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# Functionalized polyaniline-based composite membranes with vastly improved performance for separation of carbon dioxide from methane

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## ABSTRACT

Polypropylene supported polyaniline membranes photografted with 2-hydroxyethyl methacrylate and glycidyl methacrylate to produce hydrophilicity and reactivity and then reacted with diamines to provide basicity, have been prepared and used for the separation of carbon dioxide and methane. After solvation with water, these membranes exhibited a permeability of around 3400 Barrers and a separation factor up to 490. Examination by scanning electron microscopy and atomic force microscopy confirmed the absence of undesired cracks and pinholes in these membranes. The primary amine groups were further modified with 2-ethyl-2-thiopseudourea to form guanidine functionalities producing membranes with a notable permeability of 3460 Barrers and a separation factor of 540. The presence of water in these membranes promotes permeation of carbon dioxide via the facilitated transport mechanism in which both the fixed carrier amine moieties and water play the major role.

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## 1. Introduction

With the high price of oil, the abundance of cheap natural gas appears to represent a cleaner and less costly fuel alternative. Raw natural gas as it exits the well is called “sour gas”, contains up to 90% methane and other higher hydrocarbons, but has other “problematic” components which make it corrosive and more expensive to transport. As a result, sour gas must be processed using a method called “sweetening” before use. Sour gas contains acidic gases such as hydrogen sulfite, which smells and can be harmful, and carbon dioxide that decreases the overall energy content of the gas and makes it more expensive to transport. Additionally, when these acidic gases are exposed to water, they form acids that are highly corrosive to pipelines. Therefore, one of the most important parts of natural gas processing, involves the removal of these acidic gases, which contains sulfur compounds and carbon dioxide. Typically, after sweetening, natural gas contains no sulfur and less than 2 wt% carbon dioxide [1].

The three most common technologies used for the removal of carbon dioxide from sour gas are: (i) “scrubbing”, a process in which the gas is passed through amine solutions which absorb the carbon dioxide, (ii) adsorption, a process in which the gas is absorbed into solids including metal oxides, activated carbon, zeolites, and metal-organic frameworks, and (iii) cryogenic separation [2].

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Membrane-based technologies have also been proposed as an alternative to the common processing methods, all of which are energy intensive and costly [3]. Unfortunately, current membranes have limitations that hinder their wide use for the removal of CO<sub>2</sub>. For example, polymer-based membranes, which rely on a simple solution-diffusion permeation mechanism, often suffer from the trade-off between permeability and selectivity. Many industrial units designed with cellulose acetate membranes or polyimide exhibit a modest selectivity of 12–15 and 20–25, respectively, and cannot compete with the classical amine absorption [4]. This problem has been clearly demonstrated by Robenson's plots summarizing a large quantity of data from various literature. His work led to the concept of the empirical upper bound relationship for membrane separation of gases [5,6]. Thus, in order to use large-scale membrane units for separation of CO<sub>2</sub> new types of membranes affording *both* high selectivity and permeability, i.e. membranes possessing properties above the upper bound, must be developed [7].

Membranes enabling facilitated transport in which the separation includes a reversible chemical reaction, appear to provide a solution to the problems of conventional membranes. This approach originates from early work with liquid films used as a carrier [8]. Although this technology provided for both very high permeability and good selectivity, the use of mobile carriers was less practical. Therefore, new membrane-forming polymers for the separation of CO<sub>2</sub> had to be designed that incorporate carbon dioxide-philic functionalities that serve as fixed carriers [4,9]. The mechanism of the facilitated transport has been studied previously and is well described in Ref. [9]. Using this concept,

Hu et al. grafted polyethylene glycol onto ionic polymers poly(4-vinylbenzyltrimethylammonium tetrafluoroborate) and poly[2-(methylacryloyloxy) ethyl-trimethylammoniumtetrafluoroborate] and obtained membranes with good permeability and selectivity for CO<sub>2</sub> [10]. Lau et al. prepared membranes with enhanced selectivity for CO<sub>2</sub> permeation from a polyalkoxysilane and polyetherdiamine [11]. Membranes prepared from a copolymer of 2-*N,N*-dimethylaminoethyl methacrylate [12] as well as those prepared by polycondensation of 3,3'-diamino-*N*-methyl-di-propylamine and trimesoyl chloride [13] also exhibited high permeation ability for CO<sub>2</sub>. These examples selected from many others in current literature clearly demonstrate the positive effect of basic nitrogen-containing functionalities on facilitation of CO<sub>2</sub> transport.

