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Review

Topical Progression in Organic and Inorganic Membranes for Advance Application: A Review

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Abstract

Organic and inorganic nano-porous filtration membranes have been discussed in this review, as emergent water treatment technology for elite protection of human health and environment. Self-assembled block copolymer has evolved as influential tool to fabricate organic nano-porous materials with well-defined morphology, pore size and distribution, porosity and surface chemistry. These types of nano-porous materials are attractive for regulation and detection of transport at molecular level. The literature inspection presented in this article typically addressed exploration of relevant aspects such as polymerization method, surface morphology, membrane thickness, and active porosity affecting membrane performance. Similarly, considerable efforts towards fabricating ordered and water-permeable inorganic membranes were debated. In both type of membranes, fine control over pore dimensions, structural characteristics, and physical behavior of nano-structures hang about a major challenge.

Keywords: Self-Assembled Block Copolymer; Nano-Porous; Membrane; Water Treatment; Surface Morphology

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1. Introduction

1.1. Water treatment - Indispensable

One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water and sanitation. Problems with water are expected to grow worse in the upcoming decades, with water scarcity occurring globally, even in regions currently considered water-rich. Addressing these problems calls out for a tremendous amount of research to be conducted to identify robust new methods of purifying water at lower cost and with less energy, while at the same time minimizing the use of chemicals and impact on environment. Several problems associated with lack of clean/fresh water are well known as 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, and millions of people die annually from diseases transmitted through unsafe water to human [1]. Countless more are sickened from disease and contamination. Intestinal parasitic infections and diarrheal diseases caused by waterborne bacteria and enteric viruses have become leading cause of malnutrition owing to poor digestion of food due to water [2, 3]. In both developing and industrialized nations, a growing number of contaminants are entering water supplies from human activity, from traditional compounds such as heavy metals and distillates to emerging micro-pollutants such as endocrine disrupters and nitrosoamines. Consequently, an essential aspect for sustaining life is an adequate supply of clean water; however several areas of the world suffer from insufficient water supply or ineffective sanitation [4, 5]. Efforts aimed at solving the global water crisis using traditional water purification methods depending on chemical treatments [6-8].

1.2. Nanotechnology and block copolymer

Field of nano-science and nano-technology has grown progressively in the recent decades. Material science focuses the material preparation, fabrication of nanostructure, and their application. Various application of nanotechnology includes miniaturization of electronic and memory devices, fabrication of potent drugs effective diagnostic procedures, and the design of robust catalyst. Various high resolution lithographic methods are used to manipulate the nanostructure. Lithographic approach carves a large size material to smaller one with dimension to a few 100 nm at an industrial scale. By using molecular assembly, scientists have synthesized various material and nanostructures. During the last decades, block copolymers (BCPs) have been the focal point of interest owing to the miscibility between their constituent blocks [9]. In contemporary macromolecular science, BCPs have been the focus of research activity. The fundamental issues associated with the self assembly processes in both solution and bulk are molecular and structural characterization. BCPs now stand on the verge of a new generation of sophisticated material applications because of rapid progress in these areas, particularly nanostructures will play a vital role. Variety of architecture such as nano-sphere, nano-fibers, and nano-tubes can be yielded through self assembly of polymer blocks [10]. Block copolymers can also be used to make membranes that have pores on nano-scale. Block copolymers represent a subject of broad current research emphasis across the full spectrum of macromolecular chemistry and physics, ranging from development of new synthetic strategies and molecular architectures to application of advanced theoretical and computational methods. In new material science, self-assembly of BCPs is an important strategy to replace current lithographic technology. Due to the scale of microscopic domains between 10 and 100 nm, and their physical and chemical properties, BCPs have become center of attention in self assembly-based processes. Structure of micro-domains has proven to be effective in BCPs by modification of their thermodynamics through molecular weight and compositions [11]. Block copolymer/homopolymer mixtures have been of considerable interest because they can be easily modified to yield desired properties in polymeric materials such as pressure-sensitive adhesives. The phase behavior of these mixtures is generally complicated because two different transitions can occur at the same time, i.e. macrophase and microphase separations. If the molecular weight of the added homopolymer is sufficiently low compared with that of block copolymer, it tends to be solubilized into one of the microdomains. In this case, the macrophase separation is suppressed, and microphase separation becomes dominant. Various assembly techniques for nano-structure formation using block copolymers are mentioned in Figure 1.

