

# Effect of Reaction Conditions on Film Morphology of Polyaniline Composite Membranes for Gas Separation

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**ABSTRACT:** Composite membranes combining polyaniline as an active layer with a polypropylene support have been prepared using an *in situ* deposition technique. The protonated polyaniline layer with a thickness in the range of 90–200 nm was prepared using precipitation, dispersion, or emulsion polymerization of aniline with simultaneous deposition on top of the porous polypropylene support, which was immersed in the reaction mixture. Variables such as temperature, concentration of reagents, presence of steric stabilizers, surfactants, and heteropolyacid were found to control both the formation

and the quality of the polyaniline layers. Both morphology and thickness of the layers were characterized using scanning electron microscopy. Selective separation of carbon dioxide from its mixture with methane is used to illustrate potential application of these composite membranes. © 2012 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 3077–3085, 2012

**KEYWORDS:** conducting polymer; thin film; membrane; morphology; polyaniline

**INTRODUCTION** Thin film composite membranes are layered materials typically fabricated from a thin film deposited on a thicker porous support. Their early applications include systems for water purification and desalination, separators in batteries, and in fuel cells.<sup>1</sup> Several composite membranes and films containing intrinsically conducting polymers have been recently developed and used in chemical sensors,<sup>2,3</sup> anti-corrosion coatings,<sup>4</sup> pervaporation,<sup>5</sup> and gas separation.<sup>6,7</sup> To make these membranes viable, their production must be simple, and straightforward, using deposition techniques that enable the production of large areas of defect-free film with a uniform thickness.

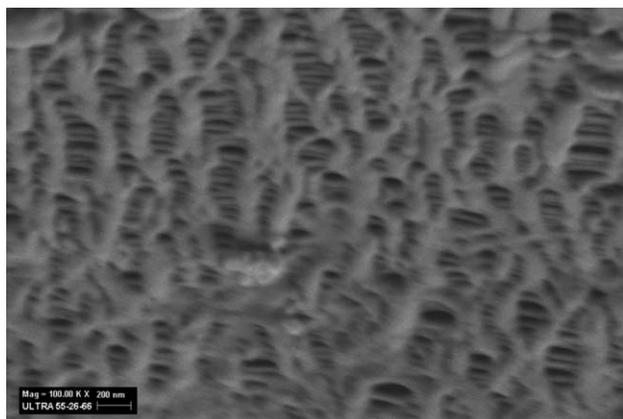
Polyaniline (PANI) is one of the most commonly studied conducting polymer.<sup>8–11</sup> Much research has focused on the modification of solid surfaces with a PANI layer which subsequently serves as the active component while the support typically provides the desired mechanical properties.<sup>12–14</sup>

Several approaches to film formation using PANI have already been reported including dip coating, drop casting, fractional thermal vacuum deposition, and electrochemical growth via galvanostatic, potentiostatic, or voltammetric routes.<sup>15–18</sup> The most common current technique used for the formation of thin PANI films is spin coating.<sup>19</sup> This approach is difficult to implement since very few solvents

allowing the dissolution PANI for subsequent spin coating are available. In addition spin-coated PANI films frequently suffer from poor adhesion to the surface of the support layer. Thus, a scalable deposition technique that allows reproducible control of thickness and morphological homogeneity of supported PANI films remains a challenge.

*In situ* deposition during polymerization of aniline has a potential to become a simple, continuous, and scalable method for the production of smooth submicrometer thin PANI films. Sapurina et al. have demonstrated that the adsorption of aniline oligomers on top of the support plays a fundamental role in film formation.<sup>20</sup> The deposition process has recently been studied in detail.<sup>21</sup> Several studies have also shown that the adsorption of hydrophobic PANI nuclei on hydrophobic surfaces was more uniform than is observed for the deposition on more hydrophilic species.<sup>9,22,23</sup> As a result, the PANI films formed on the former supports were also more homogeneous.

This communication reports the optimization of polymerization conditions enabling preparation of ultrathin, homogeneous, and defect-free PANI coatings with defined thicknesses when deposited on a hydrophobic porous polypropylene support.



**FIGURE 1** SEM micrograph of porous polypropylene support Celgard.

## EXPERIMENTAL

### Materials

Aniline and poly(*N*-vinylpyrrolidone) (PVP, molecular weight 55,000) were purchased from Aldrich (St. Louis, MO, USA). Aniline hydrochloride, ammonium peroxydisulfate (APS), and tungstosilicic acid ( $\text{H}_4[\text{Si}(\text{W}_3\text{O}_{10})_4] \cdot n \cdot \text{H}_2\text{O}$ ; HWSi) were obtained from Alfa Aesar (Ward Hill, MA, USA) while dodecylbenzenesulfonic acid (DBSA) was from TCI America (Portland, OR, USA). Microporous polypropylene film Celgard 2400 (Fig. 1) with a thickness of 25  $\mu\text{m}$  and an average pore size of 43 nm was supplied by Celgard, Inc. (Charlotte, NC, USA).

### *In Situ* Deposition of Polyaniline Films

The polymerizations of aniline hydrochloride to afford PANI coating were initiated with APS<sup>24</sup> and carried out in a simple device as shown in Figure 2. A circular piece of the polypropylene support with a diameter of 8.8 cm was placed on the top of the stainless steel base and sandwiched between the top stainless steel ring and the base. After fastening the pieces, a defined volume of the reaction mixture solution was transferred on the polypropylene support in the assembled device and aniline was polymerized.

