal chloride solution overnight. These membranes were used to investigate the photo-irradiation effect on potential response to metal ion concentrations and photo-induced potential change. The photo-induced change for the PVC membranes containing malachite green derivatives was affected by their metal–ion complexing affinity and by the pH in aqueous solution. Photo-induced switching in the potential response to metal–ion concentrations was achieved by these membranes. Photo-ionization by UV irradiation induced the release of complexed metal ions as a result of electrostatic repulsions, which strongly suggested the possibility for photochemical ion-selectivity switching between cations and anions. After UV irradiation, a positive charge from the ionized derivative was left on the membrane surface, which in turn attracted negative charge. Therefore, these membranes can be utilized as cation sensors under dark conditions and then switched to anion sensors by UV irradiation.

5.3. Membrane modification—photo-responsive membranes

Photo-irradiation enables the performance improvement of commercial polymeric membranes for applications that include gas separation, filtration, and membrane adsorption. The general strategy outlined in this section is to functionalize membrane pores/surfaces with photo-responsive polymers.

Trushinski et al. [135] fabricated thin-film composite photochemically active membranes by interfacial polymerization of 1,6-hexanediamine with light sensitive diazoketonedisulfonylchloride (DKDSC) and naphthalene-1,3,6-trisulfonylchloride (NTSC) on the surfaces of PS UF membranes. The membrane discs were soaked in 1.0% (w/w) aqueous solutions of the diamine for 2 h and then placed in carbon tetrachloride solution of the trisulfonylchloride for 25 min and then allowed to dry in air for 30 min. This protocol yielded a thin coating of a polysulfonamide polymer on the surfaces of the support membranes. Crosslinking was controlled by the addition of various amounts of NTSC to improve the strength of the polymer film. It was observed that irradiation of the modified membranes with light photochemically transformed the diazoketone functionality. It was converted to carboxylic functionality by irradiation in water producing negatively charged membranes that exhibited pH dependence. The acid membranes had more hydrophilic surfaces, which enhanced solution flux. Irradiation of the membranes in alcohols led to the formation of ester membranes that had more hydrophobic surfaces, causing a decrease in the solution flux but, in turn, enhancing the salt rejection.

Chung et al. [136] developed porous membranes grafted with poly(spiropyran-containing methacrylate) with permeability that varied with UV–vis irradiation. Copolymers of spiropyran-containing methacrylate (SPMMA) and AAm were grafted from the surface of porous PTFE membranes. The permeability of a water–methanol mixture through the modified membranes was investigated under photo-irradiation. Very little effect of irradiation on permeability was observed for PAAm-modified PTFE membranes; however, for poly(SPMMA-*co*-AAm) modified membranes, UV irradiation led to increased permeability, while visible light irradiation decreased permeability. Increased permeability was attributed to the collapse of grafted chains and the opening of membrane pores. Chain collapse occurred due to a decrease in their solubility in a H_2O/CH_3OH mixture when merocyanine groups were generated by UV-light irradiation. When the grafted chains were exposed to visible light irradiation, neutral spiropyran was formed, chain solubility increased, and the chains extended from the pore surfaces. The result was constriction of the membrane pores and a decrease in permeability.

Park et al. [137] grafted poly(spiropyran-containing methacrylate) on a glass filter to control permeation of organic liquids by photoirradiation. The glass filter was first modified with octadecyldimethyl-*N*,*N*-diethylaminosilane and then subjected to glow discharge treatment for graft copolymerization of spiropyran-substituted methyl methacrylate (SPMA), and methyl methacrylate (MMA). Surface wettability was altered by these modification treatments. An SPMA/MMA copolymer was soluble in toluene under irradiation of UV light and insoluble under irradiation of visible light. The same copolymer was soluble in DMF irrespective of photoirradiation. Therefore, toluene permeation through a glass filter grafted with SPMA/MMA copolymer was increased by UV light irradiation and decreased by visible light irradiation. DMF permeation was not affected by photoirradiation. These results indicated that the permeation of organic liquids through the modified glass filters was controlled by the solubility (extension/contraction) of the polymer chains grafted on the surface.

