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Current Patents of Dendrimers and Hyperbranched Polymers in Membranes

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Abstract: Dendrimers or other hyperbranched polymers are a new class of artificial polymers with unique properties, such as high degree of branching units, high density of surface functional groups, nano-scaled size, well-defined molecular weight and low-dispersity. These features make them attractive materials in the field of membrane science. This review is a short survey of patents on dendrimers and other hyperbranched polymers in membrane fields such as proton exchange membranes, bipolar membranes, gas separation membranes, and solid-liquid separation membranes, etc.

Keywords: Dendritic polymer, dendrimer, hyperbranched polymer, membrane.

1. INTRODUCTION

Dendritic polymers have been recognized as the fourth class of the macromolecules. They have several attractive properties, such as high degree of branching units, high density of surface functional groups, nano-scaled size and low-dispersity. Generally, dendritic polymers consist of three main structural components: a multi-functional core, repeated branching units and surface functional groups. When the generation of dendritic polymers is defined as the layer number of the repeated branching units [1] Fig. (**1a**), they are further classified into three subclasses: random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers Fig. (**1b**). Among these subclasses, dendrimers and hyperbranched polymers have been widely investigated.

Dendrimers are perfect artificial macromolecules, which are synthesized by a step-wise method. Two strategies, namely the divergent strategy and the convergent strategy, were proposed to prepare dendrimers. The divergent method starts from a central core and extends toward the surface, while the convergent one uses a top-bottom method that starts from the periphery of dendrimers. Tomalia *et al*. first reported the synthesis of polyamidoamine (PAMAM) dendrimers by using the divergent method in the early 1980s [2]. Later in 1990, Hawker *et al*. proposed the convergent method for dendrimer construction [3]. Up to now, most of the dendrimers, including the commercial available polyamidoamine (PAMAM) dendrimers and polypropyleneimine (PPI) dendrimers, are synthesized by the divergent method.

Unlike dendrimers, hyperbranched polymers with non-perfect structure are synthesized via one-step reactions. However, hyperbranched polymers and dendrimers built from AB_x functional monomers have many common features because of their similarity in branching. Compared with dendrimers, hyperbranched polymers possess economical attraction due to the much cheaper one-step synthesis. They are promising products for industrial applications.

Up to now, dendrimers and hyperbranched polymers have been widely applied in many fields including supramolecular chemistry, electrochemistry, photochemistry, nanoparticle synthesis, pollution management, dye decolorization, preparation of monomolecular membranes, curing of epoxy resins, catalysis and drug delivery. Among these applications, the use of dendrimers and hyperbranched polymers in membranes has attracted increasing interest from the increasing number of the papers published or patents issued Fig. (**2**). Therefore, this review will be a short survey of current patents on dendrimer and other hyperbranched polymers in membrane, especially in proton exchange membranes, bipolar membranes, gas separation membranes and solid-liquid separation membranes.

2. PROTON EXCHANGE MEMBRANES

Proton exchange membrane fuel cell (PEMFC) is believed to be the best type of fuel cell as a new clean and high efficient power, which will eventually replace the gasoline and diesel internal combustion engines. The function of the proton exchange membrane (PEM) is use to conduct the protons and separate the catalyst. Thus, PEM needs good proton conductivity and perfect mechanical strength. Dendrimers and hyperbranched polymers have high density of functional groups on the surface, which leads to high proton conductivity. In addition, these promising macro-molecules have spherical structures and thus can function as perfect skeletons of PEM. Up to now, dendrimers and hyperbranched polymers have proved themselves to be important components in PEM.

Lee *et al*. [4] employed PAMAM dendrimers as components of PEM for fuel cells. Compared to the traditional Nafion 117, the membrane containing PAMAM dendrimers has higher proton conductivity but lower fuel permeability even under low humidity condition and/or at high temperatures. The new type of PEMs was prepared as

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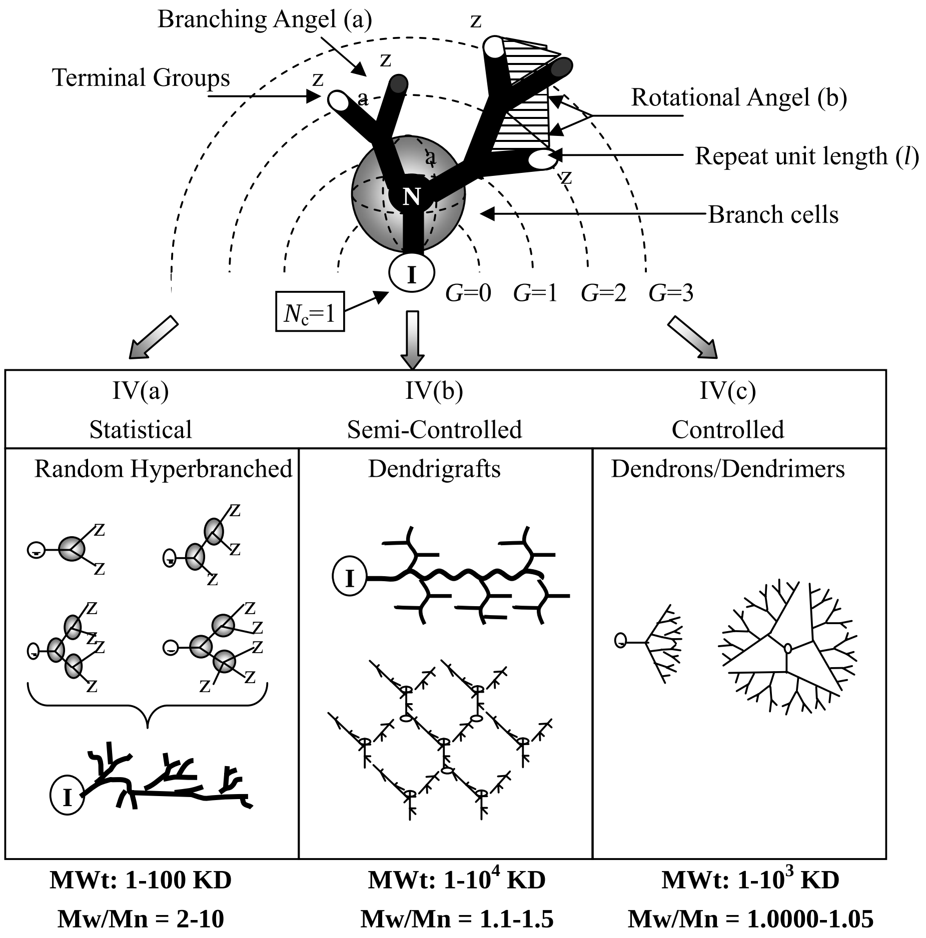


