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EFFECT OF PET SUPPORT MEMBRANE THICKNESS ON
WATER PERMEATION BEHAVIOR OF THERMALLY RESPONSIVE PNIPAM-g-
PET MEMBRANES

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ABSTRACT

In this study, a KrF excimer laser was used at 248 nm wavelength to fabricate support membranes and the final PNIPAM pore-filled thermally responsive PET membranes using a novel continuous two-step operation. Four different thickness (50, 75, 100, 125 μm) PET membranes were perforated using excimer laser ablation and 3 different mesh masks with 25, 31 and 43 μm opening sizes. The surface and cross-sectional morphologies of the ablated support membranes were elucidated using optical microscopy and micro-CT. Proper combinations of laser operational parameters (energy fluence, number of pulses, pulse frequency) and mesh size for each thickness membrane were determined based on energy required for perforation, average pore size and morphological observations.

Temperature responsive poly(N-isopropylacrylamide) (PNIPAM) hydrogel was grafted in membrane pores through pulsed laser polymerization (PLP) at 3 progressive grafting density values induced by different numbers of laser pulses. Membranes with 4 thicknesses and 4 grafting conditions (1 ungrafted and 3 grafted) for each thickness were characterized using water permeation test to yield 6-orders of magnitude membrane water permeability coefficients. Permeation behavior and thermal response were found for all 4 thicknesses of membranes at grafted state, and the permeation result displayed a decreasing trend in permeability coefficient with increasing thickness, while thermal response displayed an increasing trend with increasing thickness at higher grafting density state.

Scanning Electron Microscopy (SEM) was utilized to characterize the surface and pore grafting phenomena on membranes of different thicknesses under varied grafting conditions. Our results indicate that the film thickness has little or no effect on kinetics of PLP for given laser operation parameters, when grafting polymerization is performed on the PNIPAM monomer pool at the bottom of the support membrane which is polymerized upwards through the pores using excimer laser irradiation directed from the top of the pores. Thus, our results reveal that similar crosslink structure is obtained in PNIPAM grafted in the pores of different thickness support membranes when using the same PLP conditions.

DEDICATION

For those creative and considerate designers, especially the one who design this universe.

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CHAPTER I

INTRODUCTION

Interest in mimicking bio-membranes have been increasing due to the fascinatingly “intelligent” feature of bio-membranes^{[1], [2]}. Bio-membranes transport water, ions and even larger molecules like proteins in all kinds of living organisms. Among all approaches^{[3], [4]} to mimic bio-membranes, preparation of stimuli-responsive membranes is the easiest and most inexpensive way because it doesn’t require synthesis of artificial transferring channels or an effort on extraction of biological membrane proteins from living body. In stimuli-responsive membranes, mass transfer changes when an external stimuli, such as temperature, ph, light strength or electromagnetic field is applied^{[5], [6]}. Stimuli-responsive membranes prove effective in mimicking the way bio-membranes transfer essential molecules and the way they react to chemical cues in biological systems. Therefore, plenty of applications such as controlled transport^{[7]–[9]}, separation process^{[10], [11]}, chemical sensor^{[12], [13]} use stimuli-responsive membranes, among which controlled transport is the focus of this study. Since change in temperature is relatively easy to realize and due to general lack of severity in temperature changes observed in the biomedical field, temperature responsiveness is chosen to be the studied in this work.

Apart from synthesizing stimuli-responsive material (poly(N-isopropylacrylamide), PNIPAM), grafting it into laser-perforated support membranes (PET) is a commonly used

method^{[3], [4]}, it is also used in previous studies in our research group^{[14], [15]}, and it will be utilized in this study.

To fabricate a temperature responsive membrane, a two-step fabricating method was reported by Tiwari and Sancaktar^{[14], [15]}, in which a krf excimer laser was employed to ablate commercially available polyethylene terephthalate (PET) films to generate regular and uniform pores, and the same laser was used to graft thermo-responsive PNIPAM hydrogel into these pores. Although several techniques such as phase inversion, track-etching and electrospinning have been developed^[16] to produce porous support membranes, none of these produce the properties of porous support membranes mentioned above so as to have constant flux across the whole membrane. For example, even though track-etching^[17] might be able to manufacture regular cylindrical pores with pore size as small as 10 nm, which is a promising scale for the application of ultrafiltration, it still couldn't meet the requirement of uniformly distributed pores over the whole membrane. Additionally, the chemical etching applied after ion bombardment could lead to higher tendency of fouling as a result of this procedure, because of the morphology change on the surface of the membrane^[14]. Uniformity in pore morphology as well as pore size and size distribution ensure constant flow rate through the membranes as was achieved by masked laser ablation used in this study.

The same excimer laser is used for grafting hydrogel in the pores by Pulsed Laser Polymerization (PLP), which enables the whole processing time for grafting the thermally responsive polymeric material onto the support membranes to be shortened compared with UV photo-grafting, controlled radical grafting, plasma initiated grafting and radiation

induced polymerization. PLP allows precise and uniform grafting in all pores using krf excimer laser^[14]. With a lower critical solution temperature (LCST) at around 32°C due to its change in solubility in water to provide possibility for desired alteration of hydrophobicity, PNIPAM has been studied and employed in many researches^{[18], [19]}, and is also utilized in this study.

The works^{[14], [15]} by Tiwari and Sancaktar have shown that krf excimer laser can be multiply used in both ablation and polymerization for the process of fabricating a thermally responsive membrane using commercially acquired PET films and aqueous grafting solution consisting of the monomer of PNIPAM, crosslinker and initiator. The following conclusions were derived in their work.

- Varied pore sizes ranging from 600 nm to 25 µm could be obtained in support membranes by combining different laser operation parameters with mask mesh of various sizes.

- Permeability of water through the membrane could be tuned by modifying the laser operation to yield a 6-order difference in scale at room temperature for 25 µm thick membranes.

- Hydrogel network formation rate was positively related to the concentration of monomer in grafting solution.

- The effect of crosslinker in grafting solution on the thermo-responsiveness of those membranes were of great significance to the best of their understanding.

Based on their works, this study is focused on the thickness effect of support membranes on the water permeability and their temperature response, because different

thicknesses represent different mechanical behavior for the membranes as well as varied resistance to the extent of water flow through them. Thus, after a brief introduction to excimer laser ablation and pulsed laser polymerization in Chapter 2, applicable materials, experimental operations and characterization methods will be presented in Chapter 3. The results and discussions will be presented in Chapter 4 followed by our Conclusions Chapter 5.

CHAPTER II

BACKGROUND

In this chapter, Excimer laser will be introduced and perforation of polyethylene terephthalate (PET) film using excimer laser will be covered based on the mechanism of laser ablation of PET film. Several membrane techniques will also be introduced for comparison with the method of laser ablation. The use of excimer laser for pulsed laser polymerization (PLP) as a grafting (functionalization) method and information on the thermo-responsive hydrogel used are going to be outlined in the second half of this background Chapter. Lastly, a basic equation for laminar flow of an incompressible Newtonian fluid through a cylindrical channel driven by pressure (Hagen-Poiseuille equation) will be modified and expanded to be used in this research.

2.1. Excimer laser and laser ablation

Abbreviated from “light amplification by stimulated emission of radiation”, laser is a beam of light with extremely high energy that is generated by adding light of the same phase, same wavelength to the same propagation direction coherently through a gain medium.

Since the invention of the first laser in 1960, many different types of lasers have been developed. Based on their gain media, lasers can be classified into gas laser, solid state laser, dye laser and semiconductor laser etc. Among all these lasers, a type of gas laser, excimer laser is of great attention in the application of cutting, drilling and welding

operations^[20] owing to the high energy ultraviolet laser beam. Excimer is an abbreviation for “excited dimer”, which is used to describe excited noble-halogen gas dimer molecules. Based on the noble-halide gases mixture involved various wavelength and energy of UV-light can be obtained; commonly used ones are arf (193 nm), krf (248 nm), xecl (305 nm) and xef (351 nm)^[21].

Due to the relatively higher output pulse energy, 248 nm krf excimer laser is more widely used in polymer applications than the other types mentioned above^[22]. Involving Kr^+ , F^- and a buffer gas molecule (Ne or He in most cases), production of krf excimer laser pulse can be described simply as follows^[22].

First, a fast high-voltage electric current is discharged to excite Kr and F to obtain Kr^+ and highly electronegative F^- :

Afterwards, a three-body collision occurs and produces an excited dimer at high energy level:

Laser beam is emitted when excited molecule krf^* dissociates into atoms at ground state. The output energy of laser pulse relies on the energy difference between the excited and ground states, as shown in the graph of the potential well below in Figure 2.1^{[22], [23]}.

Figure 2.1 Internal energy of rare-gas halide molecules in excited and ground states^[22],
[23].

Excimer laser ablation removes unwanted material with least amount of collateral damage by breaking chemical bonds. Excimer lasers are most commonly used in the production of microelectronic devices. Laser aided eye surgery^[24] is another common example of excimer laser application in daily life. Since polymeric materials have relatively high absorbances of UV-light, they are very easy to be ablated by excimer laser. With this useful and interesting feature, excimer laser ablation will be one of the focus and a powerful technique employed in this research.

There are several laser operation parameters which affect the results of excimer laser irradiation. The energy per unit area of the laser beam, also known as Energy Fluence (will be denoted as F hereafter) needs to be higher than the ablation threshold of a polymeric material for ablation to occur. It is known that polymers have different absorbances at different laser wavelengths, and thus, different fluences may need to be used at different wavelengths to ablate them (see Table 2.1.1).

Table 2.1 Ablation threshold values at 248 nm laser wavelength for some polymers.

Ablation Threshold (mj/cm^2)				
PS	PC	PET	PI	PMMA
57	56	22, 30 ^a	65	200
All values taken from ref.[25]; a - from ref. [26], [27]				

The ablation fluence threshold in the case of PET with incoming 248 nm laser beam varies within 22-30 mj/cm^2 depending on the reporting source as shown in Table 2.1.1. Apart from F , the number of pulses of laser beam applied in ablation process (henceforth P for short) and the frequency of laser pulses (henceforth f for short) are two other operation parameters of importance for ablation. The process of masked excimer laser ablation on polymeric materials is shown in Figure 2.2[28].