Weh et al. [138–140] developed several photo-switchable membranes by adsorbing azobenzene (AZB) to the pore walls of membrane supports. They utilized the principle that AZB undergoes *trans*–*cis* photo-isomerization, as shown in Fig. 19. In their earlier work [138,139], they reported reversible changes in gas permeability by photo-induced switching of supported poly(methacrylate)-AZB membranes, in which the AZB was chemically bound to the polymer matrix. They later developed a principle in which they adsorbed AZB within three-dimensional zeolitic pore systems, yielding composite, photo-switchable zeolite-AZB membranes [140]. It was predicted that the *trans*-AZB isomer had a higher free volume available for the permeating gas molecules than the *cis*-AZB isomer. This prediction agreed with experimental results that showed an increase of the single gas permeance in the *trans*-state of the zeolite-AZB membranes compared to the *cis*-state. The switchable modification of the gas permeation was reversible over many cycles. Due to the reversibility of the photochemical *trans*–*cis* switching, these AZB modified membranes could be utilized as micro-valves in micro-reaction technology for dosing reactants or light controlled removal of products.

Kameda et al. [141] investigated gas permeability of membranes modified with a polymer functionalized with azobenzene chromophores (azopolymers) under different conditions of light irradiation. The azopolymer modifier layer was formed on an amide

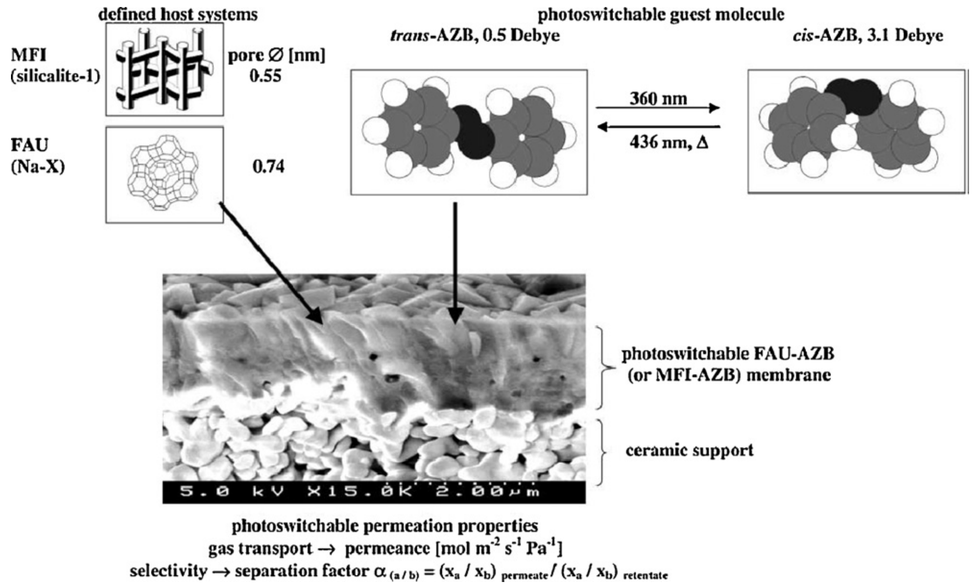

Fig. 19. Schematic of the working principle of photo-switchable zeolite-AZB membranes.
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UF membrane by spin-coating a dichloromethane solution of a random copolymer of methyl methacrylate and 2-(ethyl-[4-(4-nitrophenylazo)phenyl]amino)ethyl methacrylate. Measurements with helium showed that the permeability of the modified membranes increased by 5–10% upon irradiation with blue light, which caused cyclic photo-isomerization of the azobenzene chromophores. However, no significant change in gas permeability and no photo-isomerization of the azobenzene chromophores were observed upon irradiation with red light. It also was observed that the azopolymers irradiated with blue light spread out from the localized particulate domains, indicating the existence of photo-induced plasticization.

