Membrane is a physical barrier made of solid or liquid which separates two different distinct phases and plays the vital role to act as a selective barrier to allow the transportation of the substances through it under the influence of some driving force. The driving force may include the gradient produced as a result of pressure, concentration and electric potential. The membrane is very important and is termed as 'cause' and 'progresses' of life. Therefore, membrane is one of the simplest things to speak about but actually it is one of the busiest to deal with. As a result, membrane science is emerging today at a great pace which offers the widest spectrum of potential and realized applications than that of any other existing technology. It has enormous potentialities in particular with specific answers to today's asking scenario of the rapid social, economical and industrial transformations, such as energy problems, the rapid increase in the storage of chemical species, the treatment of industrial wastes, the development of the clean industry etc.

The field of membrane science and technology finds its existence starting from the discovery of the phenomenon of 'osmosis' in 1748 by Jean Antoine Nollet as a result of keen observation. In 1887, Van't Hoff defined osmotic pressure and derived a relation for it in context to membrane. Though, for the following 200 years after the discovery of osmosis, this was mere a phenomenon observed in laboratories. And finally in 1949, the University of California at Los Angeles (UCLA) implemented this phenomenon for desalination of seawater by using semi permeable membranes. With this initiation, the recent arena of separation science and technology takes off which is largely based on synthetic membranes. For the membrane to be used effectively and efficiently for any application it must possesses at least the following characteristics [1]:

- High separation ability
- High flux
- Mechanical stability
- Tolerance to all feed stream components (fouling resistance)
- Tolerance to temperature and pH variations

1.1.1 Diversification of membrane technology / applications

Earlier membranes were used merely for the purification of water. With the passage of time, this technology has started to prove its efficiency in other fields as a major tool and taken the dimension of an industry. In this day and age, membranes are getting more than what these are professed earlier mere as a physical barrier to allow the selective transportation of the molecules through. It has spread its wing beyond the area of separation or purification into other fields like fuel cells [2-6], bio-reactor [7-10], biosensor [11], biomedical [12], molecular imprinted polymers [13, 14]. In terms of separations these are used profoundly in various applications viz. reverse osmosis, filtration (microfiltration, ultrafiltration), pervaporation, dialysis, emulsion liquid membranes, membrane-based solvent extraction, membrane reactors, gas permeation, supported liquid membranes.

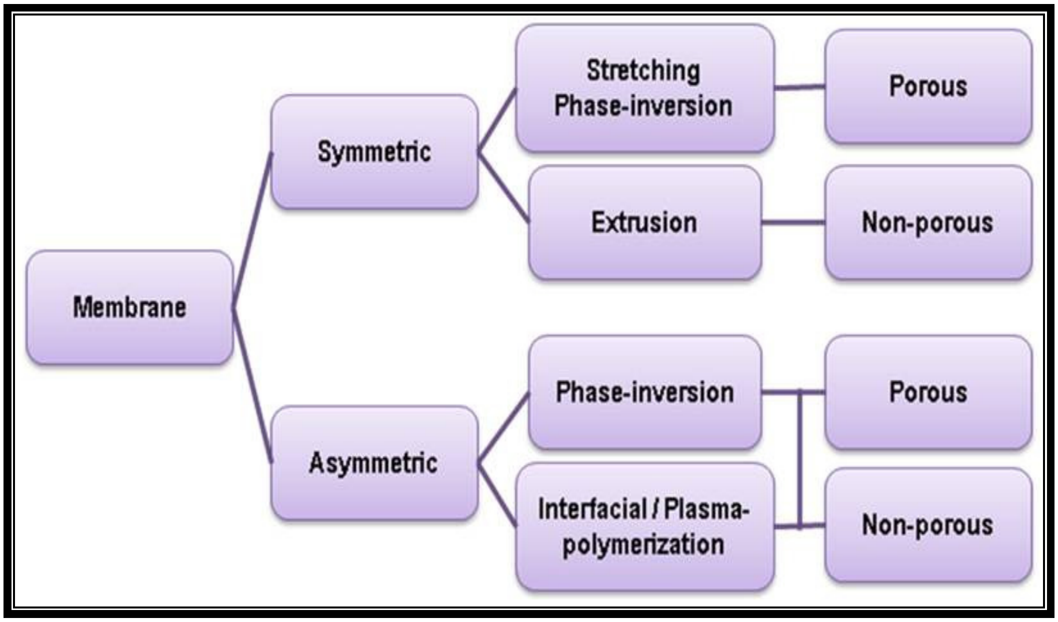
1.1.2 Classification of membranes

To make best use of the membranes for different applications, it is necessary to have an idea about the 'built in' configuration of the membranes and details about the particular target. Synthetic membrane is fabricated from organic or inorganic materials which include solids such as metal / ceramic (aluminum oxides, silicon carbides, zirconium oxides), homogenous films (polymers), heterogeneous solids (polymeric mixes, mixed glasses) [15-18], and liquids. Ceramic membranes are very stable chemically, thermally, mechanically, biologically inert and eco- friendly and have long working life. Liquid membrane refers to synthetic membranes where liquid layer works as a separation barrier. Various types of liquid membranes are reported in literature: emulsion liquid membranes, immobilized (supported) liquid membranes and hollow-fiber contained liquid membranes [19-23].

But polymeric membranes lead the membrane separation processes. This is because of being very competitive in separation performance with quality and quantity and they are very much economic. Polymeric membranes can be of various thicknesses, with homogeneous or heterogeneous structure. The way of preparation of membrane also results in the variations in membranes. This may result in dense or porous membranes.

Membranes can be used as a flat sheet or in tubular form as hollow fibre. These may have either a symmetric (isotropic / homogenous) or an asymmetric (anisotropic / heterogeneous) structure. The first of the two has uniform structure throughout in the entire thickness and its separation property is governed by entire structure. The second one has a gradient in the structure and its separation behaviour is governed by the dense region in the membrane. Membranes, in general can be classified by considering different parameters [24] as shown schematically (scheme 1.1).

Scheme 1.1 Classification scheme of synthetic membranes based on their bulk structure, production method, and separation regime

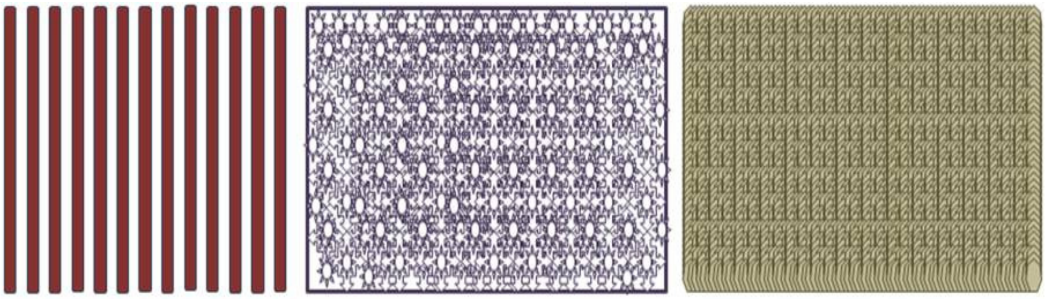


❖ **Symmetric Membranes**

These membranes have the uniform structure throughout the entire membrane thickness. Symmetric porous membranes have cylindrical, sponge, web or slit like structure as shown in figure 1.1. Common methods of their preparation are stretching of a melt-processed semi- crystalline polymer film, vapor-induced phase inversion and temperature-induced phase inversion.

Dense symmetric membranes with thicknesses larger than 10 μm can be made by solution casting and subsequent solvent evaporation or by melt extrusion. As the membranes are relatively thick, they have only limited applications in gas separation processes and electrodialysis.