In polymeric film ablation (especially PET film in this work), the polymer is covered by a metallic mask at the first stage with certain region(s) open, and the open area is exposed to the UV-light. Thus, once the incident beam hits the target material at the open

Figure 2.2 Schematic demonstration of laser ablation process for an irradiated polymer surface. Adapted with permission from reference[28]. Copyright (1989) American Chemical Society.

areas of the mask, the high energy of the laser beam is absorbed by certain depth of the affected zone based on Lambert-Beer law shown in Equation (2.1.4)[29].

$$d(F) = \frac{1}{\alpha_{eff}} \ln\left(\frac{F}{F_{th}}\right) \quad \text{Equation (2.1.4)}$$

Where $d(F)$ is the absorbing depth of polymer film per pulse (or ablation rate), F and F_{th} are the applied fluence and threshold fluence, respectively, and α_{eff} is the effective absorption coefficient.

Chemical bonds in the region of this certain depth will then be excited and start to break down due to photothermal or photochemical interactions with incoming light. Then,

the ablated small molecules eject from the original area in a burst of gas leaving an etched pit of certain depth behind. As the laser beam hits the same exposed area pulse by pulse the pit grows deeper and eventually a penetrated pore is formed through the film if sufficient number of pulses, P , is provided.

2.1.1. Morphology of ablated membrane

An optical microscopic image and an SEM image^[14] displayed below demonstrate the perforated membrane produced by excimer laser ablation. Regular and uniformly distributed pores are observed using this technique, which can be used for controlled transport study.

Figure 2.3 25 μm Support membranes fabricated using 635 mesh and Hz frequency. (a) and (b) show the pores and cross-section of a membrane fabricated using $F = 100 \text{ mJ/cm}^2$ and $P = 300$ pulses; Scale bar: 100 μm . Reproduced with permission from Ref. [14], Copyright (2018) Elsevier

2.1.2. Ablation mechanism

Plenty of works[25], [30]–[32] have been done to understand the mechanism of ablation. Basically, there are two models, photochemical and photothermal. A combination of the two is advocated by most[33]. It's generally believed that during the nanosecond time scale of an incident laser pulse photon energy primarily transforms into the energy of

electronic excitation. Subsequent step of energy transformation divides the mechanism into photochemical or photothermal categories. Based on the photochemical model, chemical bonds break directly resulting from the electronic excitation state leaving no damage to the remaining regions, which is preferred from manufacturing perspective. On the other hand, energy of bonds at excited state can also cause excited lattice vibration, thus thermal bond breakage occurs as predicted by the photothermal model.

2.2. Membrane techniques

Serving as an important part in a large number of separation processes, membrane technology has been increasingly highlighted since its first application. Membranes, considered as an interface, can be used to separate matters of great value as well as undesirable materials from their mixtures by applying pressure, a concentration gradient or an electronic field. Taking into account of the relatively low cost and ability to be manufactured extensively, polymeric materials are undoubtedly better choices than metal and ceramic for this purpose, and several methods have been developed to fabricate porous polymeric membranes in industrial practice. Some of the most widely employed techniques to produce porous polymeric membranes for controlled transport will be briefly introduced in the following sections.

2.2.1. Phase inversion

Phase inversion is a process in which a solution of polymer is triggered to undergo phase separation and the polymer-rich phase solidifies from a liquid state in a controlled manner while the polymer-lean phase (mostly solvent) is removed from the system by evaporation for its high volatility or by exchange with nonsolvent, thus a membrane of

polymeric matrix with desired microstructure is obtained[34]. Eventual membrane morphology is determined by what type of polymer, solvent and nonsolvent utilized and the composition of applicable components as well as the manner how phase transition is initiated. Usually, through: 1) cooling down the polymer solution system; or 2) by immersing the polymer solution in a non-solvent; or 3) by exposing the solution to non-solvent vapor; or 4) directly heat up solution to evaporate solvent[35], phase inversion can be initiated to achieve the desired pore morphologies and production effectiveness. Among these, the second method mentioned above is the most widely used, which is generally termed immersion precipitation. The exchange of solvent and non-solvent causes the phase separation to occur continuously when operated in a continual production manner, the producing setup and process are demonstrated in Figure 2.4.

Figure 2.4 A schematic of a roll-to-roll process for making polymer membranes by immersion precipitation. Reproduced from Ref. [36] with permission from The Royal Society of Chemistry (2017).

An SEM image of the cross-section of a typical immersion precipitation produced membrane is given in Figure 2.5 where we see different sizes of voids, these voids are the effective pores of the membrane.

Figure 2.5 The morphology of EB-cured PSU membranes as observed in SEM cross-section image. Reproduced from Ref. [37] with permission from The Royal Society of Chemistry (2016).

2.2.2. Stretching

Stretching is commonly used in producing microporous membranes in application of Microfiltration (MF) and ultrafiltration (UF) from extruded polymer film^[16]. This technique doesn't involve any solvent or other chemicals possibly used in other methods and it only requires the polymeric material to be highly crystalline so that the membrane can sustain mechanical stretching. Usually, after being molten and extruded from extruder, high crystalline polymer (such as PE and PP) will be stretched in two steps: Firstly, cold stretching of the film nucleates micropores from amorphous region of the polymer, and afterwards, hot stretching is carefully conducted to increase and finalize the pore size with consideration of thermal or mechanical properties of the precursor film such as melting point, crystallinity and tensile strength etc. Membranes produced from these procedures display an islandic structure where crystalline region is connected by fibers when observed using scanning electronic microscopy as shown in Figure 2.6[38].

Figure 2.6 Surface morphology of PP microporous membrane stretched under 105°C at different stretching rates (a: 10, b: 20, c: 30, d: 50, e: 100 mm/min). Reproduced with permission from Ref. [38] Copyright (2014) Springer.

2.2.3. Interfacial polymerization

Interfacial polymerization is an effective method people used to fabricate high performance reverse osmosis (RO) membranes^[16]. Although polymerized thin layer isn't the entire product, it serves as the effectual component on a porous substrate to provide high selectivity for this sort of membrane. The most useful material system is polyamide

due to the high reaction rate of amine-type monomer and acid chlorides. Usually, the aqueous solution with amines is adsorbed on the surface of the microporous support, and the porous membrane is then immersed in the acid chloride solution, condensation polymerization takes place immediately when two immiscible solutions come into contact, which contain the two kinds of reactive monomers. Therefore, polyamide is generated at the interface of aqueous solution and the water-immiscible solution. Once reaction ends, the membrane with freshly generated polyamide thin layer on the top will be cured at a high temperature to guarantee enough mechanical strength. A pair of the most commonly used PA polymerization monomers is m-phenylenediamine (MPD) and trimesoyl chloride (TMC), Figure 2.7^[16] and Figure 2.8[39] demonstrate the condensation reaction of this pair of reactants and the microscopic images of the resulting membrane.

Figure 2.7 Standard commercial polyamide membrane derived from m-phenylenediamine (MPD) and trimesoyl chloride (TMC) via interfacial polymerization. Reduced with permission from Ref.[16], Copyright (2013) Elsevier.

Figure 2.8 SEM and TEM images of RO membranes prepared in (a, b) hexane. Reproduced with permission from Ref. [39], Copyright (2007) Elsevier.

However, to some extent, this technique is more of functionalization than fabrication of support membranes.

2.2.4. Electrospinning

Electrospinning is a relatively new technique utilizing the physical properties (especially the ability to be charged and surface tension) of polymer solution to fabricate membrane for filtration and desalination[40]. In the process, a polymeric solution drop is charged by high voltage, and once the electric potential surpasses the surface tension of the solution droplet, a charged solution jet will be ejected and collected by a grounded plane to form fiber structure of the final membrane with solvent still in it. Upon taking away the solvent from the nanofibers, porous membrane will be obtained with certain pore morphology. This procedure is shown in Figure 2.9[41].

Figure 2.9 Schematic illustration of the basic setup for electrospinning. The insets show a drawing of the electrified Taylor cone and a typical SEM image of nonwoven mat of poly(vinyl pyrrolidone) (PVP) nanofibers deposited on the collector. Reproduced with permission from Ref. [41], Copyright (2004) Wiley-VCH.

To control the membrane porosity, average pore size, pore size distribution and certain mechanical properties, hot pressing of fabricated membranes is a critical step in post spinning treatments to reduce their thickness. An image of the cross-section of a hot-pressed electrospinning membrane[42] is presented in Figure 2.10.

Figure 2.10 Cross-section images of an electrospun hot pressed polyvinylidenefluoride-co-hexafluoropropylene (PVDF-HFP) membrane. Reproduced with permission from Ref. [42], Copyright (2013) Elsevier.

2.2.5. Track-etching

Track-etching is a method that uses high energy heavy ions from a radiation source to make atom-thick track across polymeric films. After the exposure to radiation, membranes are soaked in acidic or basic etching solution to widen the pores. This technique is very powerful in making regular cylindrical pores with very close pore size, i.e. Very sharp pore size distribution, which makes it easy to relate the transport properties through the membrane with the structural parameters such as pore size and shape. Several polymers that sustain strong acid, organic solvent have been studied and developed; PC, PET and PVDF with its copolymers are most commonly used. Membranes produced by track-

etching must be kept at a low porosity to avoid track overlapping and subsequent failure in solute transport. Irradiation duration is a very critical parameter to be controlled when processing with this technique, because it determines the pore density, and under the synergistic effect of temperature, it determines pore size of cylindrical pores. A general setup of a track-etching process with schematic demonstration is displayed in Figure 2.11, and SEM images of typical track-etched membranes are shown Figure 2.12.

Figure 2.11 (a) Track-etched membrane illustrating the porosity regime available by means of ion-track technology: single channel, non-overlapping channels, and overlapping channels. (b) Schematic of single-ion irradiation setup[43].

Figure 2.12 Trach-etched membranes prepared with (a) polypropylene substrate showing near parallel though overlapped pores, (b) polyethylene terephthalate substrate with “bow-tie” like pores, and (c) polycarbonate substrate with non-parallel oblique pores. Reproduced with permission from Ref. [17], Copyright (2001) Elsevier.

