

CHAPTER II

LITERATURE REVIEWS

This section presents literature reviews related to thermoresponsive membranes, with a particular focus on poly(N-isopropylacrylamide) (PNIPAm) and polyethylene terephthalate (PET) track-etched membranes. The discussion highlights synthesis approaches utilizing solution-based and microwave-assisted polymerization techniques. Additionally, relevant journal articles concerning the characterization and gas permeability performance of thermoresponsive membranes are critically analyzed.

2.1 Polymeric membranes

Various polymers are fabricated into membranes with distinct properties and applications, including water treatment, pharmaceuticals, food processing, and gas separation (Bernardo et al., 2009; Kotsanopoulos & Arvanitoyannis, 2015; Ma et al., 2024; Obotey Ezugbe & Rathilal, 2020). Polymeric membranes are synthetic, semi-permeable barriers composed of organic polymers such as polyethylene terephthalate, polyamide, polysulfide, polyvinylidene fluoride, or Nafion (Daud et al., 2015; Naziri Mehrabani et al., 2022; Tai et al., 2025). These membranes can be classified and distinguished based on their types and structures.

2.1.1 Types and Structures of Polymeric Membranes

Membranes can be categorized into various types based on geometry, bulk structure, production method, separation regime, and application (Pinnau & Freeman, 1999). Figure 2.1 presents the classification scheme of synthetic membranes, which include flat sheet and hollow each of which can exhibit either symmetric or

asymmetric bulk structures. Symmetric porous membranes, fabricated *via* methods such as stretched-film casting, template leaching, track-etch nucleation, sintering, or equilibrium phase inversion, feature uniform pore distribution and are widely applied in dialysis, ultrafiltration, and microfiltration. In contrast, symmetric non-porous hollow fibers are produced by extrusion or solution casting and serve principally in gas separation due to their homogeneous dense structure. Asymmetric membranes, generated most often via phase inversion, present a thin dense skin supported over a porous substructure, delivering high mechanical strength and selectivity. More advanced non-porous asymmetric thin-film composites—including those made by solution coating, interfacial polymerization, plasma polymerization, or sol-gel deposition—are tailored for reverse osmosis, pervaporation, and high-performance gas separation applications

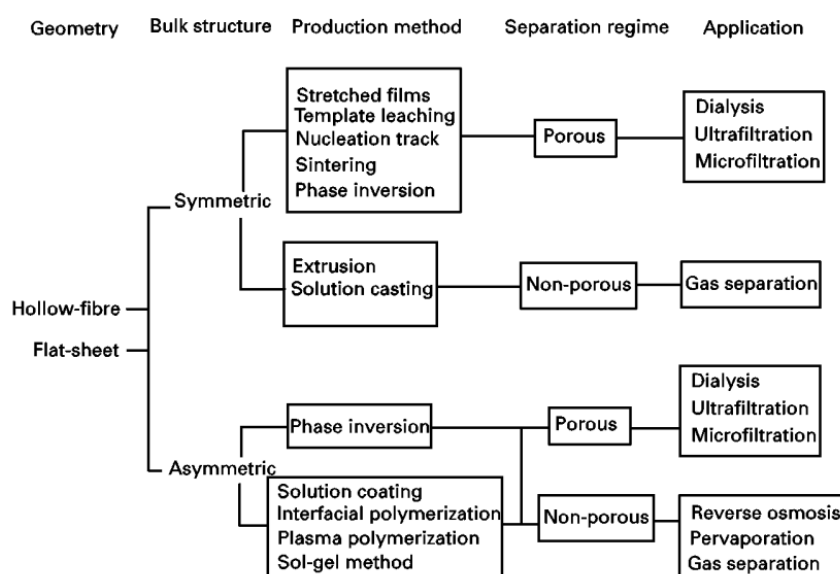


Figure 2.1 the classification scheme of synthetic membranes (Pinnau & Freeman, 1999)

Membrane structures are typically categorized into symmetric (isotropic) and asymmetric (anisotropic) structures as shown figure 2.2. Each distinguished by their internal morphology and separation performance. Symmetric membranes feature a homogeneous structure throughout their thickness—examples include porous

cylindrical arrays, porous web or sponge-like matrices, and dense polymer films. This uniform morphology offers structural simplicity and straightforward fabrication, making symmetric membranes suitable for applications where consistent permeability or mechanical integrity is prioritized (e.g., microfiltration, where uniform pore size is desirable).