Well performing membranes were also prepared using polyaniline (PANI) nanoparticles embedded in polyvinylamine [14]. We also selected PANI for our initial study due to the readily available monomer, excellent stability, simple scalable preparation, potential ability to form homogeneous thin layers, and compatibility with other polymers [15]. By varying the polymerization conditions, we optimized the in situ deposition technique that enabled formation of defect-free composite membranes combining polyaniline as an active layer with a porous polypropylene support. We also illustrated their potential in separation of CO<sub>2</sub> from its mixture with methane. While these membranes in dry state have a poor permeability and no appreciable selectivity for carbon dioxide over methane, their hydration with water helped to improve selectivity. However, the weak basicity and limited hydrophilicity of PANI were obstacles that prevented our membranes to achieve separation properties comparable with materials used by others [6]. In this report, we demonstrate that functionalization of the PANI-composite membrane using photografting with hydrophilic and reactive monomers, followed by chemical modification leading to more basic immobilized functionalities produces highly permeable membranes that readily adsorb water and significantly facilitate selective transport of CO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

Aniline hydrochloride and ammonium peroxydisulfate (APS) were obtained from Alfa Aesar (Ward Hill, MA, USA) and cystamine hydrochloride was purchased from Fluka (Buchs, Switzerland). Glycidyl methacrylate, 2-hydroxyethyl methacrylate, 1,4-dioxane, ethylenediamine, hexamethylenediamine, 2-ethyl-2-thiopseudourea hydrobromide and Dulbecco's phosphate buffered saline (D 8537) were obtained from Aldrich (St. Louis, MO, USA). Microporous polypropylene film Celgard 2400 with a thickness of 25 μm and an average pore size of 43 nm was kindly supplied by Celgard, Inc. (Charlotte, NC, USA).

### 2.2. Membrane preparation

#### 2.2.1. Composite polyaniline-polypropylene membranes.

Composite membranes combining polyaniline as an active layer with polypropylene support were prepared using an in situ deposition technique. The polymerization reaction was carried out with aqueous solutions of aniline hydrochloride (0.2 mol/L) and ammonium peroxydisulfate (0.25 mol/L). The reaction mixture was prepared by combining the monomer and oxidant solutions at 5 °C. The mixture was then poured onto the surface of the porous support film pre-wetted with methanol and placed in a simple device described elsewhere [15]. The polymerization time of 2 h afforded a thin polyaniline layer on the top of the support. This membrane

was then washed with 0.2 mol/L aqueous hydrochloric acid to remove the adhering polyaniline precipitate, and then dried in air. Finally, the protonated polyaniline was converted into an emeraldine base by treating with an excess of 0.1 mol/L ammonium hydroxide.

The absence of structural defects of these films was confirmed with failed attempts to push methanol through the membranes at a pressure of up to 0.1 MPa.

The average molecular weight of 32,000 for our polyaniline was estimated from the published linear correlation between PANI film thickness and weight average molecular mass [16]. Direct measurement of molecular weight of polyaniline in our membranes was not possible, since the amount of polyaniline in the layer ca. 150 nm thin is insufficient for size exclusion chromatography.

### 2.3. Chemical modification of polyaniline composite membranes

#### 2.3.1. Photografting of glycidyl methacrylate and 2-hydroxyethyl methacrylate

The PANI-composite membrane was wetted with a solution containing 25% glycidyl methacrylate, 25% 2-hydroxyethyl methacrylate and 50% *t*-butyl alcohol–water mixture (3:1). The wetted PANI layer was covered with a quartz plate the surface of which was treated with fluorinated silane to avoid adhesion to the membrane, and exposed to UV light at 360 nm for 15 min. After completion of the UV exposure, the membrane was immediately immersed in 1,4-dioxane for about 1 h to dissolve all soluble polymers at its surface, then washed with methanol, and dried.

#### 2.3.2. Functionalization with diamines

The PANI layer, photografted with poly(glycidyl methacrylate-co-2-hydroxyethyl methacrylate), was further modified via reaction of epoxy groups with diamines according to the scheme shown in Fig. 1a. The membranes were immersed at room temperature for 3 h in a 2 mol/L aqueous solution of ethylenediamine, hexamethylenediamine, and 1 mol/L cystamine (cystamine hydrochloride was dissolved in 10 mol/L sodium hydroxide solution).