Figure 1.1 Schematic presentations of symmetric membranes



Porous cylindrical **Porous web/ sponge** **Dense polymer film**

❖ Asymmetric Membranes

These are also known as heterogeneous membranes. These can be recognized into three basic structures (figure 1.2) as:

I. Integral-asymmetric with a porous layer,
II. Integral-asymmetric with a dense skin layer, and
III. Thin film composite membranes.

Porous integral- asymmetric membranes are developed by the phase inversion technique and are used in dialysis, ultrafiltration and microfiltration where as integral asymmetric membranes with a dense skin layer are used in reverse osmosis and gas separation.

Thin film composite membrane is made up of a thin, selective polymer layer atop a porous support. Thus the separation and mechanical functions are performed by different layers. These types of membranes are generally used in reverse osmosis purpose but are also used in nanofiltration, gas separation and pervaporation.

Integrally skinned asymmetric membranes are first developed by Loeb and Sourirajan in early 1960. These membranes are having two or more structural plane of non-identical morphologies from the same polymer material. An asymmetric membrane consists of a very thin (0.1-1μm) selective skin layer on a highly porous (100-200 μm) thick supporting substructure. The very thin skin represents the actual membrane which acts as a selective barrier. The asymmetric membranes can be achieved through four principal methods: immersion precipitation (wet phase inversion), vapor–induced phase inversion, thermally induced phase inversion and dry casting [25]. The structures of these membranes are greatly influenced by even slight change in membrane preparation conditions.

Figure 1.2 Schematic presentation of asymmetric membranes: (i) Integrally-skinned (porous skin layer), (ii) Integrally-skinned (non-porous skin layer) and (iii) Thin-film composite

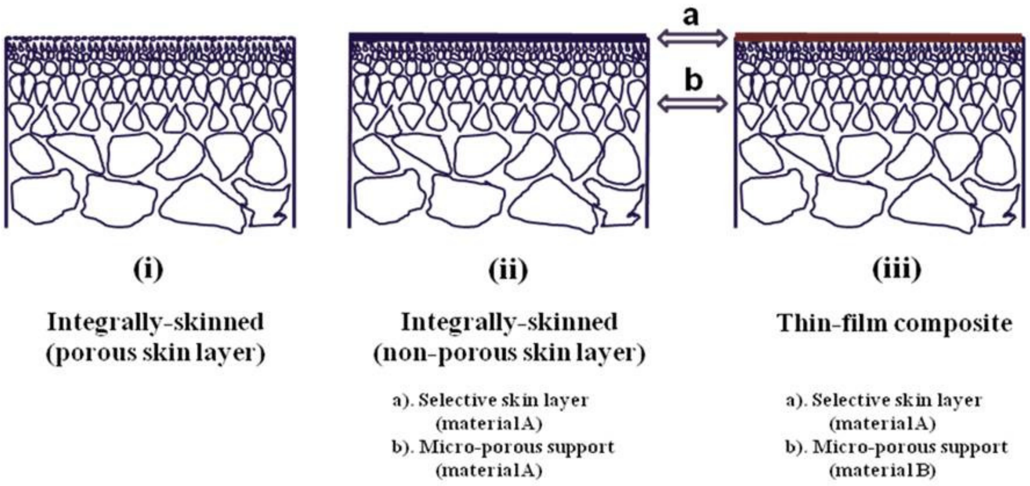
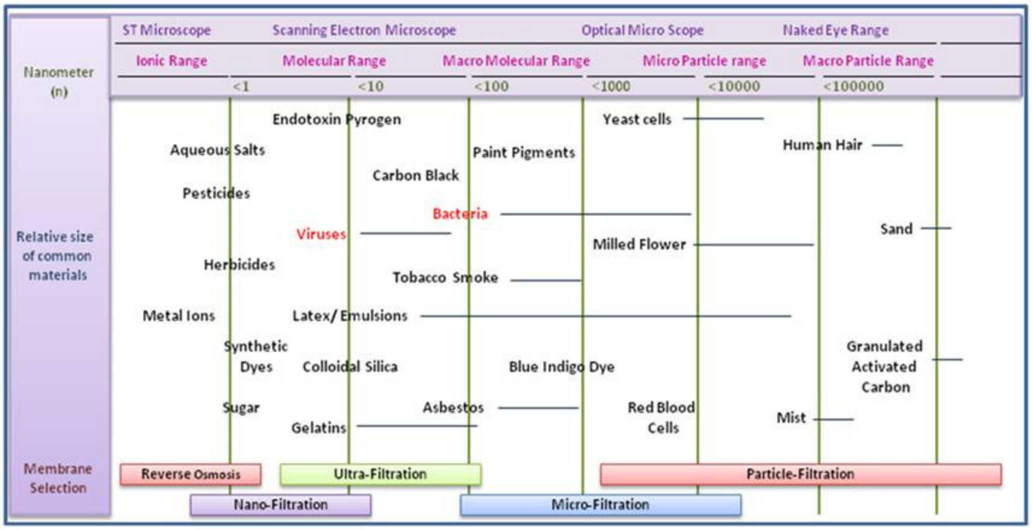


Figure 1.3 Schematic presentation of particles/material size and membranes processes of various filter ranges



Beside these, membranes can be neutral or charged, and particles transport can be active or passive. Membranes are also classified on the basis of the size of particles to be filtered through. Here pore size of the membranes can vary from 0.1 nm to 5,000 nm and above depending on the filter type. It is shown schematically for different types of particles or filter types in figure 1.3.

1.1.3 General methods of preparation of membranes

Preparatory methods govern the development of membranes in terms of porosity i.e. porous or non-porous and bulk structure i.e. asymmetric or symmetric morphology. There are various techniques to prepare the desired membranes (depending upon the polymer material used) as depicted in the scheme 1.1.

In extrusion, polymeric material is extruded to obtain polymer melt [26-29]. The polymer melt is further passed over the chill mill to form the film. Thus so formed membranes are dense, symmetric and non-porous in nature. Extrusion is used mainly for thermoplastics e.g. polypropylene, polyethylene etc. but elastomers and thermosets are also may be extruded.

In stretching, the films are prepared by extrusion methods initially and these are further stretched uni-axially or bi-axially to form the porous membranes [30-32]. This leads to a partial fracture of the film and relatively uniform pores with diameters of 1 to 20 μm.

In solution casting, an appropriate viscous polymer solution is casted on the casting plate into a film form [33-37]. Evaporation is the mechanism in which polymer precipitation takes place. The use of low boiling point solvent is preferred so that easy evaporation takes place.

***In phase inversion**,* a liquid homogeneous polymeric solution is induced to two-phase system i.e. polymer-rich phase forming the rigid matrix of the membrane and a polymer lean phase, rich in solvent and non-solvent, forming the membrane pores [38-55].There are different ways to induce the phase separation for membrane preparation like wet phase inversion (immersion) [40-44], dry phase inversion technique [45-49], vapor induced phase inversion technique [50-52], and temperature induces phase inversion technique [53-55]. In immersion method, the homogeneous polymeric solution is casted in form of membranes and immersed in the non-solvent (to the polymer) gelation bath. This leads to the diffusion and exchange between solvent and non-solvent to induce phase inversion/ separation. The phase separation is the result of the thermodynamically stable state achieved for which minimum Gibb's free energy is attained.

Dry phase inversion involves the convective evaporation to induce phase separation. The membranes prepared by this method are having a thick skin layer. In vapor induced phase separation technique, the vapors of non solvent are passed over the polymeric homogeneous solution as a coagulant and it allows the slow phase inversion of the polymer by nucleation and growth mechanism. In temperature induced phase separation, phase inversion is induced by cooling the temperature which otherwise forms a homogeneous solution at elevated temperature e.g. polypropylene dissolved in *N,N*-bis-(2-hydroxyethyl) amine. It is mainly applied to the polymer with low/poor solubility such as polypropylene Different types of membrane like symmetric or asymmetric membranes can be prepared by changing the parameters of phase inversion or by following different methods as mentioned above.

