

Polymer thermo-responsive gate membranes

Abstract

This mini review deals with advancements and importance of surface modification of porous polymer membranes especially the thermo-responsive nature of Poly (N-isopropyl acrylamide), that can be used as a gate in polymer porous membranes.

Keywords: stimuli responsive, grafted gates, grafting polymer, topography, polymerization, hydrophilic-hydrophobic, substrates, plasma

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Abbreviations: pNIPAAm, poly(N-isopropylacrylamide); PET, poly(ethylene terephthalate); LCST, lower critical solution temperature; PVCL, poly(N-vinylcaprolactam); PEO, poly(ethylene oxide); BMA, butyl methacrylate; DEAAm, poly(N,N-diethylacrylamide); AAM, acrylamide

Introduction

A stimuli responsive membrane responds to the changes in the environment such as temperature, pH, ionic strength, electric/magnetic field and light.¹ The fluctuations in the environment can trigger modification in the structure and functionality of the stimuli responsive polymer by changing their conformation and reactivity of functional groups present in the bulk or surface of the membrane. Hydrogel membranes, membranes with stimuli-responsive surface layers and porous membranes with surface grafted gates are the three types of stimuli responsive membranes.

The porous substrate membranes can be chemically modified by stimuli responsive functional gates for switching properties. This gating is produced by grafting of functional species on the external surface and pore walls. Different grafting techniques such as UV, plasma, gamma and chemical are used to produce stimulus responsive gating.^{2,3} These types of membranes neither lose the properties of base membranes nor affect the inherent response property of grafting polymer. This mini review reports the features and trends in thermo-responsive material grafted polymer porous membranes. Special attention has been given to the grafting of Poly (N-isopropylacrylamide) [pNIPAAm] on different polymer porous membranes.

Stimulus responsive gate membrane

Stimulus response gate membranes consist of grafted functional polymer chains at pore surfaces of membranes. The permeability and selectivity of the membranes are reversibly controlled by the conformational transformation of polymer chain produced due to the change in local environment. The conformational shift in the grafted polymer chains along with the backbone, side chains, segments or end groups produce variation in architecture and topography of the membrane surfaces

The responsive mechanism of the surface graft polymer chains are governed by its surface energy, entropy change and segmental interactions. The conformational change in grafted chains can change the size, structure and density of membrane pores. With the change in the environmental stimuli, these gates behave as a valve system in a reversible switching fashion.⁴ With the external chemical and physical environment, the hydraulic or diffusional permeability of the solute can be regulated by the gates in pressure driven convection or concentration driven molecular diffusion. Figure 1 shows schematic representation of opening and closing of membrane channels. Surface energy always forced to attain an orientation with minimum interfacial energy between the polymer surface and its immediate environment. Hence, polymer segments expand in good solvents and collapse in poor solvents. The stimulus responsive property change of the membranes enable it to bind and release drugs at target place in drug delivery applications or selectively adsorb certain compounds in separation processes. The switching behaviour of these membranes from hydrophilic to hydrophobic nature or vice versa with the external environmental stimuli reduces membrane fouling which may be utilized to design self-cleaning membrane surfaces. Tomicki et al.⁵ prepared a stimuli-responsive track-etched membranes via surface-initiated controlled radical polymerization of poly (2-dimethylaminoethyl methacrylate) (PDMAEMA) on poly(ethylene terephthalate) (PET) membrane surface. Two different stimuli temperature and pH can change the properties of PDMAEMA above or below the lower critical solution temperature/LCST and above or below the pK_b respectively.

Thermo responsive membranes

Many research studies have been done for the fabrication of membranes with responsive behaviour against environmental changes, whose pore or mesh size changes controllably in response to change in temperature. Surface wet ability of the membrane is switched with temperature by hydrophilic-hydrophobic transition behaviour of the thermo-responsive polymer chains grafted on the membrane surface. These membranes have applications in controlled release of drugs and chemicals, flux regulations, sensors, self-cleaning devices and size selective filtrations. Various physical and chemical techniques have been used for grafting stimulus-responsive functional polymers onto porous membrane.

