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Separation & Purification Reviews

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

Polyaniline Membranes for Separation and Purification of Gases, Liquids, and Electrolyte Solutions

Malladi Sairam[a]; S. K. Nataraj[a]; Tejraj M. Aminabhavi[a]; Sukumar Roy[b]; C. D. Madhusoodana[b]
[a] Membrane Separations Division, Center of Excellence in Polymer Science, Karnatak University, Dharwad, India [b] Ceramic Technological Institute, Bharat Heavy Electricals Ltd., Bangalore, India

To cite this Article Sairam, Malladi , Nataraj, S. K. , Aminabhavi, Tejraj M. , Roy, Sukumar and Madhusoodana, C. D.(2006) 'Polyaniline Membranes for Separation and Purification of Gases, Liquids, and Electrolyte Solutions', Separation & Purification Reviews, 35: 4, 249 — 283

To link to this Article: DOI: 10.1080/15422110600859727

URL: http://dx.doi.org/10.1080/15422110600859727

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Separation & Purification Reviews, 35: 249–283, 2006

ISSN 1542-2119 print/1542-2127 online
DOI: 10.1080/15422110600859727

Polyaniline Membranes for Separation and Purification of Gases, Liquids, and Electrolyte Solutions

Malladi Sairam, S. K. Nataraj, and Tejraj M. Aminabhavi
Membrane Separations Division, Center of Excellence in Polymer
Science, Karnatak University, Dharwad, India

Sukumar Roy and C. D. Madhusoodana
Ceramic Technological Institute, Bharat Heavy Electricals Ltd.,
Bangalore, India

Abstract: Conjugated polymers are excellent barriers for membrane separations because their porosity can be controlled at the molecular level through chemical doping. Polyaniline (PANI) is particularly attractive because simple acid/base doping/undoping enables a controllable level of doping that can be readily achieved using dopants of different sizes and shapes. PANI, which belongs to an important member of the family of electrically conducting polymers, has been studied extensively as a membrane due to its distinct electrochemical properties and environmental stability. Adding dopants to PANI leads to a decrease in gas permeability, while removal of these dopants would produce extremely high permeability. This review provides an overview of the use of PANI membrane in gas separation (GS), pervaporation (PV) and electrodialysis (ED) applications. Our discussion will be concerned with the utility of PANI as a homopolymer, blend and composite membrane, discussing a considerable amount of background information on their developments and

Received 2 January 2006, Accepted 23 May 2006

This article was the CEPS Communication # 106. The authors dedicate this review article in honor of Professor Alan G. MacDiarmid, the University of Texas at Dallas, USA (Nobel Laureate in Chemistry, 2000), who visited CEPS in December 2004. His untiring energy to visit and inaugurate the Center of Excellence in Polymer Science at Karnatak University, Dharwad has been a great inspiration to our younger students and scientists.

Address correspondence to Tejraj M. Aminabhavi, Membrane Separations Division, Center of Excellence in Polymer Science, Karnatak University, Dharwad 580 003, India. E-mail: aminabhavi@yahoo.com

applications. Various modifications of PANI as efficient membranes and their future prospects in membrane separation and purification technology are discussed.

Keywords: Polyaniline, membrane, gas separation, pervaporation, electrodialysis

INTRODUCTION

Membrane-based separation processes are simple and direct methods of purifying commercially important gaseous or liquid mixtures that are often difficult to separate by other means. Polymers have distinct advantages as membranes for purification of many liquids and gases, because they are easily synthesized and processed into different forms that allow gases or liquids to pass through them. Use of polymeric membranes for separation and purification technologies has grown exponentially over the past few decades. This is mainly attributed to the potential for tremendous savings in energy if improvements over the current membrane materials can be achieved (1). Research in this area has been mainly dealt with thermoplastic polymers, but a new class of conjugated polymer, viz., polyaniline (PANI), which can be tailored to meet specific separation applications through doping process, has received much attention in separation and purification technologies. PANIs are unique because of their wide range of structural forms and the way in which such changes can be induced. PANIs possess electrical, electronic and optical properties of a metal, while retaining their process ability, etc., commonly associated with the conventional polymer. Often, these polymers are termed as "synthetic metals," since these are different from the conventional conducting polymers, which are merely a physical mixture of a nonconductive polymer with a conducting material such as metal or carbon black powder distributed throughout the matrix. Such π-conjugated polymers have been investigated ever since the pioneering discovery of conducting polyacetylene films in the late seventies by MacDiarmid et al. (2–5). This area of research was recognized for the Nobel Prize in Chemistry-2000 awarded to MacDiarmid, Shirakawa and Heeger. Even though poly(sulfur nitride) $(SN)_x$ has shown superconducting properties at extremely low temperatures (6), polyacetylene has been the widely accepted conducting polymer. The applicability of polyacetylene was limited due to the difficulty in its processing and its rapid decrease in conductivity upon exposure to air.

Further research in this area was focused on developing environmentally stable conducting polymers such as polypyrrole (PPy) (7, 8), polythiophene (9), polyphenylene vinylene (PPV) (10) and polyaniline (11–16). The structures of these polymers are shown in Figure 1, wherein, PANI has been the most widely studied conducting polymer because of its environmental stability (17–19), controllable electrical conductivity (20, 21), interesting redox properties associated with chain nitrogen (22, 23), crystallinity (24, 25) and processibility (26–31). Electrical properties of PANI can be

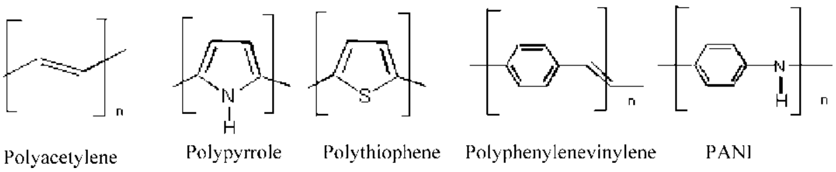


Figure 1. Structures of various conducting polymers.

improved by secondary doping (32). Various intrinsic oxidation states of PANI have been described (33–38) with alternating reduced and oxidized repeat units. The imine nitrogen atoms of PANI can be protonated wholly or partially to give the corresponding salts, but degree of protonation of the base polymer depends upon its oxidation state and pH of the aqueous acid. Complete protonation of imine nitrogen atoms in emeraldine base by aqueous acid results in the formation of a delocalized polysemiquinone radical cation is accompanied by an increase in conductivity of nearly 10 orders of magnitude or so. Various forms of PANI are shown in Figure 2.

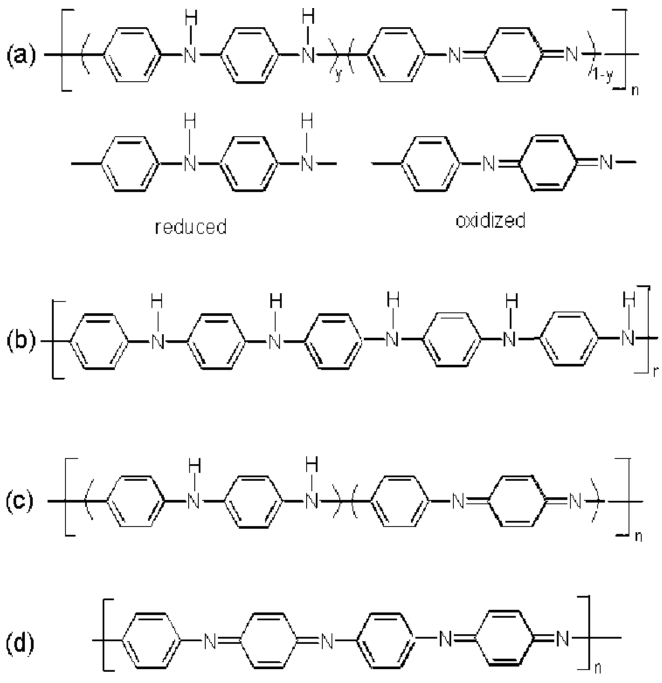


Figure 2. (a) Generalized composition of PANI indicating reduced and oxidized repeating units, (b) completely reduced polymer, (c) half-oxidized polymer and (d) fully oxidized PANI.

Applications of PANI are related to its ability to change the oxidation state, irrespective of the effect, which induces this change, standard chemical or electrochemical oxidation and reduction, variation in pH of the medium and effect of various types of energy (39, 40).

POLYANILINE AS A MEMBRANE IN SEPARATION AND PURIFICATION TECHNOLOGY

Inspiration to use PANI in separation stems from the ability to control its morphology at the molecular level via doping either during or after its synthesis. Among the many conjugated polymers, PANI appears to be the most useful for tailoring membrane properties, since it is stable in both air and water after doping/undoping processes. PANI membranes for gas separations (41, 42) and proton transport (43) have been studied, where these applications are not directly related to the change in its oxidation states. Selectivity is based on the precise control of its morphological changes due to oxidation-reduction (43) and protonation-deprotonation processes (41). In this review, we address PANI as a membrane in gas separation (GS), pervaporation (PV) separation, and electrodialysis (ED) applications. Readers may consult many noted contributions (44–49) on membrane-based separation processes, but these will not be discussed here.