In plasma polymerization, the polymerization of monomers is caused by electrical discharge in vacuum or low pressure condition [56-58]. Plasma beam tends to change the chemical and physical properties of the polymer material, due to a series of sequential reactions such as oxidation, degradation, cross-linking and results structural changes in the thin layer of the polymer surface. Thus the asymmetric non-porous membranes are formed. The conditions viz. gas pressure, temperature, kind of solid surface, monomer types, power and time of plasma action influence the polymerization process. This method offers a reliable and effective way along with reproducibility to deposit uniform and extremely thin polymer layers and is frequently used to prepare the non-porous asymmetric polymer membranes.

In interfacial polymerization**,** two different monomers, dissolved in two different solvents, immiscible to each other reacts on the porous support [59-61]. The absorption as well as reactivity depends upon the partition co-efficient of monomers. The polymerization reaction takes place at the interface of the two solutions. The thin non-porous asymmetric layer forms over the support. This interfacial polymerization is used mostly for the preparation of thin film composite membranes.

1.1.4 Functioning of membranes

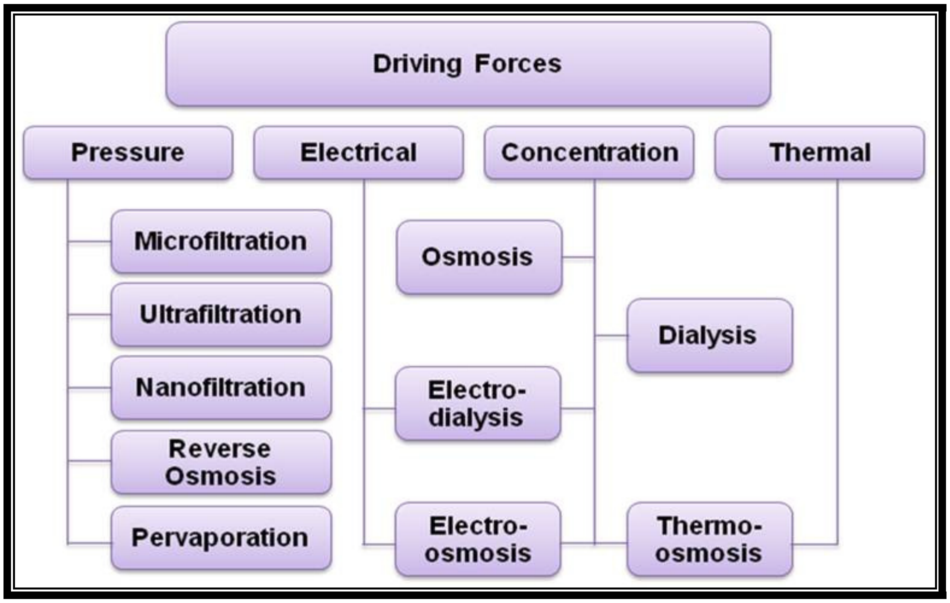
The membrane processes are controlled by several factors viz. driving forces/ gradients, pore size, membrane charge etc. Figure 1.4 displays schematic outline of various driving forces which are primary requirements towards the functioning of various types of membranes. Technically, most relevant processes are pressure driven processes such as reverse osmosis, nanofiltration, ultrafiltration, microfiltration and pervaporation/ gas separation.

- **Microfiltration membranes:** These remove particles of 50 nm or larger size. These include bacteria and suspended particles.
- **Ultrafiltration membranes:** These are capable of removing particles of roughly 3 nm or larger size. This includes removal of viruses along with bacteria and suspended particles.
- **Nanofiltration membranes:** These remove particles of 1 nm or larger size. Charged nanofiltration membranes preferentially separate multivalent ions over monovalent ions.
- **Hyperfiltration membranes:** This category of membrane filtration is known as Reverse Osmosis membranes and removes particles larger than 0.1 nm. These membranes allow only water and selectively prevent monovalent ions to pass through.
- **Gas Separation/Pervaporation membranes:** These are quite dense membranes. These are utilized for gas separations (e.g. removal of CO_2 from natural gas, separating N_2 from air, organic vapor removal from air or nitrogen stream). In pervaporation membranes, permeate generally passes through the membrane and is evaporated which are further condensed. This process helps in separation of azeotropic mixtures, drying of solvents and separation of volatile organics etc.

There are also concentration gradient driven processes (viz. osmosis, dialysis), partial pressure driven processes, (viz. pervaporation) and electrical potential driven processes, (viz. electro dialysis) [62, 63] (refer to figure 1.4). Reports are also based on their regarding thermo-osmosis and electro-osmosis in which membrane separation is combined with two different driven forces viz. for electro-osmosis, [64, 65] electrical potential as well as concentration are the driven forces, for thermo-osmosis, temperature and concentration driven forces are combined with each other [66-69].

Different models are there to explain the transport of solutes through reverse osmosis and nanofiltration membranes [70]. Here, some important of them are : (1) Solution diffusion model is basically based on the theories that ions and solvent dissolve in the polymer matrix of the membrane and diffuse independently (uncoupled) of each other through the membrane (2) In Kimura-Sourirajan model, solvent preferentially sorbs at the membrane solution interface. It then moves through the capillaries of the membrane by viscous flow in which the flux is directly proportional to the effective pressure.

Figure 1.4 Schematic presentation of various driving forces responsible for membrane functioning



The solute passes through the pore of the membrane by diffusion. (3) Nernst Planck theory dealt with the movement of ions through the membrane pores by convection, diffusion and electrical potential gradient. The ions show selectivity by Donnan Partitioning and steric effects and (4) in the irreversible thermodynamics model, membrane is treated as a 'black box' in which the solvent flux is proportional to the pressure gradient across the membrane. The solute moves through the membrane by convection and diffusion. Among the different transport models, solution-diffusion model is most widely accepted in describing pervaporation transport including preferential sorption, diffusion and evaporation steps [71].

Thus membrane functioning is regulated in terms of different properties (e.g. pore, charge and wettability). Any alteration in these properties can make a large impact on the performance of the membrane. Different controlling parameters (viz. pH, temperature) are also there in detailing the performance of the membranes. pH of the feed solution influences the polymeric membrane to acquire different surface charge. It imparts surface charge in different manner e.g. varying inbuilt functional group on the membrane [72-77]. Like pH, temperature of the solution also influences the performance of the membrane, as there is the change in swellability.

1.2 Membrane materials: development and modification

The role of membrane science and technology for what is indicated today as a sustainable development is becoming more and more evident. There are numerous polymers which are used to fulfil this very objective for various applications. Table 1.1 represents the list of various polymers which are used in various membranes based separation applications. In spite of this, for membrane science and technology to be more attractive in the future, there is a need indeed to improve the performance in terms of selectivity, stimuli, affinity, and time dependence deterioration. This can be achieved by either preparation of new material or modification of the pre-existing membrane materials.

Exploration of new materials for membranes needs various hurdles to be cleared. If these are developed in terms of performance, then it should also be taken care of in terms of other criteria of having high tensile strength, resistance towards different types of variations viz. temperature, pH, and chemicals/solutes to be separated. Moreover it should be easily commercialized.

Thus, development of new materials for membranes requires enormous efforts and also it's quite expensive. As a result, modification of pre-existing membrane according to tailor made specification becomes an important and quite prevalent criterion for various applications. The last few decades have witnessed various researches on membranes because of their versatility.