In contrast, asymmetric membranes comprise distinct layers—a thin, selective skin (which may be porous or non-porous) supported by a thicker, porous substructure. In integrally skinned asymmetric membranes, both layers are fabricated from the same material within one process, while thin-film composite (TFC) membranes involve deposition of a selective coating (material A) onto a different microporous support (material B). The selective layer governs separation (e.g., solute rejection, gas selectivity), and the porous support provides mechanical strength with minimal resistance to permeation—this dual-layer design enables high flux coupled with high selectivity, which is a significant evolution over symmetric configurations.

Functional advantages of asymmetric membranes include faster transport due to reduced diffusion resistance through the thin skin layer; this can lead to markedly improved permeability compared to symmetric counterparts. Moreover, as pioneered by Loeb and Sourirajan in the 1960s with cellulose acetate asymmetric membranes for reverse osmosis, this architecture catalyzed the commercialization of modern pressure-driven separation processes, such as desalination, ultrafiltration, and gas separation.

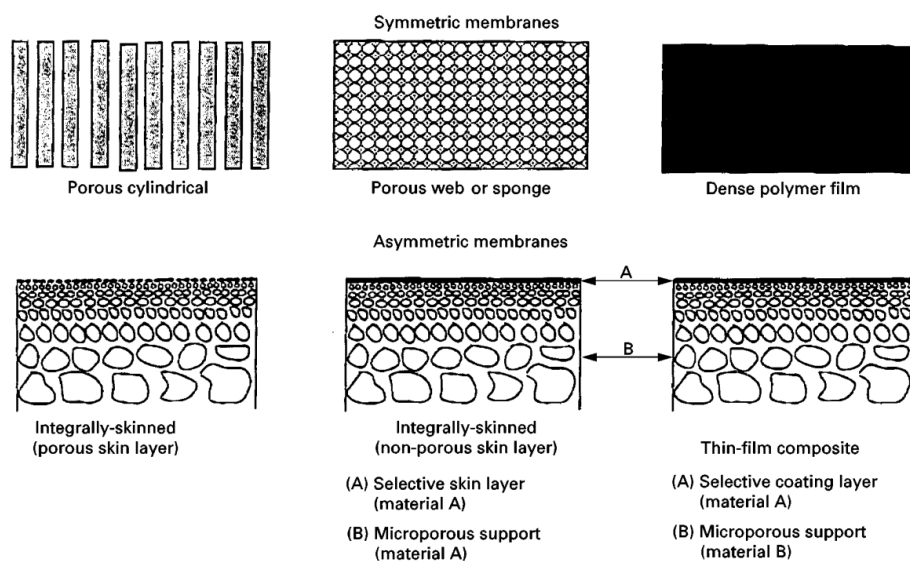


Figure 2.2 The types of the symmetric and asymmetric membrane structure (Pinnau & Freeman, 1999)

2.2 Poly (ethylene terephthalate) track-etched membranes (PET TeMs)

Poly (ethylene terephthalate) (PET) is an engineering thermoplastic polyester that is commercially available in different shapes, size, and forms (sheet, film, fiber, pellet, and etc.). The PET is an alternating copolymer including semirigid aromatic segment ($-\text{CO}-\text{C}_6\text{H}_4-$) and flexible aliphatic ester ($-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-$) (Rahman *et al.*, 2014) as show in figure 2.3. PET has excellent mechanical properties, good resistance against radiation, and good stability in bodily fluids (Gupta *et al.*, 2002). PET has been widely used in several fields including packaging, automotive, electronics, and medical applications. The hydrophobic nature of PET surface may be beneficial for some applications but unfavorable for others. Surface modifications have been carried out over the years by several research groups, which mostly aimed to increase hydrophilicity of the PET surface. Vinyl monomers such as acrylic acid (AA) (Abdolahifard *et al.*, 2011), methyl methacrylate (MMA) (Saçlak *et al.*, 1995), and acrylamide (AAM) (Zhang *et al.*, 2012) are the examples of the monomers used to graft onto the surface of PET for such purpose.

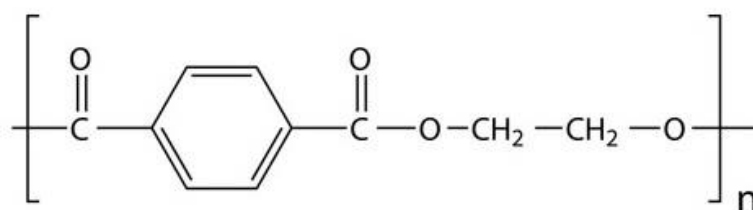


Figure 2.3 Chemical structure of Poly (ethylene terephthalate) (PET) (Rahman et al., 2014)

2.3 Thermoresponsive membrane

Thermoresponsive membranes are specialized materials that exhibit changes in their physical properties in response to variations in temperature. These membranes are primarily designed using thermoresponsive polymers, which can alter their hydrophilicity, hydrophobicity, and porosity based on temperature fluctuations. This unique characteristic allows them to be utilized in a variety of applications, including filtration, self-cleaning processes, and drug delivery systems.