#### 2.3.3. Functionalization with 2-ethyl-2-thiopseudourea

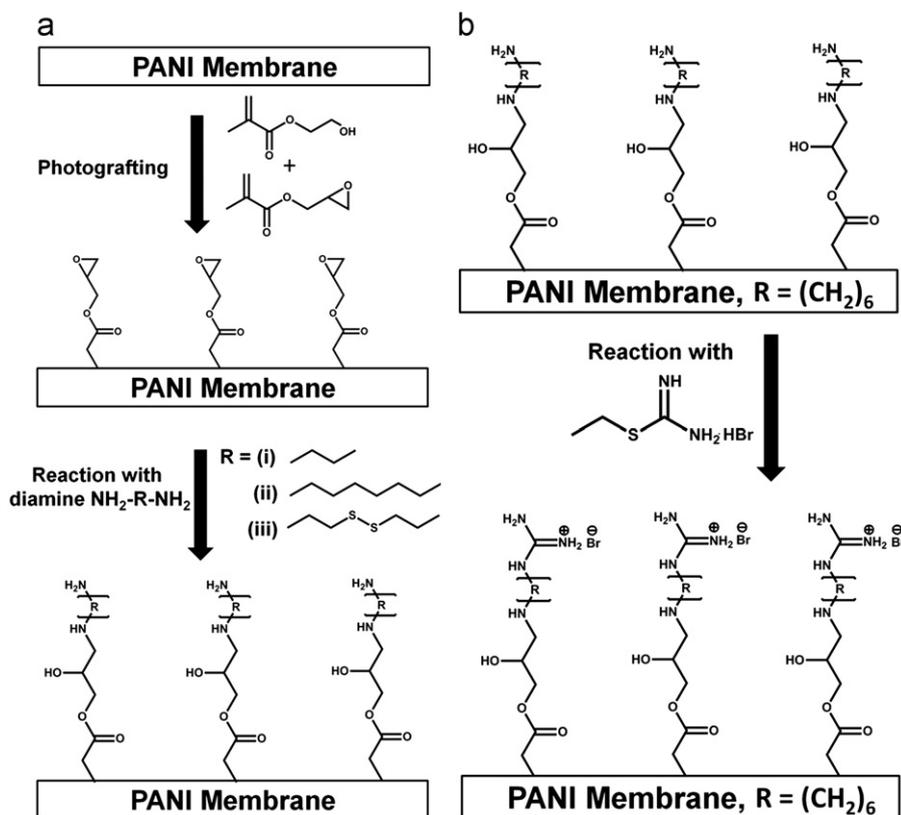
The composite polyaniline membrane, modified with hexamethylenediamine, was placed in the solution of 20 mg/mL 2-ethyl-2-thiopseudourea hydrobromide in Dulbecco's phosphate buffered saline pH 7.4, and kept at 70 °C for 3 h to afford guanidine functionalities (Fig. 1b). The functionalized membrane was then washed with methanol and dried under vacuum.

#### 2.3.4. Determination of composition

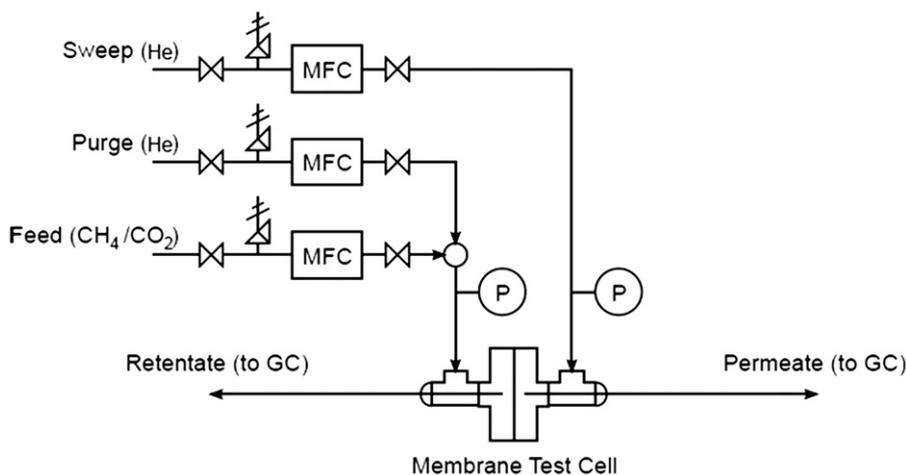
X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition of the functionalized PANI-composite membranes. A PHI 5400 ESCA system (PerkinElmer, Waltham, MA, USA) including an Al anode (primary photon energy of 1486.6 eV) and a X-ray source with a power of 150 W (15 kV at 10 mA) was used for all XPS measurements. Membranes were dried prior these measurements at 100 °C for 48 h.

### 2.4. Gas permeation

All membranes were tested for the separation of carbon dioxide from its mixture with methane (natural gas surrogate) using a home-built system shown schematically in Fig. 2 to evaluate permeability and selectivity. Steady state performance measurements were made in a flow system in which the permeate and retentate gas compositions were determined using a Model 8610C gas chromatograph (SRI International, Menlo Park, CA, USA) equipped with a 1.8 m long packed CTR column (SRI International)



**Fig. 1.** Scheme of functionalization of the polyaniline membrane first photografted with glycidyl methacrylate and 2-hydroxyethyl methacrylate and then reacted with diamines (a); as well as additional functionalization of membrane containing hexamethylenediamine with 2-ethyl-2-thiopseudourea (b).



**Fig. 2.** Experimental setup for measurement of permselectivity of membranes.

and a thermal conductivity detector. The feed gas flow was controlled by a mass flow controller (Brooks Instrument, Hatfield, PA) and the exiting flows were measured with a digital flow meter. The pressures at permeate and retentate sides were measured with pressure gauges. The feed and the sweep gas rates were kept at 10 and 2  $\text{cm}^3/\text{min}$ , respectively. The PANI-composite membranes 25 mm in diameter were mounted in a permeation cell with an effective area for permeation of 2.01  $\text{cm}^2$ . The feed gas consisted of 90% methane and 10% carbon dioxide. Helium was used as a sweep gas and was passed over the permeate side of the membrane. The total operating gas pressure was approximately 128 kPa for the feed and less than 100 kPa for the permeate. After introduction

of the feed, the system was allowed to reach a steady state. All mixed gas tests were performed at room temperature.