### Precipitation Polymerization

The reaction mixture comprising the aqueous solutions of aniline hydrochloride monomer (0.2 mol/L) and APS oxidant (0.25 mol/L) was prepared and brought alternatively to temperatures of 20, 5, or  $-2$  °C. The mixture was transferred onto the top of porous support pre-washed with methanol and the polymerization of aniline was carried out for 2 h at the specified temperature.

### Dispersion Polymerization

Dispersion polymerization was carried out in the same manner as precipitation polymerization using a reaction mixture containing in addition the steric stabilizer, poly(*N*-vinylpyrrolidone).<sup>24</sup> Aniline hydrochloride was dissolved in a 4 wt % aqueous solution of PVP to obtain 50 ml of 0.4 mol/L solution. The polymerization reaction was then initiated by adding 50 ml of 0.5 mol/L aqueous solution of APS. After

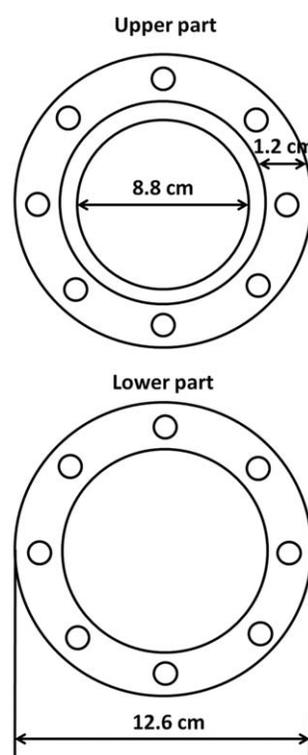
stirring briefly, the mixture was again transferred onto the top of the porous support and left to react at the desired temperature for 2 h.

### Emulsion Polymerization

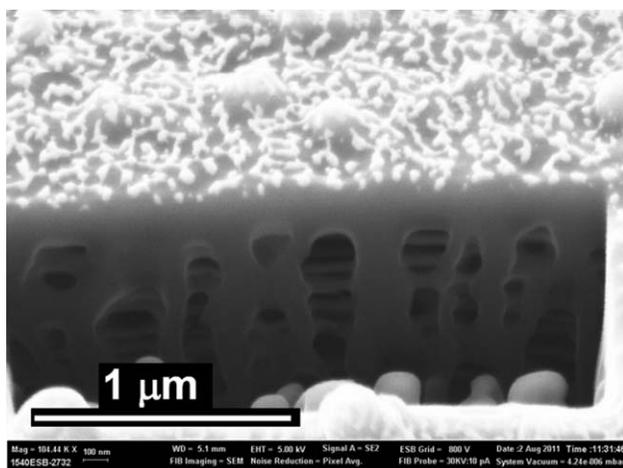
Aqueous solutions of aniline and an anionic surfactant, dodecylbenzenesulfonic acid, were mixed at different molar ratios of (1:1, 1.25:1, 2.85:1, 5:1, and 10:1). These mixtures were then sonicated to dissolve the precipitate that was observed to form immediately after the mixing. APS was then added to the emulsions and the reaction mixtures were transferred in the polymerization device containing porous polypropylene support. The polymerization of aniline was carried out for 2 h at 20 °C.

### Polymerization in Presence of Heteropolyacid

In order to increase the thickness of PANI films, aniline was polymerized in the presence of 0.2 and 0.5 mol % tungstosilicic acid with respect to aniline. Aniline hydrochloride solution (0.4 mol/L) containing heteropolyacid was mixed with the same volume of the 0.5 mol/L aqueous initiator solution at a temperature of 20, 5, and  $-2$  °C. The resulting [HWSi]/



**FIGURE 2** Scheme of device used for polymerization.



**FIGURE 3** SEM micrograph of polyaniline–polypropylene composite film after focused ion beam sectioning.

[Aniline] molar ratio equal to 0.002 (= 0.2 mol%) is equivalent to 40 mg of HWSi hydrate per 1 g of aniline hydrochloride.<sup>25</sup>

#### Treatment of Deposited Films

After the polymerizations of aniline were completed, the supported polyaniline membranes were first rinsed with 0.2 mol/L hydrochloric acid to remove the adhering PANI precipitate or colloidal particles, then with methanol, and dried in air. The protonated PANI was converted to the base by immersing the PANI-coated membrane in 0.1 mol/L aqueous ammonium hydroxide solution followed by rinsing with methanol and drying in air.

#### Characterization

The surface morphology of the films was imaged using an analytical scanning electron microscope Ultra-55 (Carl Zeiss, Peabody, MA, USA). A thin layer of gold was sputtered at the film surface before imaging. The thickness of the PANI film was estimated with an accuracy of  $\pm 10\%$  from scanning electron microscopy (SEM) images acquired with samples broken in liquid nitrogen. Focused ion beam (FIB) sections were created and imaged with a crossbeam scanning electron microscope 1540 EsB (Carl Zeiss, Peabody, MA, USA) using  $\text{Ga}^+$  beam currents of 10 pA and beam voltages of 30 kV. The films were coated with a thin gold–palladium alloy to prevent charging during exposure to electron and ion beams. Atomic force microscopy (AFM) images were obtained on SmartSPM (AIST-NT Inc, Novato CA, USA) in semi-contact mode.