2.2.6. Short summary of membrane section

Comparing the morphology of membranes fabricated through all the methods mentioned above, what is easily noticed is that there is no other methods giving rise to regular pores except laser ablation and track-etching, and that only laser ablation is able to

produce uniformly scattered pores on the membrane, though the average pores obtained through track-etching are much smaller compared to those with laser ablation.

2.3. Functionalization (grafting) by PLP

Methods used to fabricate functionalized (grafted) membrane for scientific study and industrial manufacture have been developed for many years, and several of these methods are used in large scale[20], [44]. For membrane grafted with functional polymer, UV-photo polymerization[45], controlled radical grafting[46], plasma initiated grafting[47] and radiation induced polymerization[48] are the most common techniques in practice. The simplicity, productivity and high cost-performance ratio of UV-photo polymerization distinguishes itself from all other techniques mentioned above. However, there still remains a problem that limits wide exploitation of UV-photo polymerization related to precise control of transport. Because of the use of a quartz cover, grafting solution is trapped both on the surface and inside the pores, therefore, after a long time of exposure to UV light which is necessary in UV-photo polymerization, a thick layer of grafting material forms on top of the membrane surface which covers the pores so that it blocks the transport when applied for controlled transport^[14].

Inspired by several works using excimer lasers to conduct polymerization of water-soluble monomers, especially the articles by Ganachaud F. Et al[49], [50], on pulsed laser polymerization of NIPAM with 308 nm and 355 nm laser wavelengths[49], Tiwari and Sancaktar invented a grafting method employing 248 nm wavelength krf excimer laser^[14],^[15] for grafting of NIPAM in their works, which is able to address the overly grafting problem referred above. In this way, the amount of materials grafted inside the membrane

pores or on top of the membrane surface could be controlled by the number of pulses (P) operated in one run so that no undesired overly grafting would appear. Moreover, this pulsed laser polymerization is far quicker in performing grafting procedure than UV-photo grafting. Usable grafted membranes could be prepared within 3 minutes and even in few seconds.

As for the mechanism of pulsed laser polymerization (PLP), it is a free radical polymerization technique recommended by IUPAC for determination of propagation rate coefficient (k_p), because the combination of PLP with molecular weight distribution (MWD) measurement (such as gel permeation chromatography) proved to yield accurate k_p for polymerization of many types of monomers.

Figure 2.13[51] above shows MWD of PMMA synthesized with PLP, and as displayed in this graph, the molecular weight at the first inflection point is approximately half of that obtained at the second inflection point, providing the self-consistency check for PLP and its accuracy. At low monomer concentration, both initiator concentration and solvent type wouldn't influence the coefficient of propagation rate obtained^[20]. Thus, Equation (2.3.1)[52] is proposed for variation of chain length with k_p , monomer concentration and dark time.

$$L_0 = k_p [M]_0 t_0 \quad \text{Equation (2.3.1)}$$

Where, L_0 is the chain length of polymer growing in between two pulses of laser, k_p is the rate coefficient of propagation, $[M]_0$ is the initial concentration of monomer and t_0 is the frequency of laser pulse (f).

Figure 2.13 Molecular weight distribution (MWD, dotted line) and the first derivative of MWD (solid line) measured after PLP of PMMA. M1 to M4 indicate points of inflection on the MWD curve. Reprinted with permission from Ref. [51], Copyright (2009) Wiley-VCH.

In the process of polymerization, once initiators are triggered by impinging laser pulse, free radicals are generated, and propagation of polymer chain starts. Polymer chain will continue to grow until the arrival of next pulse because termination reaction of radicals is most likely to take place when the subsequent pulse of laser approaches the polymerization system. This is an abrupt increase of radical at the moment laser pulse reaches initiators, and gradual termination occurs through the dark time before the next pulse. Repeating pulses keep the concentration of monomer changing in a periodic manner, so that most polymer chains acquire the length of L_0 . But, if one radical survives the incoming laser beam, it will then grow by another L_0 to form a chain of $2k_p[M]_0 t_0$; if once again, then $3k_p[M]_0 t_0$ And so on as given by L_n :

$$L_n = nk_p[M]_0t_0 \quad \text{Equation (2.3.2)}$$

Equation (2.3.2)[52] describes the length of polymer which survives n pulses of laser, though from a statistical perspective, this n will not be large due to highest probability of termination at the arrival of subsequent pulse.

Equations mentioned above are only used for depicting linear polymerization of monomers. In this study, a crosslinker is involved to form a network, thus governing equation will no longer be the linear form. Though not able to be directly applied in this crosslinking case, these equations are still of great significance to understand that frequency of pulsed laser is playing a big role in PLP and radicals generate and terminate at the beginning and end of each dark time, respectively. Also, to have an insight of the crosslink structure and crosslink density, Equation (2.3.1) is helpful.

2.4. Thermo-responsive hydrogel

There have been several types of stimuli-responsiveness being discovered throughout the years^[2]. Materials able to switch the configuration when external temperature, pH, ionic strength or electromagnetic field changes are the most interesting and easiest to operate ones based on material properties.

Polymeric thermo-responsive material undergoes a phase transition in solution when temperature changes. This phase transition can be recognized when focusing on the solubility of the polymer. Based on polymer intrinsic characteristics, some polymers are continuously transitioning from more soluble to less soluble as temperature varies, while others could have a critical transition temperature so that immediate alternation of polymer

solubility would be noticed around the adjacent region. There are two sorts of this critical temperature, lower critical solution temperature (LCST) and upper critical solution temperature (UCST). Solution of a polymer with a LCST starts to phase separate when temperature rises to its LCST causing precipitation of the polymer. However, polymer with a UCST in solution is utterly opposite for it would go through the transition from insoluble to soluble state with increasing temperature approaching the critical point. These can be visualized intuitively in Figure 2.14.[53]

Figure 2.14 The upper critical solution temperature (UCST) and lower critical solution temperature (LCST) phase transition behavior of polymer chains across the phase separation boundary where swelling and deswelling occurs.[53]

Hydrogel is formed by aqueously soluble polymer absorbing a great amount of water. However, different from linear water soluble polymer, it doesn't dissolve, but take in water and swell in the solvent, because the networks in hydrogel provide a resistance force for the polymer chains in it to be completely separated by water molecules. When the tendency of dissolving and the stretch of cross-linking reach a balance, hydrogel becomes stable in size, and the amount of water taken.

In the case of temperature responsive hydrogel with a critical point mentioned previously, phase transition takes place between the polymeric component of the gel and the solvent absorbed when temperature changes in the corresponding route of certain critical solution temperature. Thus, such polymer crosslinking becomes insoluble leading to the deswelling of hydrogel.

Poly(*N*-isopropylacrylamide)

Figure 2.15 Chemical structure of Poly(*N*-isopropylacrylamide).[53]

Over the years, several thermo-responsive hydrogels have been discovered and studied. Among these, poly(*N*-isopropylacrylamide) (PNIPAM) is the most attractive one because its 32°C LCST is very close to physiological temperature of human being such that effort on developing potential biological and medical application of this polymer deserves attention^[20]. The chemical structure of PNIPAM is shown in Figure 2.15 Chemical structure of Poly(*N*-isopropylacrylamide)As reported by Fujishige et al.[54], hydrogen bonds exist between the NH groups on PNIPAM and the water molecules which make polymer to go into a coil conformation below its LCST. However, at temperature higher than the LCST of PNIPAM, conformation of the polymer chains turns into folded globules owing to strong hydrophobic effect caused by carbon backbone and isopropyl groups. The reason why hydrophobicity of PNIPAM increases leading to phase separation in PNIPAM aqueous solution is that the hydrogen bonds between the amide groups and

water is weakened when higher molecular kinetic energy rising from increased temperature exceeds that for the hydrogen bonds, as shown in Figure 2.16.^[11] Thus, taking advantage of the thermo-responsiveness of PNIPAM, researchers have developed plenty of well-designed and PNIPAM-based controlled transport devices.

Figure 2.16 Schematic of the mechanism of temperature response of PNIPAM. Reproduced from Ref. [11] with permission from The Royal Society of Chemistry (2015).

2.5. Basic Equations

In this work, Equation (2.5.1)^[14] is used to determine the permeability coefficient of membranes and is combined with Hagen–Poiseuille equation[34], which constitutes a basic principle of membrane technology (Equation (2.5.2) to obtain equivalent pore size for pores in grafted membranes, as well as ungrafted ones:

$$J = \frac{m}{\rho \cdot A \cdot \Delta P} \quad \text{Equation (2.5.1)}$$

$$Q = \frac{\pi r^4}{8\mu} \cdot \frac{\Delta P}{d} \cdot N_p \quad \text{Equation (2.5.2)}$$

All physical quantities in Equation (2.5.1) and Equation (2.5.2) are listed below with their according physical meanings.

J	Permeability coefficient
M	Mass flow rate of water (slope of weight vs time curve)
P	Density of water (1 mg/ml)
A	Area of effective membrane (perforated region of support membrane)
ΔP	Pressure drop (difference between applied pressure and atmosphere)
Q	Volume flow rate through the membrane
R	Average pore radius
M	Water viscosity
D	Membrane thickness
N_p	Number of pores on a membrane

The combination of Equation (2.5.1) and Equation (2.5.2) assists in investigating the relation between water permeability and the thickness of PET support membranes.