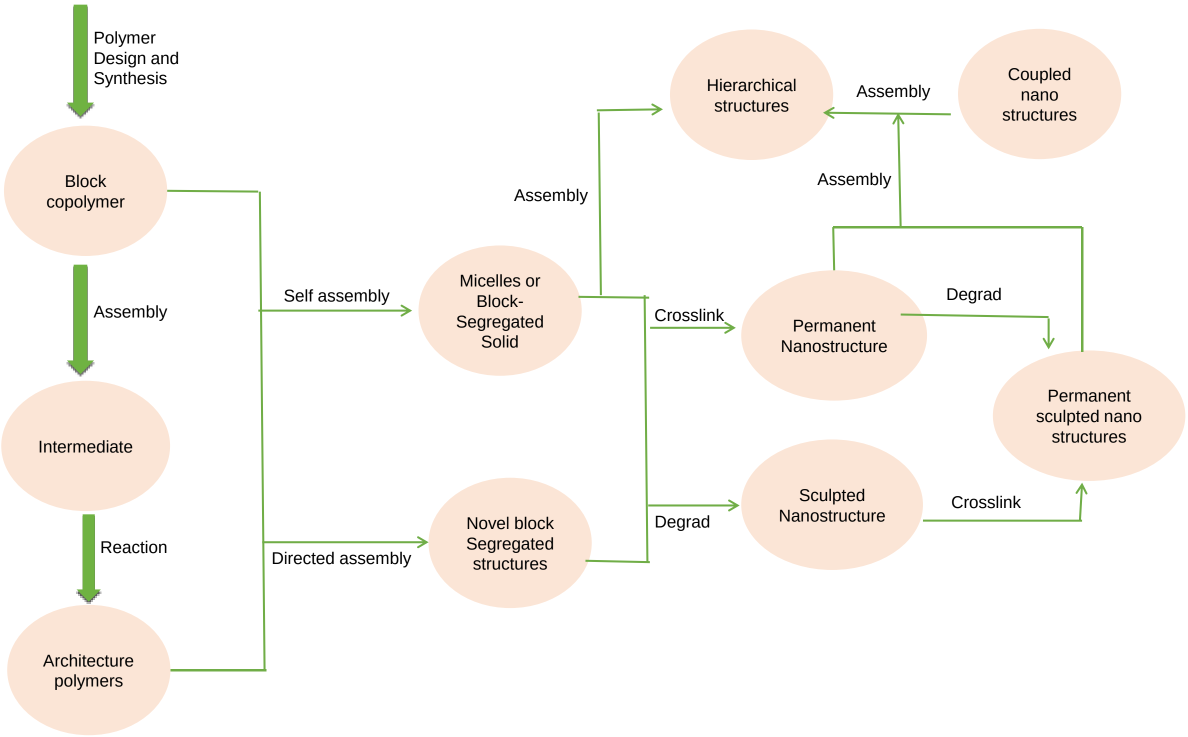

Figure 1. Methodologies for nanostructure formation *via* assembly techniques.

1.3. Water purification using organic nanostructured membrane

Large amount of waste water is generated each day by hydrocarbon processing, metallurgical, pharmaceutical, and food industries, so causing a promising source of water for beneficial use. Owing to the inherent advantages, membrane technology emerges as highly competitive candidate for reclamation and reuse of water. However, when incorporated in waste water treatment processes, the semipermeable membrane systems offer high surface areas for attachment of numerous foulants. Membrane based separations have, thus, proven to be a facile alternative for water purification capable of removing a variety of impurities including bacteria, viruses, organic molecules and dissolved salts by using the full spectrum of filtration processes [12, 13], as can be seen in Table 1. Two classes of membranes have often used in filtration processes include phase inversion and track-etched membranes. Phase inversion membranes can be made by casting a thin film of a polymer solution followed by immersing it in a non-solvent, which causes the polymer to precipitate as a web of fibers [14]. Track-etched membranes are made by exposing a thin polymer film to a beam of radiation [15]. The film is then etched in a chemical bath, which removes the polymer damaged by the radiation.

Table 1 Block copolymer membrane based separations for water purification.

Process	Microfiltration	Ultrafiltration	Nano-filtration	Reverse Osmosis
Retentate	Red Blood Cells, Bacteria, Algae, Sediment	Viruses, Proteins, Enzymes	Amino Acids, Antibiotics, Multivalent ions	Aqueous Salts
Pore Size (nm)	100-10,000	2-100	0.5-2	<0.5
Pressure (psi)	10-130	50-200	100-600	400-1000

1.3.1. Block copolymer templated membrane

A block polymer is a polymeric chain composed of at least two chemically distinct covalently bound polymer segments [16]. Variations in both the number of segments and their connectivity have resulted in a diverse array of block polymers. Simple AB diblock copolymers [17], where A is one component and B the other, have been extended to ABA triblock copolymers, ABC triblock terpolymers [18, 19], ABAB tetrablock copolymers, ABCD quarterblock polymers [20] and ABCDE pentablock polymers [21, 22] to name a few. In addition to linear block polymers, other architectures include star, [23, 24] comb or graft, [25, 26] and cyclic [27] structures. Figure 2 illustrates some block polymer architectures. An interesting aspect of block polymers is their self-assembly into ordered structures on nanometer length scales [28]. The phase separation of block polymers is driven by the chemically distinct nature of each block and is limited to microphase separation as the two blocks are covalently bound [29]. The final structure formed is a balance of minimizing the interactions between blocks by reducing their interfacial area while avoiding excessive chain stretching.

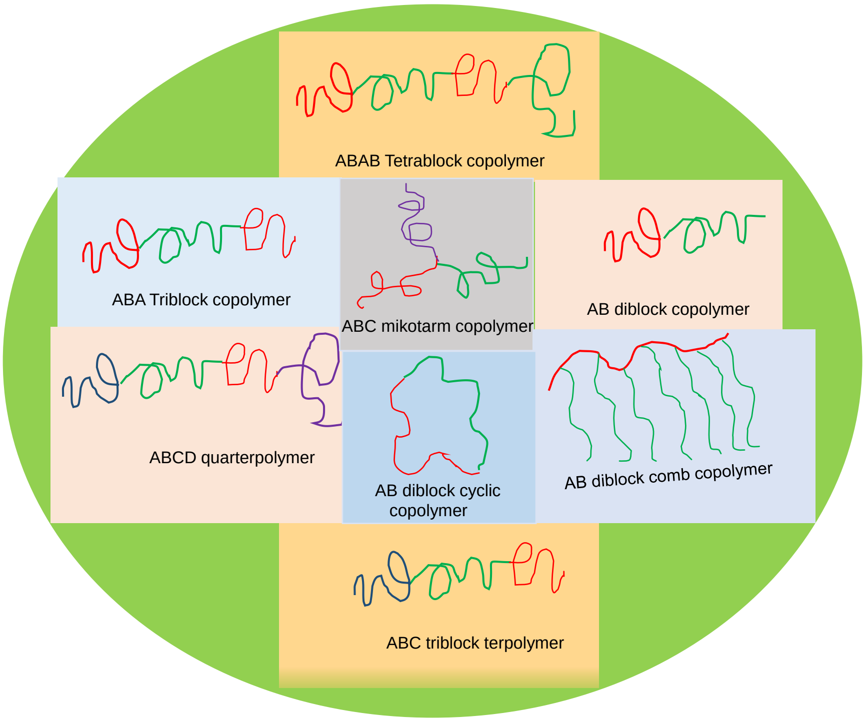

Figure 2 Block copolymer architechture; AB diblockcopolymer; ABC triblockterpolymer; ABA triblockcopolymer; ABAB tetrablockcopolymer; ABCD quarterpolymer; ABC mikotarmstar copolymer; AB diblockcomb copolymer; AB diblockcyclic copolymer.

The structure formed depends on the block compositions, degree of polymerization, segment-segment interactions χ and temperature, as χ is inversely proportional to temperature [30-32]. Equilibrium structures have been observed experimentally [33-36] and predicted theoretically [37-40] and include lamellar, bicontinuous double-gyroid, hexagonally packed cylinders and spheres on a body centered cubic lattice for AB diblock copolymers. The general theoretical phase diagram and equilibrium morphologies for AB diblock copolymers are shown in Figure 3.