The permeability coefficient of individual components in the gas mixture passing through the membrane was obtained by using

$$P_{\text{CO}_2} = x_{\text{CO}_2}^{\text{p}} S l / x_{\text{He}}^{\text{p}} A \Delta p_{\text{CO}_2} \quad (1)$$

where  $P_{\text{CO}_2}$  is the permeability of carbon dioxide,  $x_{\text{CO}_2}^{\text{p}}$  is the molar fraction of carbon dioxide in the permeate stream,  $S$  is the helium sweep gas flow rate (2  $\text{cm}^3/\text{min}$ ),  $l$  is the thickness of selective layer,  $x_{\text{He}}^{\text{p}}$  is the molar fraction of helium in the permeate stream

calculated as  $x_{\text{He}}^p = 1 - x_{\text{CO}_2}^p - x_{\text{CH}_4}^p$ ,  $A$  is the area of the membrane (2.01 cm<sup>2</sup>), and  $\Delta p_{\text{CO}_2}$  is the partial pressure difference of carbon dioxide across the membrane. The permeability  $P$  is reported in Barrer units (1 Barrer = 10<sup>-10</sup> cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cmHg or 3.348 × 10<sup>-19</sup> kmol m/m<sup>2</sup> s Pa).

The separation factor  $\alpha$  is given by

$$\alpha_{\text{CO}_2/\text{CH}_4} = (y_{\text{CO}_2}/y_{\text{CH}_4})/(x_{\text{CO}_2}/x_{\text{CH}_4}) \quad (2)$$

where  $x$  is the molar fraction of each gas on the feed side and  $y$  the molar fraction of each gas on the permeate side determined from gas chromatography measurements. The value in denominator  $x_{\text{CO}_2}/x_{\text{CH}_4} = 0.11$  remains constant in all experiments.

### 2.5. Microscopic imaging

The surface morphology of the films was imaged using an analytical scanning electron microscope Ultra-55 (Carl Zeiss, Peabody, MA, USA). A 20 nm thin layer of gold was sputtered onto the film surface before imaging. The thickness of the PANI film was estimated from scanning electron microscopy (SEM) images of cross sections acquired with membranes broken in liquid nitrogen. Atomic force microscopy images were obtained using the SmartSPM instrument (AIST-NT, Inc., Novato CA, USA) in semicontact mode.

### 2.6. Water content and contact angle

Dry membranes with known weight were immersed in water for 24 h. After the saturation, they were removed from water, the film surface was wiped with a paper tissue for a certain period of time, and the membranes were weighed again. The water content  $W_c$  in the membrane expressed as g water/g polymer was calculated using

$$W_c = (W_h - W_d)/W_d \quad (3)$$

where  $W_h$  and  $W_d$  are the weight of hydrated and dry membranes, respectively.

Easy Drop Goniometer (Krüss GmbH, Germany) was used to determine the contact angle of a water droplet with a volume of 2  $\mu$ L placed on the film surface. The measurements were carried out in air at room temperature. All reported contact angles are an average of at least five measurements taken at different locations on the polymer surface.

## 3. Results and discussion

Our initial generic PANI membranes failed to exhibit any noteworthy selectivity and permeability for carbon dioxide in the dry state and a certain improvement was observed after wetting the PANI surface with water [15]. More specifically, permeability and selectivity for CO<sub>2</sub> found for these dry composite PANI membranes at ambient temperature were 155 Barrers and 1.1, respectively. The values for the wet membrane were then 3.89 Barrers and 15 (Table 1). Clearly, these conventional membranes, which permselectivity relies solely on solution-diffusion mechanism, are not suitable for any real-life application.

As an alternative to conventional polymeric membranes, membranes enabling facilitated transport have attracted significant attention because of the potential for achieving both high permeabilities and selectivities. The selective permeation of CO<sub>2</sub> through such membranes is achieved via a reversible reaction of CO<sub>2</sub> with the help of a carrier immobilized within the membrane, whereas gases such as H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> do not react and permeate exclusively by means of the much less efficient solution-diffusion

mechanism. Therefore, we decided to functionalize the PANI membranes to achieve facilitated transport.

### 3.1. Preparation of functionalized membranes

The “classical” facilitated transport mechanism includes the reaction of CO<sub>2</sub> with water forming the bicarbonate anion that is transported across the membrane [9]. Indeed, we observed in our preliminary experiments an improvement in CO<sub>2</sub> transport when the PANI membrane was wetted with water [15]. However, a contact angle of 65° measured for water at the emeraldine base PANI film surface indicated its hydrophobicity and seriously limits the amount of water that can be accommodated within the membrane. Therefore, the first step towards the development of an efficient PANI membrane was to decrease the hydrophobicity. In an unrelated project, we have developed a simple technique for photografting polymer surfaces with a variety of monomers which result in significant changes in polarity [17,18]. Here, we chose 2-hydroxyethyl methacrylate (HEMA) as a monomer enhancing hydrophilicity of the PANI membrane. In order to allow further chemical modifications of the membranes, we mixed HEMA with glycidyl methacrylate (GMA) that provides reactive epoxide functionalities. Although not very hydrophilic by itself, this functionality forms hydrophilic moieties after its reaction with nucleophiles such as amines. Due to the reactive nature of conjugated polyaniline, no pre-activation of the membrane or addition of a photoinitiator in the monomer mixture is required to achieve efficient surface modification via photoinitiated grafting [19].