2.3.1 Mechanism of Action

Thermoresponsive membranes typically operate based on two critical solution temperatures:

Lower Critical Solution Temperature (LCST): Below this temperature, the polymer is soluble and the membrane is hydrophilic. As the temperature increases past the LCST, the polymer becomes less soluble, leading to a transition to a hydrophobic state.

Upper Critical Solution Temperature (UCST): Above this temperature, the polymer chains collapse and aggregate, resulting in a change in the membrane's structure and properties.

For instance, poly(*N*-isopropylacrylamide) (PNIPAm) is a widely studied thermoresponsive polymer that exhibits an LCST around 32°C. At temperatures below

this threshold, PNIPAm remains hydrated and hydrophilic; above it, the polymer expels water and becomes hydrophobic

2.3.2 Applications

Thermoresponsive membranes have garnered significant attention for their versatility across various fields:

Filtration: These membranes can selectively filter particles based on size and charge by adjusting their pore size through temperature changes. For example, PNIPAm-grafted membranes can separate proteins from solutions by altering their surface properties with temperature

Self-Cleaning Surfaces: The ability of thermoresponsive membranes to switch between hydrophilic and hydrophobic states enables them to repel contaminants or facilitate easy cleaning processes when exposed to heat

Biomedical Applications: In drug delivery systems, thermoresponsive membranes can control the release of therapeutic agents by responding to body temperature or external thermal stimuli. This capability allows for targeted and controlled drug release

Environmental Remediation: These membranes are also being explored for applications in water treatment processes where they can respond dynamically to varying environmental conditions

2.3.3 Recent Advances

Recent studies have highlighted several advancements in the development and application of thermoresponsive membranes: Enhanced Fabrication Techniques: Innovations in fabrication methods have improved the stability and scalability of these membranes. Techniques such as electrospinning and grafting have enabled the creation of complex structures that enhance performance

Multi-Stimuli Responsive Membranes: Research is expanding towards membranes that can respond to multiple stimuli (e.g., temperature and pH), broadening their applicability in complex environments

Environmental Impact Considerations: Ongoing research is focused on addressing limitations related to the environmental impact and longevity of these materials to ensure sustainable applications

Thermoresponsive membranes represent a significant advancement in material science with promising applications across various sectors. Their ability to adapt dynamically to environmental changes makes them invaluable for innovative solutions in filtration, self-cleaning technologies, biomedical applications, and environmental management. Continued research and development will likely enhance their functionality and commercial viability in the future.

2.3 Poly (*N*-isopropyl acrylamide) (PNIPAm)

Poly (*N*-isopropyl acrylamide) (PNIPAm) is one of the thermo-responsive polymers that can be triggered by temperature resulting in the change in their physical properties. One of the most attractive properties of PNIPAm is physical changes with a lower solution critical temperature (LCST) of 32 °C (Nagase *et al.*, 2018). Because of the chain structure of PNIPAm contain hydrophilic and hydrophobic group as show in figure 2.4. The chain of this polymer collapses when it is exposed to temperatures higher than its LCST. Hydrogen bonds are formed between water molecules and the structure of functional monomer units of the PNIPAm polymer, which are N–H and C=O as show in figure 2.5. The hydrogen bonds are primarily responsible for the LCST.

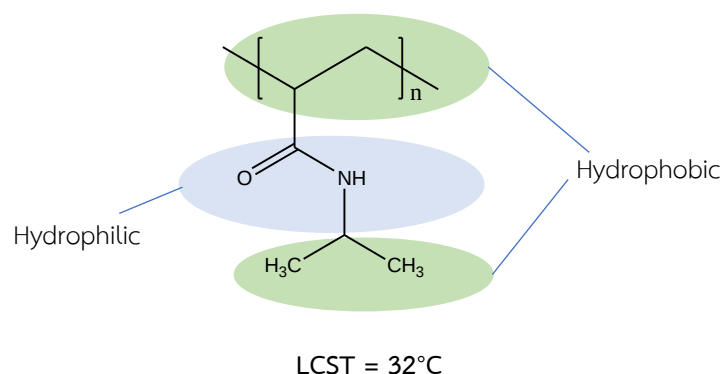


Figure 2.4 Chemical structure of Poly (N-isopropyl acrylamide) (PNIPAm) (Kita *et al.*, 2004)