Nayak et al. [142] successfully grafted optically active vinyl spiropyran (1′-(2-propylcarbamylmethacrylamide)ethyl)-3′,3′-dimethyl-6-nitrospiro[2H-1]benzo-pyran-2,2′indoline) on 30 kDa PES UF membranes by photograft-induced polymerization using UV light at 300 nm (Fig. 20). The modified membranes retained the optically switchable characteristics of the vinyl spiropyran molecules. ATR-FTIR spectra from dry modified membranes exposed to visible light for 5 min showed the peak assigned to the aromatic $C{=}O$ stretch was maximized, while the peak assigned to the carbonyl group in the monomer backbone was reduced. Similarly, spectra from dry modified membranes treated with UV radiation showed the opposite trend. Alternating the light source to UV and visible light led to reversible changes in surface wettability. Exposure to UV light led to an increase in the sessile contact angle of the dry modified membrane while exposure to visible light led to a decrease in the sessile contact angle. Finally, unmodified membranes exhibited the highest adsorbed amount of BSA protein, followed by modified membranes that had been exposed to visible light ('closed' configuration) and modified membranes that had been exposed to 254 nm UV radiation ('open' configuration). The 'closed' configuration adsorbed 26% more protein than the 'open' configuration. The 'open' configuration produced 17% more permeation flux of 10 mM phosphate buffered saline compared to the 'closed' configuration.

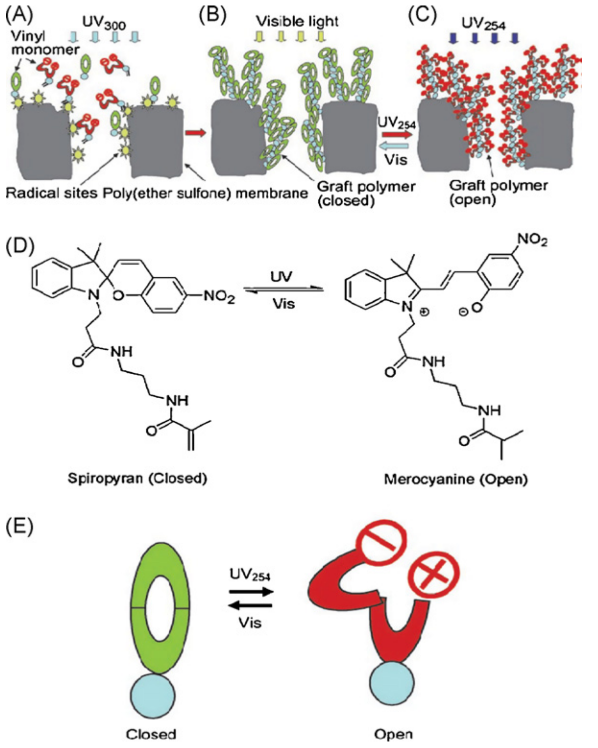

Fig. 20. Graft polymerization and switching; (A) photo-grafting of vinyl monomer onto PES UF membrane, (B) exposure of modified membrane to visible light leading to formation of 'closed' form of spiropyran (white), (C) exposure of modified 'closed' form of the membrane to UV radiation to form 'open' form of spiropyran (red), (D) the chemical structure of the two configurations of vinyl spiropyran as a function of vis and UV irradiation, (E) a schematic of the chemical structure of vinyl spiropyran in two configuration as a function of vis and UV irradiation.
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Sumaru et al. [143] developed photo- and temperature-responsive gate membranes (PTGM) by immobilizing dual-responsive hydrogels to the surface of porous, hydrophilic PTFE membranes. The hydrogel was prepared by radical copolymerization of NIPAAm, a vinyl monomer having a spirobenzopyran residue, and cross-linker. Permeability of 1 mM HCl aqueous solution through the modified membranes increased as the temperature was increased above the LCST of the PNIPAAm; however, the permeability under irradiation conditions was always larger than that measured in the dark, with largest difference at the LCST. The permeability of 1 mM HCl aqueous solution through the modified membranes doubled in response to blue light irradiation; after the light was turned off, the permeability decreased gradually to the former value.

