

Structure and Gas Separation Properties of Composite Films Based on Polyaniline

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ABSTRACT: Composite films based on the polyvinyltrimethylsilane (PVTMS) with polyaniline (PANI) coating were obtained by borderline polymerization of aniline. The obtained coating was shown to differ from the polymer forming in the reaction mixture bulk both in chemical structure and morphology. Ratio and concentration of the reagents, mixing rate, reaction time, and condition of support surface were among the investigated factors affecting the growth and quality of PANI coating. The gas separation characteristics of composite membranes, as affected by the

process conditions and the type of PANI, were investigated. It is shown that the proposed method provides a means for obtaining composite membranes that combine high selectivity, especially in O₂/N₂, He/CH₄, and CO₂/CH₄ separation, with permeability higher than that of known composite materials. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1379–1384, 2003

Key words: polyaniline; films; coatings; selectivity; permeability

INTRODUCTION

In recent years there has been increasing interest in various aspects of the chemistry, physics, and technology of polyaniline (PANI) because of the combination of valuable properties of this compound, as well as to its specific structure, characterized by the presence of a system of conjugated bonds.

Apart from its impressive electrophysical characteristics,¹ PANI possesses unique selectivity in O₂/N₂ and He/CH₄ separation.^{2–11} The analysis of published gas-transport properties of PANI films cast from the solution in *N*-methylpyrrolidinone shows some confusion in permeability/permeability experimental data. It may be connected with the high sensitivity of PANI to preparation procedure and measurement conditions. In particular, permeability of PANI was not always measured with the control of reaching equilibrium. Nevertheless, PANI is of considerable interest as a membrane material for commercial gas separation, where high selectivity and high permeability are required.¹²

Nevertheless, the wide practical use of PANI in membrane technology is impeded by such properties of this polymer as nonfusibility, insolubility in most organic solvents, poor mechanical characteristics, and low gas permeability.

One of the promising approaches to the solution of this problem is to obtain composite membranes with support from highly permeable material, coated by thin PANI film. The method of borderline polymerization of aniline developed at our facilities¹³ allows the direct preparation, during the course of synthesis, of high-quality PANI coatings on the surface of most materials, regardless of their form and chemical structure.

The purpose of this work was to obtain composite films by carrying out borderline polymerization of aniline on the surface of polyvinyltrimethylsilane (PVTMS), one of the most permeable materials. Investigation of the structure and the gas separation properties of such films was also the task.

EXPERIMENTAL

Materials and samples

Aniline (C₆H₅NH₂; reagent grade) was vacuum-distilled twice under 1.33 kPa at 323 K. Ammonium peroxydisulfate [(NH₄)₂S₂O₈; reagent grade] was purified by recrystallization.¹³ Hydrochloric acid (HCl; analytical grade) and *p*-toluenesulfonic acid (reagent grade) were used without additional purification. Degassed distilled water was used to prepare aqueous solutions.

PVTMS films were prepared by casting from a 5% solution of substance in toluene, thoroughly filtered before use, onto the cellophane support. The volume of solution and the diameter of cellophane support

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were chosen so that the obtained film was 50 μm thick. The solvent was removed and the films were dried in vacuum. Before use, the films were washed with methanol and dried under conditions excluding dust penetration.

Borderline polymerization of aniline on the surface of PVTMS film was performed by rotating the thermostated glass flask that contained the sample in rotation basket (30–40 cycles/min).

The concentrations of aniline and ammonium peroxydisulfate were varied from 0.01 to 0.2 mol/L at constant molar ratio (1 : 1); the HCl concentration was varied from 0.1 to 2 mol/L.

Solutions of the reactants were prepared and mixed immediately before casting. PVTMS film was carefully placed on the surface of the reaction mixture in the revolving flask to avoid any air bubbles. The film gained a shaped form during formation, so that the reaction mixture did not leak over the board to the outer, dry side.

When the reaction was complete, the composite PVTMS–PANI film was removed from the reaction flask, washed with HCl solution (of the same concentration as for the polymerization), and dried in vacuum over P_2O_5 .

To obtain undoped samples, the composite film after washing with HCl was rinsed with distilled water for at least 0.5 h. Then NH_4OH solution was added dropwise for 0.5 h, followed by washing with the distilled water and drying in vacuum over KOH. Redoping was performed in reverse order: the required acid was added dropwise to distilled water in a revolving flask in which the undoped sample was placed, to the required pH level.