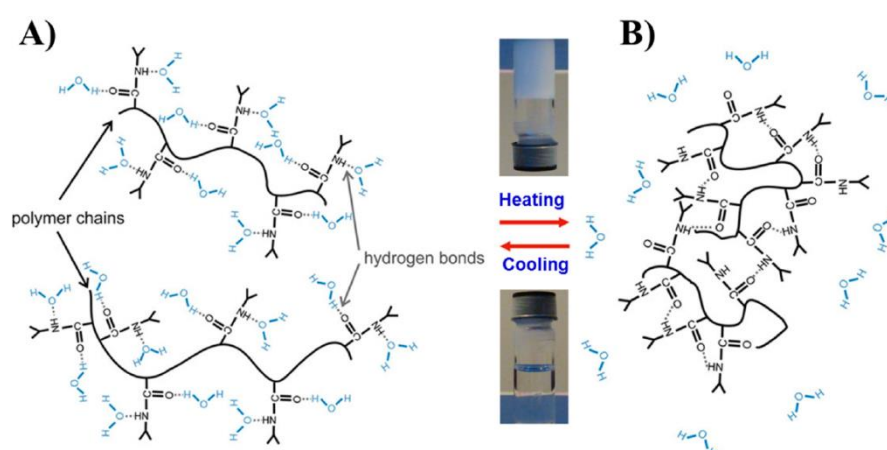


Figure 2.5 Temperature responsive behavior of Poly (N-isopropyl acrylamide) (PNIPAm)

a) the swollen PNIPAm in aqueous solution below LCST (32 °C) and

b) the shrunken PNIPAm above LCST (32 °C) (Lanzalaco & Armelin, 2017)

Many studies have shown that the LCST of PNIPAm is about 32°C, which is close to physiological temperature and easy to be adjusted. PNIPAm been used in biomedical applications such as drug delivery systems (Gandhi *et al.*, 2015), cardiovascular repair (Naito *et al.*, 2004) , sensing analysis (Shoji *et al.*, 2017), and medical imaging (He *et al.*, 2020).

2.3.1 Thermoresponsive mechanism of PNIPAm

Poly(*N*-isopropylacrylamide) (PNIPAm) is one of the most extensively investigated thermoresponsive polymers in aqueous environments. Below its lower critical solution temperature (LCST), typically around 32 °C under standard conditions, PNIPAm chains are highly hydrated, soluble, and adopt an extended, random-coil conformation stabilized by hydrogen bonding between the amide groups and surrounding water molecules. Upon heating above the LCST, the polymer undergoes a sharp coil-to-globule transition, accompanied by a loss of hydration and a significant decrease in solubility, often resulting in phase separation or aggregation. This transition is a hallmark of thermoresponsive character. PNIPAm possesses a particularly sharp demixing transition in an aqueous environment with an LCST near to 32 °C, highlighting the distinct and reproducible thermal behavior that underpins its widespread use in stimuli-responsive materials (Futscher et al., 2017).

The thermodynamic stability of a polymer in solution can be described by the Gibbs free energy of mixing (ΔG_{mix}) expressed as

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} + T\Delta S_{\text{mix}}$$

where ΔH_{mix} represents the enthalpy of mixing, ΔS_{mix} denotes the entropy of mixing, and T is the absolute temperature.

The polymer–solvent system remains miscible when $\Delta G_{\text{mix}} < 0$, whereas phase separation becomes thermodynamically favorable when $\Delta G_{\text{mix}} > 0$. In the case of PNIPAm, increasing temperature amplifies the contribution of the $T\Delta S_{\text{mix}}$ term, thereby altering the free-energy balance and driving the system from a homogeneous to a demixed state at the LCST.

2.4 PNIPAm composite membrane based on polymeric membranes

Poly(*N*-isopropylacrylamide) (PNIPAm) composite membranes have garnered significant attention in recent years due to their unique thermoresponsive properties and potential applications across various fields, particularly in biomedical and filtration technologies. This review synthesizes findings from recent studies on PNIPAm-based membranes, highlighting their fabrication, characteristics, and applications.

PNIPAm is a well-known thermoresponsive polymer that undergoes a phase transition around its lower critical solution temperature (LCST) of approximately 32°C. Below this temperature, PNIPAm is hydrophilic and swells in water; above it, the polymer becomes hydrophobic and collapses, leading to a significant change in its physical properties. This behavior makes PNIPAm an attractive material for creating responsive membranes that can adapt to environmental changes.

2.4.1 Fabrication Techniques

The fabrication of PNIPAm composite membranes typically involves:

Grafting onto Substrates: PNIPAm can be grafted onto various substrates such as nylon or polyamide to enhance their properties. For example, grafting can improve the mechanical strength and thermal stability of the membranes while maintaining their thermoresponsive characteristics

In Situ Polymerization: This method allows for the simultaneous formation of PNIPAm and another polymer, such as poly(pyrrole) (PPy), to create multifunctional hybrid membranes. These membranes exhibit not only thermoresponsive behavior but also electrical conductivity, making them suitable for applications in electrochemical devices.