Kimura et al. [144] developed a porous membrane that showed repetitive changes in permeation of hexane or ethanol by alternating UV and visible light irradiation. Photo-chromic crown ether–spirobenzopyran copolymer was coated onto porous PE membranes by soaking the membranes in a solution of the copolymer and evaporating the solvent to dryness at room temperature. The modified membranes were able to work as functional membranes since they could control solvent permeation rate photo-chemically. The authors observed that the permeation rate of hexane decreased when the modified membranes were exposed to UV light due to increasing polarity of the membrane pores as a result of photo-isomerization of the spirobenzopyran groups to the ionic merocyanine form. Irradiation of the membranes using visible light restored the hexane permeation rate. In contrast, the permeation of ethanol through the modified membranes was enhanced by UV irradiation due to the increase in the apparent pore size induced by the polymer chain contraction.

By modifying the surface of nanoporous alumina membranes using mixtures of photo-chromic spiropyran and hydrophobic molecules, Vlassiouk et al. [145] were able to show that it was possible to control the admission of water into the modified membranes using light. Alumina membrane surfaces were modified in two steps; first, the membrane surfaces were silanized with 3-(aminopropyl)-triethoxysilane. Then the spiropyran carboxylic acid was coupled to the surface-bound amino groups by immersing the membranes in an ethanol solution of the acid and using the coupling agent, 1-ethyl-3-(3-(dimethylamino)propyl)carbo-diimide. When the spiropyran was in the thermally stable, relatively hydrophobic closed form, the membranes were not wetted by water. On exposure to UV light, the spiropyran photo-isomerized to the more polar merocyanine form and allowed water to enter the pores and cross the membrane. Therefore, the photo-responsive membranes acted as burst values, allowing the transport of water and ions across them. In aqueous solutions containing ions, the modified membranes acted as electrical switches; photoisomerization led to a two-order-of-magnitude increase in ionic conductance, allowing current to flow across the membranes. Exposure to visible light caused photo-isomerization of the merocyanine to spiropyran.

Bora et al. [146] developed a simple method of activation of cellulose membranes for immobilization of biomolecules by preparing photoreactive cellulose membranes using a simple, single step procedure involving 1-fluoro-2-nitro-4-azidobenzene (FNAB). The membranes were prepared by utilizing the reaction of the fluoro groups of FNAB and the hydroxyl groups of cellulose in an alkaline medium. The cellulose membranes were washed in distilled water and methanol and then dipped in solutions of FNAB in toluene in which 30% potassium hydroxide solution was added. The azido group of the photoreactive cellulose membrane in the presence of UV light generates highly reactive nitrene. As the nitrene has a property of binding to C–H or N–H bonds through insertion reaction, the membranes developed were capable of binding any biomolecules irrespective of their functional group by simple photo-chemical reaction.

5.4. Photo-responsive carrier membranes

Photo-switchable carriers in polymeric membranes have been investigated by various groups. The transport properties of such membranes for certain ions can be switched by selective UV irradiation. We report examples of work done to develop these membranes and how they have been utilized in several tailored applications.

Shinkai et al. [147] attempted to control ion extraction and ion transport across a liquid membrane by light. They synthesized photo-responsive bis(crown ether) with an azobenzene linkage and immobilized it in liquid membranes using *o*-dichlorobenzene as solvent. The azobenzene functionalized bis(crown ether) responded to photo-irradiation and the *cis* isomers exhibited greater binding affinities than the *trans* isomers for large alkali metal cations. Transport of K^+ ions across the liquid membrane established that the transport rate was suppressed by light when a hydrophobic counter anion was used, and accelerated by light when a relatively hydrophilic counter anion was used.