The next step was to react the photografted surface with diamines, by which aliphatic amine functionalities increase basicity of the membrane and positively contribute to facilitated transport. Fig. 1a illustrates both photografting of the PANI membrane and reaction with three different diamines including ethylenediamine, hexamethylenediamine, and cystamine.

A further increase in basicity was then achieved by reaction of the free primary amine groups of the membrane modified with hexamethylenediamine with 2-ethyl-2-thiopseudourea affording guanidine functionalities as shown in Fig. 1b. Goniometric analysis confirmed the hydrophilic nature of the membrane after these functionalizations. The contact angles shown in Table 2 are close to 30° and demonstrate the desired increase in hydrophilicity of the membrane

**Table 1**

Gas transport properties of wet composite PANI membranes containing various functionalities.

Functionality	Permeability coefficient for CO <sub>2</sub> Barrer	Separation factor $\alpha$ CO <sub>2</sub> /CH <sub>4</sub>	$\Delta p_{\text{CO}_2}$ <sup>a</sup> (kPa)
None (emeraldine base PANI)	3.89	15	8.09
Ethylenediamine	3410	374	8.32
Hexamethylenediamine	3400	438	8.31
Cystamine	3470	488	8.29
Guanidine	3460	540	8.29

<sup>a</sup> Partial pressure difference of carbon dioxide across the membrane.

**Table 2**

Contact angles of composite PANI membranes containing various functionalities.

Functionality	Contact angle (°)
None (emeraldine base PANI)	65
Ethylenediamine	30.5
Hexamethylenediamine	27
Cystamine	26
Guanidine	29

surface. The functionalization of the surfaces was also confirmed by XPS analysis. Table 3 shows the elemental composition of the surface layer of these membranes. As expected, membranes containing

**Table 3**

Chemical composition of surface of functionalized polyaniline membranes determined using XPS quantitative analysis.

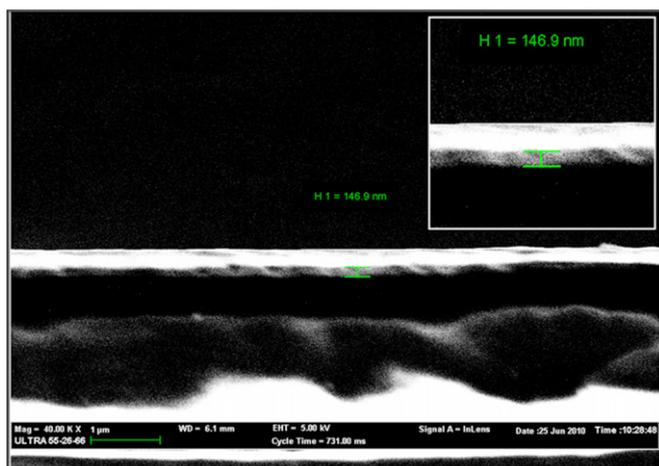
Functionality	Oxygen (at%)	Carbon (at%)	Nitrogen (at%)	Sulfur (at%)
None (emeraldine base PANI)	34	61.5	4.4	–
Photografted	28.3	66.1	5.6	–
Ethylenediamine	20.9	72.2	6.9	–
Hexamethylenediamine	20.0	74.0	5.9	–
Cystamine	28.2	60.0	8.9	2.3
Guanidine	21.8	68.6	9.6	–

guanidine functionalities include the highest percentage of nitrogen. A XPS scan of the plain emeraldine base PANI films reveals the presence of oxygen that may originate from partial oxidation of the film surface or from complexed oxygen [20].