Crosslinking: The degree of crosslinking in PNIPAm structures significantly influences their swelling behavior and mechanical properties. Crosslinked networks

tend to restrict chain mobility, which can lead to enhanced gas barrier properties but reduced permeability compared to linear structures.

2.4.2 Characterization

Characterization techniques employed for PNIPAm composite membranes include:

Scanning Electron Microscopy (SEM): Used to analyze the surface morphology of the membranes, revealing how grafting or crosslinking affects their structure.

Differential Scanning Calorimetry (DSC): This technique assesses the thermal transitions of the membranes, confirming the presence of LCST behavior.

Mechanical Testing: Evaluating Young's modulus provides insights into the flexibility and strength of the membranes under varying conditions.

2.4.3 Applications

PNIPAm composite membranes have diverse applications:

Biomedical Applications: Due to their biocompatibility and tunable properties, PNIPAm membranes are explored for cell culture systems where they facilitate cell attachment and detachment based on temperature changes. This feature is particularly useful for tissue engineering and regenerative medicine. For instance, Okano and co-workers developed PNIPAm-grafted culture dishes that enabled temperature-triggered cell detachment without enzymatic treatment, which was highly beneficial for regenerative medicine and tissue engineering (Okano et al., 1995).

Smart Coatings: The ability to reversibly modulate surface wettability by temperature enabled PNIPAm composites to act in self-cleaning surfaces and responsive drug delivery systems. For example, Zhang et al. constructed PNIPAm-based nanocomposite coatings that exhibited switchable hydrophilic–hydrophobic

transitions, thereby demonstrating effective self-cleaning and controlled drug release capabilities (Zhang et al., 2007).

Smart gating / stimuli-responsive flux control: PNIPAm composite membranes were developed for “smart gating” systems, in which permeability could be tuned with temperature. For example, Tiwari and Sancaktar reported PNIPAm-grafted temperature-responsive PET membranes, which exhibited reversible modulation of permeability with temperature due to the thermoresponsive switching of PNIPAm chains. In their study, water flux increased more than twofold when the temperature was raised above the LCST (~32 °C), and this switching behavior was fully reversible over repeated heating–cooling cycles without significant performance loss (Tiwari & Sancaktar, 2018).

Oil/water separation and anti-fouling membranes: PNIPAm composite membranes were used in separation of emulsions and in self-cleaning membranes. For example, Oral et al. prepared CA/PNIPAm membranes that demonstrated effective gravity-driven separation of oil/water mixtures and oil-in-water emulsions while resisting fouling (Oral & Basal, 2023).

2.4.4 Challenges and Future Directions

While the potential of PNIPAm composite membranes is vast, challenges remain:

Stability Under Repeated Cycling: The long-term stability of these membranes under repeated thermal cycling needs further investigation.

Scalability of Production: Developing cost-effective methods for large-scale production without compromising quality is crucial for practical applications.

Future research could focus on enhancing the biodegradability and biocompatibility of PNIPAm composites by incorporating natural polymers or

biodegradable materials. Additionally, exploring new copolymerization strategies could yield materials with tailored properties for specific applications.

In conclusion, PNIPAm composite membranes represent a promising area of research with significant implications for smart materials in biomedical and industrial applications. Their unique properties can be harnessed through innovative fabrication techniques to meet the demands of various technological advancements.

2.5 Solvent-assisted polymerization

Solvent-assisted polymerization is a technique that utilizes solvents to facilitate the polymerization process, enhancing the properties and performance of the resulting polymers. This method can be applied in various contexts, including the synthesis of new materials, improving polymer characteristics, and recycling existing polymers.

2.5.1 Hansen-solubility parameters (HSP)

The Hansen-solubility parameters or sometimes called cohesive energy parameters have developed to predict the degree of the binding between solvent and polymer which was thought to control solvent retention solvent by the notion of “like dissolve like”. The HSP based from the Hildebrand solubility parameter (denoted as δ) that provide the single numerical value of solvent. The limitation of Hildebrand model was the expression of “good solvent” only the difference of δ between solvent and polymers from $\pm 2 \text{ MPa}^{1/2}$ which was poor accuracy. Therefore, the HSP employed the three parameters represented dispersion, polar, and hydrogen bonding components.