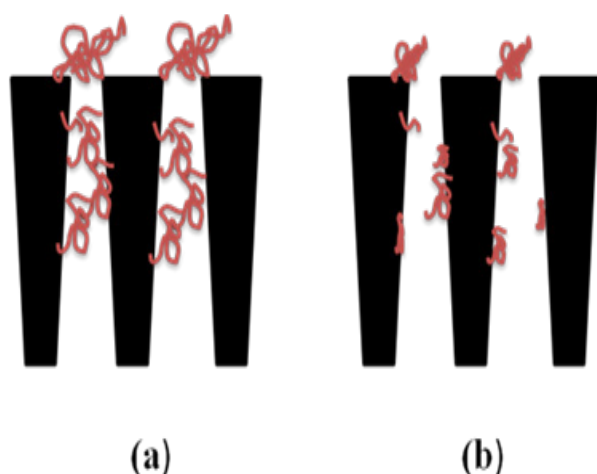


Figure 1 A Schematic of opening and closing of gates in an asymmetric membrane.

Depending on the grafting condition, the grafted polymer chains can be located mainly either on the external surface of membrane or inside the pores. Polymers such as poly (N,N-diethylacrylamide) (DEAAm) and Poly (N-isopropylacrylamide) (PNIPAAm) grafted on the membrane surface can undergo hydration-dehydration change in aqueous solutions in response to a relatively small change in temperature.⁶ Among these pNIPAAm is a widely studied thermo-responsive polymer which changes its conformation at its LCST (32°C).

Poly(N-isopropylacrylamide) [pNIPAAm]

Poly (N-isopropylacrylamide) [pNIPAAm] is a common thermo-responsive polymer which undergoes hydrophilic-hydrophobic transitions in solution in response to the temperature at around 32°C, i.e. the lower critical solution temperature (LCST) of the polymer. The LCST is the temperature at which aqueous solutions undergo a transition from a soluble to an insoluble state. In hydrogels, transition occurs from a swollen state to a contracted state as the temperature increase above their LCST. The contribution of entropy may lead to the chain contraction and phase separation if the hydrophobic and hydrophilic groups present are in the appropriate ratios. pNIPAAm is an example for non ionic water soluble polymer showing this type of phase behaviour. Other examples for thermo-responsive polymers are poly (N-vinyl caprolactam) (PVCL),⁷ poly (ethylene oxide) (PEO),⁸ PDMAEMA and poly(2-ethyl-2-oxazoline) (PEtOx).⁸ The LCST of a polymer can be changed by copolymerization.

Poly (N-isopropylacrylamide) undergo conformational changes in water by forming hydrogen bonding with amide group below LCST and polymer chains expand. Above LCST the polymer chains get collapsed entropically and expel water molecules. A schematic illustration of swelling and de-swelling mechanism of pNIPAAm chains below and above its LCST in water is shown in Figure 2. The surface confined pNIPAAm polymer chains changes its size more pronounced than that of at solution phase. Thus, grafting of pNIPAAm onto the porous membrane is advantageous to make thermo-responsive membrane. PNIPAAm have varieties of applications in separations, drug delivery systems, enzyme and cell immobilization and molecular valves.⁹

pNIPAAm modified membrane: Interesting studies

Graft polymerization of N-isopropyl acrylamide on the

membrane surface can be achieved by different techniques such as UV irradiation, plasma treatment, γ -ray, ozone treatment and chemical reaction.¹⁰⁻¹² These techniques have also been used for the fabrication of poly (N-isopropyl acrylamide) grafted chains on various substrates including polymer membranes. Wang et al.¹³ grafted pNIPAAm tubular-type porous polyethylene membrane by low temperature plasma method. The studies showed that the grafted pNIPAAm could respond immediately to surrounding temperature changes. By varying UV irradiation time and monomer concentration, the graft yield of pNIPAAm graft polymerization onto porous PE membranes can be controlled.¹⁴ For membranes with low graft yield, diffusional permeability is directly proportional to temperature and at higher graft yield, it is inversely proportional to temperature. Liang et al.¹⁵ prepared temperature-sensitive membranes by photo-induced graft polymerization of NIPAAm monomer on the surface of PP (polypropylene) microfiltration membrane. Curti et al.¹⁶ graft polymerized NIPAAm monomers on previously oxidized PET (polyethylene terephthalate) and PS (polystyrene) surfaces. It is found that the grafted surface can show hydrophobic and hydrophilic character dependant of the temperature.