Moreover, the spectrum of its uses may be still more widened considerably by taking recourse to modification. The use of different techniques in modifying membranes is currently of considerable interest that includes chemical [78], photo-irradiation [79, 80], and low-temperature plasma [81-83]. Modification by these methods has significantly contributed in development of various types of membranes e.g. for gas separation [84-87] reverse osmosis membrane [88, 89], functionalization of ultrafiltration membranes [90-92] and environmentally sensitive membrane [93-101] (pH, temperature, photo radiation). Among the above mentioned techniques, photo-irradiation mediated technique has been used more frequently in an effectively variable qualitative manner.

Table 1.1 List of different polymers used in various membrane processes

Membrane material	**Membrane process**
Cellulose regenerated	D,UF,MF
Cellulose nitrate	MF
Cellulose acetate	GS,RO, D,UF,MF
Polyamide	RO NF,, D,UF,MF
Polysulfone	GS,UF,MF
Poly(ether sulfone)	UF,MF
Polycarbonate	GS,D,UF,MF
Poly(ether imide)	UF,MF
Poly(2,6-dimethyl-1,4-phenylene oxide)	GS
Polyimide	GS
Poly(vinylidene fluoride)	UF,MF
Polytetrafluoroethylene	MF
Polypropylene	MF
Polyacrylonitrile	D,UF,MF
Poly(methyl methacrylate)	D,UF
Poly(vinyl alcohol)	PV
Polydimethylsiloxane	PV,GS

MF = microfiltration; UF = ultrafiltration; NF = nanofiltration; D = dialysis; PV = pervaporation; GS = gas separation

1.2.1 Advantages of photo-irradiation in membrane modification

Modification of the properties of membranes according to tailor-made specification is an important criterion for various applications and this can be achieved by taking recourse to grafting / cross-linking and curing which have in fact become now-a-days a popular method of modifying the properties of various high molecular weight compounds. And, modification of membrane surface can be accomplished by different techniques as mentioned above to obtain the required variable controlling parameters viz. pore size, surface charge, hydrophilicity/ hydrophobicity. Each technique has its own peculiar characteristics towards modification of membranes. Modification of membranes by applying photo-irradiation is unique among all techniques and the characteristic feature of this is described in the following:

- ***Simple and easy to set up***

The technique is simple and easy to set up even than chemical process, where it needs various arrangements. The other radiation techniques are not so simple in setting up. The photo radiation technique is the low energy consumption and man-power saving process compared to the chemical process. There is the flexibility in setting up the photo-irradiation arrangements in anywhere, comparing the other radiation techniques i.e. no constraint in location. Chemically initiated grafting process is associated with the problem of purification of the graft from the initiators. Photo-induced methods are cleaner in this respect, albeit sometimes sensitizer requirement is essential.

- ***Reaction feasibility***

The photo initiated grafting reaction is of low activation energy, rapid reaction rate, applicable to wide temperature range and easy controllable by shuttering on or off, higher monomer conversion and low monomer residue compared to chemical process. Chemical initiation often brings in problems from local overheating of the initiator. But, in photo-irradiation technique, the formation of free radical sites on the polymer matrix is not dependent on temperature, thus homogenous distribution of graft polymer is probable compared to chemical method.

- ***Reaction status***

The limitation of photo-induced grafting is of relatively poor penetration is advantageous to modify the membrane surface by not altering the bulk properties. Using this technique, the mosaic grafting is feasible, as the light can be directed to location of interest. Among the techniques, Photo-irradiation is focused because of its simple, energy efficient nature.

Moreover, along with the modification of membranes surface, photo radiations can be used as a stimuli to regulate the performance of the membrane. However, it requires the incorporation of photo-responsive moieties in the membrane.

1.3 Photo-irradiation: In membrane preparations

In photo-initiated reactions the activation of molecules is due to the collision with photons (packet of energy) of visible and / or ultra-violet radiations. These radiations have enough energy to excite an electron or to ionize / to bring some conformational changes in the atoms/ molecules [102]. Table 1.2 details about visible and ultra-violet radiations.

Table 1.2 Physical parameters of UV and visible radiations.

Radiations	Wavelengths (nm)	Frequencies (Hz)	Quantum energies (eV)
Visible	750 - 400	$4 - 7.5 \times 10^{14}$	1.65 - 3.1
Ultra-violet	400 - 10	$7.5 \times 10^{14} - 3 \times 10^{16}$	3.1 - 124

Photons of UV radiation which have more energy than those of visible light (refer to table 1.2), cause chemical changes to occur. When absorbed they supply sufficient energy to break or twist some chemical bonds and thus initiate subsequent chemical reactions. Photo-irradiations are merely not responsible enough to cause the required modification or change. It’s only a tool to work with for the required result but with specific target. To make best use of this tool in an effective manner various factors are to be taken in utmost consideration to play with. They are discussed in the following:

❖ Nature of the substrate

Presence of photo-functionality decides whether addition of photo-initiator is needed or not. Choosing of the proper substrate and initiator needs the idea of surface energy of the polymers. Most polymers, especially those of low surface energy, contain many abstractable hydrogen atoms on their backbone or surface. This increases the potential for photo-initiated grafting [103]. Here are some of the polymers (table 1.3) which can show the feasibility of photo-grafting in presence of aromatic ketone as photo-initiator. Crystalline nature of polymers has negative effect in grafting i.e. the high crystalline matrix does not allow the reacting solution to penetrate into and interact with the polymeric backbone viz. grafting on high density PE is more difficult than low density PE due to the linear chain structure and its high degree of crystallinity.

Table 1.3 Surface energy data for some polymeric materials

Membrane material	**Surface energy(MJm^{-2})**
Teflon	19.1
Styrene butadiene rubber (SBR)	29.1
Polyethylene (PE)	32.1
Poly(methyl methacrylate) (PMMA)	40.2
Polystyrene (PS)	40.6
Nylon 66	41.4
Polyvinyl chloride (PVC)	41.5

- **Nature of monomer**

The nature of the monomer also influences the grafting process. The monomer should be photoactive, but it will be beneficial if they have the less activity to combine themselves (i.e. homo-polymerization).

The nature of the hydrogen influences the grafting process e.g. allylic hydrogen containing monomer methacrylates are not better monomer with respect to acrylic acid and acylonitrile, because of lower bond strength with respect to ethylenic one and the hydrogen abstraction strength is better and thus homo-polymerization favors [104].

- **Nature of solvent**

The choice of the solvent should be proper in the grafting process i.e. it should not dissolve the matrix but swelling is necessary. For thin layer grafting, slight interaction is needed and for highly crystalline polymer and dip-routed grafting swellability is important. The solvent should not be reactive towards the photo-initiators which will retard or hang the process. The solvent should not dissolve the grafted chains. Proper choice of solvent sometimes does not need the photo initiator. Aliphatic ketones (e.g. butanone, pentanone, heptanone) with water act as sensitizer [105].