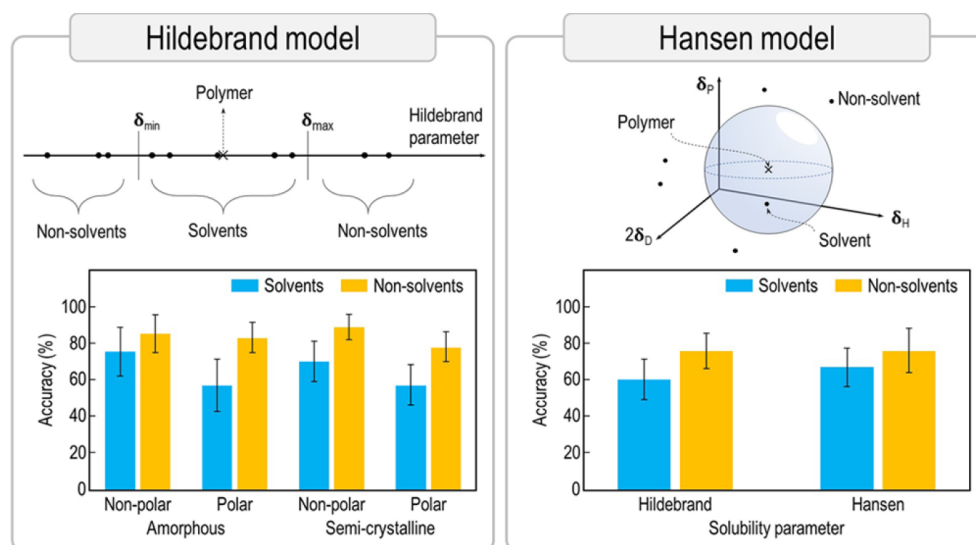


Figure 2.6 The solubility criteria and accuracy comparison between Hildebrand and Hansen Solubility parameter (HSP) (Venkatram S.,2009)

2.5.2 Mechanisms and Techniques

Chaperone Solvent-Assisted Assembly (CSAA): This innovative approach involves using multiple solvents to enable the assembly of polymers at liquid interfaces. In CSAA, a target polymer is combined with two poor solvents (α and β) that are immiscible with each other, and a third solvent (γ) that is a good solvent for the target polymer and miscible with both α and β . The diffusion of γ across the interface promotes the assembly of the target polymer at this interface, making it particularly useful for polymers that lack inherent interfacial activity.

Ionic Liquids as Solvents: Ionic liquids have emerged as effective solvents in various polymerization processes, such as Atom Transfer Radical Polymerization (ATRP). These solvents can enhance reaction control by increasing propagation rates and decreasing termination rates, allowing for high yields and narrow polydispersity in the resulting polymers.

Deep Eutectic Solvents (DES): DES are also being explored for their potential in polymer synthesis. They offer unique properties that can facilitate different

types of polymerizations, including free radical and anionic polymerizations. Their ability to dissolve a wide range of organic compounds makes them an attractive alternative to traditional solvents.

2.5.3 Applications

Fabrication of 2D Polymer Films: The CSAA method has shown promise in creating large-scale, defect-free two-dimensional (2D) polymer films applicable in fields such as photovoltaics and soft electronics. This technique allows for precise control over film structure and properties.

Reconfigurable Structures: Solvent-assisted methods can be employed to program flat polymer sheets into complex three-dimensional shapes without high temperatures or molds. This process leverages solvent-induced swelling to enable local plastic deformation, making it easier to create reconfigurable materials.

Depolymerization and Recycling: Recent studies have demonstrated solvent-assisted methods for depolymerizing plastics like bisphenol A-based polycarbonate (BPA-PC) into valuable monomers under mild conditions. This not only aids in recycling efforts but also contributes to sustainable practices in polymer chemistry.

2.5.4 Advantages

Solvent-assisted polymerization provided precise control over the kinetics of chain growth, thereby affording polymers with narrower molecular weight distributions and more predictable architectures. Dilution by solvents reduced the rate of radical termination and facilitated monomer diffusion to active sites, while appropriate solvent concentration and thermal regulation allowed researchers to tune chain propagation and minimize side reactions. For instance, in interfacial polymerization, the use of co-solvents such as ethyl formate-controlled monomer diffusion and yielded polymers with improved structural uniformity compared with single-solvent systems (Gu et al., 2023).

Another key advantage was the versatility of solvent-assisted polymerization, which enabled the selection of solvent systems tailored to specific monomers or catalytic environments. This facilitated broad applicability across diverse fields, including thin-film fabrication, membrane production, nanostructure assembly, and protective coatings. For example, chaperone solvent-assisted assembly achieved the interfacial alignment of otherwise non-assembling polymers, thereby extending the potential use of solvent-assisted methods to both two-dimensional and quasi-two-dimensional films (Zhao et al., 2024).