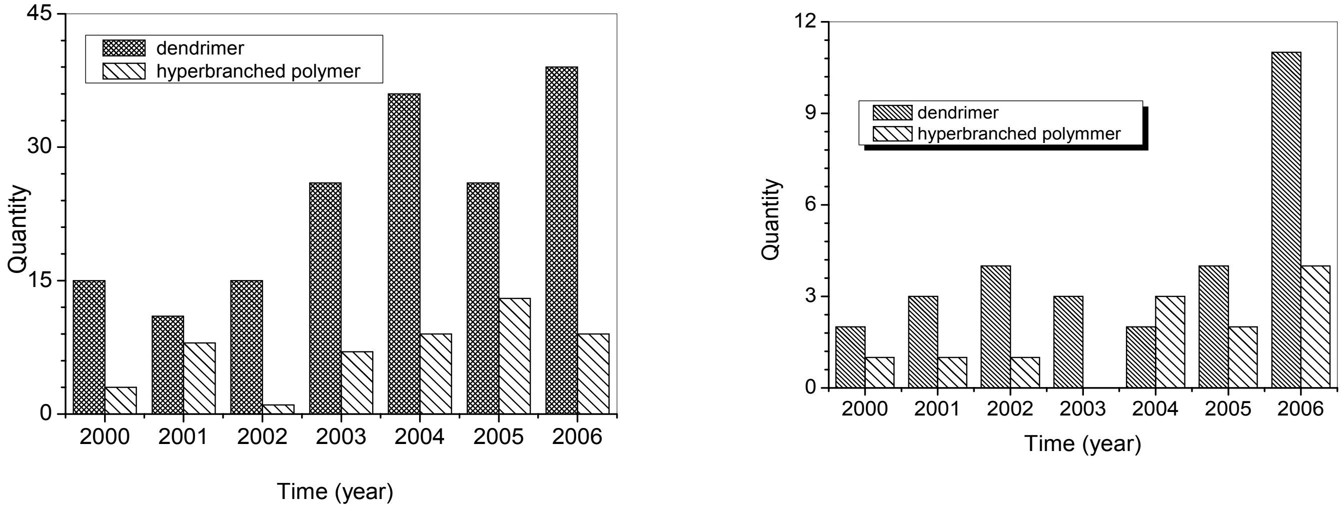
Fig. (1). The scheme and the subclasses of dendritic polymer (adapted from [1] with permission).

follows: (1) preparing the dimethylacetamide (DMA) solution of Nafion 117; (2) adding PAMAM dendrimers, into this solution, which are treated with acid in advance; and (3) mixing the resulting solution by ultrasonic pulse and preparing the proton exchange membranes according to traditional procedures. As shown in Fig. (**3**), the proton conductivity of the dendrimer-contained PEM increased faster than that of Nafion 117 with the increasing relative humidity (Fig. **3a**) while it was slightly influenced by the PAMAM contents in the experiments Fig. (**3b**). Especially, the methanol permeability of the PEM significantly decreased with the increasing of PAMAM contents Fig. (**3b**).

Colombo *et al.* prepared a new proton exchange membrane with Frechet-type dendrimer [5]. This membrane was formed by covalently linking dendrimer, which has the acid functional terminal groups, through amino or some other bridging groups. The formed membrane offered several advantages over the available commercial membranes. The present membrane can control the size of the pores and so limit the water content in the pores. In addition, comparing to the linear polymer, dendrimer can increase the ionic conductivity.

Yuki *et al*. used PAMAM dendrimer to encapsulate or adsorb metal precursors, such as $[PtCl_4]^{2-}$ [6]. The resulting complex served as the catalyst in the PEMFC. It showed high and durable catalytic activity when it was used in the electrode of a fuel cell. However, there is a limitation in the contact between the membrane electrolyte and the catalyst, which restricts the effect of the membrane electrolyte. This limitation can be improved by increasing the volume of conducting medium or by complete dispersion throughout the catalyst layer. Since PAMAM has high-density functional groups and is nano-sized, it can reduce proton transport loss in the catalytic layer by increasing the volume of conducting medium.

A new type of membrane electrolyte was prepared with Nafion 115 membrane, PAMAM dendrimers and Pt-C. As shown in Fig. (**4**), PAMAM dendrimer/Pt-C in the membrane electrolyte was employed as the catalyst [7]. Fig. (**5**) demonstrated the performance of the newly prepared membrane electrolyte. Under low current density conditions, the efficiency of the membrane electrolyte with PAMAM dendrimer was lower than that without dendrimer. At high current densities, the performance of the membrane electrolyte with 10% content of dendrimer was better than that without dendrimer. However, this performance rapidly decreased with the content of PAMAM dendrimer above 10%. The reason may be the loss of electrochemical active



(**a**) Chronology of the journal articles published on dedrimers or hyperbranched polymers.

(**b**) Chronology of the patents issued on dedrimers or hyperbranched polymers.

Fig. (2). Chronology of the journal articles published patents issued on dedrimers or hyperbranched polymers.

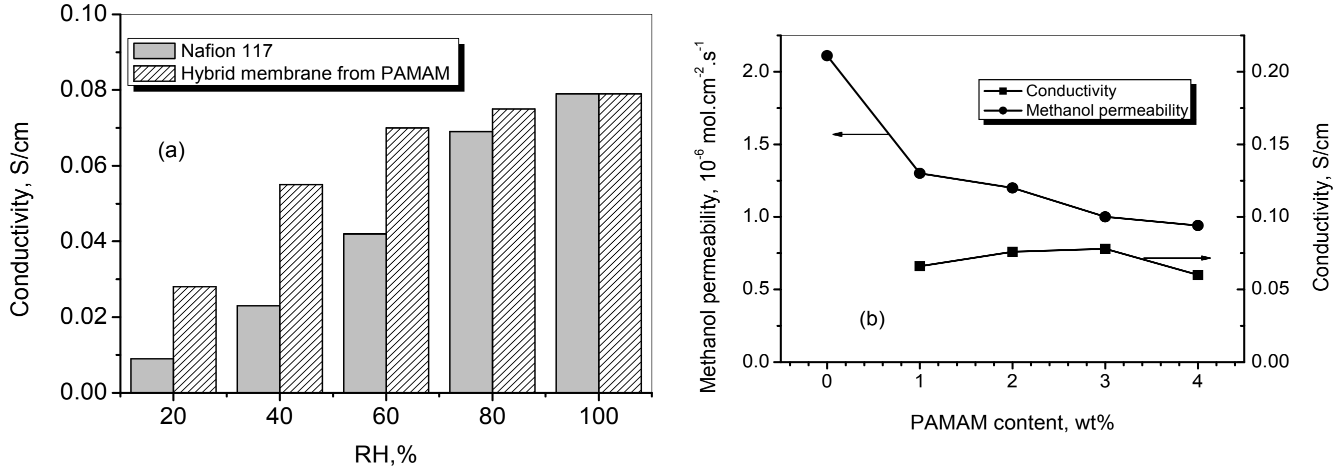


Fig. (3). a) The proton conductivity of different relative humidity, PAMAM content=0.1%; **b**). The proton conductivity and methanol permeability of different PAMAM contents at RH=60% (Data extracted from [4]).

area with the excess amount of PAMAM dendrimer, which inhibits the hydrogen adsorption reaction on to the Pt-C.