- **Nature of Photo-initiators**

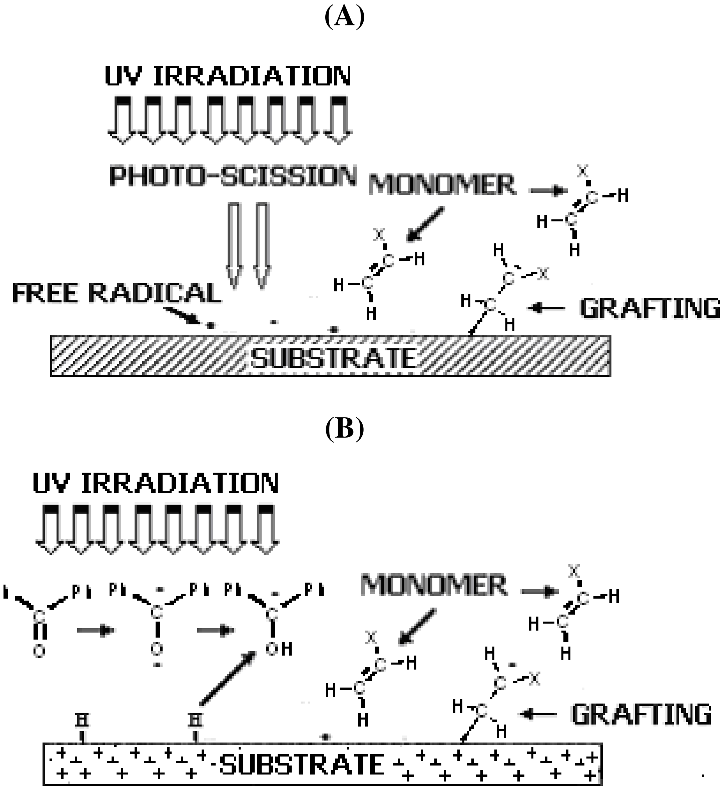
The choice of photo initiators is a matter of the properties of the polymeric substrate. Considering bulk of the reactions is free-radical reactions, two types of photo initiators are categorized. The first one undergoes homolytic bond cleavage upon absorption of light, α-cleavage takes place. It is unimolecular. Examples are Benzoin and its derivatives, hydroxyl alkyl phenyl acetophenone (HAP). The other one consists of photo-initiator and a co-initiator such as alcohol or amine combining effort forms the free radical. The reaction is bimolecular one and H-abstraction or electron transfer mechanism takes place. Benzophenone, thioxanthone are the examples in this regard.

Concentration of photo-initiator is also very crucial for grafting phenomenon. High concentration of photo initiator (benzophenone) acts as auto-retardant as it will screen UV-light to the polymeric radical and some of the ketyl radicals formed will combine with polymer radicals and prevent further reactions [106-108].

1.3.1 Mechanistic approaches

Approaches have been made to modify the membranes are of two types: with and without photo-initiator. It can be of single and two step reactions. The single step reaction is achieved either with or without photo-initiator.

Figure 1.5 Schematic diagram of grafting for (A) polymer of photo-responsive nature (intrinsic) and (B) polymer using photo-initiator



The necessity of the photo-initiator depends upon the nature of the polymeric matrix. The polymeric matrix intrinsically built with photo-active part, does not need photo-initiator additionally within the system. The schematic presentation is presented in figure 1.5 A. The incorporation of photo-initiators is possible by physical adsorption, coating or entrapping in polymer matrix while preparation or along with the solvent and monomer. Thus, the initiator remains in contact with the polymer surface in the physically adsorbed or trapped method. On irradiation, hydrogen atoms from the membrane surface are abstracted and monomer grafting takes place while along with the solvent it follows the same basic mechanism of abstracting the hydrogen (figure 1.5 B) but the abstraction of hydrogen may contribute significantly towards homo-polymerization and lesser grafting percentage.

Sometimes, the reaction system does not need photo- initiator additionally; solvent itself has also the capability to function as photo-initiator [109, 110]. Of course, this also depends upon other parameters.

The two step reaction proceeds initially by covalent attaching of the initiators on the membrane surface and then the modified membranes are further treated with monomer solution and photo-irradiated. He *et al*. has reported the modification of polypropylene (PP) membrane by attaching tertiary amines which acted as synergist to the photo-initiator (benzophenone). [109].

There are also reports of membrane modification by covalent attachment of molecules protected with photo-cleavable group by Boxus and Rajam *et al.* [112,113] in their work. These photo-cleavable groups after being fixed covalently on the matrix are irradiated and the photo cleavable groups detach on irradiation and thus impart the desired characters to the surface. It has been realized in many systems, i.e., vapor phase [114-117], batch phase [118], continuous phase [119], sandwich process [120], and bulk process [121]. By the graft method, the surface of polymeric materials can be planted a layer of new polymer chains with various functional groups in very short time according to the requirements for modification applications.

1.3.2 Contribution of photo-modified membranes

One of the critical characteristics of a synthetic membrane is its chemistry which refers to the chemical nature and composition of the surface in contact for the required function. The chemical nature of a membrane surface can be quite different from its bulk composition. This difference can result from material partitioning at some stage of the membrane's fabrication, or from an intended surface post formation modification as discussed earlier (numbering of mechanistic approach). Membrane surface chemistry involves very important properties such as hydrophilicity or hydrophobicity (related to surface free energy), presence of ionic charge, chemical or thermal resistance, binding affinity for particles in a solution, which governs the performance of the membrane. Photo-irradiation has widely contributed as a vital tool in these directions. The photo-modified membranes find applications in different aspects viz. to improve the selectivity, to minimize fouling, and permeability, immobilization on membranes, imprinted membranes etc.

Literature reports are there to prepare photo-chemically active thin film composite membranes in which the photoactive functionality is modified after the amine and sulfonyl chloride interfacial polymerization by attaching acid, ketone and ester moieties [122-126]. These membranes showed significantly towards salt rejection and separation of organic molecules. Grafting of monomers on membrane to prepare reverse osmosis (viz. 4-vinyl pyridine onto styrene butadiene-styrene triblock co-polymer membrane) [127, 128]. Nanofiltration (p-styrene sulfonate on polysulfone membrane) [129] and ultrafiltration membrane (acrylic acid on commercial Nylon, Polypropylene and Polyamide membranes, cardo polyetherketone (PEK-C) [130, 131] are good examples in this regard. The modified membranes get equipped with the capabilities towards surface and permeation properties; can be triggered by environment stimuli (viz. pH, temperature) [132-136].

Peng *et al.* has reported about the hydrogel exhibiting swelling response to both pH and temperature in Poly (N-isopropyl acrylamide)- Poly(methacrylic acid) cografted polyethylene membrane by photo-modification [136]. They have found the permeability performance of Vitamin B_{12} alters drastically due to change in swellability [135]. Polyamide microfiltration membranes photo-grafted by acrylic acid and acrylamide monomers show their dependency on pH and temperature for the permeation of riboflavin [134]. Apart from the monomers (acrylic acid and acrylamide), there are also evidence of photochemical grafting of epoxydiacrylate copolymer or one of its zeolites composites onto cellulose membrane [137].

Photo-crosslinking of monomers (Poly-(ethylene glycol) diacrylate, poly(propylene glycol) diacrylate) EPPGDA poly(ethylene glycol) diacrylate EPEGDA and poly(ethylene glycol) methyl ether acrylate EPEGMEA on the membrane developed gas separation as well as pervaporation abilities [138-140]. Liu *et al.* has achieved separation behavior for gases by photo-cross linking of various monomers e.g. Acrylonitrile, methyl methacrylate, vinylidene chloride, sodium styrene sulfonate and divinylbenzene monomers saturated on the surface of microporous support of anapore (porous alumina), gore-tex (fluoro polymer), and nucleo pore (polycarbonate) [141]. The separation of benzene/ cyclohexane mixture by photo-synthesized poly(acrylonitrile-co-butadiene-co-strene) polymer containing a photosensitive group2-(4-ethenyl)-phenyl-5-phenyl-2H tetrazole had been achieved [142]. The photo-modification by hydrophilic polyethylene glycol (meth) acrylates onto asymmetric polyacrylonitrile membrane were also been exploited to show the ability to separate methanol from less polar hydrocarbons (e.g. cyclohexane, methyl tertiary butyl ether) [143].

To counter fouling, surface modification of the membranes is one of unique approach to follow. The fouling occurs due to the deposition of the undesired materials on the membrane. It can be countered by other techniques viz. back flushing and cleaning of the membranes. But, it is of regular exercise and needs powerful cleaning agents. The photo-irradiation possesses that potential, as it can modify the surface without disturbing the bulk properties. The low fouling nature can be achieved by increasing the hydrophilicity as well as development of charge. The hydrophilicity of the membrane can be improved by the incorporation of various hydrophilic monomers (viz. acrylic acid, methacrylic acid, acrylamide etc.) [133,144].