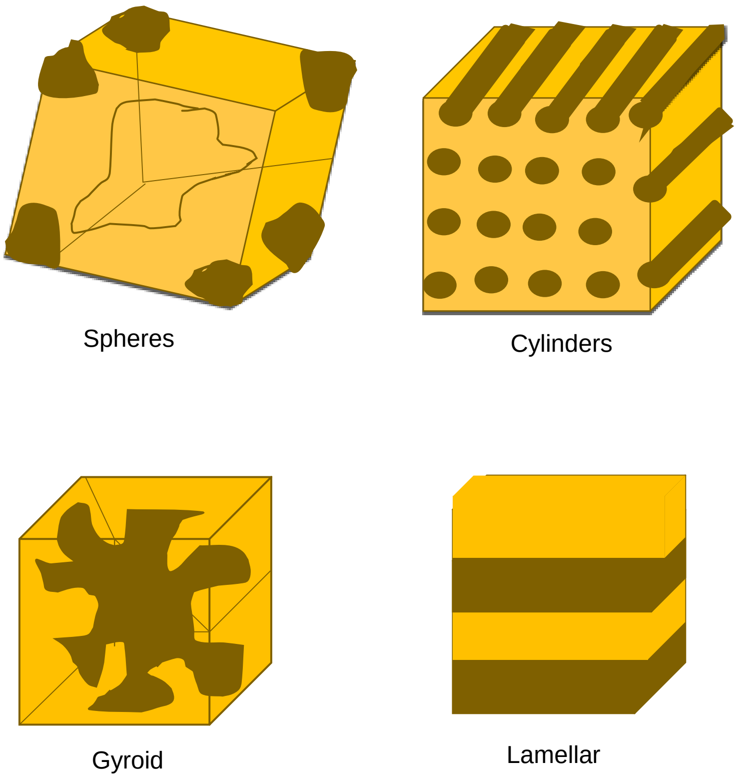
Spheres
Cylinders
Gyroid
Lamellar

Figure 3 Theoretical phase diagram for self-assembly of block copolymers.

1.3.2. Nanoporous materials from block polymer

The self-assembly of block polymers makes them attractive for a variety of technologies requiring structures exhibiting nanometer length scales [41], and one research area that exploits the nanostructures formed is nanoporous materials from block polymers. The lamellar self-assembly of an ABA triblock copolymer consist of two poly((4-vinylphenyl)dimethyl-2-propoxysilane) blocks on either side of a poly(isoprene) (PI) mid-block. Crosslinking silane block preserved lamellar microstructure, while subsequent ozonolysis removed PI block rendering material nanoporous [42]. The variety of techniques and materials used in block polymer templating of nanoporous materials has grown tremendously, but the same basic methodology remains. After a block polymer containing an etchable block self-assembles into a desired structure, the etchable component is selectively removed. Numerous methods have been employed for selective removal such as ozonolysis [43], thermal degradation [44, 45], UV irradiation [46], chemical etching [47-49], reactive ion etching [50], and single block scission [51, 52]. Figure 4 depicts the general scheme for creating a nano-porous material from a cylindrical morphology. Several literature reviews cover the development of nano-porous materials from block polymers [53].

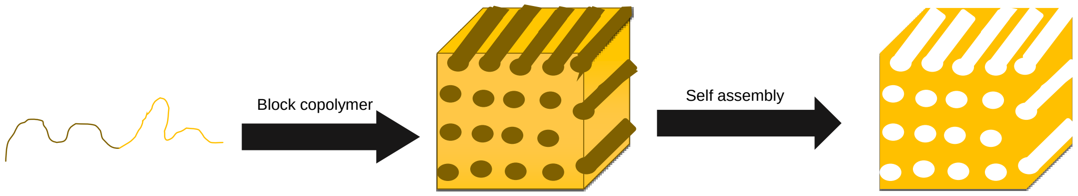

Figure 4 Scheme for the formation of nanoporous materials from a diblock copolymer.

Symmetric membranes have an isotropic structure across the thickness of the membrane. Composite membranes consist of a thin selective layer of one material with smaller pores on a thicker macroporous substructure as a mechanical support. Finally, asymmetric phase inversion membranes are composed of a single material that has a spatially varying morphology. One side of the membrane has a thin selective layer with smaller pores that transition to a thicker macroporous substructure. Figure 5 illustrates the three membrane structures.

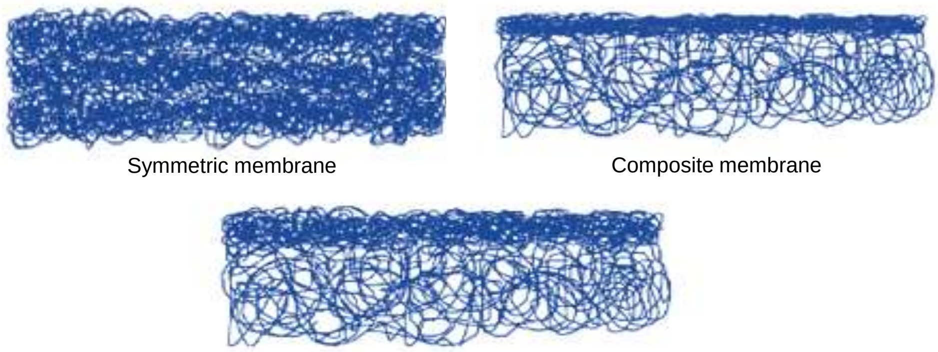
Symmetric membrane
Composite membrane
Asymmetric membrane

Figure 5 Schematic representation of basic membrane structures.

1.3.3. Composite membranes from block polymer

In addition to membrane structures, block polymer thin films have been employed as templates for forming nano-dots, nanowires and other nano-patterns for high density storage media and photonic crystals [54]. Block polymer thin films are typically formed by spin coating a block polymer solution onto a substrate. After the solvent evaporates, a block polymer coating (50-500 nm) is left on the substrate [55]. Modification of resulting thin films via selective etching renders them porous thereby creating structures useful as lithographic masks, nano-structured templates or barrier layers for membranes [56]. One of the first examples of a composite membrane with selective layer formed from a block polymer template was reported [57]. The selective layer was based on previous research into nano-porous thin films templated by poly(styrene)-b-poly(methylmethacrylate) (PS-PMMA) block polymers [58-60]. Specifically, a 2 % (w/v) solution of a PS-PMMA block polymer (89 kg/mol; 0.3 volume fraction PMMA) and a PMMA homopolymer (31.8 kg/mol and 10 wt % relative to the PS-PMMA block polymer) were spin coated onto a silicon wafer with neutral brush surface of PS-r-PMMA. The resulting 80 nm thin film had a cylindrical microstructure consisting of PMMA cylinders with perpendicular orientation with the thickness of PS matrix. Treatment of the film with an acetic acid wash removed the PMMA homopolymer creating a nano-porous layer with 15 nm pores. Figure 6 depicts the general scheme for the membrane formation. The membrane flux and separation performance was evaluated by treating membrane with phosphate buffered solution.