In addition, solvent assisted technique often yielded polymers and membranes with superior mechanical strength, enhanced thermal stability, and improved solubility characteristics. The presence of solvent facilitated the homogeneous dispersion of additives or copolymers and mitigated structural stresses during crystallization or void formation. For instance, in the fabrication of PVC/PVC-g-PEGMA blended ultrafiltration membranes, the use of the green solvent dimethyl sulfoxide (DMSO) in mixed-solvent systems ensured uniform miscibility and phase inversion behavior, which resulted in membranes exhibiting both higher pure water flux and improved solute rejection compared with conventional solvent formulations. This study demonstrated that DMSO could effectively replace traditional solvents such as DMF or NMP, thereby providing a more sustainable route to composite membrane preparation (Xie et al., 2019).

In conclusion, solvent-assisted polymerization represents a significant advancement in polymer chemistry, offering innovative solutions for material fabrication, recycling, and sustainable practices. As research continues to evolve in this area, we can expect further developments that enhance its applicability and efficiency across various industries.

2.6 Microwave-assisted polymerization

Microwaves, like light waves and radio waves, are a type of electromagnetic energy that occur within the electromagnetic spectrum. Microwaves are used to transmit long-distance phone signals, television programs, and computer data across the earth or to a space satellite. They are trained to detect speeding vehicles. The microwave, on the other hand, is arguably best known as a culinary energy source.

Free-radical polymerization and copolymerization reactions of several unsaturated monomers have been studied using microwave irradiation.

Katesripongsa and Trongsatitkul (2019) used plasma induced grafting combined with microwave-assisted polymerization technique to fabricate PNIPAM grafted onto Nylon-6 porous membranes for thermo-responsive gating application. The Nylon 6 membrane was treated with argon plasma to create hydrogen peroxide form. After that, the treated membrane was immersed in a NIPAm monomer solution (with and without *N, N* Methylenebisacrylamide as cross-linker) and then the grafting was induced using microwave irradiation. Microwave irradiation power and time were varied from 100 to 800 w and 5 to 15 min, respectively. After the microwave irradiation, the grafted membrane was repeatedly rinsed with DI water before being softly sonicated in a temperature-controlled bath and dried in an oven before being tested or characterized. The result showed that the grafted PNIPAm chains were mostly found on the membranes' top surface and at the pore entrance. The coverage of grafted PNIPAm chains on the membrane was inhomogeneous. When a crosslinker was added to the grafted membrane, it resulted in a denser grafted membrane than when it was not at all. When grafting under the conditions of a 15 min irradiation time at 800 w, the grafted membranes were fractured because the solution temperature was higher than the operational temperature of membrane. Because of their inconsistent performance, the fractured membranes were unsuitable for gating applications. The PNIPAm-grafted membranes should be produced at a proper irradiation time of 10 min and at a proper output power of 800 w to acquire the highest grafting yield. The

concentration of NIPAm required to provide the maximum yield was found to be 3 wt%

2.7 Study of water vapors transmission rate of PNIPAm composite membrane

The study of water vapor transmission rate (WVTR) in PNIPAm-based membranes has attracted considerable attention due to the unique thermoresponsive properties of PNIPAm and its potential applications in biomedical and environmental fields. Several researchers have investigated the WVTR behavior of PNIPAm composites, highlighting how structural modifications, environmental conditions, and supporting substrates influence moisture transport performance.

Zhai et al. (2022) examined the electrospun PNIPAm nanofiber membranes for wound dressing applications and reported that the WVTR values were within the optimal clinical range, enabling moisture retention while preventing wound dehydration. The fibrous morphology enhanced both permeability and breathability, thereby demonstrating the suitability of PNIPAm nanofibers for medical dressings. (Zhai et al., 2022) Similarly, Yang et al. (2008) incorporated chitosan into PU/PNIPAm thermosensitive membranes and revealed that WVTR varied markedly with temperature, reflecting the coil-to-globule transition of PNIPAm chains. This study also highlighted the dual benefit of moisture regulation and antimicrobial functionality, broadening the scope of PNIPAm composites in biomedical applications.

Beyond biomedical uses, other studies have focused on smart textiles and barrier membranes. Chung et al. (2019) grafted PNIPAm onto polyurethane substrates and showed that WVTR could be tuned according to grafting density and environmental humidity. Importantly, the membranes exhibited a distinct switching behavior near the LCST, suggesting promising applications in breathable protective clothing and adaptive coatings. Likewise, Phromphen et al. (2015) studied PVDF-g-PNIPAm membranes and

demonstrated that both liquid permeation and WVTR were thermoresponsive. Their findings emphasized that membrane thickness and grafting degree significantly affected transport properties, positioning PNIPAm-modified PVDF as a strong candidate for controlled vapor management in functional fabrics (Phromphen, 2015).