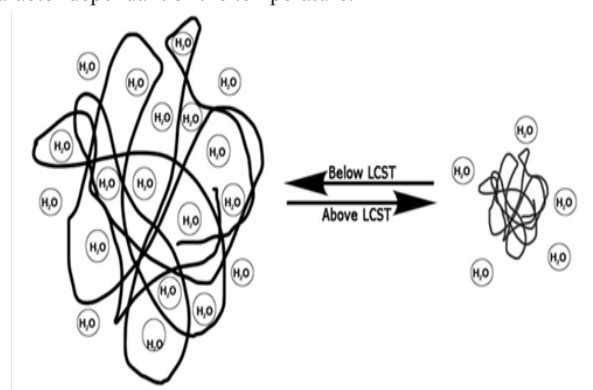


Figure 2 A schematic representation of swelling and de-swelling mechanism of poly(N-isopropylacrylamide) chains below and above its LCST in water.

The response temperature of pNIPAAm grafted membranes is normally around 32°C, the lower critical solution temperature of pNIPAAm. In practical applications different response temperatures are needed. The response temperature of the modified membrane prepared by the graft co-polymerization of NIPAAm and another monomer was found to be linearly changed with their molar ratio. A linear increase in the response temperature with molar ratio of hydrophilic monomer, like acrylamide (AAM) and a linear decrease with increase in the molar ratio of hydrophobic monomer like butylmethacrylate (BMA) were also reported.¹⁷ Some membranes have mixed polymer brushes that can respond to multiple external stimuli. Grafting of block copolymers, random copolymers, or two different homo-polymers in a sequential manner can generate multiple stimuli-responsive brushes.¹⁸ Peng et al.¹⁹ prepared a multi responsive PE (polyethylene) based membrane with temperature and pH responsive character by the sequential photo grafting of pNIPAAm and poly (methyl methacrylic acid) PMMA. The permeability of the co-grafted membrane was found to be controlled by the co-graft architecture, co-graft yield and co-graft composition. Okajima et al.²⁰ did the graft co-polymerization of NIPAAm and benzo-18-crown-6-acrylamide (BCAm) on the surfaces of porous PE membranes which can be used for regenerable cell culture membrane systems. The modified membrane surface was able to detect the cell death and selectively release dead cells. The cellular signals from the dead cells were recognized with the help of benzo-18-crown-6-acrylamide units

and the NIPAAm units functioned as the actuator to release the dead cells. In presence of potassium ions, NIPAAm/BCAm copolymer undergoes transition from hydrophobic to hydrophilic at the culture temperature 37°C.

The literature review showed that the pNIPAAm based thermo-responsive systems are getting more attention due to their wide applications from permeation to biological applications. Our research group also attempted pNIPAAm grafted on poly (ethylene-co-vinyl alcohol) membrane for biological separations and drug delivery.²¹ Membranes with self cleaning and self refreshing abilities can be fabricated using stimuli responsive membranes due to their ability of reversible changes to surface composition, surface energy, adhesion and wettability. The stimuli responsive membranes of future will move beyond barrier functions, where they respond in less well defined environments. Molecular imprinting is another interesting area for developing membranes that may act in response to chemical cues. The functions of natural receptors may be imitated by the imprinted polymer membranes and can be applied in cellular modelling transport.

Conclusion

Porous polymer membranes can be tuned by their surface functionalization especially by grafting a stimuli responsive material on the pores. This review put forward the importance and major research in this field by their versatile applications.

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Conflict of interest

The author declares no conflict of interest.