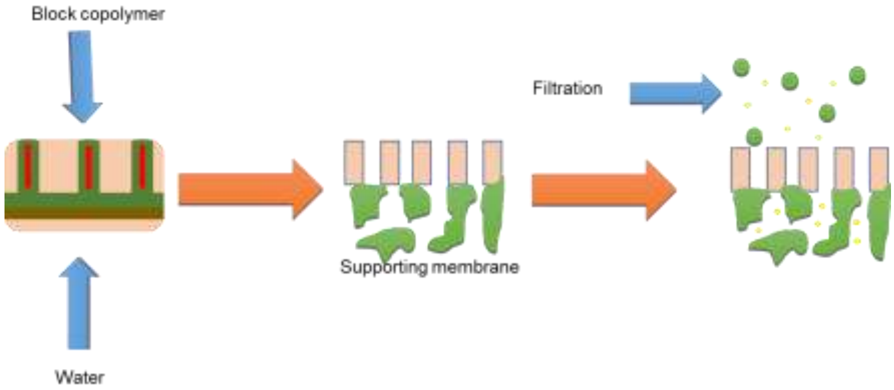

Figure 6 Illustration of the composite membrane formation.

2. Significance of Composite Membrane

On earth water is essential part of life. The continuation of life on earth is made possible because of the occurrence of clean water which is significant to metabolic processes within the body. Clean and fresh water is, thus, essential for the existence of life which is important for metabolic process within the body. In aquatic system different impurity hinder with many useful use of water. Human health and ecosystem is also affected by dangerous pollutants present in water. In this regard, waste water treatment by photo-catalytic process is relatively a new research area having huge applications. Titanium dioxide nanoparticles for water and wastewater treatment and their application mechanism and principle have also been deliberate [61]. It is well known that the current global development is not sustainable over the long time period. Potable water is a threatened but critical resource scarcity of which is devastating for the developing world. Water purification employing nanotechnology is to provide inexpensive and safe water accessible for different countries. Filtrating drinking water *via* membrane nanotechnologies have been frequently investigated. For the foreseeable future, membranes must show a number of characteristics such as high water flux, high salt rejection, mechanical stability, resistance to fouling, and low cost. Consequently, the constituents of the specific membranes must be realized and the promising nano-tech modified reverse osmosis membranes would be applicable as nano-filtration membranes in future membrane technology [62]. Various desalination technologies have been emerged to tackle the increasing water demand globally. Among them, *nano-filtration* (NF) has recently received an increased attention in the literature to desalt low salt content water. Nanotechnology based products such as nanoparticles and nano-fibers have been introduced to enhance the properties and performance of the membranes derived from conventional polymeric membrane materials and conventional phase inversion processes. When mid-layer made up of electrospun nano-fibrous membranes (ENMs) produced by electrospinning has been applied in the thin film composite (TFC) configuration in NF application; higher permeate fluxes than conventional membranes were achieved. This has been ascribed to the high porosity, low transmembrane pressure and interconnected pore structure of ENMs. The ENMs as such or after mixing with nanoparticles were also explored in the area of membrane distillation for seawater desalination [63]. A poly(vinylpopylene) (PVP)/titania (TiO_2)/Ag functional film was prepared as an antibacterial composite used in storing drinking water. The orthogonal experiment showed that the optimal conditions for preparing membranes with best antibacterial activity and tensile strength were silver nitrate ($AgNO_3$) = 0.08 %, TiO_2 = 0.20 %, and PVP = 3.00 %. Scanning electron microscopic (SEM) images showed that the TiO_2 particles were displayed on the surface and also embedded in the film. Nano-Ag was further proved through X-ray diffraction studies. The films had a favorable compatibility and heat stability. It was proved that this films possessed sustainable antibacterial activity and were safe in use [64]. A hierarchical titanate nanotube based filtration membrane was fabricated and successfully applied for bacteria removal. A facile and effective membrane fabrication method was developed to directly grow a hierarchical titanate nanotube selective layer onto a porous metal membrane substrate. The resultant membrane had a unique porous structure with strong mechanical strength, intrinsically free of cracks and pinholes, and can be readily regenerated by a simple pressure driven back-flushing process. Successful separation of Escherichia coli *(E. coli)* demonstrated the applicability of titanate nanotube membrane for waterborne pathogens removal, which would be of a great interest to the water purification applications, especially for the purified recycling water applications. The high selectivity and flux of the nanotube membrane in addition to its excellent biocompatibility and nontoxic nature render the membrane highly attractive to medical applications for removal of pathogens and other unwanted biological constituents with sizes greater than 50 nm from highly complex medium [65]. Fouling of nano-filtration membranes is still a major concern that often limits process viability. One method to minimize fouling has been to modify the filtration surface and perhaps the pores of the membrane in order to minimize adsorption of dissolved solutes. Here, nano-filtration membranes have been modified by growing acrylic acid nano-brushes from the surface of the membrane. If the pH of the feed rose above the pKa of grafted nano-brushes, the carboxylic groups would be deprotonated and swollen. Dead end filtration experiments confirmed that polyacrylic acid nano-brushes may be grafted from the surface of high flux nano-filtration membranes without significantly impacting the filtrate flux. Furthermore, swelling of the grafted nano-brushes at pH values above their pKa led to a decrease in filtrate flux. Rejection of glucose has also been investigated. For the base membrane, glucose rejection was not affected by feed pH over the range 3-7. However, for modified membranes a significant change in rejection was observed as a function of pH. Thus, pH-responsive nano-filtration membranes may be designed by surface modification [66]. Triethylene glycol dimethylether(triglyme), a polyethylene glycol (PEG)-like hydrophilic polymer, was deposited by plasma polymerization to reduce reverse osmosis (RO) membrane's organic fouling tendency. A series of plasma deposition experiments were commenced. The successful coating of the polymer was confirmed by X-ray photoelectron spectroscopy (XPS) analysis. Water contact angle measurements and permeation experiments using a protein solution were conducted to evaluate the change of hydrophilicity and anti-fouling properties. Salt rejection tests were performed to evaluate membrane performance. A reduction in contact angles from 32 ° to 7 ° was achieved for the treated membranes, indicating enhanced hydrophilicity. The permeation experiments revealed that the modified membranes attained an excellent maintenance of flux compared to the untreated membranes. Specifically, after 210 min of filtration, no flux decline was found for the modified membranes, while a 27% reduction of the initial flux was observed for the untreated membrane. Flux recovery after cleaning by water only was up to 99.5 % for the modified membranes, while for the untreated it was only 91 %. The surface hydrophilic modification of RO membranes by plasma polymerization has shown a clear improvement in membrane anti-fouling performance [67]. The production and modification of poly(vinylidene fluoride) (PVDF) membranes for liquid-liquid or liquid-solid separation have been explored. The crystalline properties, thermal stability, and chemical resistance were considered. The production method of PVDF membrane *via* phase inversion includes immersion, precipitation and thermally induced phase separation [68]. The electrospun nano-fibrous membrane (ENM) has also been classified as a microfiltration (MF) membrane, which upon further modification can be used for nano-filtration (NF) applications. The objective of this study was to investigate the suitability of ENM for water treatment applications. Different fiber sizes were obtained by varying the concentration of polyacrylonitrile solution (4 to 10 wt %) to explore the interplay between electrospun fiber size and rejected salt ions. The results indicated that as the fiber size decreased, the pore-size also decreased and the separation of salts increased. When the cross-sectional thickness of the electrospun layer was decreased together with smaller pore-size, it resulted in increased flux with high salt rejection [69]. Nano-porous membranes containing mono-disperse pores of 24 nm diameter were fabricated using poly(styrene-*b*-lactide) block copolymers to template the pore structure. A 4 µm thin film of the block copolymer was cast on microporous membrane that provided mechanical reinforcement. Exposing the composite membrane to dilute aqueous base selectively etched the polylactide block, producing the porous structure [70]. Four types of laccase-carrying electrospun fibrous membranes (LCEFMs), with high laccase-catalytic activity and sorption capacity, were fabricated by emulsion electrospinning. These LCEFMs were composed of beads-in-string structural fibers, with nano-scale pores distributed on the surface and active laccase encapsulated inside [71]. The chemically modified polyaniline (PANI) powder formed in hydrochloric acid medium was synthesized. The polymer was thermally treated in air at 180 °C that led to change in PANI structure due to crosslinking through tertiary amine groups. Different type of changes in the structure that appeared between the conventional PANI and crosslinked PANI were characterized by using spectroscopic techniques, SEM, and nitrogen adsorption–desorption isotherms. The developed material was agglomerated nanoparticles structure of size approximately 30-100 nm and pores that may render the appearance of spongy structure. The specific surface area was calculated to be 349 (m^2/g). It was utilized as adsorbent for cationic dye such as methylene blue (MB) as a model from aqueous solution [72]. The study focused on *in vitro* testing of effectiveness of nano-scale silver based filtration units for removal of bacterial pathogen contaminated water has been carried out. Clinical isolates of diarrhoegenic *E.coli* in measured volume of water was tested for most probable number (MPN) of *E.coli* by multiple tube test. The water samples were filtered through the ceramic silver nano-filter, plain polysulfone membrane and polysulfone membrane coated with silver nanoparticles with a pore size small enough to retain the pathogenic *E.coli*. Research on metal nanoparticles having significant antimicrobial effect would be utilized for making cost effective water filter systems which could protect us from the water borne diseases [73]. A commercially available lower critical solution temperature (LCST) polymer was demonstrated to preferentially adsorb water containing a reduced ion concentration, from chromium chloride salt solutions and release some of the scavenged water at higher temperature. The scavenging ability of the polymer was demonstrated to be dependent on the bulk salt concentration [74]. Nano-materials have been well suited for water purification, disinfection and wastewater treatment applications as they have as large specific surface area, high reactivity, high degree of functionalization, size dependent properties, and affinity for specific target contaminants. Membranes and filters synthesized using nano-materials have selective permeability, good flux rates, increased durability, reliability in purification and reusability. Various types of nano-materials such as carbon nanotube (CNT), nano-sorbents, dendrimers, self-assembled monolayers on mesoporous silica (SAMMS), and single enzyme nanoparticles (SENs) have been used [75]. The carbon materials have shown fine gas absorption ability towards ethylene gas at room temperature at higher temperature [76]. Amphiphilic diblock copolymers, poly(ethylene glycol)-*block*-poly(acrylate), bearing truxillic acid derivatives at junction point between two blocks, have been described. The truxillic acid junction can be selectively cut by UV light, leading to a disassembly of the nano-objects made by self-assembly of the amphiphilic copolymers in water [77, 78]. The extant application, alignment techniques and outlook toward the future have also been discussed [79, 80].