In addition to PAMAM, cyclic tertiary amine hyperbranched polymer with a structure shown in Fig. (**6**) was used as a performance additive in the fuel cell [8]. The presence of hyperbranched polymer increased the electrochemical reaction rate of the fuel cell through measuring the current density of the fuel cell. Besides, Colicchio *et al* developed new types of membrane electrolytes based on hyperbranched sulphonated polyetheretherketone (SPEEK) and poly-ethoxythsiloxane (PEOS) [9]. All kinds of the hybrid mem-branes showed ohmic-type proton conductivity. The proton conductivities of these membranes were even comparable to the Nafion 115 in humid state. In a separate study, Gode *et al.* synthesized a novel sulfated hyperbranched polymer for the PEM [10], such as sulphonated poly(3-ethyl-3-(hydroxy-methyl) oxetane) (SPTMPO). The hyperbranched polymer containing PEM showed higher proton conductivity com-pared to the Nafion 117 in humid state. The hyperbranched SPTMPO-modified membrane was more flexible and exhibited better mechanical properties than the chemical cross-linked membranes, such as the Nafion series.

By adding phosphoric acid, Zou *et al.* prepared a series of organic-inorganic hybrid membranes from hyperbranched aliphatic polyester (Boltorn^R H20) for fuel cells. The effect of temperature and incubation time on the proton conductivity of the hybrid membrane was shown in Fig. (**7**) and Fig. (**8**), respectively [11]. Obviously, higher proton conductivity of the PEM could be achieved by raising the conducting temperature, which is due to the vehicle mechanism. After being kept at 30°C or 130°C for 400 minutes, the hybrid membrane still showed a high proton conductivity of about 5×10^{-4} S·cm^{-1}, indicating that the

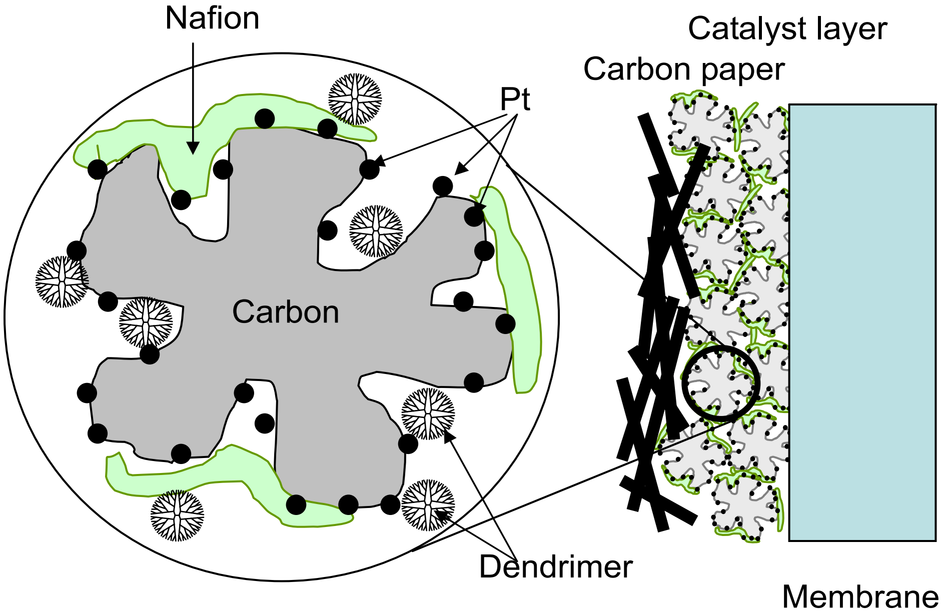


Fig. (4). The schematic drawing showing that polyamidoamine dendrimers were applied into the catalyst layer (kindly provided by the original author [7]).

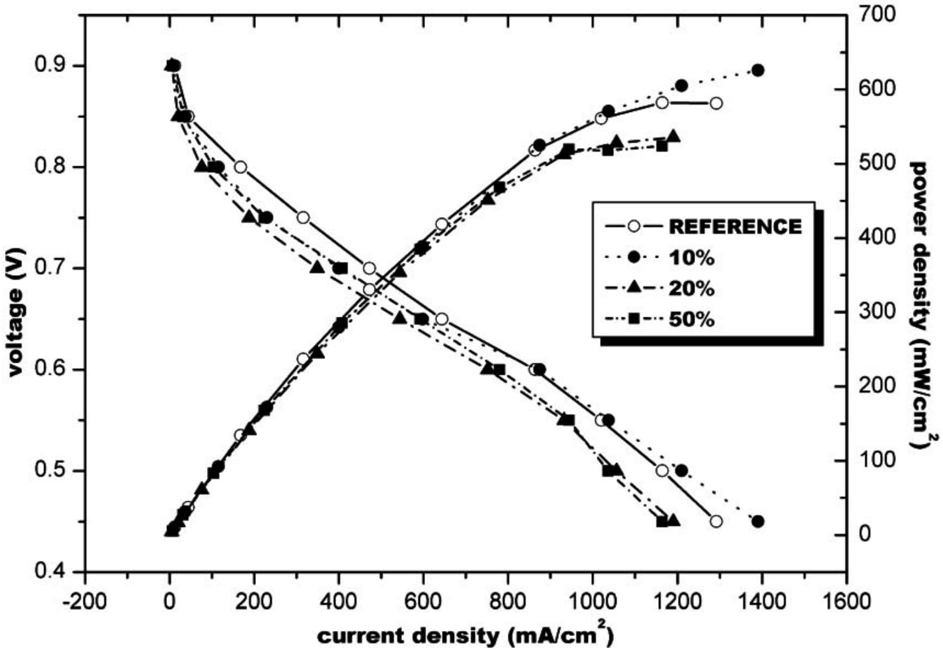


Fig. (5). Effect of PAMAM loading in the catalytic layers on cell performance (kindly provided by the original author [7]).

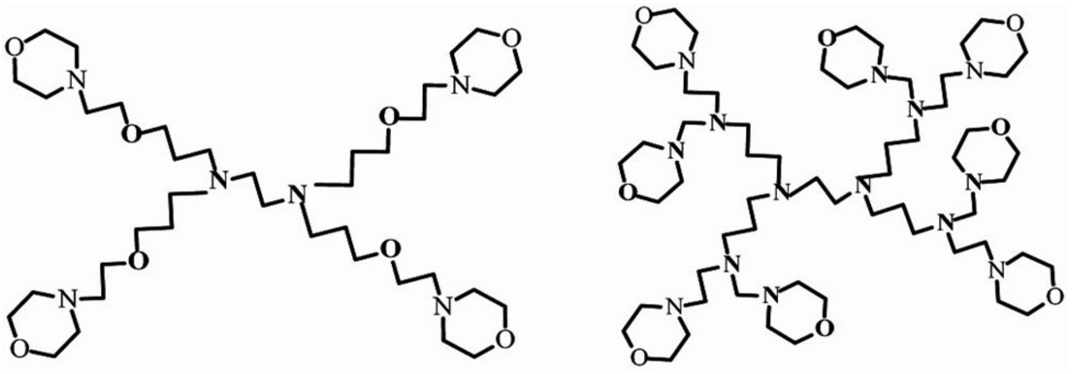


Fig. (6). The chemical structure of cyclic tertiary amine dendritic polymers.

hybrid membrane had a good water conservation property at high temperatures Fig. (**8**).