All membranes were tested for the separation of carbon dioxide from its mixture with methane (a natural gas surrogate) using a home-built system to evaluate both 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 SRI gas chromatograph (Model 8610C) equipped with a SRI packed column (6-foot CTR column) and a thermal conductivity detector. The feed gas flow was controlled by a mass flow

controller and the exiting flows were measured with a digital flow meter. The PANI-composite membranes were mounted in a permeation cell with an effective area of 2.01  $\text{cm}^2$  for permeation. 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. After introduction of the feed, the system was allowed to reach steady state. Mixed gas tests were performed at room temperature and the separation factors were calculated.

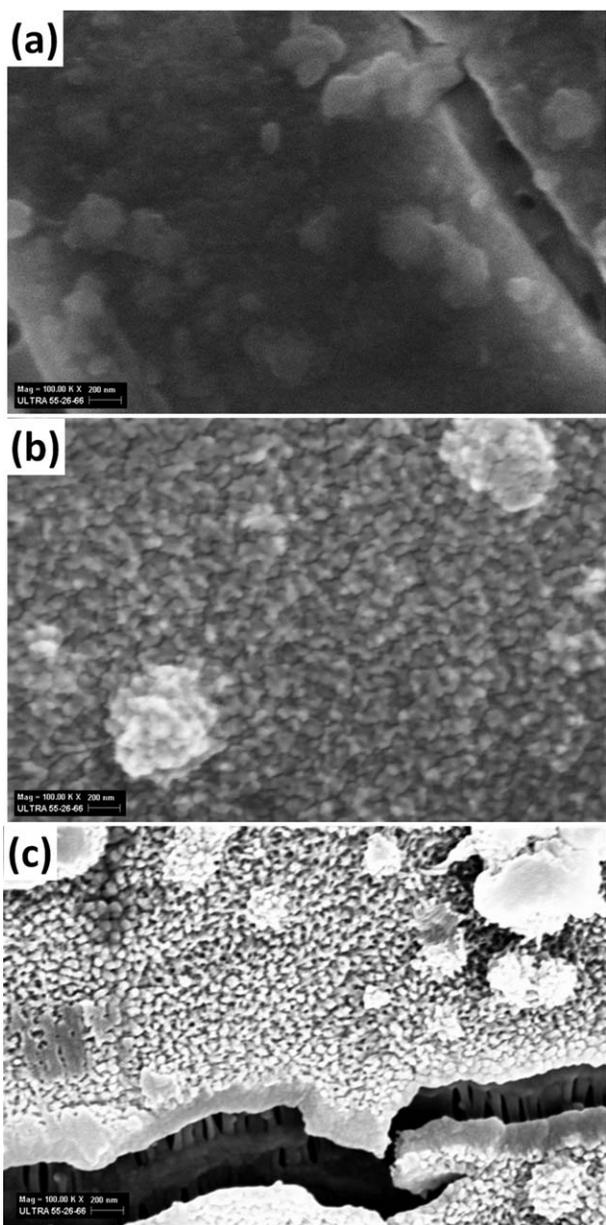
## RESULTS AND DISCUSSION

### Selection of Porous Polymer Support

The aim of this study was to prepare 100–200 nm thin defect-free PANI films. Since freestanding films of this thickness cannot be easily manipulated, they have to be deposited onto a mechanically stable support. Therefore, this support must not only allow for the direct deposition of the PANI film on its surface during the preparation, but it must also provide for good adhesion to prevent the PANI film from peeling off. For this purpose, we have selected a commercially available 25  $\mu\text{m}$  thick polypropylene film with an average pore size of 43 nm from Celgard. While similar films have previously been used for the fabrication of laminated membranes targeted to gas permeation and pervaporation,<sup>26–28(a,b)</sup> the large size of their surface pores proved to be a problem during their coating. Multilayer coating including in some cases up to 40 layers was needed to obtain a homogeneous defect-free membrane. Moreover, a detailed study of the formation of these composite membranes revealed that the polymer often penetrates into the pores of the supporting substrate during the deposition process. As a result, the effective thickness of the film could not be well controlled. In contrast, we now report the preparation of ultrathin, homogeneous, defect-free coating with defined thickness formed via direct deposition on such porous support. The dual beam electron micrograph in Figure 3 showing a cross-sectional view of the resulting PANI-PP composite membrane confirms that the PANI layer does not penetrate into the pores of the support.