References

- Wandera D, Wickramasinghe SR, Husson SM. Stimuli responsive membranes. *J Membr Sci*. 2010;357(1-2):6–35.
- Cheng JW, Rui X, Hong BW, et al. Fabrication of a thermo-responsive membrane with cross-linked smart gates via a ‘grafting-to’ method. *RSC Adv*. 2016;6(51):45428–45433.
- Chen YC, Xie R, Chu LY. Stimuli-responsive gating membranes responding to temperature, pH, salt concentration and anion species. *J Membr Sci*. 2013;44:206–215.
- Tokarev I, Minko S. Multiresponsive hierarchically structured membranes: new, challenging, biomimetic materials for biosensors, controlled release, biochemical gates, and nanoreactors. *Adv Mater*. 2009;21(2):241–247.
- Tomicki F, Krix D, Nienhaus H, et al. Stimuli-responsive track-etched membranes via surface-initiated controlled radical polymerization: Influence of grafting density and pore size. *J Membr Sci*. 2011;377:124–133.
- Puhse M, Keerl M, Scherzinger C, et al. Influence of pressure on the state of poly(N-isopropyl acrylamide) and poly(N,N-diethylacrylamide) derived polymers in aqueous solution as probed by FTIR-spectroscopy. *Polymer*. 2010;51(16):3653–3659.
- Verbrugge S, Bernearts K, Du Prez F. Thermo-responsive and emulsifying properties of poly(N-vinylcaprolactam) based graft copolymers. *Macromol Chem Phys*. 2003;204(9):1217–1225.
- Saeki S, Kuwahara N, Nakata M. Upper and lower critical solution temperatures in poly (ethylene glycol) solutions. *Polymer*. 1976;17(8):685–689.
- Heijl JMD, Prez D. Fast, multi-responsive microgels based on photo-crosslinkable poly(2-(dimethylamino)ethyl methacrylate). *Polymer*. 2004;45:6771–6778.
- Kim SY, Kanamori T, Shinbo T. Preparation of thermo responsive polypropylene membranes grafted with N-isopropyl acrylamide by plasma induced polymerization and their water permeation. *J Appl Polym Sci*. 2002;84(6):1168–1177.
- Peng T, Chen YL. Temperature-responsive permeability of porous PNIPAAm-g-PE membranes. *J Appl Polym Sci*. 1998;70(11):2133–2142.
- Yu JZ, Zhu LP, Zhu BK, et al. Poly(N-isopropyl acrylamide) grafted poly (vinylidene fluoride) copolymers for temperature sensitive membranes. *J Membr Sci*. 2011;366:176–183.
- Wang XL, Huang WJ, Chen XZ, et al. Graft polymerization of N-isopropyl acrylamide into a microporous polyethylene membrane by the plasma method: technique and morphology. *Desalination*. 2002;146(1-3):337–343.
- Koetting MC, Peters JT, Steichen SD, et al. Stimulus-responsive hydrogels: Theory, modern advances, and applications. *Mater Sci Eng R Rep*. 2015;93:1–49.
- Liang L, Feng XD, Peurrung LM, et al. Temperature sensitive membranes prepared by UV photopolymerization of N-isopropyl acrylamide on a surface of porous hydrophilic polypropylene membranes. *J Membr Sci*. 1999;162(1-2):235–246.
- Curti PS, De Moura MR, Veiga W, et al. Characterization of pNIPAAm photo grafted on PET and PS surfaces. *Appl Surf Sci*. 2005;245(1-4):223.
- Xie R, Li Y, Chu LY. Preparation of thermo-responsive gating membranes with controllable response temperature. *J Membr Sci*. 2007;289:76–85.
- Sidorenko A, Minko S, Meuser KS, et al. Switching of polymer brushes. *Langmuir*. 1999;15(24):8349–8355.
- Peng T, Cheng YL. PNIPAAm and PMAA co-grafted porous PE membranes: living radical co-grafting mechanism and multi-stimuli responsive permeability. *Polymer*. 2001;42(5):2091–2100.
- Okajima S, Sakai Y, Yamaguchi T. Development of a regenerable cell culture system that senses and releases dead cells. *Langmuir*. 2005;21(9):4043–4049.
- Riyasudheen N, Sujith A. Thermo-responsive poly(ethylene-co-vinyl alcohol) based asymmetric membranes. *RSC Adv*. 2016;6(115):114276–114285.