Various reports are there in which fouling is minimized which is caused while dealing with proteins, BSA, lysozyme and whey by photo-grafting of suitable monomers like N-vinyl -2-vinyl pyrrolidone, polyethylene glycol methacrylate dextran, polyethylene oxide, NVP, AAG [145-149] on the membrane. Membranes modified with the weakly hydrophilic acrylic acid (AA) monomer are found to reduce the fouling, with respect to strongly hydrophilic monomers like hydroxyl ethyl methacrylate (HEMA) and 2-acrylamido glycolic acid (AAG), poly(ethylene glycol) methacrylate [150-153]. Biofouling, due to microbial growth has also been reported to be minimized by grafting 2-acrylamido 2-methyl 1-propane sulfonic acid (AMPS) and quaternary 2-methyl aminoethyl methacrylate (qDMAEMA) on to polyether sulfone microfiltration membrane upon photo-irradiation [154].

Photo-irradiation has also contributed towards the immobilization of the various molecules on the membranes as surface modification is one of the pre-requisite sometime. There are lots of important studies in the literature in this regard.

PSf-g- acrylic acid and PESf-g-(acrylic acid) surfaces are found to be well suited for co-valent bimolecular immobilization [155]. Ulbricht *et al.* has reported about the feasibility of surface immobilization of BSA, γ globulin and alkaline phosphatase on to polysulfone UF membrane [156]. High binding capacities of BSA, invertase and IgG-POD (antibody enzyme conjugate) with acrylic acid modified membrane has been also observed compared to unmodified Polysulfone/Polyether sulfone [157]. PP-g-glycidyl methacrylate membranes have been studied to show the favor for affinity membranes and these are found to serve as a matrix for recombinant protein (rPA) immobilization [158].

Photo-induced surface functionalization has also been exploited to prepare molecularly imprinted polymer (MIP) membranes where the separation function is controlled by the highly specific binding of molecules which has been used as template during membrane preparation [159, 160].

Photo-reactive polymer [poly(acrylonitrile) –co-(diethylamino) dithiocarbamoyl-methyl styrene] upon photo-irradiation is the unique example of MIP membrane [161]. There are also reports of photo-assisted surface modification of polyvinylidene fluoride and polypropylene membranes with various monomers and crosslinkers for the templates (turbumenton/desmetryn) [162-164].

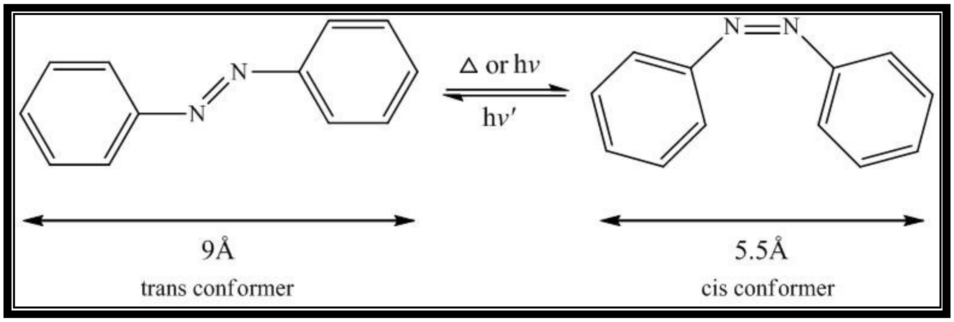
Biocompatibilities of polymers are also improved by surface modification. Grafting of hydrophilic monomers on the membrane surface makes it biocompatible as it hinders the absorption of bio-molecules also. The absorption of albumin and fibrinogen decreases with the increase of poly (vinyl pyridine) grafted on styrene-butadiene-styrene copolymer membrane [165]. Likewise, Poly(hydroxyl ethyl methacrylate) hydrogel (used in different biomedical applications) grafted on chitosan through photo-irradiation technique makes the system more biocompatible [166]. Monomers like acrylamide and methacrylic acid (MAA) are used to achieve better cytocompatible polymeric surface [167] with respect to control membrane and modified one [168].

1.4 Membranes in operation: Photo-regulation

Synthesis of the membranes showing response to the external stimuli e.g. pH, temp., conc. is well established. Along with preparation of the membranes having propensity towards light has also been exploited/worked out. These membranes are incorporated with some photo-chromic molecules to work at. When these molecules are subjected to photo-irradiations, show some interesting phenomenon like trans/cis isomerization or cyclization/ ring opening etc which are very selective, specific and rapid in action. These all in turn bring about the changes in the physico-chemical properties of the molecules and in response to this, properties of the host matrix i.e. membrane are also changed. This includes change in polarity, charge, color, wettability, and porosity of the membrane depending upon photoactive moiety. As a result, performance behavior of the membrane is also changed. This performance behavioral change of membrane in response to light is termed as photo-regulation.

The molecules which either or along with some moiety show characteristic changes in their properties in response to light are termed as chromophores / photo-antenna. The most commonly used chromophores include mainly azobenzene, spiropyran and their associated moieties. These molecules undergo reversible photo-isomerization reaction between two or more isomeric states. Different chromophore adopts different mechanisms to show the peculiar response/ behavior when exposed to photons or not.

Figure 1.6 Photo-irradiation effects on azobenzene structure: formation of different conformers (trans and cis)

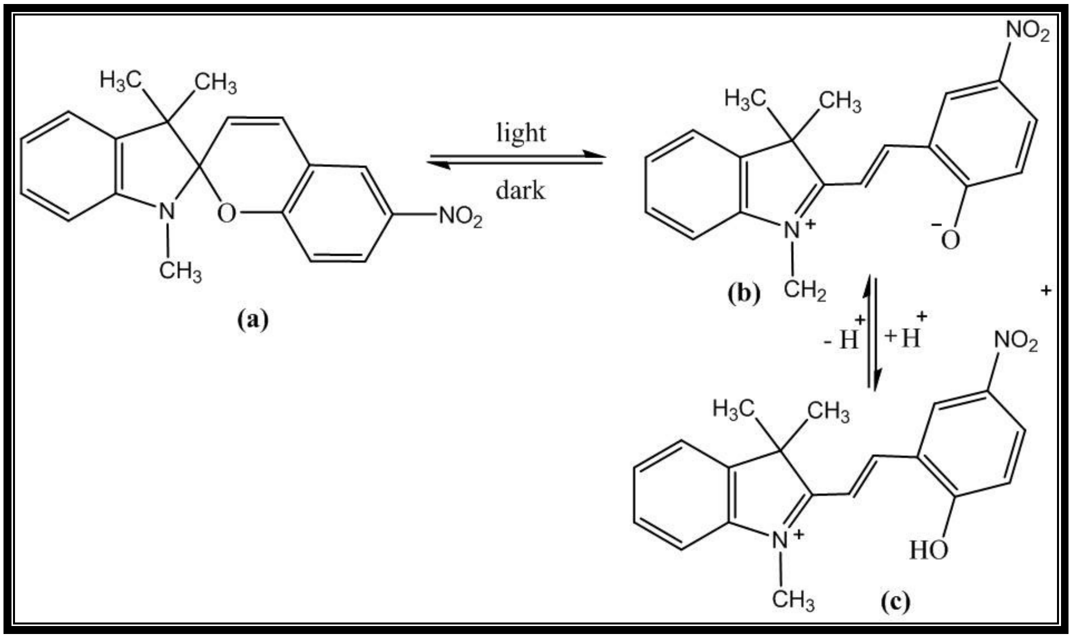


The azobenzene is such a molecule, is recognized with two phenyl rings separated by an azo (-N=N-) bond. It can exist in cis or trans form (refer to figure 1.6) and they are inter convertible by light and heat. The molecule displays a low-intensity n→ π* absorption band in the visible region and a high intensity π→ π* band in UV region [169]. The trans form of azobenzene is relatively more stable, with a difference in ground-state energies of cis and trans of 11.95 Kcal/mol [170]. The cis isomer assumes a geometry with the phenyl rings twisted at right angles to the C-

N=N-C plane [171]. Photo-induced isomerism in azobenzene results change in the dipole moment and geometry of the molecule. It involves a decrease in the distance between the 4 and 4′ ring positions from 9.0 to 5.5 A° (trans- cis) [172,173] and the local contraction may even greater [174].