In order to calculate the equivalent pore size and to relate permeability coefficient (**J**) with the thickness (d) of membrane, Equation (2.5.2) is inserted into Equation (2.5.1) to yield

$$J = \frac{\pi r^4}{A \cdot 8\mu} \cdot \frac{1}{d} \cdot N_p \quad \text{Equation (2.5.3)}$$

The assumption: $\frac{\delta(\frac{Q}{\Delta P})}{\delta \Delta P} = 0$, is made in derivation of Equation (2.5.3), which means that the variation of volumetric flow rate with pressure drop isn't a function of pressure

drop. And in the case of rectangular channel in this study, adjustment of Equation (2.5.2) is made and corresponding equation[55] is

$$Q = -\frac{h^3 l \Delta P}{12 \mu d} + \frac{16 h^4 \Delta P}{\pi^5 \mu d} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^5} \cdot \frac{\cosh(\beta_n l) - 1}{\sinh(\beta_n l)} \quad \text{Equation (2.5.4)}$$

Where $\beta_n = \frac{(2n-1)\pi}{h}$, and since pore cross-section in this study is assumed to be square, the length and width of the cross-section are equal, Equation (2.5.4) can be rearranged into:

$$Q = \frac{a^4 \Delta P}{\mu d} \cdot \left\{ -\frac{1}{12} + \frac{16}{\pi^5} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^5} \cdot \frac{\cosh[(2n-1)\pi] - 1}{\sinh[(2n-1)\pi]} \right\} \quad \text{Equation (2.5.5)}$$

Where a is the side of square, and $a = h = l$. Noticing that the term in the brackets has nothing to do with any film geometrical parameter (a or d) or any experiment operational variable (ΔP or μ), it can be simply substituted by a constant C_0 . Furthermore, because the side of a square is proportional to the diameter of a circle sharing the same area with some constant ($a = \frac{\sqrt{\pi}}{2} \Phi$), Equation (2.5.5) can eventually be transformed to the form below, because diameter of a circle is more general to describe the dimension of a pore than the side of a square:

$$Q = C \frac{\Phi^4 \Delta P}{\mu d} \quad \text{Equation (2.5.6)}$$

We found that Equation (2.5.6) meets the requirement of the assumption we stated previously when driving Equation (2.5.3). Multiplication by the number of pores on one membrane enables Q in Equation (2.5.4) be input into Equation (2.5.1) to yield an equivalent equation with Equation (2.5.3) and all parameters of this new equation are to be evaluated or calculated in this research:

$$J = C \frac{\Phi^4}{\mu} \cdot \frac{N_p}{A} \cdot \frac{1}{d} \quad \text{Equation (2.5.7)}$$

Equation (2.5.7) is simple, easy to understand and useful in characterizing the permeation related properties. However, one more simplification should to be made involving the term N_p/A in Equation (2.5.7) by replacing it with the pore density (porosity) ρ' of each membrane, to yield:

$$J = C \cdot \rho' \cdot \Phi^4 \cdot \frac{1}{\mu} \cdot \frac{1}{d} \quad \text{Equation (2.5.8)}$$

CHAPTER III

EXPERIMENTAL

3.1. Materials and equipment

Commercial PET film (Mylar® Polyester Films) with four varied thicknesses were employed in this project to study the thickness effect on membrane water permeation behavior. Film thickness varies from 50 to 125 μm in 25 μm steps. Stainless steel meshes with average open pore size of 25, 31 and 43 μm (will be denoted as “mesh 500”, “mesh 400” and “mesh 325”, respectively) were acquired from TWP Inc. (Berkley, CA, USA), and these three types of meshes with pore density of 388, 248 and 164 pores/ mm^2 , respectively, were used with different film thicknesses to attain appropriate average pore size. Ethanol was purchased from Decon Labs, Inc. (King of Prussia, PA, USA). Acetone and tetrahydrofuran (THF) were purchased from Sigma Aldrich (Darmstadt, Germany). Distilled water for grafting solution preparation was generated in our lab, and deionized water was used for other purposes with total dissolved solids content below 5 ppm.

N-isopropylacrylamide (NIPAM), N,N'-methylenebisacrylamide (mbaam), Irgacure 2959 and hydroquinone were also purchased from Sigma Aldrich (Darmstadt, Germany) as monomer, crosslinker, initiator and quenching solution solute for polymerization reaction. Their chemical structures are displayed in Figure 3.1. A 248 nm krf excimer laser (LPX 2401) used in both ablation and photo-polymerization was manufactured by Lambda Physik (Coherent, Santa Clara, CA, USA). Filtration cell

(Amicon 8010) from Millipore (Darmstadt, Germany) was used to measure the water permeability of our membranes.

Figure 3.1 Chemical structures of the constituents of aqueous grafting solution used for PLP on the PET support membranes.^[20]

3.2. Membrane fabrication

3.2.1. PET support membrane fabricated by laser ablation

Support membranes were fabricated by using the laser beam generated by excimer laser to ablate and perforate the areas of PET film not covered by the stainless steel mesh.

First, commercial PET films were cut into 30 mm × 30 mm size and then cleaned by sonicating in THF and acetone and dried up for later use. Rectangular mesh was bonded to a metal plate with a circular hole (2 mm in diameter) with the aid of double-sided tape. PET films were immobilized by a few magnets on the mesh-mounted metal plate, and then this whole setup was placed on a glass slide with another metal plate covering undesired areas of the film to protect those regions from damage of scattered or direct UV light exposure; only the 2 mm hole was exposed to the laser beam each time. The assembly of entire system is shown in the [Figure 3.2](#).

Figure 3.2. Schematic diagram of sample setup.

At this step, excimer laser was operated under constant high voltage mode at 26 kv with 1Hz frequency (f). Perforation behavior of different thickness PET films was studied at various fluences (F) between 200 mj/cm^2 and 500 mj/cm^2 . Figure 3.3[14] shows the setup of the bulk experiment. Various pore sizes and differed extent pore openings were obtained depending on the number of pulses (P , which is a changeable parameter by computer setting) and fluence (which is tuned by moving moveable stage close to or away from the focal lens above).

Different size perforated areas were obtained using various ablation conditions. A combination of certain F , P and f , such as “F350P400f1” stands for ablation operated under condition of energy fluence at 350 mj/cm^2 with 400 pulses of laser and frequency at 1 Hz. Based on Tiwari and Sancaktar’s work on 25 µm PET film^{[14], [15]}, the fluence, F , was chosen to vary at a step growth sequence from 250 to 400 mj/cm^2 with a 50 mj/cm^2 interval for each of 50 , 75 , 100 and 125 µm films. Fluences lower and higher than these preset

values were also attempted to find the best operational variable combination for each thickness. Ablated membranes cleaned in THF with sonication were then dried with air gun and set in clean petri dish for further drying. Membrane pores morphology were analyzed by optical microscopy and the average pore sizes were calculated using an image analysis software, imagej, and Excel.

Figure 3.3. Schematic diagram of the whole setup for ablation. Reproduced with permission from Ref. [14], Copyright (2001) Elsevier.

3.2.2. Grafting of NIPAM by PLP

A 2 ml grafting solution was prepared and shaken for one day to have all components dissolved before performing grafting experiment. Concentration of monomer, initiator and cross-linker are listed in

Table 3.1. Concentration of different constituents in grafting solution. Total Volume is 2ml.

Material	Function	Concentration	Amount
NIPAM	Monomer	5 w/v %	100 mg
Mbaam (10mg/ml stock solution)	Crosslinker	1 wt. % (wrt monomer)	100 μ L
Irgacure 2959 (4mg/ml stock solution)	Initiator	1 wt. % (wrt monomer)	250 μ L
Deionized water	Solvent	82.5 volume%	1650 μ L

The grafting solution was bubbled in a vial with a small surge of nitrogen for 5 minutes each time, to drive away oxygen in the solution. The cleaned and dried membrane samples were cut into a circle (25 mm in diameter) and labeled with ablation condition and grafting condition. A flat aluminum O-ring (20 mm in outer diameter; 7 mm in inner diameter) was used to store 90 μ L grafting solution at the center of a glass petri dish, which was then covered by a tube-inserted cap with a quartz window at the center, and the whole system was under nitrogen environment once the petri dish was covered. Before the petri dish was capped, support membranes were carefully placed on the O-ring with the perforated area touching the 90 μ L grafting solution from the bottom side of the membrane. Nitrogen was blown into the petri dish for 5 minutes before irradiation began. The whole setup is similar to that for the ablation procedure, as shown in Figure 3.4. ^[14]

Figure 3.4. Schematic diagram of grafting setup. Reproduced with permission from Ref. [14], Copyright (2001) Elsevier.

At this stage, the excimer laser, was operated under constant high energy mode using 100 mJ/ pulse and the fluence was set at 5 mJ/cm², which is way below the ablation threshold of PET under 248 nm UV light. With the frequency set at 25 Hz for moderate chain length based on Equation (2.3.1), several carefully arranged pulses were used to produce ungrafted samples and various degrees of grafting, or more precisely, varied water permeability coefficients to be achieved in the subsequent water permeation tests. Grafting conditions for films of all thicknesses are listed in Table 3.2. Conditions for grafting NIPAM on support membrane.

Table 3.2. Conditions for grafting NIPAM on support membrane.

Grafting condition	F (mj/cm ²)	P	F (Hz)	Operation time (s)
Ungrafted	5	0	25	0
F5P300f25	5	300	25	12
F5P600f25	5	600	25	24
F5P900f25	5	900	25	36

After grafting, the processed membranes were soaked in 5 mg/ ml hydroquinone quenching solution to quench polymerization immediately to avoid overgrafting. Then, flushed with DI water, grafted membranes were kept in hot water bath at 50~60 °C in order to let go of the remaining monomers or quenching liquid.

3.3. Characterization

3.3.1. Optical microscopy

In this study, an optical microscope (Olympus BX-51, Olympus Corporation) was used to obtain images of the perforated region of the support membrane before it underwent grafting procedure. The pictures were taken under 200x magnification in transmission mode at several different areas on a sample to obtain an average pore area with the help of the greyscale pixel analysis function in imagej software (NIH). Afterwards, the average pore areas were also used to determine the equivalent circular pore diameters of pores under

every condition. Average equivalent pore sizes under different fluences, F were then plotted versus the number of pulses, P , to see the effect of F and P on the pore sizes for each film thickness.

3.3.2. Water permeation

To characterize how well grafted membranes perform, water permeability of samples at various grafting conditions were tested with a filtration cell (Amicon 8010, Millipore). Samples were placed in the filtration cell with the perforated and grafted area being at the center of the base where the outlet of cell locates, and the cell was tightly sealed with a rubber O-ring preventing any possible leakage. The whole cell was kept in a temperature controlled water bath. There was a preheated water reservoir at the upstream of the cell, and the reservoir was pressurized by a nitrogen tank under certain preset values between 0.034 mpa (5 psi) and 0.31 mpa (45 psi) depending on the degree of grafting. At the end of water tube was a weighing balance set to collect outcoming water weight every few seconds, and with the weight and time listed on a PC, a weight-time curve was easily plotted, so that water permeability coefficient could be evaluated from the slope of the weight-time curve at 23°C and 45°C using Equation (2.5.1):

$$J = \frac{m}{\rho \cdot A \cdot \Delta P} \quad \text{Equation (3.3.1)}$$

Where m is the slope of weight versus time curve; ρ is the density of water (1 mg/ml); A is the area of perforated region; ΔP is the applied pressure.