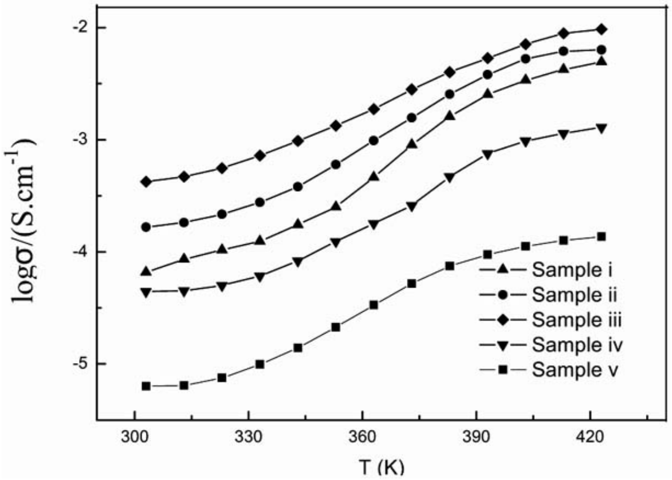


Fig. (7). Temperature dependence of the proton conductivity of hybrid membranes from hyperbranched aliphatic polyester (Boltorn^R H20) for fuel cells (kindly provided by the original author [11]). The molar ratios of the membranes compositions are : H_3PO_4 3; GPTMS 1.5; TEOS varying from 0.5,0.4,0.3 to 0.2 for samples i-v and H20-$Si_{0.5}$ varying from 0, 0.1,0.2,0.3 to 0.4 for samples i-v, respectively [11].

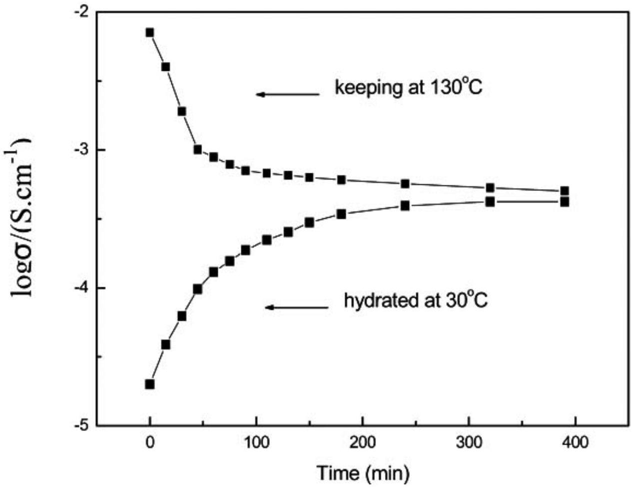


Fig. (8). Variations in the proton conductivity of sample iii with the time for the hybrid membranes from hyperbranched aliphatic polyester (Boltorn^R H20) kept at 30 and 130°C under 30% relative humidity (kindly provided by the original author [11]).

Recently, Itoh *et al.* synthesized two novel hyperbranched polymers with sulfonic acid or acryloyl groups at the end of chains [12]. Their structures were shown in Fig. (**9**). It was reported that the ionic conductivity of these two novel hyperbranched polymers increased with the increasing temperature Fig. (**10**) and the thermal stability of these materials was perfect up to 200°C. These hyperbranched polymers can be further modified with phosphonic acid groups on the surface [13]. The newly synthesized polymer was even thermal stable up to 300°C. These hyperbranched polymers will work as useful components of the high temperature PEMFC in the future.

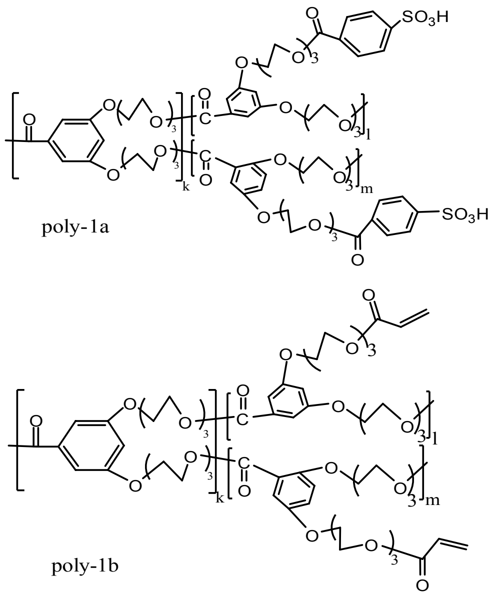


Fig. (9). The chemical structure of poly-1a and poly-1b.

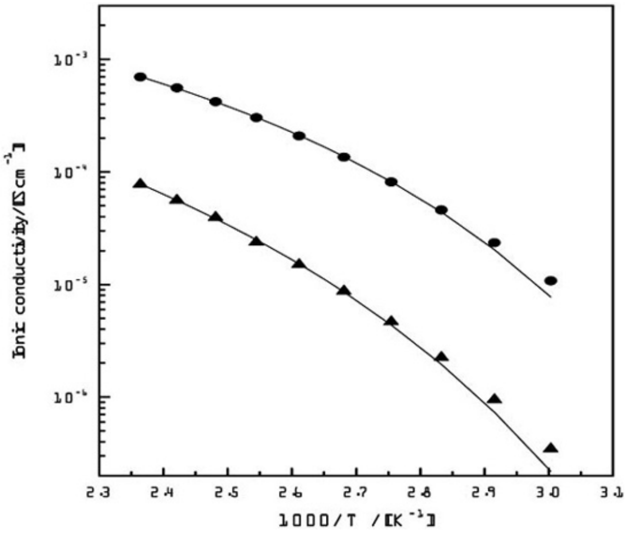


Fig. (10). Temperature dependence of the ionic conductivity for the poly-1a (●) and the poly-1a/poly-1b membrane (▲). The solid lines are the result of fitting the ionic conductivity data on the VTF equation. (kindly provided by the original author [12]).