Spiropyran is another interesting chromophore and it absorbs in the UV region. Their photochromic reaction involves inter-conversion of colorless isomer (spiropyran) to colored isomer (merocyanine) as shown in scheme 1.2 through the heterolytic cleavage of the NO bond. Here, photo-isomerization results the change in molecular geometry. The merocyanine isomer is planer, while in spiropyran parts of the molecule are perpendicular to the other part. It is also accompanied by changes in charge distribution, increase in molecular volume as well as change in dipole moment from 4.3 to 17.7D [175].

Scheme 1.2 Reversible photo-conversion of closed- Ring Spiropyran (a) into the Bipolar open Merocyanine (b); under acid conditions, the Bipolar Merocyanine (b) turns into the Monopolar N$^+$ Merocyanine (c)



The azobenzene and spiropyran moieties when attached with other molecules like polypeptides, crownethers or polymers as pendant don’t lose their characteristics upon photo-irradiation. Their photo-chromic behavior is expressed in a specific way and in a more refined manner which results a great impact on the surrounding.

The polypeptides attached with photo-chromic units respond to light by showing photo-induced structural change to destabilize the helix and promotes an extended coil structure due to change in size, charge, polarity as a result of different conformations depending upon the nature of the photo-chromic molecules attached e.g. azobenzene, spiropyran [173, 176, 177]. These also result in the apparent pK value for the ionization of the unmodified –COOH groups due to the variation of the local dielectric constant [173, 178,179].

Similarly, crown ethers and calixarene incorporated with photoactive moieties like azo and spiropyran [180-186] upon photo-irradiation causes geometrical changes in these moieties due to photo-induced transformation of the azobenzene/ spiropyran unit.

1.4.1 Conditions to photo-responsive membranes

The performance of membranes is either the result of inbuilt chemistry of the membrane matrix or due to external factors which on incorporation causes the desired effect. To work with the membranes for different applications, these are monitored accordingly.

Figure 1.7 Schematic presentations of the photo-induced changes in photo-responsive system

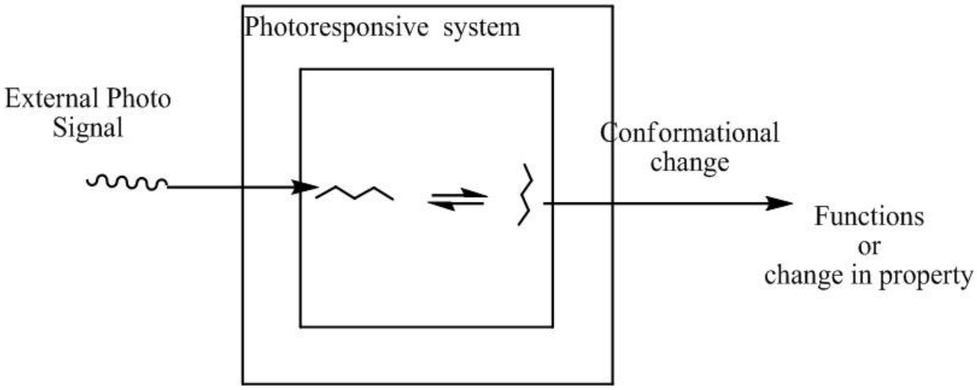


Photo-responsive Membrane works in response to the photons which it receives and results various transformation/ changes as shown schematically figure 1.7. The mechanism of stimulus-response coupling is basically the change in conformation/ geometry or molecular size as well as of the dipole-moment of the photo-responsive molecule, thus causing the characteristic changes which influence other properties within the membranes due to external photo stimulus. For the photo-regulation property of membrane, it is needed that the polymeric materials should be photo-responsive intrinsically or photo-responsive part is added to it, so that it can "trigger" to induce changes which can be light driven. There are certain other parameters to be considered to make membrane work in response to light. These are as follow:

- ❖ The membrane matrix should be inert to photo-irradiation, transparent and not alter the course of the photo-chromic reaction.
- ❖ The adsorption of the photo-chromic molecule also should not compromise the mechanical properties of the polymer backbone.
- ❖ Photo responsive molecule has to be adsorbed in an optimal amount in the polymeric membrane, so that changes can be fruitful in terms of the application.
- ❖ The incorporated photo-responsive molecule has to be reversibly photo-switchable in to same configuration must have a sufficient life time for the practical experiments.

1.4.2 Approaches in preparation

Development of photo-responsive membranes by incorporation of photo-responsive molecules require one of the crucial issue to be taken care is to choose a solid host that allows the photo-chromic reactions to occur nearly at the same rate and efficiency as those found in solution. Generally, the fast response to light exposure is no longer achievable when photo-responsive molecules are adsorbed on solid matrices or supports. The response time varies depending on the type of materials used [187-193]. The photo-responsive molecules are incorporated by the two approaches viz.

- ➢ Covalent attachment between polymer and chromophores.
- ➢ Non-covalent modification (doping of conventional materials e.g. formation of usual materials for membrane preparation in the presence of photo-responsive compounds and

The size of a chromophore, its conformation, and point of attachment to a polymer chain also play the role in determining the effective free volume available to an isomerizable group. These properties when manifested in polymers are useful probes of conformational dynamics of macromolecules for site specific photolabeling, in estimating the free volume in cross-linked networks and in designing photo-reactive polymers responsive to external stimuli.

1.4.3 Performances of photo-responsive membranes

On photo-irradiation, the photo-responsive molecule (photoreceptor) captures optical signals and converts them to chemical signals. These may involve change in wettability, change in polarity, increase / decrease in free volume space in polymer due to conformational change, change in swelling behavior of polymer, change in potential across the membrane etc. As a consequence, the performances of the membranes are altered upon photo-irradiation.

Covalent attachment of photochromes is one of the approaches to prepare photo-responsive membranes. The photo-responsive membranes show different performances in terms of their behaviors. The membrane prepared from methyl methacrylate and 2-(ethyl-[4-(4- nitrophenylazo) phenyl] amino)ethyl methacrylate show more permeability towards helium upon UV light exposure due to photo-isomerization of azo moiety and also shows plasticization effect [194]. Polymethacrylate-azobenzene membranes show different gas permeability in terms of photo-induced isomerization. The trans form is of having more free volume shows better gas permeation in presence of UV-light [195, 196]. The polyvinyl/polypeptide graft copolymer (β-p-phenylazobenzyl L-aspartate and β-benzyl L-aspartate attached to a poly(butyl methacrylate)) based membranes immersed in trimethyl phosphate (TMP) are found to improve the permeation rate of mandelic acid across by about six times upon UV-irradiation and get suppressed upon visible irradiation light due to photo-induced inversion of the helix sense of polypeptide chain in membrane. This is due to possible change in the helix size which induces the decrease in the volume occupied by polypeptide chains. The permeation rates of other polar and nonpolar substrates such as (N-(benzoyloxy)carbonyl)-D,L-alanine, acetone and biphenyl are also found to depend upon the conformational change of the polypeptide chains in the membrane [197]. Membrane based on [4-(phenylazo) phenyl]carbamoylated cellulose and amylase has been studied for their ability for chiral responsive reversible behavior upon photo-irradiation [198].