Preparation of PANI Membranes

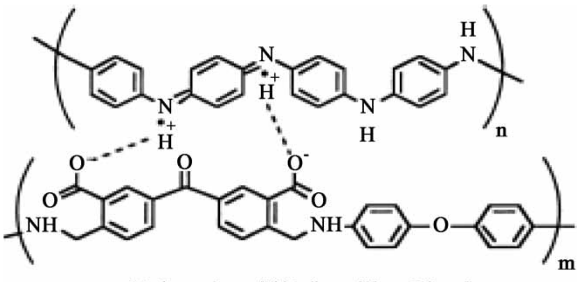
Polyaniline can be prepared by chemical, electrochemical or oxidative polymerization of aniline. Chemical oxidative polymerization of aniline is the most preferred route, since it facilitates the preparation of PANI on a large scale. Chemical oxidative polymerization is usually carried out in aqueous acidic medium with oxidizing agents like $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, $KClO_3$, $KBrO_3$, $KMnO_4$, KIO_3, $FeCl_3$, H_2O_2-$FeSO_4$, H_2O_2-Fe, etc. PANI salt synthesized this way is intractable and infusible, which poses difficulties in its processing. The undoped PANI is soluble in *N*-methylpyrrolidone (NMP), which offers the possibilities to produce stable, freestanding films and fibers. This approach has been used to prepare PANI membranes. PANI can be cast as a freestanding, dense film with pore sizes (<20 Å dia) falling in the useful range for reverse osmosis, pervaporation and gas separation applications (41, 42). However, pristine PANI membranes (50), PANI blends and composites have been used in gas, liquid and ED applications as well as in other purification technologies.

Pristine PANI Membranes

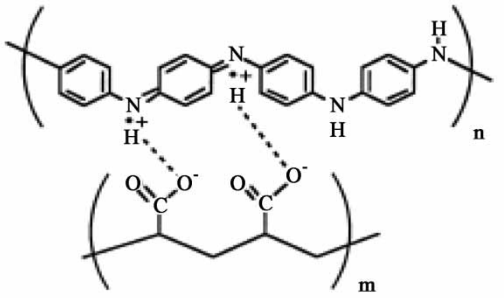
Separation and purification systems utilizing membranes are of great value for developing more energy-efficient technologies. PANI can be synthesized in emeraldine oxidation state by oxidative polymerization of aniline in an acidic medium (51). Unfortunately, it is very difficult to process PANI when it is present in its salt form. Research efforts in this direction have led to the discovery of several solvent systems, which can be used for solution processing of conducting PANI. PANI base when added to acetic acid or formic acid undergoes protonation with simultaneous dissolution (52). However, films obtained from these solvents have low mechanical strength properties. Similar is the case with the films prepared from PANI/camphorsulfonic acid (CSA)/*m*-cresol (53, 54). Attempts were also made to prepare freestanding films of PANI with CSA/hexafluoro-2-propanol (55) and 2-acrylamido-2-methyl-1-propanesulfoic acid/dichloroacetic acid systems (56). Several attempts were also made to develop new polyaniline systems, which would lead to films of high conductivity and good mechanical strength properties. Dodecylbenzenesulfonic acid (57), dialkyl phosphates (58), camphorsulfonic acid (53, 54), 1,2-benzenedicarboxylic acid, 4-sulfo-1,2-di(2-ethylhexyl) phosphoric acid ester (DEHPA) (59), etc., were used as plasticizer dopants to get the less brittle PANI films. Highly flexible PANI films were obtained by doping with DEHPA in dichloroacetic acid or difluoroacetic acid. Films prepared with other dopants in various solvents were reported to be mechanically strong, but the separation characteristics of these films have not been explored yet. Films can be formed from a dispersion of the emeraldine (base) form of PANI in NMP by grinding in a mortar and pestle. This dispersion can be poured into a Petri dish and heated until the film becomes dry. After cooling to room temperature, the film can be removed from glass by soaking in water. Fully dense, freestanding as-cast PANI membrane in purple-bronze color can be obtained. These films can be doped in 1.0 M HCl aqueous solution and the resulting doped films are deep blue in color. To prepare the undoped films, fully doped films can be placed in 0.1 M NH_4OH aqueous solution for at least 4 h; these undoped films are gold-bronze in color. Doping process removes the residual NMP from PANI film. PANI membranes with thicknesses ranging between 40 and 100 μm can be prepared by solution casting method.

PANI Blend Membranes

In order to improve their mechanical strength properties of PANI films, blends and composites of PANI were prepared. It was found that small molecular dopants like HCl are prone to leach out from the HCl-doped PANI membranes during PV experiments, which lead to a decline in permeation rates over time (60). Since decline in permeation rate is unacceptable for separations by PV membranes, two possibilities can be considered to eliminate the leaching problem: (1) use of self-doped PANI (sulfonated PANI i.e., SPANI) or (2) blending PANI with a polymeric dopant such as polyamic acid or polyacrylic acid. Figure 3 shows an ideal scheme to prepare



Polyamic acid/Polyaniline Blend



Polyacrylic acid/Polyaniline Blend

Figure 3. Doping interaction of PANI-blend systems (61, 93).

polyacrylic acid (PAAc) doped PANI. Even though self-doped PANI with dopant being covalently attached to polymer backbone would prevent dopant leaching, only thin films of SPANI can be spun or solution cast. However, PV studies have been hampered because the films of self-doped PANI cannot be readily formed from NMP or aqueous base solutions.

Alternatively, PANI blends have been prepared to eliminate the problem of dopant leaching from a membrane. However, the way a conducting blended PANI will behave in a process can be controlled by a neat dopant. Small molecular dopants used for doping PANI gradually decrease their conductivity due to evaporation at room temperature or even at high temperature. Polymeric acid doping could overcome the shortcomings related to long-term stability. Also, due to interaction and steric hindrance, polymeric dopants could enable PANI to lose its inter-chain distance. It was found that polyacrylic acid as a polymeric dopant is compatible with PANI over the whole range of mixing ratios (61). Blends of PANI and PAAc as polyanion-polycation complexes have shown macroscopically soluble aggregation. Therefore, PANI/PAAc blend films can be easily prepared. Despite the hydrophilic character of low molecular weight acid doped PANI, the PANI/PAAc membrane has shown low permeability and low long-term

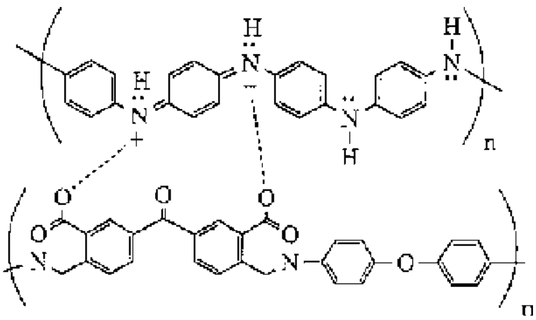


Figure 4. Idealized structure of PANI/polyimide blend.

stability. Hydrophilic PAAc as a polymeric dopant provides affinity to water and exhibits long-term stability to PANI membrane.

PANI blends have been prepared by mixing appropriate amount of other polymer with PANI or PANI solution and casting the solution on a glass plate. For instance, blends of PANI with polyamic acid, polyacrylic acid (61) and 3,3′,4,4′-benzophenonetetracarboxylic acid (BDTA)/4,4′-oxydianiline (ODA) have been prepared as membranes in PV separation and purification studies. PANI/polyimide blends have also been prepared (62) by mixing an appropriate amount of BDTA/ODA solution with 10 % (w/v) solution of PANI. Films were cast by spreading the solution on a glass plate and drying at 100°C for 1 h at room temperature, at 200°C for 1 h, and finally to 300°C for 15 min, resulting in an imidized blend. The idealized structure of PANI/polyimide blend is shown in Figure 4.

PANI Composite Membranes

PANI laminar-composite membranes have been prepared by using polystyrene (PS) as a carrier substrate and PANI as the active gas separation constituent in which PS imparts good mechanical strength. To fabricate PANI/PS composite (63), the first PANI membranes of appropriate thickness were prepared and then PS solution in benzene was cast on the previously prepared PANI membranes. Then, benzene was evaporated at ambient temperature to obtain PANI composite membranes with thicknesses ranging from 40 to 65 μm. The PS layer thickness of 35 μm provides a good mechanical strength even if the quantity of active constituent is small.

Hybrid nanocomposite polymeric membranes containing nanosized PANI particles dispersed in PVA have been prepared by *in situ* polymerization of aniline in the PVA matrix in acidic media (64). Aniline as a monomer was introduced into PVA matrix and by *in situ* polymerization outside the mesopores of the polymer matrix, a nanocomposite structure was formed.

The organic phase extends along the channels to the openings in the nanocomposite structure due to strong interactions between the nanoparticle formed and continuously polymerized PANI nanoparticles.

The utilization of conducting polymers to fabricate ion-exchange membranes combines the electrochemical properties of conducting polymers with mechanical properties of the conventional polymers. However, utilization of conducting polymers makes the membrane more ion-selective, thus improving its separation selectivity for anions or cations of different valences. Cationic membranes doped with different acids have been prepared (65) for ED separation applications by extruding high impact polystyrene (HIPS) with 20 wt.% of PANI in a single screw extruder, preheated at 180°C under 30 rpm speed and then palletized. In order to prepare membranes, pellets were heat-pressed at 160°C to avoid the degradation of PANI.

Solvent welding process was used to prepare PANI/porous-nylon composite membrane with a PANI skin layer thickness of 5 μm. PANI powder was slowly added to 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) with a constant stirring (66). The solution was filtered through 0.2 μm syringe filter, cast on a glass plate, and dried in vacuum oven at 60°C. Before removing the PANI film from the glass plate, a nylon membrane was attached to PANI film, which was previously soaked with a 20 wt.% aqueous NMP solution. The nylon-attached PANI film on the glass plate was again dried in a vacuum oven at 60°C to remove water and NMP. Water evaporated much faster than NMP because of its lower boiling point. As water evaporates, the concentration of NMP increases. NMP located between the PANI surface and the nylon membrane dissolved the PANI surface. After full NMP evaporation, the nylon membrane was adhered and welded onto the PANI film. The PANI composite membrane was peeled off from the glass plate and dried.