In subsequent work, Kumano et al. [148] investigated the photo-responsive and facilitated transport of K^+ ions through ternary composite membranes containing immobilized azobenzene-bridged crown ether (AZO-CR). These membranes exhibit *trans–cis* photo-isomerization on irradiation with UV and visible light. The membranes were prepared by coating a PVC support membrane with a liquid crystalline layer of either 4-cyano-4′-n-pentylbiphenyl (CPB) or N-(4-ethoxybenzylidene)-4′-n-butylaniline (EBBA) as a liquid crystalline layer, followed by AZO-CR. It was observed that the UV and visible light irradiations facilitated permeation of K^+ ions through the PVC/CPB/AZO-CR ternary composite membrane, and this was due to the *trans–cis* configurational change of AZO-CR induced by photo-irradiation.

Oosaki et al. [149] reported that neutral carrier type ion-selective, liquid-crystalline, ion-sensing membranes containing azobenzene derivatives as photosensitive chromophores showed remarkable changes in their ion selectivities on photo-irradiation. These membranes consisted of 4-cyano-4′-hexylbiphenyl as the liquid-crystal membrane solvent, 4-butyl-4′-methoxyazobenzene as the azobenzene derivative, 4′-[(4″-octyloxy)biphenyloxycarbonyl]-benzo-15-crown-5 as the liquid-crystalline neutral carrier and potassium tetrakis(*p*-chlorophenyl)borate as the anion excluder.

5.5. Summary—photo-responsive membranes

This section covered the development and use of membranes that respond reversibly to photo-stimulation. Photo-chromic units undergo reversible photo-isomerization reactions on absorption of light. Examples in this section illustrated how reversible photo-isomerism leads to switching between two or more states of the photo-chromic moieties, leading to molecular changes in group polarity, charge, and size that are observed as measurable changes in barrier properties.

In these cases, the membrane barrier properties are adjusted with an external stimulus (light energy).

6. Electric and magnetic field-responsive membranes

In this section, we review work done to develop charged membranes and study how an electric field applied to these membranes affects their barrier properties. Work done to develop magnetic field-responsive membranes and their applications in various fields is also summarized. Two general approaches used in the design of electric/magnetic field responsive membranes are considered. The first approach utilizes surface coatings or bulk materials that undergo reversible molecular transitions when subjected to an electric/magnetic field. The second approach takes advantage of anisotropic nanoparticles that can change surface properties if oriented at an interface in a controlled way due to an electric/magnetic force field (Fig. 21). Like with photo-irradiation, using electric fields and electromagnetic radiation to induce changes in membrane barrier properties is appealing because the response is not limited by mass transport of a change agent.

6.1. Electric field-responsive membranes

Yamauchi et al. [150] introduced the concept of electrically controlled protein permeation through PVA/PAA composite membranes. They prepared PEL gel membranes that could be activated electrically to allow the diffusion of proteins as high-molecular-weight ionic solutes. PEL hydrogels undergo significant reversible contraction and expansion in response to an electric field; therefore, application of an electric field to membranes prepared from PEL hydrogels can be used to control solute permeation based on size. The PAA/PVA PEL hydrogel composite membranes were prepared through the iterative freezing–thawing of an aqueous solution containing 10% (w/w) each of PAA and PVA. The polymer solution was poured into the space between two glass plates and cooled from room temperature to −30 °C. The frozen polymer solution was then thawed at room temperature for 5 h. This freezing and thawing process was repeated 15 times. The permeability of the membranes as a function of electric field strength was studied in a 150 mM phosphate buffer using trypsin with a molecular weight of 23 kDa as the protein solute. The membranes exhibited permeability only under an applied electric field. This suggests that the application of an electric field brought about the formation of pore channels within the membranes due to electrochemically generated contractile stress through which the trypsin molecules could permeate. The permeation rate of the trypsin increased with increasing applied electric field. This effect was most significant when trypsin was transported towards an electrode that was opposite in charge to the net protein charge. Therefore, using these membranes, the protein permeation could be turned on and off by switching a direct current source on and off.