3. BIPOLAR MEMBRANES

Bipolar membrane is a type of composition membrane, which contains a cation-exchanging layer, an anion-exchanging layer and an interfacial layer [14]. The novel property of a bipolar membrane is that the water molecules can be dissociated efficiently into the hydrogen ions and hydroxyl ions under reverse potential bias. As shown in Fig. (**11**), by establishing a reverse electric field across the membrane (the anode and cathode close to the anion selective layer and cation selective layer, respectively), charged species can be removed from the contact region between the two ion-exchange layers. When all salt ions are removed from the interface (contact region), further transport of electric charge can only be accomplished by protons and hydroxyl ions, which are produced in the contact region by water dissociation. The consumed water is replenished by transportation from the surrounding solutions. This process is called "water dissociation" and the technology is also called electrodialysis with bipolar membrane (EDBM), a simple, energy saving and environmental-friendly technology, which is being applied in many fields.

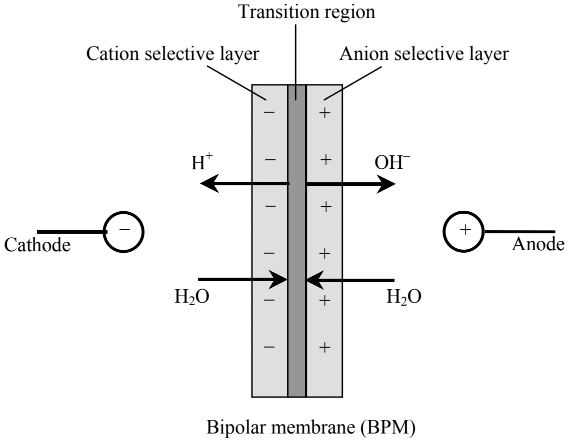


Fig. (11). Water is dissociated into hydrogen ions and hydroxyl ions in a bipolar membrane under reverse bias.

It has been well known that water dissociation reaction occurs in the so-called contact region of the bipolar membrane, which is located between the cation exchange and anion exchange layers and thus the composition of this junction plays the decisive role in the function of a bipolar membrane. To improve the water dissociation ability of a bipolar membrane, PAMAM dendrimers were used as catalysts of the water dissociation process in the intermediate layer of a bipolar membrane by Fu *et al.* [15,16]. They prepared the new bipolar membrane by immersing the heterogeneous anion exchanging membrane into PAMAM dendrimer aqueous solutions and casting the N,N-dimethylformamide (DMF) solution of sulphonated poly(phenylene oxide) (SPPO) onto the dendrimer treated anion exchanging membrane. It was found that there were two reversed effects: the high-density amino groups of PAMAM was positive for water dissociation but its steric hindrance was negative. So its catalytic effect was dependent on both the concentration and generation. As shown in Fig. (**12**), at a given PAMAM generation, taking G2 as an example, voltage, which decreased with PAMAM concentration at low concentration range, is due to an increase in catalytic sites from amino groups; and the voltage, which increase with PAMAM concentration at a high concentration range, is due to an increase in steric effect. There exists a transitional concentration for each generation of PAMAM. Below this transitional concentration, PAMAM has a catalytic function; above it, there is a hindrance effect, and at it, the voltage across a bipolar membrane reaches a minimum and the catalytic effect is highest. This transitional concentration decreased with an increase in the generation of PAMAM as demonstrated in Fig. (**13**), in which voltage dependence on concentration for different generations was plotted at a given current density.

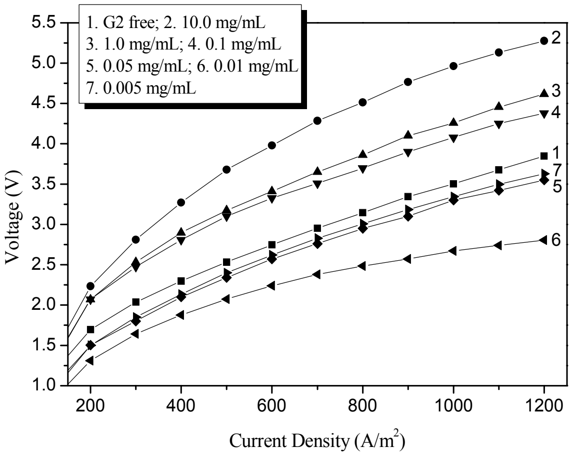


Fig. (12). The I-V curves of bipolar membrane in which the anion exchange membranes have been immersed in different concentration solutions of PAMAM G2. (taken fom [16]).

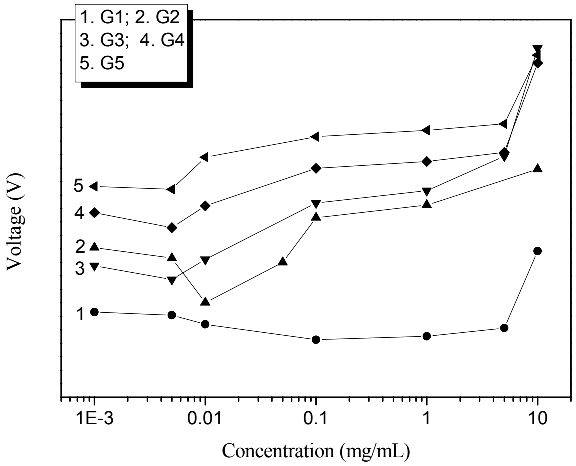


Fig. (13). The relation between the potential drop and the PAMAM concentration at the current density of 120 mA/cm^2. (taken from [16]).

In a separate study, PAMAM dendrimer-heavy metal ion complexes were used in the intermediate layer of a bipolar membrane as catalysts by Xu *et al.* [17,18]. Although heavy metal ions also had the catalytic effect in the intermediate layer, it rapidly leached out of intermediate layer during conducting the experiments and thereby caused a gradual increase of water dissociation voltage. PAMAM dendrimers can prevent the heavy metal ion from escaping by forming coordinated complexes. Thus, the newly prepared bipolar membranes using the complexes as catalysts exhibited lower membrane voltage, longer lifetime, and more stability than bipolar membranes treated with PAMAM dendrimers and heavy metal ion solutions did Fig. (**14**).

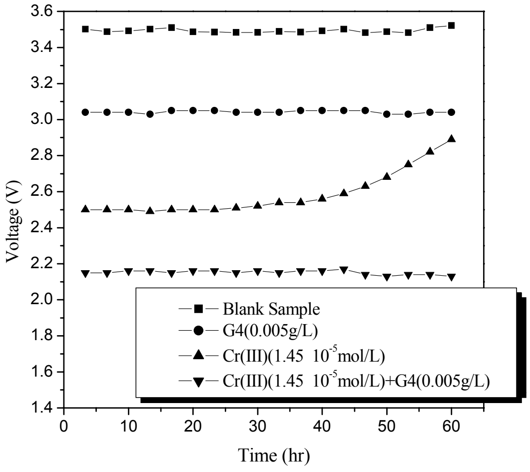


Fig. (14). V-t curves of the bipolar membranes modified by 0.005 g/L G4 solution, 1.45×10^{-5} mol/L Cr(III) solution and the complex solution with 0.005 g/L G4 and 1.45×10^{-5} mol/L Cr(III) at the current density of 100 mA/cm^2. (taken from [18]).