Orlov et al. used an oxidative polymerization method to prepare PANI/polyvinyl trimethylsilane (PVTMS) composite membranes (67). First, PVTMS membranes were prepared by casting from 5% solution and cast on a cellophane support in toluene. The volume of solution and diameter of cellophane support were optimized to have membranes with a thickness of 50 μm. The solvent was removed and membranes were dried in vacuum. Before use, the membranes were washed with methanol and dried in dust-free atmosphere. During polymerization of aniline on the surface of PVTMS film, the concentrations of aniline and ammonium peroxydisulfate were varied from 0.01 to 0.2 mol/L at a constant molar ratio of 1:1, but HCl concentration was varied from 0.1 to 2 mol/L. Reactants were prepared and mixed immediately before casting. The PVTMS membrane was then carefully placed on the surface of the reaction mixture in a revolving flask to avoid any air bubbles. When the reaction was complete, the PVTMS/PANI composite membrane was removed from the reaction flask, washed with HCl solution and dried in vacuum over P_2O_5. To obtain the undoped samples, the composite film after washing with HCl was rinsed with distilled water for at least 30 min. Then,

NH_4OH solution was added dropwise for 30 min, followed by washing with distilled water and drying in vacuum over potassium hydroxide.

Composites of PANI/ceramic membranes have been prepared (68) to enhance the properties using PANI as the pore surface modifier, by diffusing ammonium peroxydisulfate and aniline into ceramic membrane disks. Ceramic disks (mullite) were weighed and sandwiched between cells A and B with the help of vacuum oil greased O-rings and a clamp. The idealized structure of CMX-PANI composite membrane is shown in Figure 5. For a typical intercalation reaction, 2.855 g of ammonium peroxydisulfate was dissolved in 50 mL of 1 M HCl to which 5.06 mL aniline dissolved in 50 mL of 1 M HCl was added. The above two solutions were poured into cells A and B, respectively of the set up shown in Figure 5. The reaction was carried out for some desired time and stopped by discarding the residual solution in the reactor and rinsing the ceramic disk with water. PANI-intercalated ceramic disk was soaked in water overnight to remove any soluble monomer or oligomers inside the disk. The washed disk was heated to dryness at 80°C for few hours and was scraped to get rid of any PANI grown on its surface. It was reheated again at 80°C for few hours before it was weighed again. The amount in intercalated PANI was obtained from the difference in weights before and after the reaction.

Phase inversion technique followed by *in situ* polymerization was also adopted to prepare PANI/polyethylene (PE) composite membranes. Here, a substance was used to fill the PE pores first and then the desired coating material replaced it in the pores. For PANI/PE composite (69), PE membrane was immersed in a non PE solvent, such as ethanol, to fill the pores. Then, *in situ* polymerization was performed by transferring the ethanol-soaked PE membrane into acidic solution of aniline hydrochloride (0.2 M), which replaced ethanol in the pores. After replacement, an ammonium peroxydisulfate solution (0.2 M) (oxidant) in 1 M HCl was

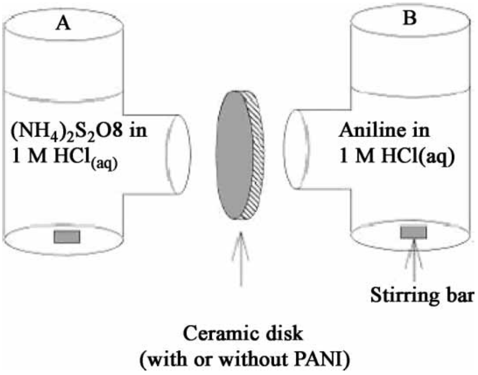


Figure 5. Schematic representation of the preparation of PANI/ceramic composite (68).

introduced to start the polymerization. PANI will then start coating as the polymerization proceeds in pores as well as at the outer surface of the PE membrane at room temperature for about 20 h. The composite formed was taken out, rinsed in 1 M HCl to remove the adhering precipitate of PANI and immersed in acetone to remove the aqueous phase, which later prevents the shrinkage and possible deformation of the composite while drying. The same procedure was used to modify the only surface of PE without pre-treating the membrane with ethanol. The membranes prepared this way contained 8.3% PANI in the pre-treated PE and 1.6% in the untreated PE. These composite membranes have been used to study the diffusion permeability of the electrolyte solution as shown in Figure 6.

In an attempt to prepare a defect-free ultra-thin PANI composite membrane, Illing et al. have developed a novel process (70). In their study, approximately 0.5 wt.% of emeraldine base was dispersed in NMP, which was spread onto a glass-plate and solvent was evaporated. Approximately, 0.1 mL dispersion/cm^2 of the substrate was required to create a 2–3 μm thick film. The PANI membrane thus obtained after evaporating NMP was dried for 2 h at 125°C. The copper colored PANI membrane was then coated with a solution of the dissolved support material. A solution of 3 wt.% of poly(vinylidenefluoride) (PVDF) was prepared in NMP/ DMSO (3:1) mixture, which was poured onto PANI membrane to adhere to the glass substrate. The PANI base cast from the NMP solution did not redissolve in

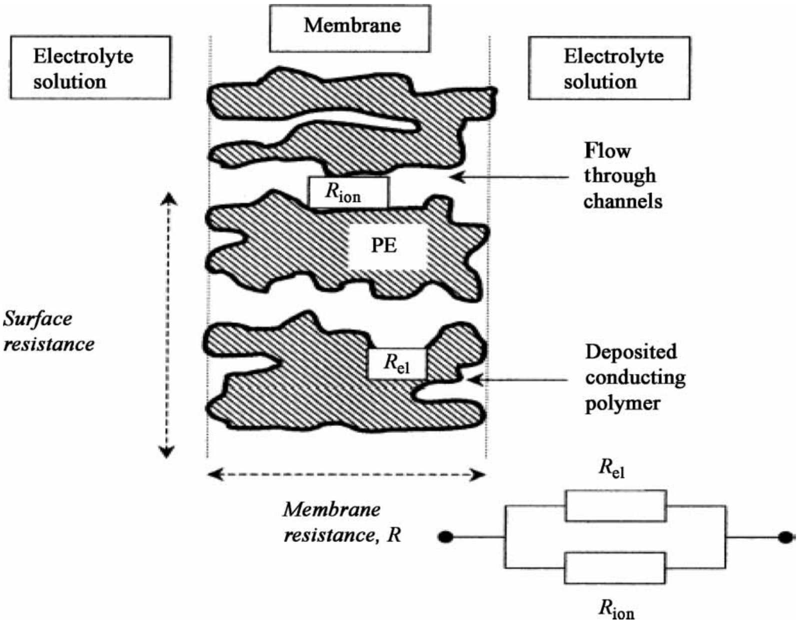


Figure 6. Schematics of PANI layer deposition on and in the pores of PE film (69).

NMP/DMSO mixture because by casting (and drying) the PANI membrane, amorphous PANI was transformed as a highly crystalline material, which could not be dissolved (71). To support 100 cm^2 pre-prepared PANI thin membranes, approximately 20–25 mL of the solution was used. The composite membrane was then dried at 60°C for several hours, until the solvent had evaporated. During evaporation, a spongeous support film was formed, which was combined with PANI. Thus, PVDF gave a stable and spongeous carrier structure, which could allow gases to pass through with negligible resistance. Finally, the composite membrane was separated from the substrate by immersing the coated glass-plate for several hours in a mixture of *n*-propanol and demineralized water.

PANI IN GAS SEPARATION

Membrane gas separation and purification has been emerged as a commercially viable process on a large scale during the seventies and eighties. However, significant progress has been made in this area, including improvements in membrane formation processes, chemical and physical structures, configurations and applications (72, 73). Chemical structures coupled with subtle physical properties of the membrane material could influence the permeability and selectivity of a gas. The responses of a polymeric material to permeation are strongly influenced by the polarity and steric characteristics of the polymer and permeate. The size and shape of bulky groups in both the polymer backbones and side chains would determine certain fundamental properties like packing density and rigidity, which in turn, would influence the permeability. These parameters along with the diffusion coefficient, governs the separating capabilities of polymers for He, H_2, O_2, N_2, CH_4, and CO_2 gas pairs. As the polymer molecular spacing becomes tighter the permeability decreases due to decreasing diffusion coefficients, but the separation characteristics are enhanced (74, 75).

Membrane-based gas separation is a pressure-driven process in which gaseous mixture is fed into membrane module under high pressure, typically between 10 and 200 bars. The driving force for separation is partial pressure difference of gases in the feed and permeates. Separation is thus based on the relative permeation rates of feed components. If membrane is to reach equilibrium, permeation would continue until pressure and concentration of gases on both sides are equal. The two main parameters defining the membrane performance are selectivity and permeation rate. In a binary system consisting of gases, "a" and "b", with gas "a" as the faster permeating component, separation factor, $\alpha_{\mathrm{a/b}}$ is defined as the concentration ratio of "a" to "b" in the permeate over the concentration ratio of "a" to "b" in the feed side given by (45),

$$\alpha_{\mathrm{a/b}} = \frac{y_{\mathrm{a}}/y_b}{x_{\mathrm{a}}/x_{\mathrm{b}}} \qquad (1)$$

where y_a and y_b are concentrations of gases "a" and "b" in the permeate; x_a and x_b are concentrations of gases, "a" and "b" in the feed. Permeation is thus defined as the volume of the feed passing through unit area of membrane at unit time under unit pressure given as:

$$P = v/A\, t\Delta p \tag{2}$$

where P is permeability ($cm^3/cm^2.s.cmHg$), v is volume of gas (cm^3), A is area (cm^2), t is time (s) and Δp is pressure difference (cmHg) (76).