3. Challenges Regarding Block Copolymer Membrane

Even with the promise shown by block polymer templated membranes, they are not without their challenges. First, their mechanical toughness is low as many membranes have inherently brittle polystyrene (PS) matrix. Although microporous membranes are often used for mechanical support, any cracks in the selective layer could significantly impact membrane selectivity. Another major challenge is forming block polymer layers thin enough so that the theoretical permeability can be realized. Many composite membranes reported are able to attain permeability on the order of phase inversion membranes or higher, but forming these membranes requires involved processes that maybe difficult to scale up for membrane production. A final challenge is forming aligned cylindrical domains that span the entire membrane. Many methods have been developed for aligning block polymer structures including shear, e-fields, temperature gradients, solvent evaporation, and neutral surface layers, but the effectiveness of these methods is variable as structures produced often have defects [81]. Additionally, many of these alignment methods add processing steps, which are either cumbersome or unfeasible for forming thin selective layers at larger scales. Many of these challenges are shared with other applications utilizing nano-porous materials from block polymers, and several methodologies have been employed to address these issues. Increase in mechanical integrity has been achieved by crosslinking the polymer matrix [82]. Efforts aimed at overcoming the challenges associated with domain alignment have focused on developing bicontinuous morphologies. While a bicontinuous structure would have more tortuous path through the membrane, avoiding often awkward alignment procedures might prove pivotal in further development of block polymer templated membranes. Mao et al., for instance, accessed the bicontinuous gyroid morphology for poly(styrene)-*b*-poly(ethylene oxide) (PS-PEO) BCPs [83]. The limited region of stability for gyroid structures made accessing the bicontinuous morphology difficult. Another example of achieving a bicontinuous structure employed a bicontinuous microemulsion. Zhou et al. formed a bicontinuous microemulsion from a ternary blend of PI and PS homopolymers and a PI-*b*-PS diblock copolymer. Subsequently, PI domains were crosslinked using sulfur monochloride, and the PS homopolymer was dissolved in hexane rendering the material nano-porous. Additionally, the bicontinuous membranes developed by Uehara et al. not only avoided the need to align the structure, but tensile tests of the semicrystalline polyether (PE) matrix exhibited marked improvements in mechanical toughness over brittle PS. Another improved nano-porous material has been templated by a metathesis reactive block polymer [84]. This material incorporated crosslinked dicyclopentadiene (DCPD) into the matrix to improve both mechanical and thermal stability, and fashioned a bicontinuous morphology, which prevented the need to align the sample. The material was templated by poly (norbornenylethylstyrene-*s*-styrene)-*b*-poly(lactide) (PNS-PLA) where the PNS block was metathesis reactive. The PNS-PLA block polymer was included during the metathesis polymerization of DCPD in tetrahydrofuran (THF) using the second generation Grubbs catalyst. The authors hypothesized that the metathesis crosslinking of DCPD and PNS induced PLA to phase separate from the forming matrix due to reaction induced phase separation. Phase separation was limited to the nano-scale by incorporation of PNS into the matrix, and removal of PLA using base mediated hydrolysis left a bicontinuous nano-porous structure.