Besides PAMAM dendrimers, hyperbranched aliphatic polyesters (Boltorn® series) were also used in the analogous way by Xue *et al.* [19]. It was found that there existed a transitional concentration: at a fixed generation, the catalytic function first increased and then decreased Fig. (**15**). The transitional concentration of Boltorn® series polymers was relatively higher than that of PAMAM dendrimers. Furthermore, the higher the generation was, the lower the voltage dropped across the bipolar membrane and the higher the transitional concentration was exhibited. The distinction is related to the competition between two counteracting factors: hydrophilicity and the steric effect. Compared with PAMAM dendrimers, Boltorn® series polymers are the most effective and economical catalysts for water dissociation when they are used as the junction of a bipolar membrane.

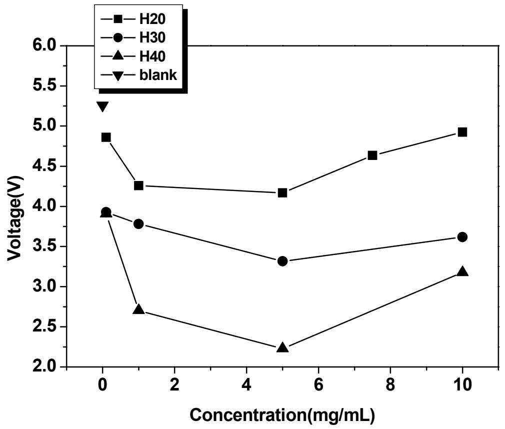


Fig. (15). The relation between the potential drop across bipolar membrane and the hyperbranched polyester concentration at the current density of 120 mA/cm^2. Blank sample (not treated with hyperbranched polyester) was considered to treat with 0 mg/ml hyperbranched polyester. (taken from [19]).

4. GAS SEPARATION MEMBRANES

Membrane based gas separation has attracted more attention for the last two decades and has developed into a new unit operation since then. Compared to traditional separation processes, it has many significant advantages, such as low investment cost, low energy consumption, simply operation, etc. Dendrimers have many unique properties for membrane based gas separation, such as open nano-scaled structures and interior accessible cavities.

Carbon dioxide was successfully separated from a gas mixture by using G0 PAMAM dendrimer [20]. Fig. (**16**) demonstrated the flow diagram of industrial equipment for separate CO_2 from CO_2-N_2 mixture with G0 PAMAM dendrimer. G0 PAMAM dendrimer aqueous solution was used as absorbent liquid, circulated between the absorber and the stripper and served as a mobile liquid membrane. The results showed that the G0 PAMAM dendrimer aqueous solution was quite efficient on removing CO_2 from the gas mixture, and the absorption stripping behavior remained unchanged over a long time.

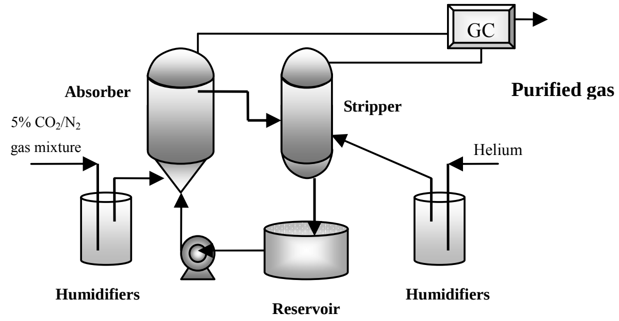


Fig. (16). The schematic process of separation equipment of CO_2-N_2 mixture (adapted from [20]).

PAMAM dendrimer was also employed as component gas selectivity membrane by the group of Kazama [21]. An *in situ* modification method, which utilizes interfacial precipitation of membrane material on the surface of commercial polysulphone (PSF) ultrafiltration hollow fiber membrane, was used to prepare the PAMAM dendrimer containing gas selective membrane. A layer of amphiphilic macromolecule-chitosan was added between PAMAM dendrimer and PSF membrane. The final obtained membrane exhibited a CO_2 permeance of 4.6×10^{-7} m^3(STP)m^{-2}s^{-1}kPa^{-1} and a CO_2/N_2 selectivity of 230 at the conducting pressure of 97 kPa at 40^{o}C (Table **1**), which can meet the needs for practical CO_2 and N_2 separation. The high gas selectivity of the dendrimer-contained membrane may be due to the interactions between the CO_2 molecules and PAMAM dendrimers. Furthermore, the gas selectivity of the membrane can be improved up to 400 at the operation pressure of 100 kPa at 40^{o}C by optimizing the membrane preparation conditions including dendrimer concentration and molar ratio [22]. Additionally, some new gas separation membranes with PAMAM derivations Fig. (**17**) were prepared for carbon dioxide and hydrogen [23]. The new gas separation membrane has higher selectivity of CO_2 compared to the membrane without PAMAM derivations.

Table 1. CO_2 Permeance and CO_2/N_2 Selectivity of PAMAM Dendrimer Composite Membrane (Taken from [21] with Permission)

Membrane	Q_{CO2} (m^{3}·(STP)·m^{-2}·s^{-1}·k·Pa^{-1})	$\alpha_{CO2/N2}$
PSF-substrate [a]	2.3*10^{-4}	1
CTS-substrate [b]	1.8*10^{-5}	1
PAMAM dendrimer composite membrane	4.6*10^{-7}	230

Feed gas: water saturated mixed gas of 5% of CO_2 and 95% of N_2 at 101 kPa.
Permeate: evacuated at 4 kPa. Testing temperature: 40℃.
[a] PSF hollow fiber membrane as dried.
[b] CTS-substrate with chitosan gutter layer.

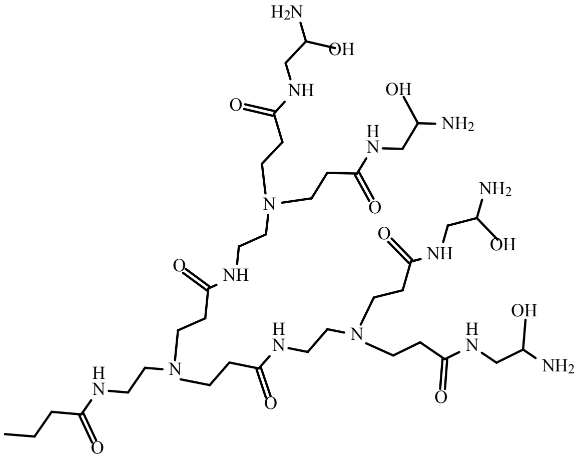


Fig. (17). The chemical structure of PAMAM derivation (branched unit).