For investigating gas transport properties, the π-conjugated polymers present the highest ideal separation factors. Much of the research on gas separation have dealt with π-conjugated poly(trimethylsilylpropyne) (PTMSP) membranes. This glassy polymer has remarkable gas permeability, but its gas selectivity is poor. Among other conjugated polymers such as PANI, poly(dimethoxy-*p*-phenylenevinylene) [DMPPV], and poly(*N*-methylpyrrole) [PMPY], PANI exhibits low gas permeability with high selectivity due to its post membrane formation involving doping. Once exposed to either an oxidizing or a reducing agent or in the special case of emeraldine base form of PANI to an acid, the polymer would become electrically conducting. Interest in PANI as a membrane for separation stems from its high selectivity towards gases, including oxygen/nitrogen, where partially doped PANI had among the highest separation factor reported ($\alpha_{O_2/N_2} \geq 12$) (40). However, PANI can be tailored after its synthesis through doping/undoping. The doping process, in which counterions are added uniformly throughout the material on a molecular level, will decrease the permeability to all gases, while undoping was found to increase the gas permeability. These effects are due to morphological changes induced in PANI by the dopants. These changes are not reversible upon undoping, since there is a tremendous driving force for adding protonic dopants to imine nitrogens on PANI backbone (e.g., 5 kcal/mol for doping with HCl, the polymer chains are pushed apart by the incoming dopants). Treating PANI with NH_4OH removes the dopants. Thus, undoping leaves PANI with increased free-volume, since there is no driving force for PANI to return to its original conformation. This accounts for high gas permeability observed for the undoped PANI.

The large difference in permeability of gases through doped and undoped PANI membranes observed by Anderson et al. (41) led to a more detailed investigation of PANI for gas separation applications. A correlation between the size of the counterion and permeability is observed for a wide range of gases where larger the dopant counterion, higher will be the permeability of gases through the undoped PANI membrane. The highest selectivity ($\approx$9) was found for O_2/N_2 through redoped PANI. Anderson et al. (77) also studied the gas permeability of PANI membranes in its emeraldine oxidation state and found substantial improvements in gas selectivity for mixtures of He/N_2, H_2/N_2, O_2/N_2 and CO_2/CH_4. The doping procedure, which enabled conductivity of the membrane, could cause significant concurrent changes in membrane morphology, resulting in its improved gas selectivity. These morphological changes could primarily influence the permeant diffusivity as shown by a comparison to kinetic diameter of the permeant. The authors (78) also have studied the effect of the dopant size in a systematic manner. For instance, PANI membranes have been fully doped with halogen acids such as HF, HCl, HBr and HI, which were then completely undoped by NH_4OH. In contrast to halides in a crystalline lattice, these acids have shown a steady progression of lower permeabilities in the order: HF > HCl > HBr > HI.

Kuwabata and Martin (42) reported that both permeation rate and selectivity are dependent upon the level of doping. Permeability of O_2 and N_2 decreased with increasing doping level. Different dopants exhibited different selectivities. For instance, 36% H_2SO_4 doped PANI had a selectivity of 13.4 for N_2/O_2 separation, while thin composite membrane doped with 38% HNO_3 gave a selectivity of 14.8 for the same mixture. The free-standing membranes of $<10\ \mu m$ thickness have shown Knudsen-diffusion with a microporous structure with increased selectivity after increasing membrane thickness. Thus, repeated doping and undoping of PANI membranes could potentially enhance its selectivities. According to Rebattet et al. (79) doped, undoped and redoped PANI increased $\approx 15\%$ permeability for H_2, CO_2 and O_2 gases with a 45% decrease in permeability for N_2 and CH_4. Differences in the reported O_2/N_2 selectivity values are due to different conditions adopted to prepare the membrane; inhomogeniety in doping process and uncertainty in low nitrogen permeability. Rebattet et al. (80) studied the variations in permeation and selectivity properties during doping, undoping and redoping processes in order to explain the microstructural modifications induced by doping. Electron spin resonance (ESR) studies indicated that polaron-oxygen interaction was the dominating mechanism for O_2 permeability of PANI membrane when redoped with HCl. In any case, doped PANI membranes gave about 15% increase in permeability of H_2, CO_2 and O_2 gases with 45% decrease in permeability of N_2 and CH_4 gases.

Liang and Martin (81) reported that by reducing the thickness of PANI membrane from 5 to 1 μm, a remarkable increase in total gas permeation rate was observed, but the O_2 selectivity was lower because some non selective pinholes were formed in thin PANI membranes. A threshold membrane thickness of 3 μm was favorable for permeability-selectivity studies. The α_{O_2/N_2} ratio was around 10 for PANI membrane having a 3 μm thickness. Upon doping with a large dopant (dodecylbenzenesulfonic acid), the membrane did not offer any improved performance, but the permeability increased greatly with a sacrifice in O_2 selectivity (82). Polymers of this study have been prepared by interfacial polymerizations, resulting in thin film composite membranes, wherein microporous support provided the required mechanical strength in addition to conductive nature and good chemical selectivity.

Dense PANI membranes when cast from NMP dispersion gave an average pore size of 20 Å (48). Permeabilities of these membranes were found to depend upon the size of the entrant gas. Permeabilities ranging from 20 Barrers for a small gas such as helium (2.6 Å) up to 0.03 Barrers for much larger gas like methane (3.8 Å) have been reported. Anderson et al. (77) reported high O_2 selectivities for PANI membranes. PANI membrane in doped, undoped and redoped forms with HCl. exhibited a selectivity of 30 towards O_2 over that of N_2, which is one of the highest values known so far (79). On the other hand, Liang and Martin (81) reported PANI membrane exhibiting a very low permeability of $10-12\ \mathrm{cm}^3\ (\mathrm{STP}) \cdot \mathrm{cm}/\mathrm{cm}^2 \cdot \mathrm{s} \cdot \mathrm{cmHg}$, a value that is close to semicrystalline poly(ethylene terephthalate) (PET) and cellulose membranes. They obtained O_2 selectivity of 15, but never obtained α_{O_2/N_2} of 30 as Kaner (83) originally reported.

Permeability data for H_2, He, CH_4, CO_2, O_2, N_2, and CH_4 were reported by Mettes et al. (84) for PANI membranes treated with perchloric acid. A large increase in permeability to all gases was observed following doping and undoping treatment cycles. Moreover, controlled redoping (of the undoped films) resulted in large separation factors for industrially important gaseous mixtures. These results are consistent with the model based on dopant occupation in the free-volume of pinhole free membranes. Another important variable for gas transport properties of PANI films is the film curing time. Permeability data for PANI films cured at 125°C for 2, 3 and 6 h, and then cycled, indicated that a three-h cure time produced the most fully dense PANI films. Mattes et al. (84) prepared asymmetric PANI hollow fibers to increase O_2 permeability by decreasing thickness of the active skin layer. Su et al. (62) used the freestanding films of PANI and its blends (50:50) with polyimide and found that H_2 and O_2 permeability of the blend was higher than observed for pure PANI base. Selectivity of the blend membranes are comparable to PANI (except in case of CO_2/CH_4), which is contrary to the observations made by Kim et al. (85), who showed that increase in permeability has occurred at the expense of selectivity.

Gas permeation experiments (80) with H_2, O_2, CO_2, N_2 and CH_4 have been carried out on the annealed, HC1 (4 M)-doped, NH_4OH (1 M)-undoped and HC1 (10^{-2} M)-redoped PANI membranes. Permeability coefficients were influenced by diffusivity and these depend on the statistical distribution of free volume spaces within the polymer matrix. Despite different affinities with PANI membrane, all the analyzed gases obeyed the Fickian transport equation. Heavy doping treatment leads to a drastic decrease in gas fluxes and diffusivities, but transport properties have been mostly regained by removing chloride ions upon undoping in the basic medium. Variations in permeability coefficients with doping-undoping-redoping processes allowed the classification of gases into two subgroups: (i) H_2, O_2 and CO_2 (smaller gases) and (ii) N_2 and CH_4 (larger gases). After doping-undoping-redoping treatments, gas fluxes were improved by 15% for smaller gases with a 45% decrease for larger gases. This was explained by the partial filling of the large-sized free volumes under moderate redoping and by a hysteresis phenomenon due to strong treatment with doping acid. Thus, doping cycle could modify gas selectivities because separation factor can be almost doubled for a gas mixture involving two subgroups, whereas it was unchanged for a gas mixture involving only one subgroup. The highest selectivity values for O_2/N_2 and CO_2/CH_4 mixtures were, respectively, 14 and 78 (80), whereas Kuwabata et al. (42) observed the respective selectivity values of 15 for O_2/N_2 and 55 for CO_2/CH_4. Such values are due to very low permeability of N_2 and CH_4 through PANI membrane. If the number of large-sized free volumes in the polymer matrix is very poor, a small variation results in large improvement of separation factors. By reporting separation factors as: selectivity vs permeability curves, as suggested by Koros (86), it turns out that for the redoped PANI, separation factors are good for N_2 separation, but these are not particularly attractive for methane separation. Despite its low permeability to gases, redoped PANI was recommended as a promising membrane to separate N_2.