4. Future Potential of Organic Nano-Structured Membrane

A family of crosslinked poly(ethylene glycol) diacrylate (XLPEGDA) materials was synthesized *via* free-radical photopolymerization of poly(ethylene glycol) diacrylate (PEGDA) solutions in water. These materials were potential fouling-resistant coatings for ultrafiltration (UF) membranes. Both variables can be used to tune water permeability properties of the resulting films. Their water permeability significantly increased as pre-polymerization water content and PEGDA chain length increased as pre-polymerization water content and PEGDA chain length increased. The separation performance of various XLPEGDA materials, compared using a selectivity–permeability plot, indicated a tradeoff between water permeability and solute rejection for materials prepared with the same PEGDA chain length. XLPEGDA samples prepared with longer chain PEGDA have both higher water permeability and better solute rejection at the same time relative to XLPEGDA primed with short-chain PEGDA. Contact angle measurements indicated that the surfaces of XLPEGDA materials formed at higher pre-polymerization water content and longer PEGDA chain length were more hydrophilic, and these surfaces generally exhibited less BSA adhesion [85]. High performance thin film composite (TFC) membranes for reverse osmosis applications were fabricated by coating solutions of highly chlorine-tolerant disulfonated directly copolymerized poly(arylene ether sulfone) random copolymers on a commercially available porous polysulfone support. Finally, water-miscible glycerin was eliminated *via* water treatment. The newly developed coating method formed ultra-thin and defect-free layers on a micro-porous Udel® support membrane. Furthermore, decreasing the amount of coating solution resulted in improved pure water flux. The TFC water flux was further improved and was accompanied by small reduction in salt rejection after various TFC membrane treatments (e.g., *in situ* acidification) [86]. Report has been found in literature describing the development of advanced membranes for water treatment through modification of low molecular weight cut-off regenerated cellulose ultrafiltration membranes with uniquely structured block copolymer nano-layers. Poly(N-isopropylacrylamide)-block-poly((polyethyleneglycol) methacrylate) nano-layers were grafted from the membrane using surface-initiated atom transfer radical polymerization. Membrane performance was evaluated by measuring water flux using deionized water [87]. Planar biomimetic membranes consisting of Aquaporin Z (AqpZ) were fabricated on cellulose acetate membrane substrate functionalized with methacrylate end groups. By vesicle rupture of triblock copolymer (ABA) vesicles and UV polymerization, a selective layer upon the substrate for nano-filtration was formed. It was found that the NF membranes can give an impressive water permeability of 34 LMH bar^{-1} and sodium chloride (NaCl) rejection of more than 30 %. The study opened up new possibilities of using AqpZ embedded biomimetic membranes for water purification with advantages that include high throughput with lesser energy consumption [88]. The effective removal of ionic pollutants from contaminated water using negatively charged nano-filtration membranes was demonstrated. Block copolymers comprising polystyrene (PS) and partially hydrogenated polyisoprene (hPI) were synthesized by varying chain architectures. The control of chain architecture allowed creating a synergetic effect on optimizing charge densities of the membrane, water permeability, and mechanical integrity under water purification conditions [89]. A facile *in situ* approach for constructing tunable amphiphilic or hydrophilic antifouling membrane surfaces was demonstrated by exquisitely manipulating the microphase separation and surface segregation behavior of the tailor-made ternary amphiphilic block copolymers during the commonly utilized wet phase inversion membrane-formation process. The water permeation flux was slightly decreased during operation (total flux declined was 6.8 %) and almost completely recovered to the initial value (flux recovery ratio was more than 99 %) after simple hydraulic washing [90]. In a related attempt, blends of polystyrene and high-impact polystyrene (HIPS) with poly(styrene-ethylene-butylene) (SEBS) triblock copolymer were fabricated. After sulfonation, blends were used to produce ion-exchange membranes. The morphology and structure of the blends were investigated by SEM and spectroscopic analysis. Furthermore, thermal transitions and stability of all the blends were characterized using calorimetric techniques and compared with those of the individual polymers. Analyses of the physical properties (i.e. ionic conductivity, ion-exchange capacity, water uptake, dimensional stability, mechanical properties, etc.) showed that the performance of the PS-containing membranes was, in general, higher than that of HIPS. Additionally, the highest sulfonation degree was found for PS/SEBS membranes. The membranes efficiency was tested by investigating the extraction of Na^+ by electrodyalisis. Comparison of the percentage of extracted ions indicated that the incorporation of SEBS results in a significant improvement with respect to membranes made of individual polymers [91]. Block and random PEGylated copolymers of poly(ethylene glycol)methacrylate (PEGMA) and polystyrene were synthesized with a controlled polydispersity using an atom transfer radical polymerization method and varying molar mass ratios of PS/PEGMA. Two types of PEGylated copolymers were self-assembly coated onto the surface of poly(vinylidene fluoride) (PVDF) ultrafiltration membranes for enhancing biofouling resistance [92]. It was found that the adsorption capacity of random copolymers on PVDF membranes was higher than those of block copolymers. However, the specific and overall protein resistance of bovine serum albumin (BSA) on PVDF membranes coated with block copolymers was much higher than that with random copolymers. The PVDF membrane coated with the copolymer owned excellent biofouling resistance to BSA, humic acid, negatively surface charged bacteria *E. coli*, and positively surface charged bacteria S. maltophilia [93]. The feasibility of adopting biomimetic membranes for water purification driven by a mechanical pressure, i.e., filtration has been explored. The use of a commercial nano-filtration membrane as a support for biomimetic lipid bilayer membranes to render them robust enough to withstand the required pressures was purposed. By properly tuning molecular interactions supported phospholipid bilayers (SPB) can be prepared on a commercial NF membrane. The presence of SPB on the surface was verified and quantified by several spectroscopic and microscopic techniques. It was shown that the hydraulic permeability of the SPB supported on the NF membrane (NTR-7450) approached the values deduced from typical osmotic permeability of intact continuous bilayers. The oxidized multi-walled carbon nanotube was loaded into poly(vinyl alcohol) (PVA) barrier layer for ultrafiltration (UF). The same approach was extended by substituting oxidized carbon nanotube with ultrafine cellulose nano-fibers (diameter about 5 nm). The resulting thin-film nano-fibrous composite (TFNC) membranes exhibited permeation flux significantly higher than those of conventional thin-film composite membranes for nano-filtration while maintaining the same rejection capability [94]. The synthesis and characterization of well-defined polyacid-based block copolymers containing polyisoprene was reported. The challenge of maintaining the integrity of the polydiene while producing polyacid from the tert-butyl ester precursor was addressed in this communication. A general purification method was also developed, taking the advantage of different polarities of each block. The polystyrene-*b*-polyisoprene-*b*-poly-(acrylic acid) (PS-b-PI-b-PAA) triblock terpolymers formed multicompartmental micelles *via* aqueous self-assembly [95]. Water permeability and salts rejection of NF membrane was measured under low transmembrane pressures. The resulting NF membranes showed significantly enhanced water permeability while maintaining high rejection of salts. The salts rejection increase was accompanied with the flux decrease when TMC dosage was increased. The flux and rejection of NF 1 for Na_2SO_4 (1 g/L) reached to 79.1 l/m^2 h and 85.4% under 0.3 MPa. The results encouraged the further exploration of NF membrane preparation using hyperbranched polymers (HBPs) as the selective ultra-thin layer [96]. The modification of commercial nano-filtration membranes with shape-persistent dendritic molecules has been reported. As the water flux is inversely proportional to the thickness of the active layer, the amount of dendrimers deposited for specific contaminants were optimized to improve the solute rejection while maintaining high water flux [97]. In another investigation, polyaniline nanoparticles were used to improve the separation figures of merit of polysulfone membrane. Polyaniline nanoparticles were dispersed into polysulfone matrix for the development of nano-composites through solution blending. A wet phase inversion method was used to fabricate a flat sheet polysulfone and nano-composite membranes. The uniform dispersion of polyaniline nanoparticles (<20 nm) into polysulfone matrix was ascertained by transmission electron microscope (TEM). Compared with polysulfone membrane, nanocomposite membranes had more hydrophilicity and smooth surface, and honeycomb cross section structure. Therefore, the nanoparticles inclusion in the polysulfone membrane showed significant effect on hydrophilic property as well as membrane morphology, which resulted in improvement of permeability characteristics of polysulfone membrane [98]. The water-facilitated ion transport in polymeric membranes has provided some directions for future endeavors in the field, such as anion exchange membranes [99, 100]. Formation of self-supporting, double stimuli-responsive ultrafiltration membranes *via* non-solvent induced phase separation (NIPS) process was reported. The polymers, polystyrene-*block*-poly (*N*,*N*-dimethylaminoethyl methacrylate) (PS-*b*-PDMAEMA), were synthesized using living anionic polymerization using *sec*-butyllithium as initiator [101]. The hierarchical co-assembly strategy demonstrated the feasibility of synchronizing multiple self-assembly processes to achieve hierarchically structured soft materials with molecular level control [102]. With nano-scale pores, high porosity, narrow pore size distributions, and tunable chemical and mechanical properties, block copolymers hold tremendous potential as efficient separation membranes. Nano-porous membranes derived from block copolymers have been pursued as desirable materials for controlled separations due to pore size tunability, narrow pore size distributions, and ability for selective functionalization [103, 104].