To evaluate the average pore size for grafted membranes, Hagen-Poiseuille's equation is needed:

$$Q = \frac{\pi r^4}{8\mu} \cdot \frac{\Delta P}{d} \cdot N_p \quad \text{Equation (3.3.2)}$$

We can rearrange Equation (3.3.2) to have a useful form:

$$\Phi = 2r = \sqrt[4]{\frac{8\mu Q}{\pi N_p} \cdot \frac{\Delta x}{\Delta P}} \quad \text{Equation (3.3.3)}$$

Where Φ is the equivalent average pore diameter; r is the average pore radius; μ is water viscosity; Q is the volume flow rate through membrane; Δx is the membrane thickness; N_p is the number of pores; ΔP is the applied pressure.

In addition to determining the permeability coefficient and equivalent pore size for each membrane, thicknesses of membranes are also taken into account through Equation (2.5.8) to determine the relation between the thickness and the permeability coefficient. Moreover, to avoid variations in pore density (ρ'), pore size (Φ) and viscosity (μ) resulting from temperature differences, permeability coefficient needs to be normalized with these 3 parameters.

Therefore, the permeability coefficient normalized with ρ' and Φ is denoted as J'' :

$$J'' = \frac{J}{\rho' \cdot \Phi^4} \propto \frac{1}{\mu} \cdot \frac{1}{d} \quad \text{Equation (3.3.4)}$$

Subsequently, J''' is the permeability coefficient that is further normalized with μ (where μ is a function of temperature):

$$J''' = J'' \cdot \mu \propto \frac{1}{d} \quad \text{Equation (3.3.5)}$$

Based on Equation (3.3.4) and Equation (3.3.5), J'' and J''' are both plotted versus thickness (d) to determine how thickness affects the membrane permeability coefficient.

3.3.3. Scanning electronic microscopy (SEM)

SEM was employed in this study to examine the surface morphology of membranes under various steps, as well as to examine the cross section of an ungrafted support membrane.

Table 3.3 depicts the grafting condition and thickness of typical samples examined in this manner. These membranes were broken into 2 pieces when they became brittle at extremely low temperature with the aid of liquid nitrogen, and then were taped with electro-conductive tapes on SEM stubs. To guarantee their electro-conductivity for successful observation, these membranes were also coated with a thin layer of gold on their surfaces before mounting onto the SEM sample stage. SEM examination was conducted under 2 kv voltage. Liquid nitrogen was used to make sure that vacuum pump could take out as much air as possible; only when pressure decreases to 6.9×10^{-7} Mpa (1×10^{-4} psi) can SEM electron beam be operated.

Table 3.3. SEM observation samples.

<i>P</i>	Ungrafted	300	600	900
D50	T; B	T	T	T
D75	T; B	T	T	T
D100	T; B	T	T	T
D125	T; B; C	T	T	T

T: top side is observed; B: bottom side is observed; C: cross-section is observed

3.3.4. Micro-computed tomography (Micro-CT) scanning

Micro-CT scanning was used in this study to obtain additional insight into the pore morphology of ablated support membranes. Samples were cut into a 10 mm $\times$ 4 mm

rectangular piece on which the perforated area was at the center of the specimen. Afterwards, testing sample was mounted on top of a stick shaped sample stage using clay. Specimen had to be perfectly straight vertically along radius direction so that homogeneous scanning could be performed to yield clear images. Scanning resolution of 0.75 μm and scanning area at perforated area were selected to find the finest and clearest view of perforated region.

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1. Ablated support membranes

After ablation with krf excimer laser and careful cleaning in THF, average pore sizes of PET membrane of each thickness were calculated by using imagej from micro images taken under an optical microscope.

These pore size data were plotted in graphs shown in Figure 4.1 as a function of number of pulses (P). In each graph there are plots corresponding to 3 different laser energy fluences. These different fluences were selected by calculating the energy required to perforate through the whole thickness of these films. Since there are 4 different thicknesses with a constant increment of 25 μm between each two nearby thicknesses, the medium energy fluence (in red color in each graph) is also taken in this stepwise rising manner with a step increment of 50 mJ/cm^2 .

Figure 4.1 reveals that films of all thicknesses have a “pore-open” P under each given fluence, with this “pore-open” P being the number of pulses before which the pores are not yet completely open under a certain F . Since higher fluence represents more focused energy, the ablation rate is accordingly higher, i.e. A thicker layer of material is activated and ablated by one pulse of laser beam of higher energy fluence. Therefore, with

Figure 4.1 Average pore size vs. Number of pulses for each thickness at various Fluences. (a) membrane thickness of 50 μm; (b) membrane thickness of 75 μm; (c) membrane thickness of 100 μm; (d) membrane thickness of 125 μm.

a higher fluence, the “pore-open” P happens to be lower, which can be most obviously noticed in the graphs of 125 μm film, in Figure 4.1(d), where films started to be perforated thoroughly at P300, P350 and P400 under F450, F400 and F350, respectively. Figure 4.2 show optical micro images for three “pore-open” stages of 125 μm ablated support membrane. These stages correspond to: (a) pores are not open yet, but just about to (F350P200f1); (b) Pores are half open (F350P300f1); (c) Pores open completely (F350P350f1).

Figure 4.2 Optical micro images for 3 “pore-open” stages of 125 μm ablated support membrane. (a) Pores are not open yet, but just about to ($F350P200f1$); (b) Pores are half open ($F350P300f1$); (c) Pores open completely ($F350P350f1$).

Secondly, it can be noticed that as the applied P reaches the “pore-open” P , subsequent pulses of laser beam would merely increase the pore size a little bit or even keep them almost constant for each and every thickness of film under certain F with a given mesh. The reason why this happens is quite intuitive because once the pores deepen, there will be less membrane material blocking the incoming laser beam by absorption. However, the presence of tapered pore wall displayed in images of Figure 4.3. Taken under SEM and reconstructed from micro-CT scanning images, does cause some loss of laser energy.

Figure 4.3 (a) SEM image for clear-cut view of 125 μm ungrafted PET membrane ablated under F350P400f1; (b) Micro-CT scan image for cross-sectional view of 75 μm PET membrane grafted under F5P600f25. Stripes in the red box in (a) are caused by the cutting process and also, possibly, because of the layer-wise crystalline structure of PET film.

Lastly, comparing the average pore sizes represented by the three colored curve-plateaus in each graph in Figure 4.1, conclusion is easily drawn that a higher F results in a larger average pore size when the total energy eventually applied is the same. Thus, the effect of fluence is more dramatic than that of P . Figure 4.4 shows that the increase of average pore size from the lowest fluence (black) to the medium one (red) is a bit larger than that from medium to highest fluence (blue). Observation of the pore morphology in Figure 4.4 also suggests that film ablated under a higher F would have more well-defined and more clean-edged pores, which are desirable for controlled transport. We note, however, that in order to obtain smaller pores, the applied F can't be too high. Therefore, the optimal combinations of F and P were determined for each thickness PET film for our study, and the results are shown in Table 4.1.

Figure 4.4 Optical micro images of 50 μm PET membrane ablated using 350 pulses of laser beam at 1 Hz frequency, and (a) $F = 200 \text{ mj/cm}^2$, (b) $F = 250 \text{ mj/cm}^2$, (c) $F = 300 \text{ mj/cm}^2$. (d) Average pore size vs P plot for 50 μm support membranes at various fluences.

Table 4.1 Mesh, mesh size, ablation condition of each thickness of film in ablation.

Thickness δ (μm)	Mesh	Mesh Opening Size (μm)	Fluence (mj/cm ²)	Number of Pulses	Frequency (Hz)
50	500	25	250	350	1
75	400	31	300	350	1
100	325	43	350	375	1
125	325	43	400	375	1

All these conclusions drawn from the pore size vs P plot remain consistent with those in works of Tiwari and Sancaktar^{[14], [15]}, in which they studied the effect of P and F on the pore size of ablated 25 μm PET membrane.

Because this step of PET film ablation is a procedure to prepare porous support membranes for the subsequent step, which is the pulsed laser polymerization (PLP) grafting, the principle for selecting best ablation operation condition remain the same as in [14] and [15], though thickness of film and lowest energy to perforate each thickness film change. The lowest energy for perforating each thickness of film is calculated from the smallest product of fluence and the corresponding number of pulses in each graph in Figure 4.1. It is plotted vs. Thickness in Figure 4.5.

Figure 4.5 Lowest energy per unit area required to completely perforate each thickness of film (Data are chosen from Figure 4.1.).

For efficiently controlled transport, clean and clear edged pores are desired in membranes which are fabricated as efficiently as possible without making the pores too large. Comparing all the average pore sizes and micro images of membranes prepared under every ablation condition, the optimal operation parameters selected for the perforation step were listed in Table 4.1. Table 4.2 lists the average pore size, consumed time and the total ablation energy needed for perforated films of each thickness fabricated at the corresponding conditions listed in Table 4.1.

Table 4.2 Production time, total energy required per unit area and average pore size of each thickness of film perforated by ablation.

Thickness δ (μm)	Time of Production (min-s)	Total Energy per Unit Area (mj /cm ²)	Average Pore Size (μm)
50	5-50	87500	12.90 ± 1.42
75	5-50	105000	21.01 ± 2.21
100	6-15	131250	23.81 ± 3.49
125	6-15	150000	25.02 ± 1.66

In our study, the laser pulse frequency was fixed at 1 Hz to produce clean edged pores since ablation under higher frequency such as 5 Hz or 10 Hz both gave rise to irregular or wavy edges. Ablation is a process of activating PET polymer chain such that undesired part of PET films is caused to degrade into low molecular weight substances such as gas (H₂O, CO, CO₂, etc.) Or smoke[28]. Without enough time interval between two pulses, the produced gas can't be fully vacuumed away by the vacuum bump. Therefore, some parts of the targeted area might be missed by the laser beam which has been scattered by the

small molecules mentioned above. Therefore, in order to create uniform and well-defined pores for constant flow rate material transport, a wider interval is needed.