Permeation experiments on O_2 and N_2 have been performed using PANI composite membranes prepared on a porous nylon membrane as a support (66). A novel solvent welding process was used to prepare PANI composite membranes. After doping and dedoping, the permeability of dedoped PANI membrane decreased, while its selectivity slightly increased, due to morphology changes of the PANI membrane. The X-ray *d* spacing of PANI membrane decreased from 4.89 to 3.67 Å after doping, dedoping and redoping. As redoping continued, the degree of doping increased, while *d* spacing has decreased, resulting in a dramatic increase of selectivity. The highest O_2/N_2 selectivity and permeability obtained from PANI redoped for 2 h were 28 and 0.13 Barrers, respectively. The O_2/N_2 permeation experiments with different upstream pressures and temperatures were carried out. Permeability of PANI membrane was highly dependent upon the level of doping. A selectivity of O_2 of 28 was obtained by redoping PANI membrane for 2 h in 0.02 M HCl solution to conclude that doping-dedoping of PANI has enhanced the O_2 permeability considerably.

Permeability and ideal selectivity obtained for a large number of gaseous mixtures through dedoped and redoped PANI membranes of varying thicknesses have been reported. For instance, microporous membranes showed (42) Knudsen diffusivity, but membrane thickness did not affect the ideal separation factors. No significant change in selectivity with increasing film thickness was observed. Rebattet et al. (79) stated that the selectivities observed were quite comparable with those of Martin et al. (81, 82), but they did not succeed in reproducing the exceptional separation factors as obtained by Anderson et al. (41, 77). Selectivities of 7.6 for H_2/CO_2 mixture for the dedoped PANI membrane and 6 for O_2/N_2, 10 for H_2/CO_2, and 200 for H_2/N_2 mixtures in case of redoped PANI membranes have been reported. Thus, PANI membrane has outperformed over the conventional membranes in H_2 separation by over 600%. Similar separation factors are also observed for CO_2/O_2, CO_2/N_2 and O_2/N_2 mixtures. However, correlations between solubility in PANI and boiling points of the gases or their critical temperatures are nearly identical with those found for natural rubber membranes. Linear relationships have been established between logarithmic reduced diffusion coefficient and diameter of gaseous molecules in addition to activation energy for diffusion, E_D. The higher E_D value indicates higher energy required to form holes of sufficient size for diffusion of large gaseous molecule. As a result of doping, inter-chain distance in PANI is reduced, which alters the solubility of H_2 in PANI. However, undoping could increase permeabilities of gases having kinetic diameters smaller than 3.5 Å, with a decrease in permeability for large gaseous molecules. It is noticed that D decreased, but E_D increased in the doped PANI membranes.

Stolarczyk and Lapkowaski (87) studied the gas separation properties of PANI/PS laminar composite membranes. The assumption was that PANI layer acts as a gas-separating barrier, while PS as a substrate. Because of its thin-film forming properties, possibilities of obtaining much higher permeability and satisfactory mechanical strength are good. The influence of protonation-deprotonation on permeability was studied. Protonation of PANI showed a decrease in permeability; large differences in permeabilities of gases were observed with the large diameter size gases. The selectivity and permeability of PANI membranes have shown a dependence on degree of protonation, but no significant effect of size on doping with the anion was noticed.

Orlov et al. (67) prepared PANI/PVTMS (polyvinyltrimethylsilane) composite membranes and tested their gas transport properties for O_2/N_2, He/CH_4, He/N_2 and CO_2/CH_4 mixtures. The doped composite membranes have shown very similar properties to those of PVTMS membranes to separate O_2/N_2 and CO_2/CH_4 mixtures. In case of He/N_2 and He/CH_4 mixtures, the selectivity of composite membrane was markedly higher due to the fact that permeability of He decreased only slightly as compared to O_2, N_2, CO_2 and CH_4. Permeability coefficient was lower for all gases in case of composite membrane as compared to pure PVTMS membrane. In the undoped state, these samples exhibited better selectivities of gas separation for O_2/N_2 and CO_2/CH_4 mixtures than those of PANI membranes cast from the solution. However, changing the process conditions did not improve their gas-transport properties. Gas permeability of O_2 and CO_2 are twice as high, whereas those of N_2, CH_4 and He changed only slightly. This could be due to the possible interaction or doping of emeraldine PANI by O_2 and CO_2. Authors concluded that the composite membrane was only slightly less permeable than PVTMS membrane, whereas its separation selectivity was 2–5 times higher. Efforts were made to study the changes in conditions of polymerization such as reagent concentration, acidity of the medium and duration of reaction, which affected not only the quality of PANI coating in the composite membranes, but also its gas transport properties.

Illing et al. (88) have developed a novel method to prepare ultrathin PANI/PVDF (polyvinyledine fluoride) composite membrane and tested their gas permeation rates for H_2, CO_2, O_2 and N_2 at the upstream side pressure of 1–1.5 bars. The membranes of thicknesses ranging between 62 and 105 μm with a PANI layer of thickness 0.8 to 10.5 μm were used. The fluxes of all gases increased linearly with decreasing thickness of the membrane, indicating a constant permeability. The spongeous support material used did not affect the gas permeability and even the thinnest composite membrane of PANI (thickness $> 0.8\ \mu m$) preserved its gas selective properties.

Pellegrino and Radebaugh (89) studied the effects on pure gas permeabilities resulting from the treatment of PANI-emeraldine base (EB) membranes. These include: (i) permeability of He, H_2, CO_2, O_2, Ar, N_2, and CH_4 through "as-cast" PANI-EB membranes, which followed size-dependent (kinetic diameter) relationship, (ii) changing film from the as-cast EB form to a fully doped (FD) emeraldine salt (ES) form with halogenic acids caused a decrease in gas permeability. This decrease depends upon both the gaseous molecules as well as the halogenic acid, (iii) undoping PANI-ES/FD film (by the addition of NH_4OH) back to EB form yielded an "undoped" EB membrane. Gas permeabilities of these membranes were uniformly larger than those found for the original as-cast membranes. Additionally, the ratio between pure gas permeabilities for various mixtures (ideal separation factor) decreased in the undoped films relative to either the as-cast or FD-ES forms, (iv) permeability of any gas in the undoped EB film varied with halogen acid used to dope it. A clear trend of decrease in permeability in the order: $F^- > Cl^- > Br^- > I^-$, as the acid anion changed, followed the size order of the solvated halogen ion, which was quite opposite the normal order of counterion size in a crystal lattice and (v) re-exposing the undoped film to a halogen acid (called redoping) was used to modify pure gas component's permeability through the resulting film.

An optimum in ideal separation factor for several gas pairs, including O_2/N_2 and H_2/N_2, with respect to the amount of redoping has been reported (90). Oxygen solubility of the as-cast film was higher than that of the as-made powder or the undoped film. Nitrogen solubilities in both the as-made powder and the as-cast film were about the same, but significantly greater than those found in the undoped film. Pure component permeation measurements on these films gave ideal O_2/N_2 selectivities (permeability ratios) of $\sim$7 for the as-cast film and $\sim$9 for the undoped film. Permeability difference for both the species is lower in the undoped film, but the decrease is greater for N_2 than O_2. Thus, it is concluded that observed ideal O_2/N_2 selectivity in the as-cast film is primarily based on the differences in diffusion selective rates with respect to sorption as well as diffusion coefficients, while in the undoped film and solubility selectivity controlled the permeability ratio. The differences in solubility for various combinations of mixtures and the forms of PANI-EB membrane were attributed to the physical properties of gas critical temperature and its molecular size that is accessible to polymer free volume. Thus, doping and undoping of PANI films can be used to create a molecular size selective environment with respect to sorption and diffusion.

Table 1 lists the ideal O_2/N_2 solubility selectivity (ratio of pure component solubilities) as $\sim$1.8 for the as-cast film and 3.8 for the undoped

Table 1. Separation factors of redoped PANI membranes for selected gaseous mixtures

PANI membranes	H_2/CO_2	H_2/O_2	H_2/N_2	CO_2/O_2	CO_2/N_2	O_2/N_2	Ref.
Microporous PANI	4.52	3.65	3.54	1.32	1.41	1.07	(88)
Microporous PANI	4.69	4.00	3.74	1.17	1.25	1.07	(88)
Undoped	N/A	N/A	N/A	N/A	N/A	53	(41)
Redoped	9	20	14,100	2	1560	700	
Doped	N/A	29	73	N/A	N/A	2.5	(79)
Undoped	N/A	30.2	283	N/A	N/A	9.4	
Redoped	N/A	30.6	436	N/A	N/A	14.2	
Undoped	1.59	0.172	N/A	N/A	N/A	N/A	(105)
Redoped	120	144	71,800	1	600	500	
Undoped	N/A	N/A	314	N/A	N/A	13.5	(104)
Redoped	N/A	N/A	N/A	N/A	N/A	N/A	
Polyimide	N/A	N/A	120	N/A	N/A	6.2	(63)
PANI (base)	N/A	N/A	240	N/A	N/A	9.1	
PANI/polyimide	N/A	N/A	270	N/A	N/A	10	
PANI_{Cl}	N/A	N/A	84.2	N/A	N/A	0.50	(75, 83)
$\text{PANI}_{\text{Cl dep}}$	N/A	N/A	224	N/A	N/A	0.17	
$\text{PANI}_{\text{ClO}_4}$	N/A	N/A	84.3	N/A	N/A	0.57	
$\text{PANI}_{\text{ClO}_4}$ dep	N/A	N/A	231	N/A	N/A	0.21	
PANI_{PTS}	N/A	N/A	93.2	N/A	N/A	0.83	
$\text{PANI}_{\text{PTS dep}}$	N/A	N/A	220	N/A	N/A	0.20	
$\text{PANI}_{\text{DBSA}}$	N/A	N/A	92.3	N/A	N/A	0.83	
$\text{PANI}_{\text{DBSA dep}}$	N/A	N/A	220	N/A	N/A	0.20	
Redoped	9	31	151	3.5	17	5	(88)
Cellulose	1.4	3.1	2.0	2.2	1.5	0.7	(61,88)
Polycarbonate	1.5	8.6	40.0	5.7	26.7	4.7	
Polybutadiene	0.3	N/A	6.5	7.2	21.4	3.0	
Polydimethylsiloxane	0.2	1.1	2.3	5.4	11.5	2.1	
LDPE	N/A	3.0	8.8	4.2	12.3	2.9	
HDPE	0.7	5.9	16.7	4.1	11.7	2.8	