5. Inorganic Nano-Structured Membrane

The increasing interest in the use of inorganic membranes in separation processes for several industrial and laboratory applications is due to many properties which make them superior over their organic counterparts. These membranes allow better separation characteristics and a higher flux because of relatively narrow pore size distribution and higher porosity. These also have higher mechanical stability which includes resistance to compaction under high pressure which is a prerequisite for separations requiring high pressures. Their better chemical and the thermal stability and the resistance to the bacterial actions allow them to be used for a longer time hence they are cost effective. But apart from the above mentioned properties one of the drawbacks of these inorganic membranes is that they are brittle, hence, more sophisticated membrane casting methods are required which make them cost inefficient. Inorganic membranes can be prepared from metals and ceramic materials. Finely porous metallic membranes have been often made of stainless steel and palladium and are mainly used in gas separations, but they can also be used for water treatments at high temperatures or as a membrane support materials. Ceramic membranes are mostly made from the following materials e.g. TiO_2, ZrO_2, Al_2O_3 and SiO_2. The chemical and mechanical stability depends on the membrane structure, with finer structures being less stable. Current state of research in the field of inorganic membranes has been focused on the commonly used materials for membranes like TiO_2, ZrO_2, Al_2O_3 and SiO_2. A short overview about these membranes casting, physical and chemical properties and morphological variations used for the micro or nano-filtration process for the treatment of waste water have been presented here [105, 106]. Sodium zeolite microfiltration membranes were prepared on Al_2O_3 tube by *in situ* hydrothermal synthesis method and investigated for water separation and recovery from oily water. Sodium/Al_2O_3 membranes with average inter-particle pore sizes of 1.2 μm, 0.4 μm and 0.2 μm were prepared. The membranes were characterized by SEM and the inter-particle pore size distribution was determined by gas bubble pressure method. Membranes with pore sizes of 1.2 μm and 0.4 μm were used to treat an oil-in-water emulsion containing 100 mg/L oil. 99 % oil rejection was obtained and water containing less than 1 mg/L oil was produced at 85 Lm^{-2} h^{-1} by NaA1 at a membrane pressure of 50 kPa. Consistent membrane performance was maintained by a regeneration regime consisting of frequent backwash with hot water and alkali solution [107]. Two 50 kDa polyacrilonitrile ultrafiltration membranes, one cationic (CM) and the other anionic (AM), have been tested in order to study the removal of humic acid or natural organic matter and to examine their applicability for water purification. Experiments were carried out using synthetic water formulated from humic acids, and two natural source waters having different physical and chemical characteristics. The effect of the pressure (ranging between 100 kPa and 400 kPa), ionic strength (p*I*) (1.4×10^{-3} mol L^{-1}, 2.5×10^{-2} mol L^{-1}, and 4.1×10^{-2} mol L^{-1}; expressed as KCl) and pH (2.7, 5.8, 6.8, 7.8 and 8.8), on synthetic water ultrafiltration, were investigated. The membranes tested produced high permeate flows, higher in the case of AM. Pressures increased did not greatly enhance permeate flow. In general, a slight decrease in flux resulted for an increase in p*I* (8% and 6% in the case of CM and AM, respectively if the p*I* increased from 1.4×10^{-3} Mto 4.1×10^{-2} M). At pH 2.7, the flux reductions were in excess of 42 % for both membranes, whereas at pH 8.8, the flux reduction was a minimum; 11% with CM and 4% with AM. AM membrane underwent a greater permeate flux reduction than CM in natural water ultrafiltration experiments, in contrast to assays with humic acid. This was probably due to the high hydrophilicity of the anionic membrane, and the different nature (hydrophilic character in these waters) and molecular weight distributions of the organic matter [108, 109]. Nano-filtration by highly concentrated (11–17% w/v) mixture of organic/inorganic salts, generated from pharmaceutical industries to separate mineral salts (sodium acetate and sodium chloride) from heteroaromatic quaternary ammonium chloride salts soluble in water. The process, using a spiral-wound nano-filtration module, consisted of a diafiltration step until the mineral salts were almost completely eliminated followed by a concentration step. To optimize the process transmembrane pressure, velocity and pH were studied. The retention of organic salts was higher than 99.5%. The flux and rejection showed that it was not necessary to increase transmembrane pressure to obtain the faster salt elimination. The best result was obtained with the highest velocity which reduced membrane fouling. Changing pH from 3 to 4.5 had little effect on permeate flow; however, the purification of a solution at pH 5.4 was difficult because of a very low permeate flow. Less than 2% of the ammonium salts entrapped in the membrane were lost. Under optimal experimental conditions, more than 99 % of mineral salts can be eliminated [110]. Ultrafiltration membranes used for drinking water treatment needed to have high rejection for microbial species. The effect of various inorganic halides added to a casting solution of poly(acrylonitrile) in *N*,*N*-dimethyl formamide was examined by measuring changes in the intrinsic viscosity, concentrated solution viscosity and the ternary phase boundary [111]. In another study, nano-filtration membrane and reverse osmosis membrane were tested to investigate the optimal operating conditions, color, salt rejection and permeate flux and evaluate the feasibility of nano-filtration and reverse osmosis membrane combined process to improve the permeate flux and separation efficiencies in reactive dye manufacturing. Effects of pressure, types of membrane and dye solution on flux and rejections were investigated. Experiments showed that the type of membrane had significant effect on both permeate flux and rejection efficiencies [112]. The membrane purification of the water contaminated by Co(II)-ions have also been studied. Both the ceramic and polymeric membrane modified by different additives has been used. In case when the polymeric membrane made use of, as the high degree of water purification as 92.8% was reached. An addition of the clay minerals into the system subjected to separation resulted in an essential increase of the water purification degree (up to 98.2%) [113]. The retention of inorganic salts was primarily affected by membranes fixed charge and sieving effect.

6. Conclusion

Nanotechnology is revolutionary scientific and engineering venture that invariably impacts the existing infrastructure of consumer products, manufacturing methods and materials usage. Understanding and manipulating the transport of various type of chemical species at nano-scale have enabled the design of new systems and devices proficient of dealing chemical separations for example water purification/treatment, bio-separation, and molecular sensing. Progression towards the fabrication and characterization of high-performance nano-porous materials is an indispensable step for the accomplishment of skills exploiting transport phenomena at the nano-scale. Recently, membrane technology has been comprehended as a functional gadget in various relevance including sustainable water treatment, energy conversion, energy storage, health zone, food trade, etc. Widespread use of this technique, though, has been obstructed by cost, performance and durability issues. The foremost intention of this chapter has been to explore potential of block copolymer templated nano-porous polymers in water filtration membrane applications. Advances in the design and fabrication of nano-porous materials were predictable to inaugurate new opportunities for the development of membrane techniques. Two different emerging water treatment technologies i.e. *organic and inorganic nano-porous filtration membranes* clasped immense pledge to afford superior protection of communal health and environment. Essential kinds of membrane filtration processes included reverse osmosis, ultra-filtration, micro-filtration and nano-filtration. A large amount of fundamental research from literature has been undertaken to study block polymers in the aspects of production, characterization, modification and property enhancement. Block copolymers have proven particularly advantageous for templating porous membranes. With nano-scale pores, high porosity, narrow pore size distributions, and tunable chemical and mechanical properties, the block copolymer derived nano-porous polymers hold tremendous potential as robust, efficient, and highly selective separation membranes. We have been, thus, motivated to systematically investigate membrane property and performance of these materials for water filtration applications. The basic concepts and definitions have been described to understand membrane transport in relation to the membrane structure and chemistry, consequently membrane performance in relation to the water purification.

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