Figure 4.6 Average pore size plots of 75 μm PET membrane ablated with (a) mesh 500 (m500) and (b) mesh 400 (m400); Example of optical microscopic image of bottom surface of ablated support membrane ablated with (c) mesh 500 (mesh open size of 25 μm) and (d) mesh 400 (mesh open size of 31 μm).

When performing grafting and post-grafting Water Permeation Test, mesh selection for the previous perforation step manifests its importance for improving productivity and quality. For example, pore size plot for 75 μm membrane ablated under two different size meshes (mesh 500 with 25 μm opening size; and mesh 400 with 31 μm opening size) shown in Figure 4.6 illustrates this observation. Figure 4.6 reveals that the difference in average pore size when using these two different support membranes is ~10 μm, which is much larger than the difference in the mesh opening sizes (~6 μm). Furthermore, the use of mesh

500 (Figure 4.6 (c)) results in much larger heat-affected zone (the dark area around the pores) in comparison to mesh 400 (Figure 4.6 (d)).

Although a denser mesh (mesh 500) gives rise to smaller pores with which transport through the membranes will be less, if desired, the water permeation results shown in the following section suggest that an optimum combination of thickness with average membrane pore size is crucial for fabricating membranes with wider range of permeability.

4.2. NIPAM grafted PET membranes

Using PLP, NIPAM was grafted in the pores of different thickness PET support membranes. For PLP, various pulse numbers (P s) were used at constant laser energy fluence of 5 mJ/cm^2 and constant laser pulse frequency of 25Hz. , PNIPAM was grafted from the grafting solution reservoir at the bottom of membrane pores and the PNIPAM hydrogel network grew upward inside the pores of these support membranes to fill up the whole pore by PLP. Thus, varied grafting densities were obtained to yield a large range of water permeability in the Water Permeation Test. Also, it was reported[15] that PNIPAM pore-grafted PET membranes have temperature responsive water permeation behavior, and likewise, thermo-responsiveness was also observed in this study and will be addressed by PLP grafting different thickness membranes using several different PLP pulses.

4.2.1. Water Permeability of NIPAM-grafted PET membranes versus P

From graphs in Figure 4.7, for each thickness, it's clearly seen that water permeability coefficient (J) and the equivalent pore size decrease with increasing number of pulses (P)

Figure 4.7 Permeability coefficient and the equivalent pore size for various grafting conditions thicknesses of membrane at both room temperature (23°C, black) and a higher temperature (45°C, red). (a)(c)(e)(g) are permeability coefficient at varied P_s of 50, 75, 100 and 125 μm membranes, respectively; (b)(d)(f)(h) are equivalent pore size at varied P_s of 50, 75, 100 and 125 μm membranes.

when a fluence ($F = 5\text{mj/cm}^2$) below PET ablation threshold and a mild laser beam frequency ($f = 25\text{ Hz}$) are used. The same composition of grafting solution (5% monomer; 1% crosslinker; 1% initiator) is used during these tests (Figure 4.7).

The reason for the trend of decreasing J with increasing P is very straightforward; as P increases, more monomers are polymerized onto the hydrogel network mass, filling up the pores from grafting solution reservoir. On one hand, this growth of network reinforces the overall strength of the grafted materials such that less material might be washed away when conducting water permeation test; on the other hand, the additional PLP of the hydrogel increases crosslink density, which in turn increase the extent of resistance to water flow through the network. Therefore, decreases in permeability coefficient can be noticed with every thickness of PET support membranes as P increases.

Also, an abrupt drop of permeability from the magnitude of 10^6 to 10^3 is observed in Figure 4.7 when comparing the permeability of an ungrafted state ($P = 0$) with that of the first grafted state under 300 pulses ($P = 300$); afterwards, permeability rolls down gradually as P increases. In other words, Figure 4.7 (a) shows that the permeability (J) vs. P variation with 50 μm thickness PET membrane exhibits a drop of approximately 2 million $\text{L/m}^2\text{hrbar}$ for J in $P = 0$ to $P = 300$ interval, while the drop of J value is merely several thousands in the $P = 300$ to $P = 600$ interval. An explanation for this huge difference is that, according to Equation (2.5.7), permeability coefficient is proportional to the 4th power of pore size (Φ). This pore size value changes significantly from clear pores to hydrogel grafted pores as shown in Figure 4.7 (b). The pore size drops by about 10 μm in the case of 50 μm membrane and membranes of larger thicknesses could have an even larger decrement. However, as the grafted hydrogel grows strong enough to sustain the high pressure of water,

the change in pore size is relatively small, e.g. 1 μm in the $P = 300$ to $P = 600$ interval for 50 μm membrane, as shown in Figure 4.7 (b). Therefore, the corresponding permeability drop of these two pore size changes exhibit such a high difference for the same P increment.

By looking into the differences between the “ J vs. P ” graphs corresponding to 23°C and 45°C conditions in Figure 4.7, positive thermal response of PNIPAM-g-PET membrane can be recognized throughout all P s, and the absence of negative thermo-responsiveness at the highest P employed suggests that grafting density of PNIPAM hydrogel caused by 900 pulses of laser beam is still moderate with the given grafting concentration.

The observed variation in permeability is consistent with that was reported earlier by our group^{[14], [15]} using a thinner PET support membrane (25 μm).

We note that, pursuant to PLP, and depending on the amount of hydrogel material grafted, the membrane pores may be partially or fully filled, lengthwise, as displayed in Figure 4.8. SEM images of top surface of ungrafted membranes and grafted membranes at each grafting condition for all four thickness membranes are displayed in Figure 4.9. Membrane pores under each grafting condition for all thicknesses were fully filled with PNIPAM hydrogel, but not necessarily flush with or flowing over the support membrane, as observed in Figure 4.9.

Figure 4.8 schematic of partially (left) and fully (right) filled pores.

Figure 4.9 SEM images of top surface of ungrafted membranes and grafted membranes at each grafting condition ($P = 300$; 600 ;and 900) for all four thickness membranes. Scale bar: 50 μm .

4.2.2. Thickness effect on Water Permeability of PNIPAM-g-PET membranes

In order to have a clear and straightforward idea of how thickness affects the transport behavior of membrane, permeability coefficient data were replotted in the manner of “ J vs d ” which is displayed in Figure 4.10. However, the pattern of how J varies with d displayed in Figure 4.10 shows no trend at all.

Figure 4.10 Permeability coefficient plotted vs. Thickness under various grafting conditions at a) room temperature (23°C) and b) 45°C.

Tracing back to Equation (2.5.8) we can see that J is proportional to the inverse of thickness, which doesn't coincide with graphs demonstrated above. Considering the 4th power influence of pore size on J (Equation (2.5.8), it is necessary to eliminate the impact of both pore size (Φ) and pore density (N_p/A) on J . Therefore, we let the first normalized permeability coefficient J'' to be equal to the permeability coefficient J divided by the 4th power of original pore diameter ($[\Phi]$) and the pore density (N_p/A):

$$J'' = \frac{J}{[\Phi]^4 \cdot \rho'} \quad \text{Equation (4.2.1)}$$

Where $\rho' = \frac{N_p}{A}$ Is the pore density.

From the new plots in Figure 4.11, an obvious negative correlation of J'' and d can be observed for each P at both room temperature and a temperature higher than the LCST of PNIPAM (45°C). Since viscosity term remains unchanged at one certain temperature, second normalized permeability coefficient J''' will be considered only when discussing the effect of thickness on the thermo-response behavior of membrane permeability coefficient.

Figure 4.11 Permeability coefficient normalized with pore density and pore size for all thicknesses of membranes under varied grafting conditions at a) room temperature (23°C), and b) 45°C.

Since water transport in ungrafted pore channel is typically laminar flow, resistance to the flow arises from friction between water molecules and the inner surface of membrane pores. Therefore, the thicker the membrane is, the more mass transport delayed is observed, and the permeability coefficient is lower. This is predicted by Equation (3.3.4) and demonstrated in Figure 4.11 for the ungrafted membranes.

As a matter of fact, the actual water flow path (d_x) is much longer than the nominal path (d , thickness of membrane)[56] for a molecule to travel in hydrogel micro pores. The attraction force between the water molecules and the side groups of PNIPAM is stronger than that between water and PET, because water share more affinity with the amine groups on PNIPAM hydrogel network due to molecule polarization, while PET chain is nonpolar. Thus, the grafted hydrogel will have stronger resistance for water to transport through the pore due to affinity-induced delayed migration of water molecules inside the hydrogel. This accounts for the huge difference in J'' between the ungrafted membranes and the grafted ones.

In the case of grafted membranes, it's no longer plausible to simply use a model of laminar flow through regular tube to describe the water flow in the hydrogel. Therefore, the reason why water permeation decreases with increasing membrane thickness has to be considered with respect to the crosslink structure of grafted hydrogel. In order to discern the effect of the hydrogel structure, the percent void volume in hydrogel, termed as porosity (ε), is calculated based on the equivalent pore size calculated using Hagen-Poiseuille equation and the corresponding data of Figure 4.7 (b) (d) (f) and (h). The approximation in effective change in pore size is demonstrated by the diagram in Figure 4.12.

Figure 4.12 Schematic demonstration of approximation in effective change in grafted membrane pore size. The Hagen-Poiseuille equation is applied to calculate equivalent pore size and porosity.

With the approximation described above, average porosity of hydrogel grafted at three grafting conditions were calculated and plotted vs. Thickness in Figure 4.13.

As shown in Figure 4.13, porosity of network grafted using 300 laser pulses are around 2.5-3.0%, 600 pulses 1.25-2.3% and 900 pulses 1-1.25% for the range of membrane thickness used. This porosity data corresponding to a certain P can be treated practically as constant with membrane thickness, which indicates that crosslink structure of hydrogel at certain P in varied membrane thicknesses are similar. Therefore, the effect of membrane

thickness on the grafting of hydrogel is rather small or even none. Based on this observation, the explanation for the decrease of water permeation with thickness increase should focus on the actual pathway of water through the grafted PNIPAM and the thickness itself.

Figure 4.13 Average porosity of hydrogel network grafted at $P = 300$; 600; and 900 for all four membrane thicknesses. Original data were collected at 23° C.