Kokufuta et al. [151] used the PAA/PVA PEL hydrogel composite membranes for electrically controlled separation of maleic

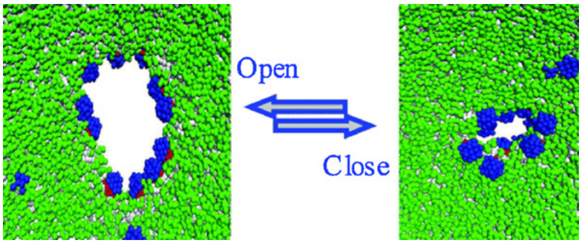

Fig. 21. Smart membrane system consisting of anisotropic nanoparticles that respond to an electric/magnetic force field.
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acid (MA) and fumaric acid (FA). Separation was based on the differences in the molecular weights and dissociation characteristics of the solutes; MA and FA are isomers that have different hydrodynamic radii and dissociation constants. Permeation of MA and FA was not observed without the application of an electric field, indicating that the membranes exhibited permeability only under an applied electric field. It earlier had been suggested that the size of the pore channels in the membranes under an applied electric field of 6 V is large enough to permit the diffusion of MA and FA. The separation of MA from an equimolar mixture of MA and FA using the composite membranes was performed under different conditions of pH and electric field strength. It was found that MA was separated from the mixture at pH 2 under an applied electric field greater than 2 V because only the COOH groups of MA were dissociated at pH 2 and the MA^- ions were transported through the membrane towards the electrode opposite in sign to their charge. The highest separation coefficients for MA were observed under conditions of pH 2 and 6 V.

Bohn and co-workers [152] presented work on electric field-induced permeability modulation in pure and mixed Langmuir–Blodgett (LB) multilayers of hemicyanine dyes and octadecanoic acid on nanoporous membranes. Composite membranes were prepared by coating nanoporous membranes with LB barrier layers. PC track-etched membranes were coated with poly(styrene sulfonate) (PSS) by adsorption from aqueous solution. LB films of hemicyanine dyes, 4-(4-dioctylaminostyryl)-*N*-propylsulfonate pyridinium or 4-(4-dihexadecylaminostyryl)-*N*-methylpyridinium iodide, mixed with octadecanoic acid were then deposited on both sides of the PSS-coated membranes. The response in permeability of the resulting composite membranes to both *ac* and *dc* electric fields was characterized. It was shown clearly that imposing *ac* or *dc* electric fields across the membranes led to large changes in permeability. The results also supported electroporation (field-induced structural changes in membranes) over iontophoresis (field-driven motion of ions across membranes) as the dominant mechanism for field-mediated increases in permeability. Field-induced permeability changes in phosphate buffer and deionized water suggested that at least two effects were important in determining the transport behavior in the composite membranes: field-induced structural change in the barrier layer that mediated the electroporation and field-mediated alteration in transport through nanopores of the membranes.

Chen et al. [153,154] reported on the electro-sensitive permeability of a new class of polymer–polymer nanocomposite membranes with oriented PEL nanodomains normal to the plane of the membrane. Track-etched membranes with oriented, low porosity structures were used as the matrix to provide mechanical durability. A PEL gel filled the pores and regulated the transport properties. The membranes were synthesized using oxygen plasma-initiated surface graft polymerization. Polyester track-etched (PETE) membranes were used as the matrix, and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and N,N′-methylenebis(acrylamide) (BisA) were used as the monomer and cross-linker. Transport rates of dimethyl methylphosphonate (DMMP) in the original PETE and nanocomposite membranes were measured. The permeability of the nanocomposite membranes was affected by electric actuation; whereas, no actuation behavior was observed with the original PETE membrane. When an electric field of 10 V was applied, the membrane became nearly impermeable (Fig. 22). Without voltage, the PAMPS gel in the pores swells in water and the mesh size of this swollen network allows for the diffusion of molecules. With voltage, the PAMPS gel on the external membrane surface and in the pores of the membrane contracts resulting in increased diffusion resistance.