PPI dendrimers were employed as components of gas separation membrane by Chung *et al.* [24] to improve the gas separation ability of the membrane. Different generations of PPI dendrimers (Fig. **18**), such as G1, G2 and G3, were dissolved in methanol. The polyimide membranes were then immersed in these solutions and washed with fresh methanol after the incubation period. Gel content and gas separation capability of these dendrimer containing gas separation membranes showed that the gel content increased in the order of G1>G2>G3 with the same incubation time and the gas separation capability increased over or near to the super bound materials. In addition, the gas separation property was further improved and located well above the permselectivity-permeability trade-off line with an increase in cross-link time. For example, the maximum increase was about 74% after 20 minutes of incubation with G1 PPI dendrimer solutions.

Hyperbranched polymers have similar structural properties compared with the dendrimers. Therefore, some research groups investigated the gas selectivity properties of membranes prepared from the hyperbranched polymers. For example, Suzuki *et al.* synthesized a novel hyperbranched material with 4,4′-(hexafluoroisopropylidene) diphthalilc anhydride (6FDA) and 1,3,5-tris(4-aminophenoxy)benzene (TAPOB) Fig. (**19**) [25-27]. They prepared a hybrid membrane with the 6FDA-TAPOB hyperbranched material and silica. Compared with linear type polyimides, such as the novel 6FDA-TAPOB, hyperbranched polyimide had a better thermal stability and a higher fractional free volume. The prepared membrane exhibited considerably high gas solubility, resulting in high gas permeability (Table **2**). It was shown that after incorporation of silica in the 6FDA-TAPOB-silica hybrids, both the diffusion and selectivity increased with the increasing content of the silica in the hybrids. In addition, the properties of oxidiphthallic anhydride (ODPA)-TAPOB hyperbranched membrane and the corresponding silica hybrid membrane were investigated in the same group and the result is similar to that of above-mentioned hyperbranched membrane [28].

Hyperbranched neopentyltetraethylene diamine was used to prepare membrane for carbon dioxide separation by Wang *et al.* [29]. Such membrane was prepared by casting the solution, which consists of dendritic neopentyltetraethylene diamine and polyvinyl alcohol, onto the polysulphone membrane or polyethersulphone membrane matrix. Compared to traditional gas separation membrane without the dendritic polymer, the new membrane had better permselectivity, higher stability and compression resistance.

5. SOLID-LIQUID SEPARATION MEMBRANES

Solid-liquid separation, a traditional unit operation, has been attracting increasing attention with the developments of membranes. It exists in many industrial fields, such as chemical engineering, environmental protection, pharmaceutics, etc. The dendrimer has high density of surface functional groups, which can bond to some other compounds, so it can play an important role in solid-liquid separation. For example, PAMAM dendrimer was used in water purification through its binding the contaminants [30,31]. The purified water can thus be separated by conventional separation and PAMAM dendrimer be recovered simultaneously. The flow sheet was shown in Fig. (**20**). The system contains three unit operations: a reaction unit, a filtration unit and a dendrimer recovery unit. The solid-supported filters contain many different dendrimers, including but not limited to cation/anion-binding dendrimer, organic compound-binding dendrimer and so on. The system can purify the water containing heavy metal ions such as Cu(II). Co(II), Ag(I), Fe(III), Ni(II), etc. [30] and the factors to be considered include dendrimer generation, terminal functional group, two-site model of uptake, solution pH, molecular weight cut-off and membrane type, etc.

A new semipermeable composite membrane was prepared from dendrimer by Zwijnenburg *et al.* [32]. Due to the amine-terminal structure of dendrimers, some compounds, such as isophthalyl chloride (IPC), trimesoyl chloride (TMC), can be polymerized into the new semipermeable composite membrane and thus the obtained

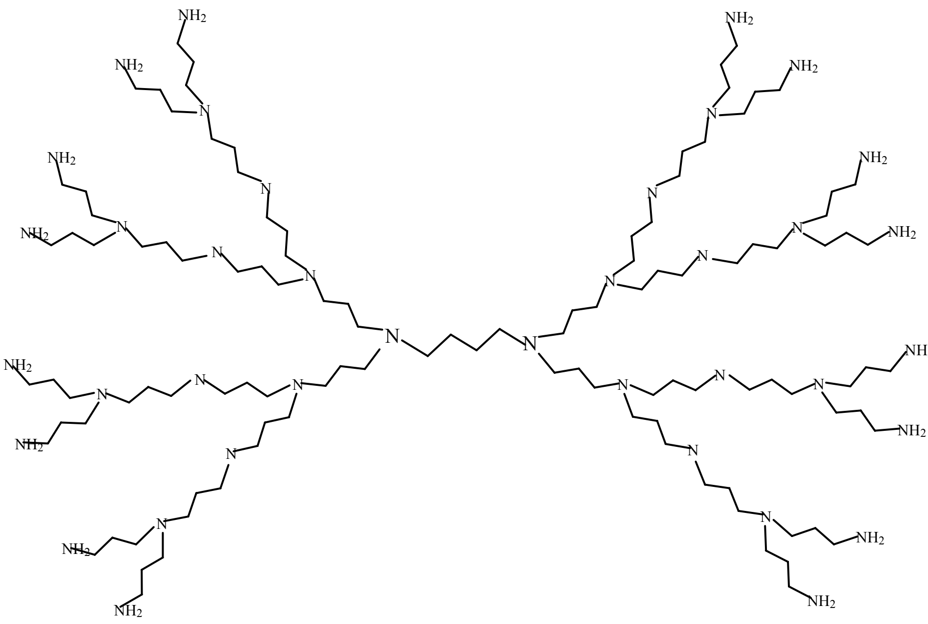


Fig. (18). The chemical structure of polypropylenenimine.