Since the hydrogel structure in different thickness membranes are similar at a given grafting P , and mutual attracted molecule types don't change, we can assume that a constant tortuosity τ exists for a certain grafting condition for all thicknesses. According to the definition of tortuosity[56] shown in Equation (4.2.2), and the schematic demonstration in Figure 4.14, τ must be greater than unity and the amount of τ is determined by grafting density, or grafting P from an operational point of view when grafted materials remain unchanged and water is the only tested media.

$$\tau = \frac{d_x}{d} \quad \text{Equation (4.2.2)}$$

Where τ is the tortuosity of a water molecule in a hydrogel of certain grafting density; d_x is the actual pathway that water travels through in the hydrogel; d is the nominal flow path, which is exactly the thickness of membrane.

Figure 4.14 Schematic illustration of the difference between the nominal flow path (membrane thickness d) and possible actual flow path (d_x).

Once τ is fixed by grafting P , there is no doubt that thicker membrane provides longer pathway for water molecules to move from one side to the other side of the hydrogel network in the pores. Accordingly, a longer time delay is observed for certain amount of water to permeate through a thicker membrane, and therefore, a thicker membrane with the same grafting (crosslink) density hydrogel would yield lower water permeation.

4.2.3. Thickness effect on temperature response of Water Permeability coefficient for NIPAM grafted PET membranes

Tested with filtration cell under two different temperatures, below and above the LCST of PNIPAM, water permeability coefficients of all thicknesses of grafted membranes were obtained. These values were normalized with pore density, pore size and viscosity of water at those two temperatures. The second normalized permeability coefficient J''' obtained in this manner is plotted vs. Thickness (d) in Figure 4.15 (a) (b) and (c), and the percent increment of J''' is calculated by dividing the difference of J''' between two

temperatures with the J'''' at room temperature and is plotted in Figure 4.15 (d) to illustrate the effect of thickness on thermo-responsiveness.

Figure 4.15 Normalized permeability coefficient J'''' vs. Thickness d for 3 different grafting conditions (a) $P = 300$; (b) $P = 600$; (c) $P = 900$ at two varied temperatures, and (d) the percent increment of normalized permeability coefficient J'''' vs. Thickness d at 3 different grafting P values.

The temperature response of the normalized permeability coefficients exhibiting increases when testing temperature increases above the LCST of PNIPAM remains the same for grafted membranes of 4 different thicknesses under all 3 grafting conditions used (P s = 300, 600 and 900). Variation at certain thicknesses under a given grafting P might not be so huge as others, such as the difference in J'''' values for 50 μm membranes under 300, 600 and 900 pulses of PLP, and between 23°C and 45°C; but they still display positive temperature response.

We should note, however, that the temperature response appears to improve when thickness increases, and this behavior is more manifested at higher grafting P . This behavior can be observed from the percent increment of normalized permeability coefficient J''' vs. Thickness d plot in Figure 4.15 (d).

CHAPTER VI

CONCLUSION

5.1. Ablation section

We found the ablation process to be similar for PET films of various thicknesses. Variation in thickness only led to varied energy needed to perforate film of certain thickness. Therefore, a proper combination of laser energy fluence (F), number of pulses (P) and laser pulse frequency (f) values were found for each thickness of membrane to obtain well-defined, clean-edged pores on support membrane.

Apart from laser operation parameters, mesh size for certain thickness should also be carefully selected to attain pores desired for efficient water permeation and a larger selection of permeability coefficients when the membranes are grafted. For example, the pore size plot for 75 μm membrane ablated under two different sizes meshes (mesh 500 with 25 μm opening size; and mesh 400 with 31 μm opening size) revealed that the difference in average pore size when using these two different support membranes is ~ 10 μm , which is much larger than the difference in the mesh opening sizes (~ 6 μm).

5.2. Grafting and water permeation section

We found that permeation decreases as membrane thickness increases at both room temperature and above the lower critical solution temperature (LCST) for PNIPAM (32°C), under every grafting condition (ungrafted and grafted at $P = 300, 600, 900$ pulses), in agreement with the Hagen–Poiseuille equation.

Thickness of film has little or no effect on the PLP process for a given set of laser parameters, i.e., various thicknesses of membranes have similar crosslink density of hydrogel grafted from the monomer reservoir at the bottom of the pore crosslinked by the laser pulse coming from the top. We make this conclusion based on the fact that our porosity data corresponding to a certain number of laser pulses, P , for PLP can be treated as practically constant with membrane thickness, which indicates that crosslink structure of hydrogel at certain P in varied membrane thicknesses are similar. Therefore, the effect of membrane thickness on the grafting of hydrogel is rather small or even none. Since the hydrogel structure in different thickness membranes are similar at a given grafting P , we can assume that an approximately constant tortuosity should exist for a certain grafting condition for all thicknesses. Consequently, we conclude that for a given set of PLP parameters, the film thickness has little or no effect on the kinetics of PLP and similar crosslink structures are obtained in length and radial directions within the pores (note that the effective permeation coefficient values were normalized w.r.t. The pore diameter leading to constant porosities).

Grafted membranes share the same temperature responsive behavior; that is, permeation appears higher at temperature above LCST of PNIPAM because of shrinkage of PNIPAM network. Also, thermo-responsiveness appears to be more prominent with thicker films pulse-laser polymerized using higher grafting pulses. We make this conclusion based on our “percent increment of normalized permeability coefficient J'' ” vs. Thickness d ” plots which are approximately linear with constant positive slopes up to a certain (termination) thickness value. These termination thicknesses increase with

increasing number of PLP pulses which likely cause higher crosslink density in the hydrogel.

5.3. Future work

The absence of negative thermo-responsiveness at the highest ***P*** employed in this research suggests that grafting density of PNIPAM hydrogel caused by 900 pulses of laser beam is still moderate with the given grafting concentration, such that number of pulses can be increased to investigate the possible negative temperature response in future work. However, higher ***P*** couldn't be achieved as time was limited in this study, and also because this negative response is much easier to be observed if model drug diffusion test is conducted, which will be much more time-consuming.

REFERENCES

- [1] C. G. Palivan, R. Goers, A. Najer, X. Zhang, A. Car, and W. Meier, “Bioinspired polymer vesicles and membranes for biological and medical applications,” *Chem. Soc. Rev.*, vol. 45, no. 2, pp. 377–411, 2016.
- [2] M. Karimi *et al.*, “Temperature-Responsive Smart Nanocarriers for Delivery Of Therapeutic Agents: Applications and Recent Advances,” *ACS Appl. Mater. Interfaces*, vol. 8, no. 33, pp. 21107–21133, Aug. 2016.
- [3] Y. Shen, P. O. Saboe, I. T. Sines, M. Erbakan, and M. Kumar, “Biomimetic membranes: A review,” *J. Membr. Sci.*, vol. 454, pp. 359–381, Mar. 2014.
- [4] J. Zhao *et al.*, “Biomimetic and bioinspired membranes: Preparation and application,” *Prog. Polym. Sci.*, vol. 39, no. 9, pp. 1668–1720, Sep. 2014.
- [5] Z. Liu, W. Wang, R. Xie, X.-J. Ju, and L.-Y. Chu, “Stimuli-responsive smart gating membranes,” *Chem. Soc. Rev.*, vol. 45, no. 3, pp. 460–475, 2016.
- [6] D. Wandera, S. R. Wickramasinghe, and S. M. Husson, “Stimuli-responsive membranes,” *J. Membr. Sci.*, vol. 357, no. 1–2, pp. 6–35, Jul. 2010.
- [7] S. Aluri, S. M. Janib, and J. A. Mackay, “Environmentally responsive peptides as anticancer drug carriers☆,” *Adv. Drug Deliv. Rev.*, vol. 61, no. 11, pp. 940–952, Sep. 2009.
- [8] J. Kost and R. Langer, “Responsive polymeric delivery systemsq,” *Adv. Drug Deliv. Rev.*, p. 24, 2001.
- [9] E. Fleige, M. A. Quadir, and R. Haag, “Stimuli-responsive polymeric nanocarriers for the controlled transport of active compounds: Concepts and applications,” *Adv. Drug Deliv. Rev.*, vol. 64, no. 9, pp. 866–884, Jun. 2012.
- [10] L. Chu, R. Xie, and X. Ju, “Stimuli-responsive Membranes: Smart Tools for Controllable Mass-transfer and Separation Processes,” *Chin. J. Chem. Eng.*, vol. 19, no. 6, pp. 891–903, Dec. 2011.
- [11] Y. Wang, C. Lai, H. Hu, Y. Liu, B. Fei, and J. H. Xin, “Temperature-responsive nanofibers for controllable oil/water separation,” *RSC Adv.*, vol. 5, no. 63, pp. 51078–51085, 2015.

- [12] I. S. Han *et al.*, “Constant-Volume Hydrogel Osmometer: A New Device Concept for Miniature Biosensors,” *Biomacromolecules*, vol. 3, no. 6, pp. 1271–1275, Nov. 2002.
- [13] S. Herber, W. Olthuis, P. Bergveld, and A. Van den Berg, “Exploitation of a pH-sensitive hydrogel disk for CO₂ detection,” *Sens. Actuators B Chem.*, vol. 103, no. 1–2, pp. 284–289, Sep. 2004.
- [14] A. Tiwari and E. Sancaktar, “Poly (N -isopropylacrylamide) grafted temperature responsive PET membranes: An ultrafast method for membrane processing using krf excimer laser at 248 nm,” *J. Membr. Sci.*, vol. 552, pp. 357–366, Apr. 2018.
- [15] A. Tiwari and E. Sancaktar, “Poly(N -isopropylacrylamide) grafting solution parameters for controlling temperature responsiveness in PET membranes fabricated using 248 nm krf excimer laser,” *Eur. Polym. J.*, vol. 103, pp. 220–227, Jun. 2018.
- [16] B. S. Lalia, V. Kochkodan, R. Hashaikeh, and N. Hilal, “A review on membrane fabrication: Structure, properties and performance relationship,” *Desalination*, vol. 326, pp. 77–95, Oct. 2013.
- [17] P. Apel, “Track etching technique in membrane technology,” *Radiat. Meas.*, vol. 34, no. 1–6, pp. 559–566, Jun. 2001.
- [18] L.-Y. Chu, T. Niituma, T. Yamaguchi, and S. Nakao, “Thermoresponsive transport through porous membranes with grafted PNIPAM gates,” *aiiche J.*, vol. 49, no. 4, pp. 896–909, Apr. 2003.
- [19] S. Ohya, S. Kidoaki, and T. Matsuda, “Poly(N-isopropylacrylamide) (PNIPAM)-grafted gelatin hydrogel surfaces: interrelationship between microscopic structure and mechanical property of surface regions and cell adhesiveness,” *Biomaterials*, vol. 26, no. 16, pp. 3105–3111, Jun. 2005.
- [20] Tiwari, A. (2018) *Fabrication of temperature responsive membranes using 248 nanometer Krypton fluoride excimer laser* (Doctoral dissertation) Available from [ohiolink.edu. \(akron1529323637791699\)](http://ohiolink.edu. (akron1529323637791699))
- [21] R. Russo, “Laser ablation in analytical chemistry—a review,” *Talanta*, vol. 57, no. 3, pp. 425–451, May 2002.
- [22] W. Li and E. Sancaktar, “Orderly Perforation of Polyester Films by Excimer Laser,” in *Volume 4: 20th Design for Manufacturing and the Life Cycle Conference; 9th International Conference on Micro- and Nanosystems*, Boston, Massachusetts, USA, 2015, p. V004T09A030.
- [23] “Understanding Lasers: An Entry-Level Guide, 4th Edition | Photonics & Lasers | General & Introductory Electrical & Electronics Engineering | Subjects | Wiley.” [Online]. Available: <https://www.wiley.com/en->