### Precipitation Polymerization

The simplest approach to PANI film deposited on surface of the PP support involves the direct polymerization of an aniline hydrochloride solution on the polypropylene support itself. The scanning electron micrograph of Figure 4(a) shows that the PANI film in the composite membrane prepared by precipitation polymerization at 20 °C with subsequent deprotonation using ammonium hydroxide has a granular morphology and displays numerous defects. Removal of the acid molecules from the inter-chain space during deprotonation results in a significant decrease in both mass and volume of the film.<sup>29</sup> The volume change causes strain resulting in film deformation and cracking with the formation of defects, which are not desirable for membrane applications. However, we found that the uniformity of the PANI films improves when the polymerization is carried out at a lower temperature of 5 °C. Also, the films prepared at lower temperature are generally thicker.<sup>27</sup> The PANI film shown in



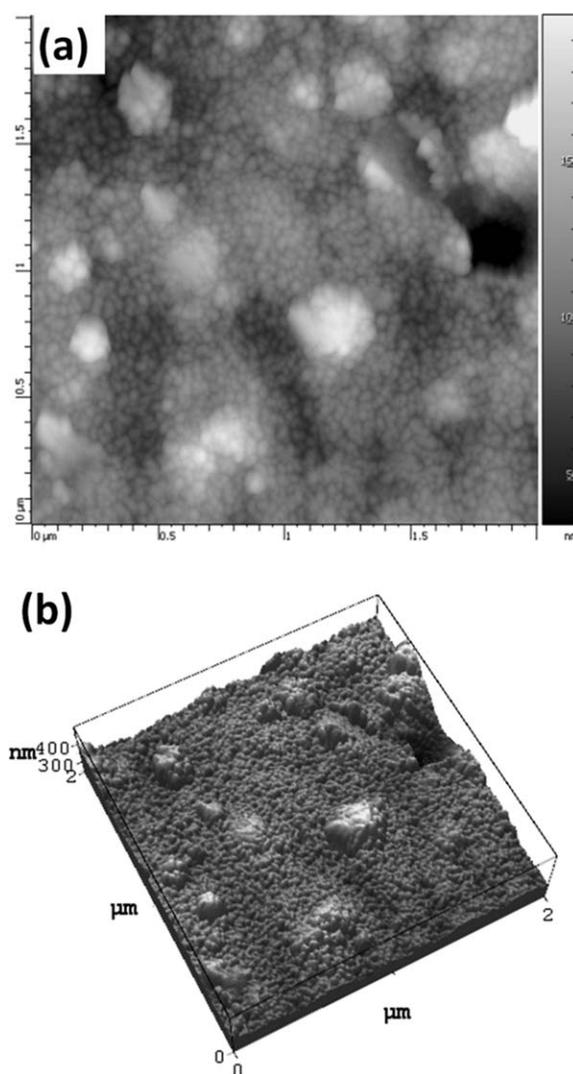
**FIGURE 4** SEM micrographs of polyaniline films deposited on polypropylene support by precipitation polymerization of aniline at 20 (a), 5 (b), and  $-2$  °C (c).

Figure 4(b) appears more uniform and more compact, consisting of small clusters with diameters in the range of  $150 \pm 50$  nm, distributed over the scanned area as can be seen from AFM images [Fig. 5(a,b)]. A further decrease in polymerization temperature to  $-2$  °C affords again PANI film with cracks [Fig. 4(c)]. These cracks likely originate from gas microbubbles that adhere to the support and preclude the adsorption of aniline oligomers during the initial step of formation of the PANI layer.

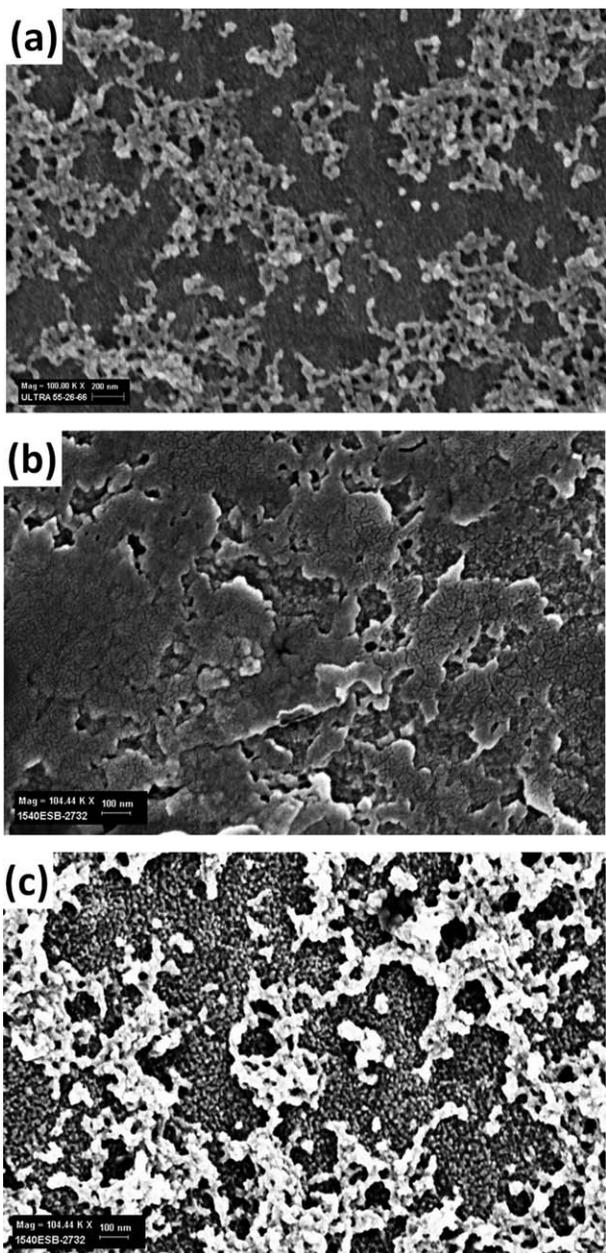
#### Dispersion Polymerization

Because the quality of PANI film proved to be difficult to control during precipitation polymerization, we also tested