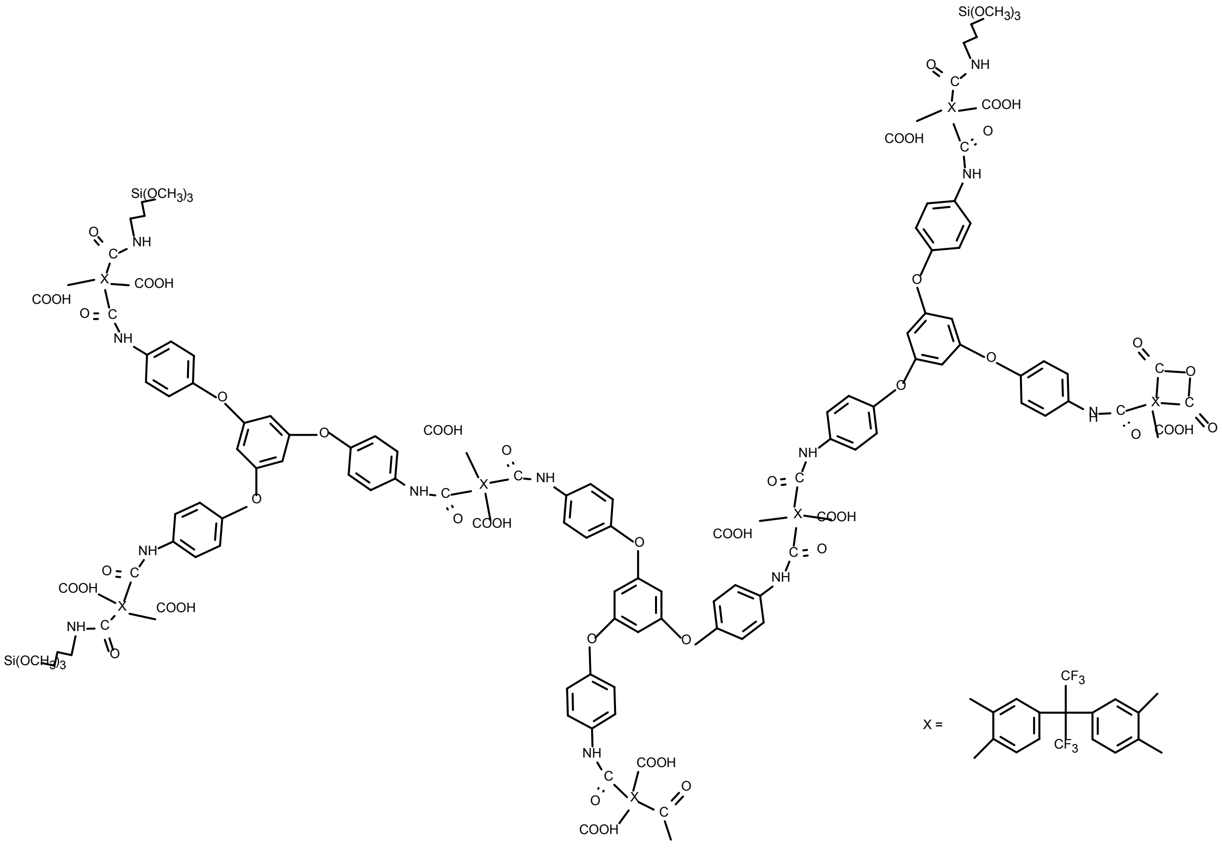


Fig. (19). The chemical structure of 6FDA-TAPOB hyperbranched polyamic acid.

Table 2. Gas Transport Properties of 6FDA-Based Polyimide-Silica Hybrid Membrane at 76 cm Hg and 25°C (Adapted from [27])

Sample	$P*10^{10}$ [$cm^3(STP)cm/cm^{2}\cdot s\cdot cm/cm^{2}\cdot s\cdot cmHg$]				$D*10^8$ [cm^2/s]				$S*10^2$ [$cm^3(STP)\cdot cm^3_{polym}\cdot cmHg$]			
	CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4	CO_2	O_2	N_2	CH_4
6FDA-TAPOB	7.4	1.5	0.23	0.098	0.30	1.4	0.25	0.028	25	1.1	0.92	3.5
10 wt % SiO_2	10	2.0	0.31	0.13	0.35	1.5	0.29	0.026	30	1.4	1.1	5.0
20 wt % SiO_2	13	2.1	0.32	0.16	0.37	1.3	0.25	0.030	35	1.7	1.3	5.2
30 wt % SiO_2	23	3.0	0.46	0.24	0.57	1.7	0.29	0.040	41	1.8	1.6	6.0

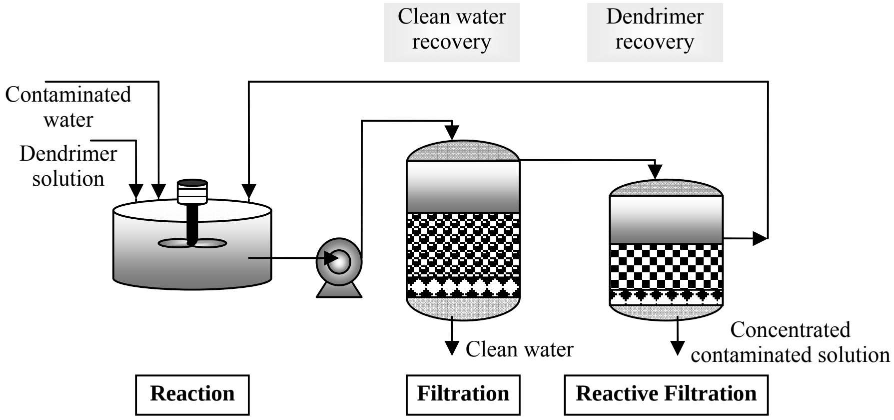


Fig. (20). The schematic process of water purification (adapted from [30]).

membrane can be used in nanofiltration and reverse osmosis processes.

Besides the general filtration by PAMAM modified membranes, recently, novel nanofiltration membrane was prepared from PAMAM dendrimer by Li *et al.* [33,34]. Such nanofiltration membrane (PEK-C NF membrane) was prepared with PAMAM and trimesoyl chloride (TMC) by in situ interfacial polymerization on phenolphthalein poly(ether ether ketone) (PEK-C) ultra filtration membrane. It was reported that the flux and rejection of the resulting membranes increased with increasing concentrations of PAMAM and/or generation numbers of PAMAM for NaCl concentration. Both rejection and flux decrease with an increase in $MgSO_4$ concentration. As for different type of salts, rejections follow the order of $MgCl_2 > MgSO_4 > NaCl > Na_2SO_4$, indicating that the resulting membranes were all positively charged. Especially, such membranes can work under hard conditions such as high temperature (e.g. 80°C) and acid medium (pH=2-9)). The long-term test was investigated at an operating pressure of 0.6 MPa with 1000 mgL^{-1} NaCl solution and showed that the novel nanofiltration membrane maintained flux around 45 $kg.m^{-2}h^{-1}$ and rejection ratio around 35% after over 1.5 months of operation at 30°C [32].

6. CURRENT AND FUTURE DEVELOPMENTS

Although dendritic polymers only have a short history of nearly two decades, the amount of patents and papers is increasing every year, which makes continuous progresses on their applications in both academic researches and industry processes. From the mentioned examples, dendritic polymers have proved themselves to be promising materials in the fields of membranes, but they are limited to in an embryonic stage.

The properties of dendrimers are almost the same as the hyperbranched polymers, but they are synthesized by a stepwise strategy and are expensive, while hyperbranched polymers are synthesized by one-step strategy and are very cheap. Therefore, hyperbranched polymers can be a good candidate of dendrimers and should receive more attention in membrane fields. Therefore, in the future, more attention should be paid to improving the synthesis of novel dendritic polymers and inventing the new methods for membrane formation with dendritic polymers. In particular, future developments will focus on the following aspects: (1) Reducing the synthesis costs of dendrimers so that they can be extensively applied in membranes and other fields; (2) Enlarging the application of the membranes from hyperbranched polymers to the fields of resources and environments, such as fuel cell-membranes, liquid separation membranes; (3) Exploiting the new applications of dendritic polymers in the other fields of membrane. As a general rule, the structure and properties of membranes from dendritic polymers should also be correlated.

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