us/Understanding+Lasers%3A+An+Entry+Level+Guide%2C+4th+Edition-p-9781119310648. [Accessed: 12-Jul-2019].

- [24] “Eye surgery,” *Wikipedia*. 04-Apr-2019.
- [25] S. Lazare and V. Granier, “Ultraviolet laser photoablation of polymers: a review and recent results,” *Laser Chem.*, vol. 10, no. 1, pp. 25–40, 1989.
- [26] S. Petit, P. Laurens, J. Amouroux, and F. Are, “Excimer laser treatment of PET before plasma metallization,” *Appl. Surf. Sci.*, p. 4, 2000.
- [27] H. Watanabe and M. Yamamoto, “Laser ablation of poly(ethylene terephthalate),” *J. Appl. Polym. Sci.*, vol. 64, no. 6, pp. 1203–1209, May 1997.
- [28] R. Srinivasan and B. Braren, “Ultraviolet laser ablation of organic polymers,” *Chem. Rev.*, vol. 89, no. 6, pp. 1303–1316, 1989.
- [29] R. Srinivasan and B. Braren, “Ablative photodecomposition of polymer films by pulsed far-ultraviolet (193 nm) laser radiation: Dependence of etch depth on experimental conditions,” *J. Polym. Sci. Polym. Chem. Ed.*, vol. 22, no. 10, pp. 2601–2609, Oct. 1984.
- [30] T. Lippert, “Interaction of Photons with Polymers: From Surface Modification to Ablation,” *Plasma Process. Polym.*, vol. 2, no. 7, pp. 525–546, Aug. 2005.
- [31] P. E. Dyer and J. Sidhu, “Excimer laser ablation and thermal coupling efficiency to polymer films,” *J. Appl. Phys.*, vol. 57, no. 4, pp. 1420–1422, Feb. 1985.
- [32] R. Srinivasan and V. Mayne - Banton, “Self - developing photoetching of poly(ethylene terephthalate) films by far - ultraviolet excimer laser radiation,” *Appl. Phys. Lett.*, vol. 41, no. 6, pp. 576–578, Sep. 1982.
- [33] T. Lippert, “UV Laser Ablation of Polymers: From Structuring to Thin Film Deposition,” in *Laser-Surface Interactions for New Materials Production*, vol. 130, A. Miotello and P. M. Ossi, Eds. Berlin, Heidelberg: Springer Berlin Heidelberg, 2010, pp. 141–175.
- [34] J. Mulder, *Basic Principles of Membrane Technology*. Springer Science & Business Media, 2012.
- [35] I. M. Wienk, R. M. Boom, M. A. M. Beerlage, A. M. W. Bulte, C. A. Smolders, and H. Strathmann, “Recent advances in the formation of phase inversion membranes made from amorphous or semi-crystalline polymers,” *J. Membr. Sci.*, vol. 113, no. 2, pp. 361–371, May 1996.

- [36] D. R. Tree, K. T. Delaney, H. D. Cenicerros, T. Iwama, and G. H. Fredrickson, "A multi-fluid model for microstructure formation in polymer membranes," *Soft Matter*, vol. 13, no. 16, pp. 3013–3030, 2017.
- [37] V. Altun, M. Biemann, and I. F. J. Vankelecom, "Study of phase inversion parameters for EB-cured polysulfone-based membranes," *RSC Adv.*, vol. 6, no. 112, pp. 110916–110921, 2016.
- [38] Shuqiu Wu *et al.*, "Study of structure and properties of polypropylene microporous membrane by hot stretching," *Polym. Bull.*, vol. 71, no. 9, pp. 2205–2217, Sep. 2014.
- [39] A. K. Ghosh, B.-H. Jeong, X. Huang, and E. M. V. Hoek, "Impacts of reaction and curing conditions on polyamide composite reverse osmosis membrane properties," *J. Membr. Sci.*, vol. 311, no. 1–2, pp. 34–45, Mar. 2008.
- [40] R. Gopal, S. Kaur, Z. Ma, C. Chan, S. Ramakrishna, and T. Matsuura, "Electrospun nanofibrous filtration membrane," *J. Membr. Sci.*, vol. 281, no. 1–2, pp. 581–586, Sep. 2006.
- [41] D. Li and Y. Xia, "Electrospinning of Nanofibers: Reinventing the Wheel?," *Adv. Mater.*, vol. 16, no. 14, pp. 1151–1170, Jul. 2004.
- [42] B. S. Lalia, E. Guillen-Burrieza, H. A. Arafat, and R. Hashaiekh, "Fabrication and characterization of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) electrospun membranes for direct contact membrane distillation," *J. Membr. Sci.*, vol. 428, pp. 104–115, Feb. 2013.
- [43] M. E. Toimil-Molares, "Characterization and properties of micro- and nanowires of controlled size, composition, and geometry fabricated by electrodeposition and ion-track technology," *Beilstein J. Nanotechnol.*, vol. 3, pp. 860–883, Dec. 2012.
- [44] N. Nady, M. C. R. Franssen, H. Zuilhof, M. S. M. Eldin, R. Boom, and K. Schroën, "Modification methods for poly(arylsulfone) membranes: A mini-review focusing on surface modification," *Desalination*, vol. 275, no. 1, pp. 1–9, Jul. 2011.
- [45] M. A. M. E. Vertommen, H.-J. L. Cornelissen, C. H. J. T. Dietz, R. Hoogenboom, M. F. Kemmere, and J. T. F. Keurentjes, "Pore-covered thermoresponsive membranes for repeated on-demand drug release," *J. Membr. Sci.*, vol. 322, no. 1, pp. 243–248, Sep. 2008.
- [46] K. Pan, R. Ren, Y. Dan, and B. Cao, "Synthesis of controlled thermoresponsive PET track-etched membranes by ATRP method," *J. Appl. Polym. Sci.*, vol. 122, no. 3, pp. 2047–2053, Nov. 2011.

- [47] R. Xie *et al.*, “Temperature-dependent molecular-recognizable membranes based on poly(N-isopropylacrylamide) and β -cyclodextrin,” *J. Membr. Sci.*, vol. 326, no. 2, pp. 618–626, Jan. 2009.
- [48] Z. Lin, T. Xu, and L. Zhang, “Radiation-induced grafting of N-isopropylacrylamide onto the brominated poly(2,6-dimethyl-1,4-phenylene oxide) membranes,” *Radiat. Phys. Chem.*, vol. 75, no. 4, pp. 532–540, Apr. 2006.
- [49] F. Ganachaud, R. Balic, M. J. Monteiro, and R. G. Gilbert, “Propagation Rate Coefficient of Poly(N-isopropylacrylamide) in Water below Its Lower Critical Solution Temperature,” *Macromolecules*, vol. 33, no. 23, pp. 8589–8596, Nov. 2000.
- [50] “Pulsed - laser polymerization (PLP) of N - isopropyl acrylamide (NIPAM) in water: a qualitative study - Ganachaud - 2000 - Macromolecular Symposia - Wiley Online Library.” [Online]. Available: <https://onlinelibrary.wiley.com/doi/abs/10.1002/1521-3900%28200002%29150%3A1%3C275%3A%3AAID-MASY275%3E3.0.CO%3B2-U>. [Accessed: 12-Jul-2019].
- [51] S. Beuermann, “Solvent Influence on Propagation Kinetics in Radical Polymerizations Studied by Pulsed Laser Initiated Polymerizations,” *Macromol. Rapid Commun.*, vol. 30, no. 13, pp. 1066–1088, Jul. 2009.
- [52] O. F. Olaj, I. Bitai, and F. Hinkelmann, “The laser-flash-initiated polymerization as a tool of evaluating (individual) kinetic constants of free-radical polymerization, 2. The direct determination of the rate of constant of chain propagation,” *Macromol. Chem. Phys.*, vol. 188, no. 7, pp. 1689–1702, 1987.
- [53] M. I. Gibson and R. K. O’Reilly, “To aggregate, or not to aggregate? Considerations in the design and application of polymeric thermally-responsive nanoparticles,” *Chem. Soc. Rev.*, vol. 42, no. 17, pp. 7204–7213, Sep. 2013.
- [54] S. Fujishige, K. Kubota, and I. Ando, “Phase transition of aqueous solutions of poly(N-isopropylacrylamide) and poly(N-isopropylmethacrylamide),” *J. Phys. Chem.*, vol. 93, no. 8, pp. 3311–3313, Apr. 1989.
- [55] “Hagen–Poiseuille equation,” *Wikipedia*. 13-May-2019.
- [56] A. A. Merdaw, A. O. Sharif, and G. A. W. Derwish, “Water permeability in polymeric membranes, Part I,” *Desalination*, vol. 260, no. 1–3, pp. 180–192, Sep. 2010.