dispersion polymerization. The polymerization mixture includes a surface active component, poly(*N*-vinylpyrrolidone), which improves the quality of the deposited PANI films. This steric stabilizer prevents the macroscopic precipitation of PANI leading to the formation of polymer colloids instead of precipitated polymer particles, thus reducing the contamination of films with PANI precipitate.<sup>9</sup> In addition, the surfactants reduce the surface tension at the interface between the polypropylene support and the aqueous polymerization mixture, thus decreasing the adhesion of microbubbles, which could block access of the polymerization mixture to the surface of the support film. The absence of microbubbles also reduces the number of undesired defects.<sup>30</sup> Indeed, Figure 6 shows that the morphology of PANI composite membranes prepared in the presence of a steric stabilizer are different from those prepared under similar conditions using plain precipitation technique shown in Figure 4. Here again, films prepared at 5 °C [Fig. 6(b)]



**FIGURE 5** AFM images of polyaniline-polypropylene membrane prepared by precipitation polymerization at 5 °C with a scanning window of  $1 \times 1$   $\mu\text{m}$  (a) and 3D AFM image (b).



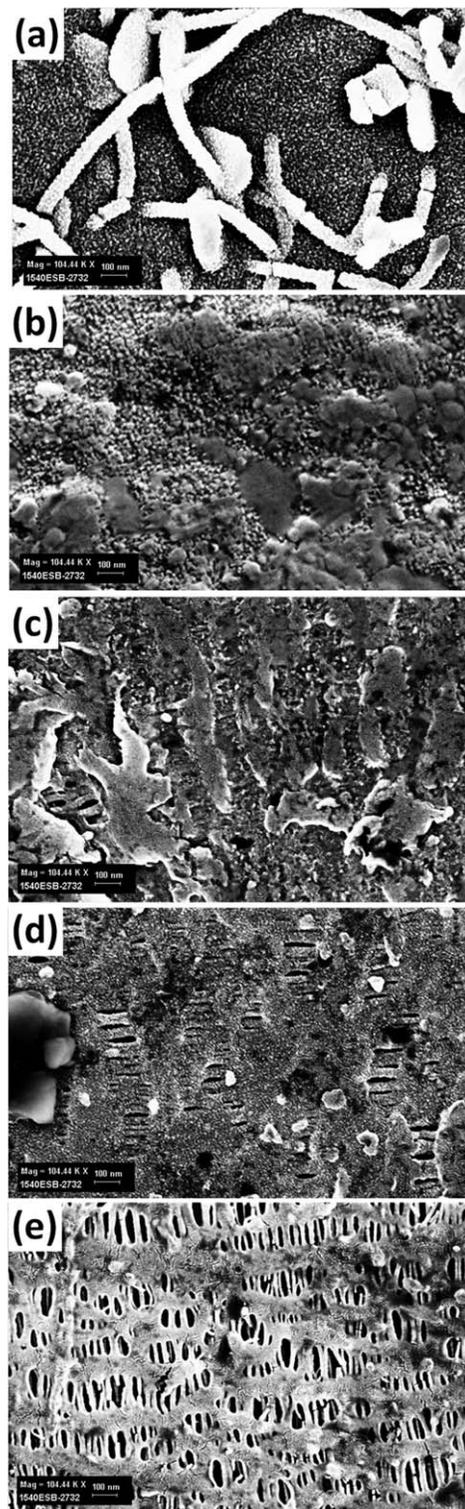
**FIGURE 6** SEM micrographs of polyaniline-polypropylene films prepared using dispersion polymerization at 20 (a), 5 (b), and  $-2$  °C (c).

exhibit the best homogeneity. In general, we observed that films prepared using the dispersion polymerization were thinner than those prepared using precipitation polymerization.<sup>9</sup>

#### Emulsion Polymerization

Dodecylbenzenesulfonic acid (DBSA) is another surface active additive we tested as an aid to the polymerization process under emulsion polymerization conditions. SEM micrographs in Figure 7 reveal that the morphology of PANI films prepared using emulsion polymerization is strongly affected by the molar ratio of DBSA to aniline in the

polymerization mixture. With a [DBSA]/[aniline] molar ratio of 1:1, the film has a crack-free nanofibrillar morphology [Fig. 7(a)]. This evolves to a compact morphology with some



**FIGURE 7** SEM micrographs of polyaniline films prepared using polymerization mixtures with dodecylbenzenesulfonic acid to aniline molar ratios of (a) 1:1, (b) 1.25:1, (c) 2.85:1, (d) 5:1, and (e) 10:1.