N/A-Not available, dep-doped, Cl-chlorine.

membranes. Kaner et al. (83) reported the highest separation factors, while Anderson et al. (77) for various gaseous mixtures using redoped PANI membranes (see Table 1), which are higher than other polymer membranes studied. Table 2 documents the permeability data for different gaseous mixtures.

PERVAPORATION

Pervaporation (PV) is a membrane-based technique used for the separation and purification of liquid mixtures, azeotropes, etc., by using dense

Table 2. Comparison of permeability of PANI and modified PANI membranes for different gaseous mixtures

	Permeability (Barrers)						
Membranes	O_2	N_2	H_2	CO_2	CH_4	He	Ref.
PANI redoped	0.142	0.01	4.35	0.547	0.007	—	(79)
PANI undoped	—	0.016	4.53	0.568	0.011	—	(79)
PANI undoped	0.172	0.0032	10.6	1.59	0.608	11.5	(41)
PANI/PI blend (50:50)	0.282	0.027	7.40	1.281	0.015	—	(86)
$PANI_{Cl}$	0.004	0.008	0.650	—	—	—	(88, 75)
$PANI_{Cl\ dep}$	0.003	0.018	4.394	—	—	—	
$PANI_{ClO_4}$	0.004	0.007	0.590	—	—	—	(86)
$PANI_{ClO_4\ dep}$	0.004	0.019	4.395	—	—	—	
$PANI_{PTS}$	0.005	0.006	0.559	—	—	—	
$PANI_{PTS\ dep}$	0.004	0.020	4.400	—	—	—	
$PANI_{DBSA}$	0.005	0.006	0.554	—	—	—	
$PANI_{DBSA\ dep}$	0.004	0.020	4.408	—	—	—	
Polyimide	0.174	0.028	3.33	0.979	0.017	—	

polymeric membranes. The feed liquid diffuses through the membrane and vaporizes on the downstream side, where the applied pressure is much lower than the saturation vapor pressure. Recently, PV has received considerable attention in view of its environmentally benign nature and developments of newer membranes. The solution-diffusion model has been widely employed to study the mass transport in PV. The chemical potential gradient across the membrane is the driving force for mass transport, which is created by applying either vacuum or using an inert purge (normally air or gas stream) on the permeate side to maintain permeate vapor pressure lower than the partial pressure of the feed. Different liquids permeate through membranes at different rates, leading to the separation of a liquid component from the mixture. Separation characteristics of a membrane strongly depend upon its chemical properties and morphology. PV has been discussed at various lengths in the earlier literature, but the present review addresses the use of only PANI membrane in PV separation and purification applications.

PANI Membranes in Pervaporation

Since most liquids are in the same size regime as gases (2–10 Å), PANI can be used for liquid separation as well. It is well known that the undoped and doped forms of PANI have different chemical characteristics. For example, undoped form of PANI is hydrophobic, while doped form is hydrophilic.

Hence, doped PANI preferentially permeates water over organic acid like acetic acid.

Water-Acetic Acid Separation

Distillation is the most widely used primary unit operation process for acetic acid separation, but the products of distillation tower are the bottom streams of concentrated acetic acid and an overhead stream is ideally pure water. Efforts have been made to find suitable alternatives to solve this problem (1). Among them, azeotropic distillation was used, which involves the addition of a third component to distillation tower to improve the relative volatility of separation and thereby reduce the separation requirements. While this would help to reduce the operating costs, it adds to the environmental pollution problems (90, 91). Thus, from an energy savings point of view, PV is suitable as an alternative to azeotropic distillation. The membranes used for this purpose (92–99) are polymeric, which have failed often (100–105). While dehydrating acetic acid at higher temperatures, chemical and thermal resistance of the membrane is important (93).

To examine the effect of membrane thickness on permeation rate asymmetric PANI membranes have been used (50) in PV applications. PANI powder in its emeraldine-base form was dispersed in NMP with grinding. This PANI/NMP dispersion was poured into a petri dish and heated; it was then removed from the oven. After the dispersion had cooled to room temperature, about 5 mL of either methanol or toluene was added to petri dish to extract the residual NMP. Methanol or toluene was left in the petri dish for 3 min, after which the liquid was decanted. The petri dish was placed back in the oven and heated at 110°C for 1 h. The resulting asymmetric membrane was removed from the glass dish by soaking with water. After the film formation, a sample of the asymmetric PANI membrane formed was freeze-dried.

Huang et al. (68) used pure PANI membrane for the PV separation of water from carboxylic acids. These studies have been carried out with the doped (salt) and undoped (base) forms of PANI having different chemical characteristics. High selectivity ($\alpha = 1370$) from the doped PANI (salt) membrane for acetic acid/water mixtures have been reported (92). Doping interactions and high selectivity for water have increased due to the cooperative action of water as illustrated by the high selectivity of >1300 for 50:50 (wt.%) acetic acid/water mixture. To improve the relative low permeation rates (flux) obtained with the dense membranes (79 μm), asymmetric membranes (73 μm) have been developed and the rate of permeation through the asymmetric membrane (7.4 $g/m^2 \cdot h$) was higher than that of the dense membrane (3.9 $g/m^2 \cdot h$). The asymmetric membrane displayed somewhat lower separation factor (($\alpha_{H_2O} = 2.4$) as compared to dense membrane with a α_{H_2O} of 3.7. The ratio of asymmetric membrane selectivity (α_{asym}) to that

Table 3. Permeation rates (flux) and selectivities of water/acetic acid feeds for doped and undoped PANI membranes (50, 92)

Feed (wt.% of water)	Doped selectivity (α_{H_2O})	Flux (g/(m^2 · h))	Feed (wt.% water)	Undoped selectivity (α_{H_2O})	Water flux (g/(m^2 · h))
(a)					
0.0	N/A	0.000	0	N/A	3.560
12	4000	1.016	12.9	3.8	10.503
29.36	1600	3.359	19.4	2.7	7.936
47.62	1400	4.064	31.87	2	11.688
66.84	230	8.038	44.24	3	8.563
80.84	240	6.588	47.62	2.4	13.123
100	N/A	10.637	61.8	3.8	7.002
			81.25	23.0	2.351
			100		1.706
(b)					
44.44	180	0.21	44.44	2.50	0.41
48.00	2.7	0.70	N/A	N/A	N/A

N/A- Not available.

of intrinsic selectivity (α_{int}) as measured from the dense film i.e., $\alpha_{\text{asym}}/\alpha_{\text{int}}$ was 0.65, which indicates that membrane resistance of the porous PANI support plays a significant role in overall selectivity of the asymmetric membrane. With dense membranes of doped PANI, permeation rate ranged from 0 for conc. acetic acid to $>10\,\text{g}/(\text{m}^2 \cdot \text{h})$ for pure water. While permeation through undoped PANI membrane became slightly enriched with water, the selectivity of undoped PANI for water was low. Selectivities of doped PANI membranes are thus far superior to those of the undoped membranes. Permeation rates and selectivities of water/acetic acid feed for the doped and the undoped PANI membranes are summarized in Table 3(a).

Ball et al. (93) have tested PANI and their blend membranes for the separation of acetic acid, propionic acid and water/acetic acid feeds under different conditions. Permeation of formic acid through the undoped PANI membrane was not measured because PANI could swell more, due to its solubility in formic acid particularly, in the undoped form so that membrane would become porous. Permeability of acetic acid for 44.4/55.6 (w/w) water/acetic acid feed mixture through the undoped PANI membrane varied widely from a high value of 0.53 g/m^2.h to a low value of 0.04 g/m^2 · h ($P_{\text{ave}} = 0.3 \pm 0.2$ g/m^2 · h) [see Table 3(b)]. Composition of permeates after 76 h was 66 wt.% of water with $\alpha_{H2O} = 2.5$. The low permeability of water results from the undoped PANI, which is hydrophobic and reduced the solubility of water with an overall lowering of permeability to water in the undoped PANI membranes. Permeability flux of acetic acid through HCl-doped PANI approached zero; whereas water had comparatively higher permeability flux. This variation indicated that dopant leaching could have taken place in the feed solution as confirmed by separate experiments. Such a higher permeability flux of $P = 0.3\ \mathrm{g/m^2 \cdot h}$ for acetic acid in the undoped PANI membrane than water even though acetic acid (4.2 Å diameter) is significantly larger in size than water, is due to the hydrophobic nature of the membrane. Flux and selectivity from PV experiments reported in the literature for acetic acid/ water mixtures using different polymeric and inorganic membranes are compared in Table 3.