Photo-responsive membranes are reported to be prepared by using the cross-linker along with the photo-functional monomer. This includes preparation of MIP membranes from p-phenyl-azoacrylanilide (PhAAAn) as the photosensitive functional monomer, dansylamide (DA) as the template, and mixtures of EGDMA and tetraethylene glycol diacrylate (TEGDA) as cross-linker [199]. This membrane shows the reversible change in the recognition to dansylamide upon irradiation by UV and visible light. The azoaromatic polymer membrane prepared from polar poly(hydroxy ethyl methacylate) and p-phenyl azobenzoyl chloride are studied to function as a permeable membrane in the dark of the proteins of various molecular weight(viz. insulin (Mw 6000), lysozome (Mw 14,500), chymotrypsin (Mw 23,000) with a linear increase in their permeation with time [200]. But under UV- irradiation, it works as semi-permeable membrane and allows only insulin to pass through although it is accompanied by overall decrease in permeation than dark. The decrease of permeability depends upon the degree of swelling of the polymeric membrane. It has been reported that degree of swelling of azo aromatic polymer membrane in water decreases upon UV-irradiation and recovers upon visible irradiation due to photo-isomerization of azo moiety which in turn alters the permeability of the membranes. The photo-responsive membranes based on poly-L-glutamic acid with azobenzene in side chain are found to show the increase in water uptake upon UV-irradiation. This has been reported due to change in the polarity due to photo-isomerization which results in the increase in the pK_a value of the L-glutamic acid moieties and increase in the negative charge on the membrane [201, 202]. The coupling of spiropyran carboxylic acid on silanized alumina membrane surface result the flow of water and ions through the membrane upon UV-irradiation due to photo-isomerization to more polar merocyanine form [203].

Various researchers have utilized the technique of grafting to incorporate the photo-active onto the different membranes [204-206]. The porous PTFE membrane prepared by grafting of spiropyran containing methacrylate (SPMMA) and AAm show the increase in permeability upon UV-exposure due to merocyanine formation. It governs pore generation/opening and decreases with visible light after attaining initial spiropyran form. Like-wise grafting on porous glass filter by spiropyran substituted methyl methacrylate (SPMA), and methyl methacrylate (MMA) on a glass filter by glow discharge show photo-regulated permeability of organic liquids due to solubility of graft chain altered upon photo-irradiation as a result of contraction or expansion of the chains [205]. In the same way adsorption of BSA is also found to vary reversibly on Polyether sulfone (PES) membranes photo-grafted with optically active vinyl spiropyran (1-(2-propylcarbamylmethacrylamide) ethyl)-3,3-dimethyl-6-nitrospiro[2H-1]benzo-pyran-2,2-indoline) upon photo-irradiation [206].

Non covalent modification approach is followed by adsorption, coating or blending of the photoactive moiety into the polymer matrix. Reports are there about the photo-responsive membranes by adsorption of photo-active azo compounds in the pores of membranes [207]. It shows reversible trans-cis isomerization to govern gas separation upon photo-irradiation. Membranes prepared by immobilizing hydrogel prepared from N-Isopropylacrylamide, allylamine, *N,N'*-methylenebisacrylamide, and spirobenzopyran with COOH residue on PTFE membrane are found to show increase in permeation of 1mM HCl upon photo-irradiation [208]. Photo-responsive polyethylene membranes are prepared by coating of crown-ether-spirobenzopyran copolymer solution which governs the permeability of hexane and it is found to decrease upon UV-irradiation due to increase in polarity and vice-versa [209]. The plasticized poly(vinyl chloride) membranes [210-214] of entrapped photo-responsive bis-(15-crown-5) with an azo linkage upon UV or visible light irradiation show the reversible affinity towards ion permeability along with the change in the membrane potential. Upon photo-irradiation, the selective K^+ permeation through the membrane is found to accelerate. The membrane potential also shifts more in the positive direction upon UV-light irradiation in presence of KCl or RbCl with respect to LiCl and NaCl. This is found due to higher binding ability of the potassium and rubidium ions than lithium and sodium ions. Subsequent visible light irradiation recovers the original value of the membrane potential. In the plasticized poly(vinyl chloride) membranes containing a lipophilic spiro-benzopyran with and without crown ether moiety [215], the potential for membrane with crown moiety in the presence of alkali metal ions is found to increase followed by a decrease on photo-irradiation. This is also affected by the type of metal ions and pH of the aqueous phase and it's found due to fast proton exchange followed by slow metal-ion exchange of its merocyanin form. While the system without crown ether moiety exhibits a steady potential photo-response which is dependent on pH of the aqueous phase.

1.5 Scope and objective

The aims of the present research are to develop tailor-made polymeric membranes using photo-irradiation techniques and the photo-regulated performances of the photo-responsive membranes. The achievements of these objectives are targeted more or less to exploit these in terms of separation of different water pollutants along with the membrane's versatility towards the external stimuli like pH and light. This has been focused by taking into the account the various isomers of the specific pollutant and the pH sensitive charged species other than pollutants e.g. natural colors (anthocyans).

The thesis has been outlined to study the following objectives in respect to photo-irradiation. The first working part deals with the achievement of Photo-modification of membranes. The photo-modification is done without any sensitizer. The prior art of preparation of asymmetric polysulfone membranes is exploited in proto-type casting machine. The photo-modification of membranes by photo-responsive monomer (acrylic acid) is done. The membranes are subjected to study to fulfill the scope for the removal of water pollutants along with the study of effect of external stimulus (i.e. pH) during the separation of floral pigments from the extract of rose petals. The natural pigments anthocyanins are also pH responsive. In the same context, piperazine based thin film composite polyamide membranes have also been photo-modified by acrylic acid and identification of the proper step of modification has been done. The water separation of water pollutants (viz. simazine, atrazine, 2,4,6-trichlorophenol, 2,4-dichlorophenol) is carried out and their different separation behavior in terms of physical parameters is tried to explain.

The second part deals with the polyamide based thin film composite membranes. This part of the thesis details about the study of use of some technical approaches for better performances of membranes. Here, photo-irradiation technique is employed instead of heat-curing to form the cross-linked network of polyamide from the monomers m-phenylene diamine and trimesoyl chloride during interfacial polymerization. These photo-treated low pressure thin films composite membranes are used for the removal of water pollutants. In this study, the experimental solution is also dealt technically by adding surfactant into the solution to increase the size of the solutes. The role of surfactants is exploited in terms of energy efficient technique.

Surfactants have the ability to interact with the organics, generally hydrophobic in nature. The aggregated surfactant molecules with the organics are easy to separate at comparatively (with respect to the required) low pressure. The separation behaviors of pentachlorophenol, simazine by the thin film composite membranes are studied in presence of sodium lauryl sulfate. The later study also unfolds the separation behavior in terms of nature of surfactants (cationic (cetyl tertiary ammonium bromide, CTAB) and anionic (SDS).

The third part deals with the development of membranes by incorporating the photoactive azo-moiety. In this case the unique and unconventional approach is followed. The azo-moiety is incorporated into the pores of the asymmetric polysulfone membranes. These Membranes are further used towards the separation of isomeric water pollutants (2-chlorophenol and 4-chlorophenol). The separation behavior is studied in dark and photo-irradiation conditions without applying pressure and it is explained in terms of photo-isomerization effect of the azo-moiety. The characterization of the particular azo incorporated membrane has also been carried out and possible exploitation regarding its biocidal activity is also done as an extension to the study towards new application.

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