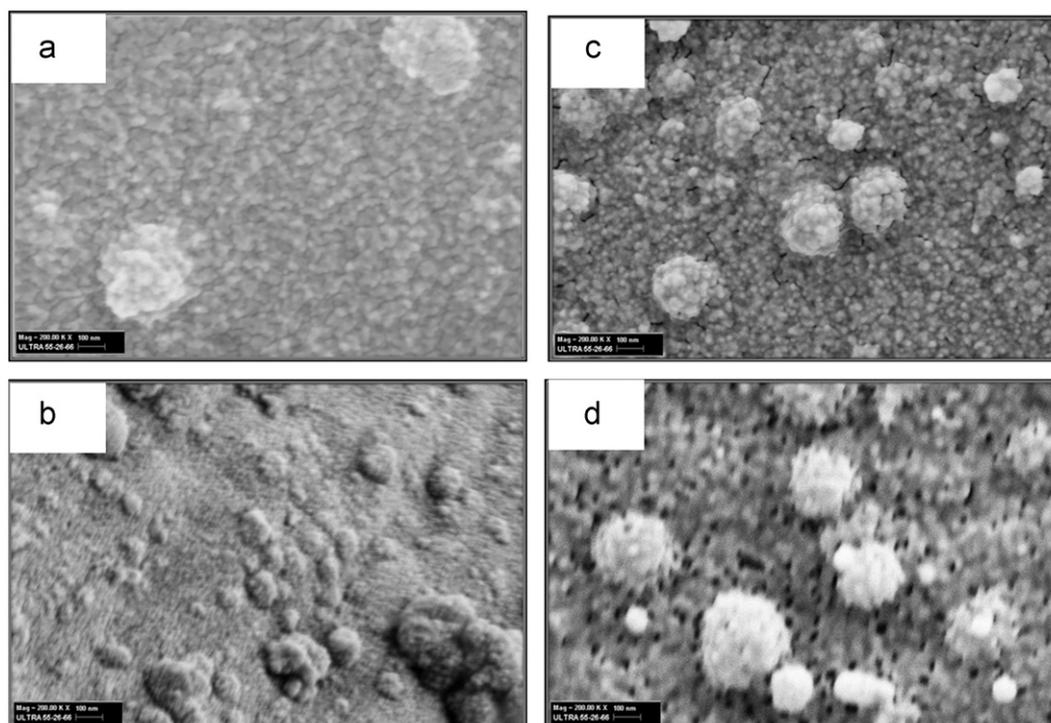
### 3.2. Imaging membrane surface

The separation performance of a membrane is determined by both its chemical structure and morphology. Therefore, special attention has to be paid to the completeness of coatings, its integrity, and the absence of defects. Fig. 3 shows the SEM image of the cross-section of a supported PANI membrane that consists of two layers. The top layer is the dense active PANI layer, which enables separation, while the bottom layer is the polypropylene support, which provides for mechanical strength. The thickness of that PANI layer is 147 nm. The scanning electron micrographs in Fig. 4 shows surface morphology of the original polyaniline film prepared by precipitation polymerization at 5 °C, and after modification with cystamine, hexamethylenediamine, and additional treatment with 2-ethyl-2-thiopseudourea. All membranes exhibit a globular morphology with some precipitated PANI particles adhering to the surface. The average size of the globules is 55 nm for parent PANI film and 56 nm for PANI film modified with hexamethylenediamine. The surface of the parent membrane and those modified with diamines remains smooth with no significant changes resulting from the modifications. The surface roughness is about 20 nm. In contrast, a significant increase in size of the globules to 130 nm is observed for membrane containing the guanidine functionalities indicating changes in the morphology resulting from the additional reaction and leading to more massive aggregation of globules.

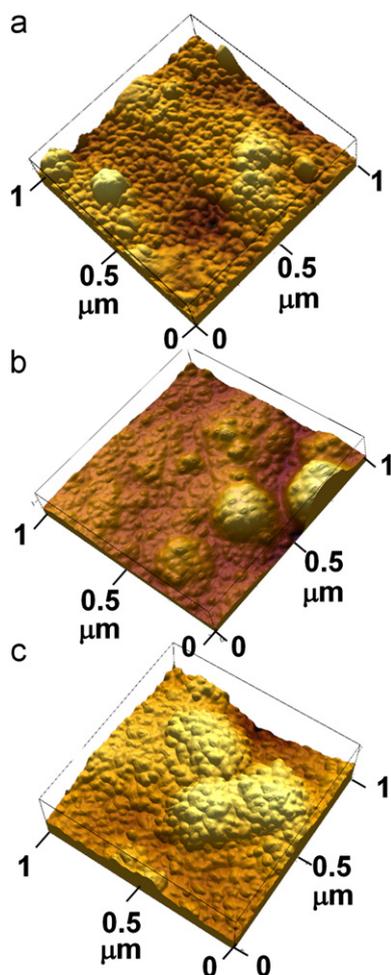
Similar granular patterns of surface morphology were also observed using an AFM. The images of polyaniline membranes shown in Fig. 5 presents a relatively smooth and regular structure consisting of small clusters distributed over the entire scanned area. Table 4 shows the root-mean square roughness and mean



**Fig. 3.** Cross-section SEM micrographs of PANI-composite membrane.



**Fig. 4.** SEM micrographs of original PANI film, after modification with cystamine (b), hexamethylenediamine (c), as well as with hexamethylenediamine and 2-ethyl-2-thiopseudourea (d).



**Fig. 5.** Topographic AFM images of original polyaniline layer (a), after photografting with glycidyl methacrylate and 2-hydroxyethyl methacrylate followed by modification with hexamethylenediamine (b), and with hexamethylenediamine and 2-ethyl-2-thiopseudourea (c). The size of scanned window is  $1 \times 1 \mu\text{m}$ .

**Table 4**  
Mean roughness  $R_a$  and root-mean square roughness  $R_{\text{rms}}$  determined from AFM images for polyaniline films before and after modification.