**TABLE 1** Thickness of the Polyaniline Film Prepared by Precipitation and Dispersion Polymerization

Temperature (°C)	Thickness (nm)	
	Precipitation Polymerization	Dispersion Polymerization
20	119	83
5	147	92
-2	156	138

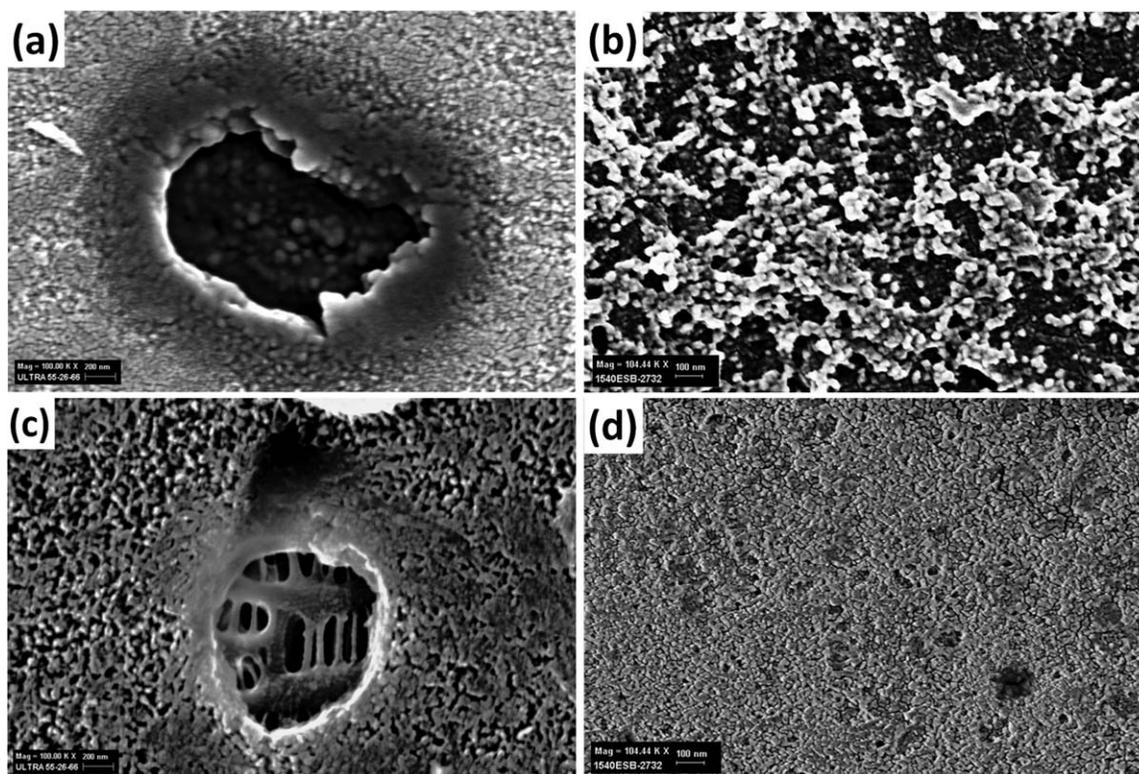
surface roughness [Fig. 7(b)] when the [DBSA]/[aniline] molar ratio is changed to 1.25:1. A further increase in [DBSA]/[aniline] molar ratio to 2.85:1 affords films with a smooth surface [Fig. 7(c)]. However, no film is formed at much higher ratios of 5:1 and 10:1 [Fig. 7(d,e)]. At such high ratios it is likely that the surface of the polypropylene support becomes mostly covered with adsorbed surfactant molecules leaving no space for the adsorption of aniline oligomer nuclei.

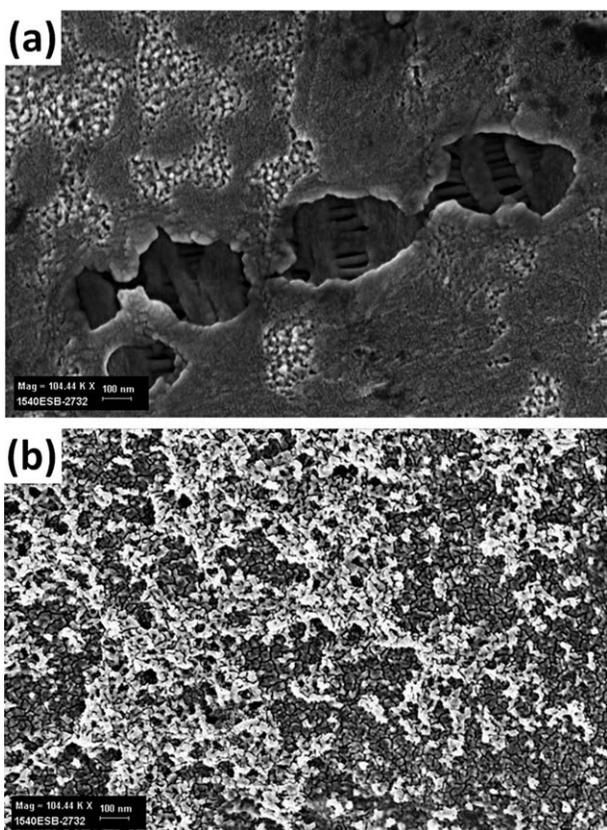
#### Control of Film Thickness

The presence of a water-soluble polymer during film preparation affects the thickness of the deposited film and also avoids the adhesion of a PANI precipitate.<sup>26</sup> Indeed, the PANI films deposited on polypropylene support prepared using dispersion polymerization are always thinner than those prepared via precipitation polymerization (Table 1). This effect

results from the reduced density of nuclei at the support surface controlled by presence of the steric stabilizer. Thus, homogeneous films prepared using both dispersion and emulsion polymerizations are very thin which makes them susceptible to mechanical damage.