Temperature-dependent permeability on 50:50 (w/w) acetic acid: water mixture has been studied by Ball et al. (93) over the temperature range of 20° to 80°C. The permeation of water through doped PANI membrane increased from 10 to $70\ \mathrm{g/m^2 \cdot h}$. Conversely, the undoped PANI membrane gave 1.2 to $3.9\ \mathrm{g/m^2 \cdot h}$ between 20° to 90°C. Selectivity remained the same for doped PANI and it decreased slightly than that of the undoped PANI at these temperatures. However, high temperature operations did not change any physical characteristics of the membranes, considering the high thermal stability of PANI up to 425°C in nitrogen (94).

Kaner (83) studied the selectivity of water over that of carboxylic acid mixtures containing acetic acid, formic acid and propionic acid in feeds containing water. Water content of the permeant increased from 28 to 94 wt.% with a decrease in formic acid concentrations from 21.8 to 4.3 wt.%, acetic acid concentration from 26.6 to 1.1 wt.% and propionic acid concentration from 24.0 to 0.2 wt.%. Such a dramatic increase is due to the change in chemical nature of the doped and the undoped PANI membranes. Water transport through the doped PANI membrane was favored by a combination of favorable diffusion, water's small size and favorable solubility, resulting in the hydrophilicity of PANI induced by doping. Doped PANI effectively blocked larger carboxylic acid such as propionic acid, but smaller acid like formic acid, permeated to some extent. It was found that PV separation of all the three carboxylic acids from water confirmed that the doped PANI membrane was effective in blocking acetic and propionic acids. The permeability of carboxylic acids over water, despite their larger sizes than water, through the undoped PANI are highly sensitive to the morphology of PANI and high affinity between the undoped PANI and carboxylic acids. The difference in permeabilities through the undoped PANI and the HCl-doped PANI membranes was due to leaching of the dopant ions from the HCl-doped membranes. However, permselectivity was not affected by leaching in case of carboxylic acids.

Su et al. (62) studied the PV separation of acetic acid-water mixtures using PANI/polyimide blends in which polyamic acid was used as a polymeric dopant. The 25/75 ratio of PANI/polyimide blends in their imidized forms have shown higher permeability for 50:50 (w/w) acetic acid:water compositions, which was indeed higher than that observed for the pure PANI membrane. Selectivity of PANI/polyimide membrane has shown a higher magnitude than the undoped PANI. This could be due to possible interactions between the nitrogen-containing moiety of PANI backbone and oxygen of the other counterpart, which could reduce the free volume, resulting in higher selectivity than that of PANI. These interactions are displayed in Figure 4.

Alcohol-Water Separation

Ball et al. (60) studied the solubility of liquids using different PANI membranes through PV separation technology. The selectivity of doped PANI varied widely from membrane to membrane for 50:50 (w/w) of ethanol: water feed composition. The α values ranged between 1.7 and 17. The leaching effect of doped HCl into ethanol/water mixture resulted in a variable solubility as well as rate of permeation with time. The undoped PANI was impermeable to ethanol, but it displayed high selectivity ($\alpha_{H_2O} = 1100$) for water over that of ethanol. Permeate collected was 99.99% water for the same feed composition, but permeation rate was relatively lower. In order to overcome the leaching effect of the HCl-dopant, polymeric dopants have been used and blends of PANI with polyamic acid and acrylic acid have been tested. Blends were stable with linear fluxes and selectivities in between those of the doped and undoped PANI membranes. Also, the doped PANI showed highest intrinsic permeability of ~1.0 with a lowest value of 0.07 for the undoped PANI, whereas intermediate values were observed for PANI blend membranes as given in Table 4. Results for blends exhibited higher selectivity, but the leaching effect was avoided by replacing polymeric dopants.

Nanocomposite membranes of doped PANI nanoparticles dispersed in PVA have been used in PV separation of water-isopropanol feeds by Naidu

Table 4. Permeation rates and selectivities of water/ethanol feeds for different PANI membranes (60)

PANI membrane	Feed (wt.% of water)	Selectivity (α_{H_2O})	Permeability ($g \cdot mm/m^2$ h)
Doped PANI	50.0	1.717	1.0
Undoped PANI	49.9	>10,000	0.07
10% Polyamic acid/90% PANI	50.0	22	0.20
10% Polyacrylic acid/90% PANI	50.0	5.6	0.30

et al. (64). PV separation of feed mixtures with varying compositions ranging from 10 to 50 wt.% of water were performed. The membrane containing 40:60 surface atomic concentration ratio of PANI has shown a highest selectivity of 564. Time-dependent permeation experiments revealed a two-fold increase in flux by raising the temperature from 30° to 40°C with a considerable loss in selectivity from 564 to 181. The increase in flux over the studied temperature range was observed due to increased diffusion of feed molecules. However, in the complex nanocomposite membrane, slight changes in fractional free volume with increasing temperature resulted in an increased permeation flux.

Lee et al. (61) obtained a flux and water in the permeate of 300 $g/m^2 \cdot h$ and ~100 % water in the permeate with PAAc doped PANI membranes for the feed mixtures of water/isopropanol. The results suggested a strong interaction between PANI and PAAc polymers by complexation. When the amount of PAAc in the doped membrane was 20 wt.%, water concentration in the permeate decreased to 97 wt.%, while permeate flux increased to 200 $g/m^2 \cdot h$ due to the affinity of PAAc to water. As the water concentration in the feed mixture increases, amorphous region of the membrane swells, resulting in a flexible polymer with a decrease in energy required for the diffusive transport through PANI membrane. The temperature effect indicated that PANI/PAAc membranes followed the same general trends as observed for other polymer membranes. Thus, by increasing temperature, the permeate flux also increased, but permeate water concentration decreased.

Mirmohseni and Saeedi (95) studied the PV separation of nitric acid from the aqueous mixtures of nitric and phosphoric acids. Permeation rate for nitric acid was 1.21×10^{-10} mol/cm^2 h (approximately 0.004 $g/m^2 \cdot h$), while the permeation rate for phosphoric acid was essentially negligible. Investigations utilizing other conjugated polymers as membranes to separate liquid or ionic mixtures have been reported (78, 85). Poly-(3-methylthiophene) and poly(*N*-methylpyrrole) membranes have been used to separate acetone/water, 2-butanol/water and 2-butanol/heptane feed mixtures. Doping poly(3-methylthiophene) with perchlorate ions gave a two-fold increase in the permeation rate of acetone (from ~70 to ~180 mL/min). However, an opposite behavior was observed for poly(*N*-methylpyrrole) for which the permeation rate was higher in the undoped form. The rates of transport of methanol and methyl-*t*-butylether using thin films of polypyrrole, poly(*N*-methylpyrrole) and PANI have also been reported (72). Polypyrrole films did not show any separation capability; but, both poly(*N*-methylpyrrole) ($\alpha = 3.9$) and PANI ($\alpha = 4.9$) have shown the modest separation abilities. Electrochemically synthesized PANI and polypyrrole films have been used in PV separation studies to separate methanol/water mixtures (96). Permeation rates of methanol and water were larger for oxidized PANI membranes than for the reduced PANI. Conversely, methanol had a higher permeation rate in the reduced (undoped) form of polypyrrole than that in its oxidized form (96).

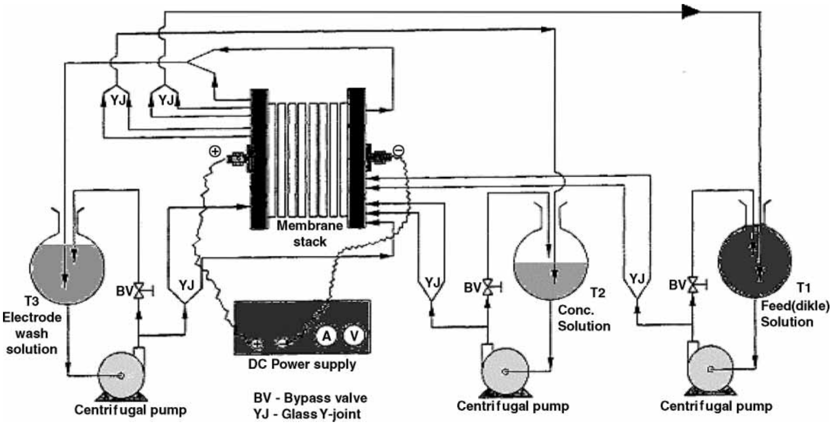


Figure 7. Schematics of our indigenously developed ED pilot plant.

PANI AS MEMBRANE IN ELECTRODIALYSIS

Electrodialysis (ED) is a membrane-based electrochemical separation process in which ionic species are transported across ion-selective (permeable) membranes from one compartment to another under the influence of an electrical potential gradient. Electrical charges on the ions allow them to be driven through the membranes fabricated from ion-exchange polymers, since membranes used in ED have the ability to selectively transport ions having positive or negative charges and reject ions of opposite charges. In a typical ED stack shown in Figure 7, cation and anion-selective membranes are alternately arranged in stacks to form diluate and concentrate compartments between the membrane pairs. Electrodes are placed at the extremes of the stack, which are in contact with the electrode rinse solution continuously. When a potential difference is applied between both the electrodes, cations migrate through cation-exchange membranes, which have negative fixed groups, while they are retained by anion-exchange membranes. Anion-exchange membranes allow only anions to pass through and the cation-exchange membrane retains these. The increasing utilization of ED technique in the treatment of industrial wastewater or effluents/discharges is due to the developments in newer types of ion-exchange membranes and modifications of the existing commercial membranes to improve their transport properties.