Functionality	$R_a$ (nm)	$R_{\text{rms}}$ (nm)
None (emeraldine base PANI)	20.6	26.22
Hexamethylenediamine	15.20	21.53
Guanidine	39.74	48.98

roughness for PANI films before and after modification. Once again, a significant increase in both values is observed after surface modification leading to guanidine functionalities.

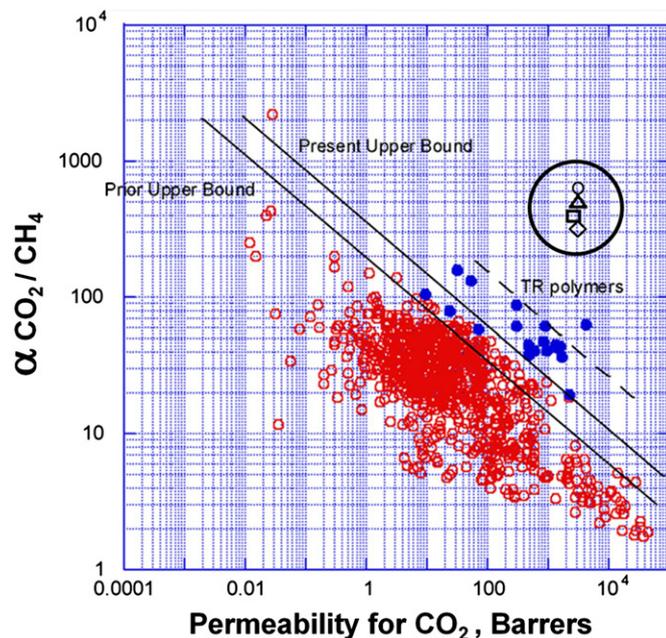
### 3.3. Gas permeation

The wetted parent PANI membrane did not exhibit reasonable permselectivity for separating  $\text{CO}_2$  from methane. In order to increase the permselectivity, we studied the effects of modifications of photografted polyaniline membranes and the amount of adsorbed water on gas transport and efficiency of the separation.

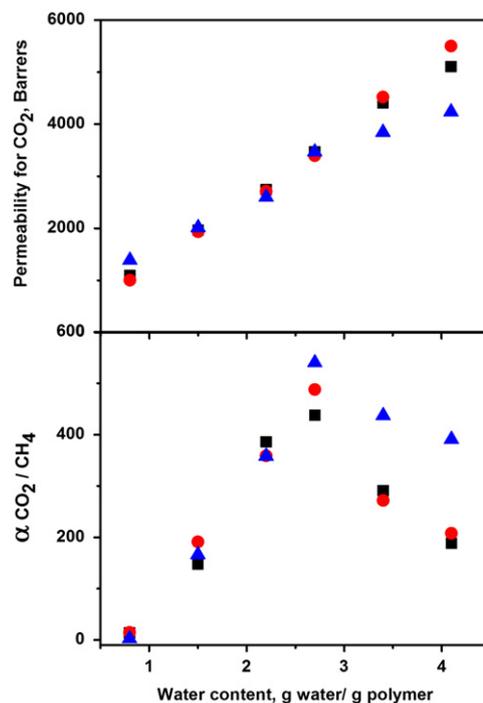
#### 3.3.1. Effect of amines

Photografted PANI-composite membranes reacted with ethylenediamine, hexamethylenediamine, and cystamine as well as

those modified to form guanidine moieties were first tested for the gas separation in dry state. Once again, these membranes did not exhibit sufficient permselectivity. Drying the membranes may



**Fig. 6.** Robeson's plot of the empirical permeability/separation factor and upper bound relationship for separation of  $\text{CO}_2/\text{CH}_4$  using membranes. Experimental points within the circle in the trade-off map represents permeability and separation factor  $\alpha$  determined for polyaniline membranes photografted with glycidyl methacrylate and 2-hydroxyethyl methacrylate reacted with ethylenediamine (diamond), cystamine (triangle), hexamethylenediamine (square), as well as with hexamethylenediamine and 2-ethyl-2-thiopseudourea (circle). Adapted from Ref. [6].



**Fig. 7.** Effect of water content in the membrane on  $\text{CO}_2$  permeability (top) and  $\text{CO}_2/\text{CH}_4$  separation factor  $\alpha$  (bottom) for polyaniline membrane photografted with glycidyl methacrylate and 2-hydroxyethyl methacrylate and reacted with hexamethylenediamine (squares), cystamine (triangles), as well as with hexamethylenediamine and 2-ethyl-2-thiopseudourea (circles).

**Table 5**  
Comparison of membrane separation properties of membranes containing different fixed carriers with current work.