Recent report has shown that the polymerization of aniline in solution is significantly affected by the presence of tungsten containing compounds.<sup>25</sup> For example, the use of 2 mol % of sodium tungstate relative to aniline was found to increase the induction period from 5 to 30 min and even to 120 min if tungstosilicic acid (HWSi) is used at the same molar concentration. Because this retardation of aniline polymerization also decreases the rate of nucleation during the induction period, we assumed that further delaying the onset of polymerization might help in the formation of thicker PANI films. We envisioned that extending the nucleation period, during which the insoluble oligomers containing phenazine are formed, provides more time for these initial nuclei to adsorb at the support surface. The longer the nucleation period, the more nuclei adsorb at the surface and the thicker the PANI film. The effect of tungstosilicic acid on morphology of the deposited PANI film is shown in Figures 8 and 9. PANI films prepared by precipitation polymerization in the presence of 0.2 and 0.5 mol % HWSi (relative to aniline) at 20 °C [Fig. 8(a)] and 5 °C [Fig. 8(c)] have a compact structure with a number of pinholes that make the films useless for membrane applications. The thickness of the layer prepared at 20 °C with an addition of 0.2 mol % HWSi is 129 nm

**FIGURE 8** SEM micrographs of polyaniline films prepared by precipitation polymerization (left) and dispersion polymerization (right) in the presence of 0.2 mol % of tungstosilicic acid at 20 °C (a, b) and 5 °C (c, d).



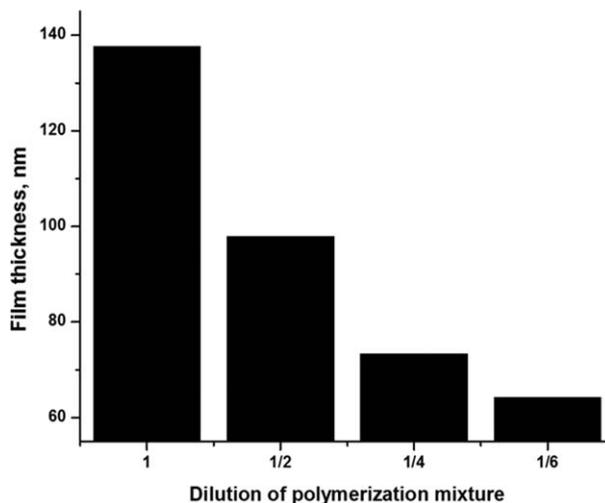
**FIGURE 9** SEM micrographs of polyaniline films prepared by precipitation polymerization at 5 °C (a) and by dispersion polymerization at 20 °C (b) in the presence of 0.5 mol % tungstosilicic acid.

while at 5 °C and 0.5 mol% HWSi the thickness is 174 nm. In contrast, PANI films prepared via dispersion polymerization in the presence of 0.2 and 0.5 mol% HWSi at 20 °C feature a highly porous homogenous structure [Figs. 8(b) and 9(b)] and a thickness of 96 and 138 nm, respectively. Films prepared in the presence of 0.2 mol % HWSi at 5 °C have dense homogeneous structure [Fig. 8(d)]. No film formation was observed at 5 °C using polymerization mixtures in which the concentration of HWSi exceeded 5 mol %. It is likely that a high concentration of the heteropolyacid interferes with the frequency of formation of nuclei and/or initiation centers. As a result, the propagation of PANI chains is reduced.

The film thickness can also be controlled via other parameters such as reaction temperature and concentration of the

**TABLE 2** Thickness of the Polyaniline Film Prepared in the Presence of Tungstosilicic Acid

Type of Polymerization	Concentration of HWSi (mol/L)	Temperature (°C)	Thickness (nm)
Precipitation	0.02	20	128
Precipitation	0.05	5	174
Dispersion	0.02	20	95
Dispersion	0.05	20	138