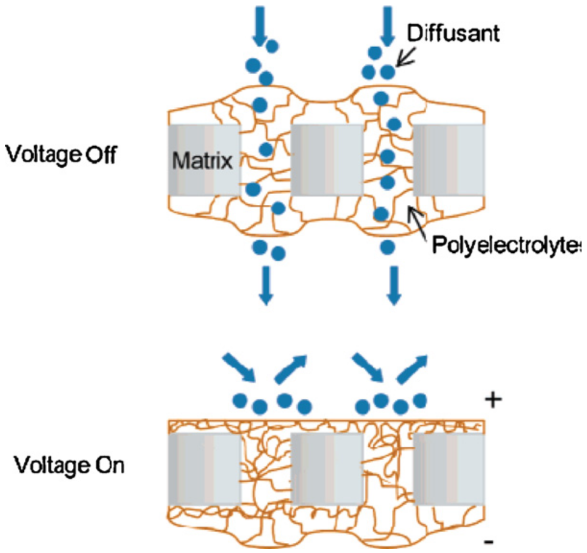

Fig. 22. Schematic diagram showing the electrosensitive permeability in PAMPS gel-*g*-PETE nanocomposite membranes.
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6.2. Magnetic field-responsive membranes

Ozeki et al. [155] demonstrated how relatively low magnetic fields may be used to regulate the electrical properties of lipid membranes. The membrane potential and resistance of black lipid membranes (BLM), comprising didodecyl phosphate (DP) or dipalmitoylphosphatidylcholine (DPPC) changed up to 50% and 4%, respectively, on application of steady magnetic fields. Diamagnetic lipid molecules are well-known to align under steady magnetic fields. The addition of molecules having different magnetic anisotropy to the BLM modified the magneto-responses of the membranes since the magnetic-field effects occur by cooperative orientation of the lipid molecules. The magnetic regulation of the functions of lipid membranes makes it possible for these membranes to be applied as molecular devices and sensors.

Khoo and Liu [156] designed and developed microfabricated, membrane-type magnetic actuators that could be used to fabricate tetherless micropumps for microfluidic systems. The membranes were prepared by embedding magnetic pieces of electroplated permalloy ($Ni_{80}Fe_{20}$) in thin, flexible membranes made of silicone elastomer, PDMS. Large membrane displacements of the order of 80 μm were produced by these membrane actuators when an external magnetic field was applied.

Yang et al. [157] prepared a dual stimuli-responsive microcapsule with a superparamagnetic porous membrane and linear-grafted PNIPAAm gates in the membrane pores. Oleic acid (OA) modified Fe_3O_4 nanoparticles were embedded into the polyamide microcapsule membrane during interfacial polymerization, and, then, plasma-induced grafting polymerization was used to graft PNIPAAm into the pores of the microcapsule membranes. The final microcapsule membranes exhibited time-independent superparamagnetic properties with good magneto-responsive ability. The microcapsules dispersed in deionized water at 25 °C. When an external magnetic field was applied, the microcapsules aggregated at the membrane surface. On removing the magnetic field, the microcapsules redispersed in the deionized water. Even after applying magnetic stimulus to the membranes 30 times, the magnetic responsiveness of the membranes remained nearly constant. Therefore, the magnetic nanoparticles embedded into the membranes did not leach out over time; the van der Waals attractive forces between the OA-modified Fe_3O_4 nanoparticles and the polyamide polymers kept the Fe_3O_4 nanoparticles tightly fixed in the membranes. These membranes are being examined for applications like controlled release of chemicals, microreactors, biomedical or chemical sensors, and in separation processes.