Membrane	Gas	$P_{\text{CO}_2}^a$ (Barrer)	Selectivity	$\Delta p_{\text{CO}_2}^b$ (kPa)	Ref.
Polyvinylamine on polysulfone porous support	Pure CO <sub>2</sub> and CH <sub>4</sub>	$8.4 \times 10^{-3c}$ $1.0 \times 10^{-2c}$	1100 700	200–400	[21]
AIBA-K/polyallylamine/poly(vinyl alcohol) <sup>d</sup>	20% CO <sub>2</sub> , 40% H <sub>2</sub> , 40% N <sub>2</sub>	6000 1800	280 1800	24.32	[22]
Functionalized polyaniline	10% CO <sub>2</sub> , 90% CH <sub>4</sub>	3460	540	8.29	This study

<sup>a</sup> Permeability coefficient (1 Barrer =  $10^{-10}$  cm<sup>3</sup>(STP) cm/cm<sup>2</sup> s cmHg).

<sup>b</sup> Partial pressure difference of carbon dioxide across the membrane.

<sup>c</sup> Permeance in m<sup>3</sup>(STP)/m<sup>2</sup> bar h units.

<sup>d</sup> AIBA-K Potassium salt of 2-aminoisobutyric acid.

also lead to formation of minute defects and microvoids in the extremely thin active layer due to shrinkage. In contrast, hydration of these membranes with water dramatically improves permselectivity of all modified membranes as shown in Table 1. The amine groups, that also contribute to the high hydrophilicity, now serve as fixed carriers to bolster the CO<sub>2</sub> transport via the facilitated transport mechanism [21].

Our results indicate that the amount of CO<sub>2</sub> separated from the feed directly relates to the type and quantity of amine functionalities in the membrane. The composite membranes containing ethylenediamine, hexamethylenediamine and cystamine moieties featured selectivities of 370, 440 and 490 and permeabilities of 3410, 3400 and 3470 Barrers, respectively (see Table 1) when membrane were impregnated with sufficient amount of water (about 2.7 g water/g polymer). The presence of two amine groups in the guanidine functionality enhanced the separation factor to a remarkable value of 540 while retaining a high permeability of 3460 Barrers. The apparent increase in permeability of methane compared to that observed for the non-functionalized polyaniline membrane is likely to result from the significant error in measurements of the very small permeations through a membrane.

Fig. 6 shows these values placed in the trade-off plot [6]. The exceptional performance of our membranes significantly exceeds all other results included in the plot.

### 3.3.2. Effect of water content

Water represents an important factor in the facilitated transport of CO<sub>2</sub> through a membrane since in the presence of basic functionalities, it enables rapid formation of permeable carbonate ions [8]. The effect of swelling of polymer-based membranes containing amine groups and used for facilitated transport has been investigated extensively in recent years. The results confirmed an increase in permselectivity after switch from dry state to swollen conditions [21–26]. This is also true for membranes in our current work.

Fig. 7 shows that water content in our polyaniline-based membranes has a significant effect on both CO<sub>2</sub> permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity. The membranes are rather hydrophilic and can absorb significant volumes of water. Their permeability is directly proportional to the water content. The more water the membrane contains, the larger the inter-chain spaces in the polyaniline matrix, and the easier the gas permeation. This is confirmed in Fig. 7 by the linear increase in permeability with the water content corresponding to the increase in diffusivity in the more swollen membrane. In contrast, hydrophobic methane neither forms an ionic compound nor dissolves in the hydrated

membrane and its permeability controlled by the solution-diffusion mechanism is very low [22].

Fig. 7 shows that selectivity for CO<sub>2</sub> also depends on water content in the membrane. The separation factor increases with the increasing water content in membrane until it reaches about 2.7 g water/g polymer. However, with the further increase in water content, the selectivity for CO<sub>2</sub> decreases. The initial increase of the selectivity for CO<sub>2</sub> is likely due to an increase in the amount of water in the membrane that can accommodate more CO<sub>2</sub>. However, when water content further increases, the distance between carrier functionalities increases and they are distributed in a larger volume. As a result, the reaction kinetics is slower and the separation factor is reduced.

## 4. Conclusions

We demonstrated that separation performance of supported polyaniline membranes is significantly enhanced by the chemical modification and the presence of water. Photografting the surface with a poly(2-hydroxyethyl methacrylate-glycidyl methacrylate) chains makes it both hydrophilic and reactive. Subsequent reaction of the epoxide group with diamines increases the basicity of the membrane and introduces functionalities serving as fixed carriers. Further enhancement in basicity is achieved through transformation of primary amine in guanidine functionalities. These membranes can accommodate significant amounts of water that react with CO<sub>2</sub> and promotes CO<sub>2</sub> transport. In contrast, permeation of methane is not facilitated by this modification. As a result, the membranes exhibit permselectivity way above the upper bond in the trade-off plot. As a reference, Table 5 shows examples of the results found in literature for membranes containing fixed carrier that comprised polyvinylamine crosslinked with ammonium fluoride on polysulfone porous support [22] and crosslinked poly(vinyl alcohol) containing both mobile and fixed carriers [23]. Although the accuracy of our measurements may be limited by the relatively small area of the membrane given by our experimental setup, our results clearly demonstrate success of our approach.

Our continuing research is directed towards extending the selection of liquids promoting permeability that are used to swell the membrane. We are specifically focusing on those liquids that are less volatile than water.

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