PANI Membranes in Electrodialysis

In ED, the presence of PANI layer on the surface of commercial sulfonated cation exchange membranes (PANI-modified CMX) (97) led to an improved selectivity for several divalent and monovalent cation species. To study the effect of polymerization time, single face modification was carried out in a two-compartment cell made of Teflon containing 40 mL of reagents in one compartment and 40 mL of water in the other. The first step consisted of exchanging protons that are initially present in CMX membrane with anilinum species using 10% (v/v) aniline in 1M HCl solution added in the reagent compartment, while stirring for 1 h at room temperature. In the second step, polymerization was induced by replacing aniline solution with 1 M $(NH_4)_2S_2O_8$ aqueous solution and stirring for various times at room temperature. The cell was rinsed with water between both steps. Before use, the composite membranes were conditioned in 1M HCl aqueous solutions for 40 h or longer to ensure the complete protonation of PANI. The modified membranes were identified as P*X*-*Y*; P for PANI, *X* for time (h) of immersion in 10% (v/v) aniline solution (1 h in most cases), and *Y* for time (h) of polymerization. Polymerization time is the time required for which the membrane is in contact with the oxidant, or it could also imply degradation. The idealized structure of CMX-PANI composite is shown in Figure 8.

In ED, the presence of PANI layer at the surface of commercial sulfonated cation-exchange membranes (Neosepta) led to improved selectivity for specific ion transport. Permselectivity of this composite membrane (Neosepta CM-1-PANI) for Na^+ in the presence of Ca^{2+} ions for electrodialysis in neutral solutions was reported by Sata and Yang (98). They demonstrated that Zn^{2+} and Cu^{2+} ion leakage can be reduced by a factor of at least 20 for ED using PANI-modified CMX membrane as compared to the virgin Neosepta CMX membrane. These data showed that the time required for H^+ ions within

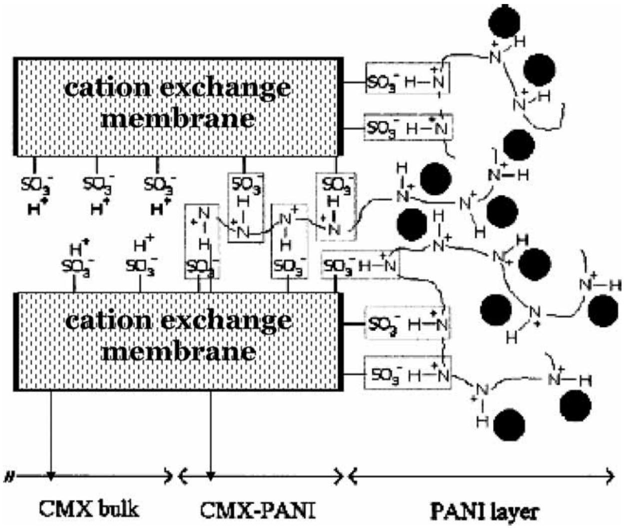


Figure 8. Idealized schematic structure of CMX-PANI composite membrane (97).

the membrane to exchange with anilinum species in 10% (v/v) aniline and 1 M HCl solution. Based on the experimental results, the modification of membranes and ED methods have been proposed and practiced in the literature.

Tan et al. (97) modified the commercial sulfonated cation-exchange membranes by polymerizing a thin layer of PANI in the presence of high oxidant concentration on a single face of a sulfonated cation-exchange membrane. A decrease in membrane ion-exchange capacity (IEC) was observed due to the presence of cationic PANI acting as counterions for sulfonate groups of the membrane at a maximum PANI loading. For longer polymerization times, degradation of PANI layer at the surface was demonstrated. Optimum membrane permselectivity for protons against the bivalent metallic cations viz., Zn^{2+} and Cu^{2+} was found. A three-layer model for the most permselective CMX-PANI composite membrane was proposed based on XPS and IEC data. The outer layer was constituted with a positively charged PANI doped with the chloride ions. The fixed sulfonate groups of the CMX as shown in Figure 8 compensated the intermediate layer of the positively charged PANI.

Amado et al. (65) prepared membranes using high impact polystyrene and PANI for use in ED. These membranes exhibited an initial degradation at 230°C and have a high mechanical resistance. These membranes also showed a good chemical stability in acidic and alkaline media. When dipped in strong oxidant media, loss in mechanical resistance was observed due to chromium absorption by the membrane. PANI-camphorsulfonic acid and PANI-*p*-toluene sulfonic acid membranes exhibited a good zinc ion transport as well as extraction compared to the Nafion-450 commercial membrane. PANI-camphorsulfonic acid membrane was swollen more than other membranes with PANI, demonstrating its usefulness in ion transport. On the other hand, PANI-dodecylbenzenesulfonic acid membrane had a low transport number for Zn^{2+} ions, even with a low electrical resistance, probably due to the fact that functional groups have excessively scattered within the polymer matrix. However, low values of transport numbers for CN^- and $Zn(CN)_4^{2-}$ anions demonstrated its excellent selectivity. For instance, zinc transport in cationic form is an evidence of good selectivity for PANI-*p*-toluenesulfonic acid and PANI-camphorsulfonic acid membranes, while low selectivity was observed for PANI-dodecybenzenesulfonic acid membrane. Dodecybenzenesulfonic acid-doped PANI/HIPS membrane demonstrated a high IEC than other doped PANI systems, even though camphorsulfonic acid-doped membrane had higher swelling in the presence of a hydrophilic SO_3 group. This was due to higher dimensional stability of the system.

CONCLUSIONS

PANI has great many potential advantages as a membrane material in separation and purification technologies. Many researchers working in this area have attempted to improve the permeation properties of PANI membranes by adapting to various chemical processes. However, the number of advantages of using PANI as a membrane material are innumerable compared to the conventional polymeric membranes, especially in terms of selectivity, flux as well as thermal and chemical stability. Comparing the membrane separation characteristics of PANI and several of its modified membranes with those of a large number of polymeric materials, it is apparent that PANI membranes have an appropriate combination of gas separation selectivity and permeability for most gases, liquids and electrolyte solutions. Literature in this area is huge and is still accelerating at a rapid rate to compete with other conventional type polymeric membranes or modules. Variation of the oxidation state of PANI as a membrane results in changes of the whole spectrum of chemical, physicochemical properties and a host of potential applications that would arise due to the presence of various redox states from its interconversions. In addition, charge transfer interactions taking place in PANI have been a matter of great academic interest.

Overall, the present review emphasizes that PANI membranes are effective in gas and neutral solute separations as well as electrolyte solutions. However, selectivity of PANI is based on the precise control of its morphological changes due to oxidation-reduction and protonation-deprotonation processes. Recently, the application of PANI as a coating material in other filtration techniques such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis in different ceramic modules is an upcoming area of research, which needs to be pursued vigorously. Different types of spiral-wound or tubular modules of ceramic nature can be attempted for coating with PANI. More opportunities are possible on PANI or PANI modified coated membranes over the ceramic supports in more intricate separation and purification problems. The exploitation of this type of approach will offer greater challenges for the benefit of future researchers working in this fascinating area. Polyaniline can also be used as a surface pore modifier for different ceramic modules, which can be used in various filtration processes mentioned here. However, no such data are available on these aspects.

ABBREVIATIONS

BDTA	3,3′,4,4′-benzophenonetetracarboxylic acid
ClO_4	Perchlorate ion
CMS	Carbon molecular sieves
CMX	Commercial sulfonated cation-exchange membrane
DBSA	Dodecylbenzenesulfonic acid
DEHPA	Diethylhexylphosphoric acid
DMPPV	Poly(dimethoxy-para-phenylene-vinylene)
DMPPV	Poly(dimethoxy-*p*-phenylenevinylene)

DMPU	1,3-Dimethyl-3,4,5,6-tetrahydro-2 (1H)-pyrimidinonePE-Polyethylene
DMSO	Dimethylsulfoxide
EB	Emeraldine base
ED	Electrodialysis
ES	Emeraldine salt
ESR	Electron spin resonance
FD	Fully doped
GS	Gas separation
HIPS	High impact polystyrene
IPA	Isopropanol
NMP	N,N'-Dimethyl pyrrolidone
ODA	4,4′-Oxydianiline
OMS	Organic molecular sieve
PAAc	Polyacrylic acid
PANI	Polyaniline
PET	Poly(ethyleneterephthalate)
PI	Polyimide
PPV	Polyphenylene vinylene
PPY	Poly(*N*-methylpyrrole)
Ppy	Polypyrrole
PS	Polystyrene
PTMSP	Poly(trimethylsilylpropyne)
PTSA	*p*-Toluenesulfonic acid
PVDF	Poly(vinyledinefluoride)
PV	Pervaporation
PVTMS	Poly(vinyltrimethylsilane)
SN	Poly(sulfur nitride)
SPANI	Sulfonated polyaniline

ACKNOWLEDGMENTS

The authors (Professor T.M. Aminabhavi, Dr. M. Sairam and S.K. Nataraj) thank University Grants Commission (UGC), New Delhi, India for major funding (Grant No: F1-41/2001/CPP-II) to establish Center of Excellence in Polymer Science (CEPS) at Karnatak University, Dharwad. Part of this work is a result of consultation project between BHEL and CEPS. We also thank Mr. G. Swaminath, AGM., BHEL, Bangalore, India.

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