More recently, Ranganath et al. (2023) developed Janus membranes composed of PVDF/PNIPAm blends with asymmetric wettability. These membranes exhibited directional vapor transport dependent on temperature gradients, expanding the design space of PNIPAm-based systems into next-generation adaptive textiles and vapor-regulating devices. The anisotropic behavior of such membranes provided an advanced level of control compared to conventional homogeneous systems (Ranganath et al., 2023).

Taken together, these studies confirm that PNIPAm-based membranes possess intrinsic thermoresponsive properties that can be exploited to regulate water vapor transmission near physiological or environmental temperatures. Key factors governing WVTR performance include polymer composition (e.g., chitosan, polyurethane, PVDF blends), structural design (electrospun fibers, grafted layers, Janus configurations), and operational conditions such as temperature, humidity, and thickness. While electrospun and grafted systems provide reversible switching behavior, the incorporation of supporting polymers or asymmetric architectures enhances functional versatility. Overall, the literature suggests that PNIPAm-based composite membranes are promising candidates for wound dressings, breathable barriers, and smart textiles, though careful optimization is required to balance mechanical stability with thermoresponsive performance.

2.8 Study of gas permeability of PNIPAm composite membrane

Porous membranes are rigid which highly voided structures with randomly distributed interconnected pores. This reason, porous membranes exhibit very high

levels of gas permeability. The various parameters affect the properties of the membrane, such as the molecular size of the membrane polymer, pore size, and pore size distribution (Ismail et al., 2015).

The diffusion mechanism of gas permeation through the porous membrane can be divided into 4 types as show in figure 2.4:

1) Knudsen (or free molecule) diffusion occurs when the mean pore diameter of the porous media is smaller than the mean free route of the gas particles. The mean free path gets large in low permeability porous media with a small pore radius and low gas pressures, this form of diffusion occurs. In soils, Knudsen diffusion could happen in clays, silts, and rocks. Sub-atmospheric pressures, such as those created by soil vapor extraction, could boost the effect of Knudsen diffusion in these materials even more. Due to a reduction in the mean pore diameter and an increase in the tortuosity (λ), it has also been hypothesized that Knudsen diffusion could be a substantial flow mechanism in fine sands at high levels of water saturation. (Reinecke & Sleep, 2002)

2) Surface diffusion occurs when molecules that have been absorbed by a porous medium are transported across the surface of the porous as a result of a two-dimensional or surface gradient of concentration. Generally, surface diffusion plays a minor role in the diffusion in a porous medium unless there is a large amount of absorption by the solid phase of the medium.

3) Capillary condensation occurs when a condensed phase partially fills the membrane pores. Only species soluble in the condensed phase can pass across the membrane if the holes are filled with condensed phase. For capillary condensation, fluxes and selectivity are often high. The emergence of capillary condensation, on the other hand, is highly dependent on gas composition, pore size, and pore size uniformity.

4) Molecular sieving occurs when pore sizes are small enough (3.0–5.2 Å), resulting in the separation of molecules with different kinetic diameters: Only the smallest gas molecules can pass through the membrane when the pore size so small. Solution casting, sintering, stretching, track etching, and phase separation are all methods for making porous polymeric membranes. Depending on the properties of the materials used and the process parameters used, the final shape of the membrane formed will vary substantially.

Transport in membranes is described by a variety of methods, including bulk material transport (dense membranes), Knudsen diffusion in narrow pores, viscous flow in large pores, and surface diffusion along pore walls.

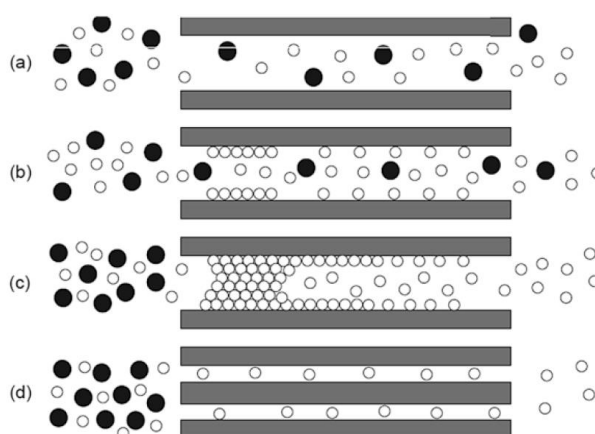


Figure 2.7 The diffusion mechanism of gas permeation through the porous membrane (Reinecke & Sleep, 2002)

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|---|----------------------|
| A) Knudsen (or free molecule) diffusion | B) Surface diffusion |
| C) Capillary condensation | D) Molecular sieving |