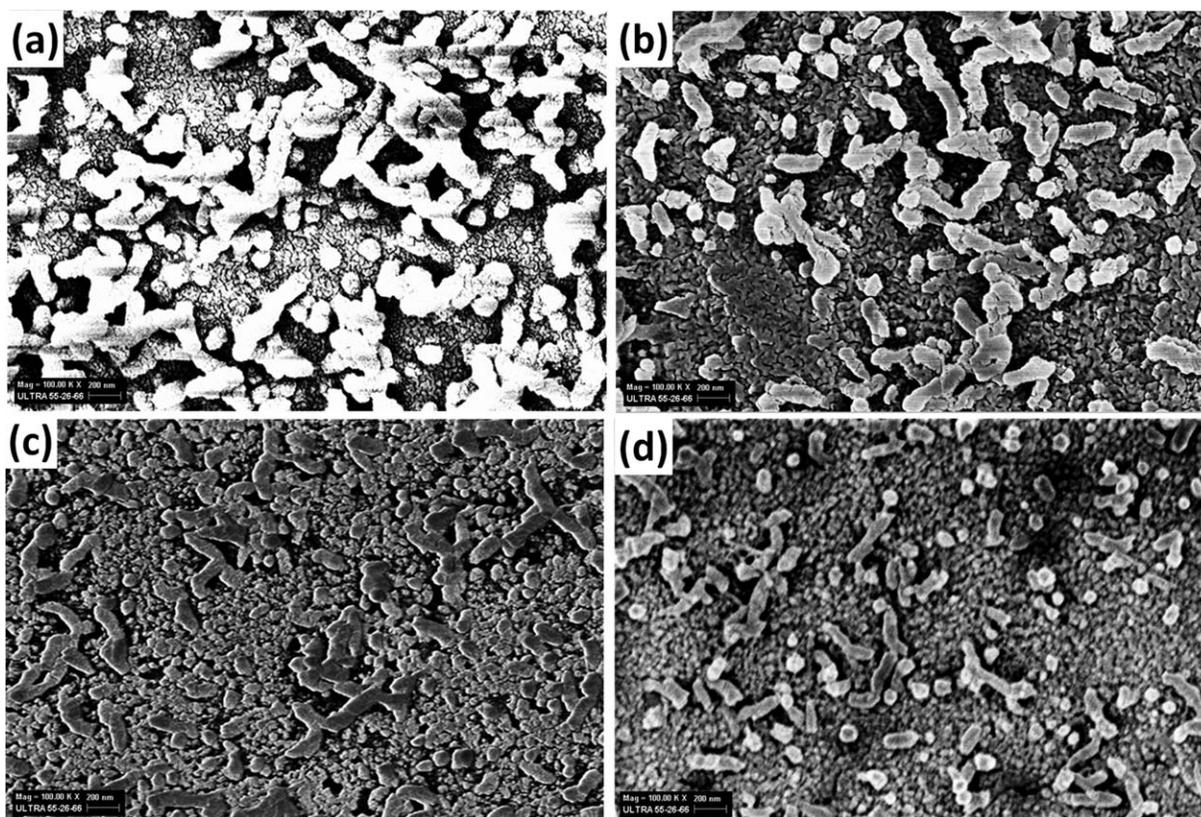
**FIGURE 10** Thickness of supported polyaniline films prepared *in situ* using dispersion polymerization of reaction mixture without dilution, diluted 2, 4, and 6 times. Conditions: Polymerization mixture: aniline hydrochloride 0.2 mol/L, ammonium peroxydisulfate 0.25 mol/L, poly(vinylpyrrolidone) 2 wt %, in 1 mol/L hydrochloric acid, temperature 20 °C.

reagents in the polymerization mixture.<sup>27</sup> As shown above, a decrease in reaction temperature affords an increase in the film thickness (Table 2). Similarly, an increase in concentration of the reagents leads to an increase in the film thickness. Figure 10 demonstrates the direct proportionality between the film thickness and the concentration of reagents in the polymerization mixture. Interestingly, morphology of the PANI films shown in Figure 11 is not significantly affected by the changes in concentration of components of the polymerization mixture.

### Gas Transport Properties

The performance of our composite membranes is demonstrated with the separation of carbon dioxide from its mixture with methane. This separation is important in processing of natural gas because CO<sub>2</sub> decreases the energy content, reduces transport capacity of pipelines, and forms a corrosive acid in presence of water. Since carbon dioxide is known to interact with basic nitrogen-containing compounds such as amines, this property is used for its capture. Polyaniline also contains amine functionalities and therefore it has a potential in the separation of CO<sub>2</sub> from its mixtures with methane.

Initial experiments aimed at the separation of carbon dioxide from methane using dry PANI membranes demonstrated that all composite polyaniline–polypropylene membranes had poor permeabilities and no appreciable selectivity for carbon dioxide. For example, Table 3 shows the transport properties of a PANI-composite membrane prepared by precipitation polymerization at 5 °C. However, once the membranes were hydrated with water, the selectivity values increased and reached up to 15.4. This increase in interaction of carbon dioxide with amines in the presence of water was also reported in the literature.<sup>31</sup> Polyaniline is a weak base, and



**FIGURE 11** SEM micrographs of composite polyaniline–polypropylene films prepared by dispersion polymerization using (a) standard, (b) 2, (c) 4, and (d) 6 times diluted polymerization mixture. For conditions see Figure 10.

carbon dioxide dissolved in water forms a weak carbonic acid. These properties then represent the basis for the mutual interaction that enables the transport of carbon dioxide through polyaniline films that differ in dry and wet state.<sup>32</sup> In contrast, transport of hydrophobic hydrocarbon methane is less favorable in wet membranes.

## CONCLUSIONS

Our study demonstrates that PANI composite membranes with well-defined morphology can be prepared using a single step *in situ* polymerization. Temperature, concentration of reagents, steric stabilizers, surfactants, and heteropolyacid are tools enabling control of both morphology and thickness of the PANI layers. This ability to deposit the defect-free PANI films on surface of a support is desirable for potential applications including composite membranes for gas separations. While the dry membranes have a poor permeability and no appreciable selectivity for carbon dioxide over meth-

ane, their hydration with water significantly increases both these parameters. Current experiments focus on chemical modification of the PANI surface which leads to new chemistries optimized for CO<sub>2</sub> transport.

## ACKNOWLEDGMENTS

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**TABLE 3** Properties of Polyaniline–Polypropylene Composite Membranes Prepared by Precipitation Polymerization at 5 °C

Membrane	Permeability for CO <sub>2</sub> , Barrer	Selectivity CO <sub>2</sub> /CH <sub>4</sub>
Dry	155	1.1
Wet	3.89	15.3

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