Rybak et al. [158] reported a new concept in which polymer membranes filled with neodymium powder and magnetized ('magnetic membranes') were used for air enrichment. The idea of 'magnetic membranes' was introduced based on the observation that oxygen and nitrogen have quite different magnetic properties; oxygen is paramagnetic, whereas nitrogen is diamagnetic. This difference provides a mechanism for their separation. Magnetic membranes were made by pouring a solution of 3% ethyl cellulose (EC) in 40:60 ethanol/toluene with dispersed, magnetic neodymium powder into a petri dish and then evaporating the casting solvents in a stable external magnetic field for 24 h. Magnetic membranes were obtained with 1.0–10.5% neodymium powder content (wet basis) and 19.1–73.0% neodymium powder (dry basis). Permeation measurements were carried out using the membranes before and after magnetization in a magnetic field. Almost 56% oxygen enrichment was attained through the magnetic membranes for a magnetic induction of 2.25 mT, compared to only 24% oxygen enrichment for the non-magnetic EC membranes prepared without neodymium powder.

6.3. Summary—electric and magnetic field-responsive membranes

This section described the relatively few examples of electric and magnetic field-responsive membranes. Two approaches have been utilized to develop electric/magnetic field-responsive membranes: (i) using surface coatings or bulk materials that undergo reversible molecular transitions on exposure to an electric/magnetic field and (ii) utilizing anisotropic nanoparticles that change surface properties if oriented at an interface in a controlled way by an electric/magnetic force field.

7. Future directions and conclusions

7.1. Future directions

Responsive membrane systems with changing barrier properties and highly adaptive surfaces have been created using different approaches in recent decades, but most of the work has been focused on how the different responsive interactions within the membranes can be tuned and monitored in controlled environments. The next generation of responsive membranes will move towards advanced functions, i.e., beyond barrier functions, in less well-defined environments. Innovations will lead to the design of more complex membrane systems capable of mimicking functions of living systems.

Stimulation of responsive membranes will shift from non-specific triggers such as temperature and pH to specific, affinity type triggers. Molecular imprinting is one platform that may see growth for developing membranes that respond to such chemical cues. Imprinted polymers made to mimic natural receptors may find applications in modeling cellular transmembrane transport.

A less well developed research area that is ripe for exploration is the fabrication of membranes that respond to biochemical stimuli, such as enzyme substrates and antibodies/antigens. Membrane design might involve immobilization of a biomolecule (enzyme/antibody/antigen) onto the membrane surface. Interaction of the immobilized agent with a substrate or biochemical in solution would elicit a conformation change directly or indirectly by generating a reaction product that elicits the change. Such membranes could be used to regulate the transport and release of chemicals, e.g., drugs, by receiving and responding to biochemical cues.

Stimuli-responsive membranes have strong potential for future applications in tissue engineering, bioseparations, antifouling surfaces, and drug delivery among others. Reversible changes to surface composition, surface energy, adhesion and wettability of stimuli-responsive membranes will provide ways of fabricating membranes with new functions, such as self-cleaning and self-refreshing abilities. Switchable membrane surface properties will improve the efficiency of many technological processes.

7.2. Conclusions

This review has examined in detail the significantly important and rapidly developing field of stimuli-responsive membranes. We used physical polymer science to explain the conformational changes in membrane materials that result in reversible microphase segregation, hence, leading to responsive behavior (Section 1). The responsive properties can be controlled by direct manipulation of the chemistry of membrane materials, structural and morphological factors, and external stimuli.

Myriad ways of designing and fabricating stimuli-responsive membranes were discussed in Section 2. These were generalized into two categories: membrane synthesis from stimuli-responsive materials and membrane modification to incorporate stimuli-responsive materials.

Membrane that respond to changes in temperature were considered in Section 3, where we looked at work done to develop these temperature-responsive membranes and some applications as biomaterials or drug-delivery systems.

pH- and ionic strength-responsive membranes are used widely in various applications such as controlled release of chemical and drugs, flow regulation, sensors, self-cleaning surfaces and selective filtration. Section 4 summarized how these membranes have been fabricated and their applications.

Photo-responsive membranes were covered in Section 5, including ways to develop them and a look at reversible photo-stimulated changes of membrane barrier properties and functions. Section 6 discussed approaches to design and use electric and magnetic field-responsive membranes.

Finally, this review is meant to provide a better understanding of stimuli-responsive membranes and to encourage further development efforts. The untapped potential of stimuli-responsive membranes is great.

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