Methods

Morphology of the films was studied by scanning electron microscopy (SEM) using a scanning electron microscope JSVU3 (JEOL, Japan). The conducting carbon layer ($d = 100 \text{ \AA}$) was sputtered onto the samples in advance by thermovacuum sputtering of graphite.

FTIR spectra were obtained by use of a spectrometer (IFS-113v; Bruker Instruments, Billerica, MA). Break total inside reflection (BTIR) spectra were obtained using an attenuated total reflection unit with 45° prism from KRS-5.

Gas permeability of composite films was studied by the differential permeability method with gas chromatography analysis of exiting gases under partial pressure (1 atm) at room temperature.¹⁴

RESULTS AND DISCUSSION

Special conditions for preparation of PANI coating on the surface of PVTMS support

The method of borderline polymerization developed at our facilities¹³ makes possible the preparation of

PANI coatings directly during the course of synthesis, thus avoiding the stages of polymer isolation, neutralization, dissolution, and casting of films from solvents with high boiling point.

To obtain high-quality PANI coating on the PVTMS surface a number of requirements must be met, the most important of which are the ratio of reaction mixture volume to the interfacial surface area and concentrations of the reagents.¹³ The first factor is rather strictly defined by the geometrical properties of the chosen sample and flask. Only reagent concentrations and duration of reaction can be varied.

It was found that borderline polymerization is favored in the range of decreased reagent concentrations and reaction time. In this case, a dense, uniform polyaniline layer forms on the support surface.

An increase in reagent concentrations and reaction time makes the other processes, adsorption polymerization and destruction, more influential. The first process facilitates precipitation of a loose, irregular layer of polymer from the solution bulk on the evolving PANI surface, whereas the second process decreases the quality of PANI coating.

The products of borderline and adsorption polymerization are visually distinctive: a shiny, glazed coating and a matted coating, respectively.

Thus, the composite film obtained under the conditions of borderline polymerization ($[\text{aniline}] = 0.02 \text{ mol/L}$, $[(\text{NH}_4)_2\text{S}_2\text{O}_8] = 0.02 \text{ mol/L}$, $[\text{HCl}] = 0.1 \text{ mol/L}$, reaction time 1 h) should be a thin layer of PANI on PVTMS support.

SEM study of PANI layer

According to electron microscopy data, the obtained dense PANI coating is about 0.5–1 μm thick. Its surface reproduces the morphology of the PVTMS support. To study the structure of the coating, samples of composite material were extracted with hexane until the support was fully dissolved. It is difficult to identify the supermolecular structure of the PANI layer, even at magnifications of $\times 20,000$. This means that PANI formed by borderline polymerization has dense, finely structured texture of unresolved morphology, whereas the polymer formed in the solution bulk in the meantime is of globular structure, with characteristic dimension of 0.5 μm .

FTIR study of chemical structure

To investigate the chemical structure of composite films, their FTIR spectra were analyzed. Regardless of polymerization time, the spectrum of the composite film is the superposition of two spectra, that of initial PVTMS and that of polymerization products, which include PANI and PVTMS modified in process. Table I depicts the time dependency of the fraction of

TABLE I
Fraction of Unchanged PVTMS Film in the Composite Film (x) Versus Polymerization Time as Found from FTIR Spectroscopy Data

Time (h)	x^a (%)	
	Doped form	Undoped form
0	100.0	100.0
0.6	99.4	99.6
1	97.6	96.9
2	95.4	95.1
4	93.0	93.3

^a In service program of subtraction by Bruker, x is found automatically.

PVTMS that retained its initial structure. It is seen that during 4 h of polymerization, about 7% of PVTMS undergoes modification. If a frontal mode of support modification is supposed, it means that during this time the thickness of the PVTMS layer decreased from 50 to 46.5 μm , whereas the thickness of the layer consisting of PANI and modified PVTMS increased to 3.5 μm .

It was found from BTIR spectral studies (Fig. 1) that peaks 1247, 841, and 751 cm^{-1} , which are characteristic of modified PVTMS, are poorly presented in the spectra of the surface layer after 4 h of borderline polymerization, in contrast to PANI peaks.

Thus on the basis of SEM and BTIR spectroscopy data the conclusion can be made that, in all probability, the borderline polymerization of aniline forms the three-phase system on the support surface. It consists

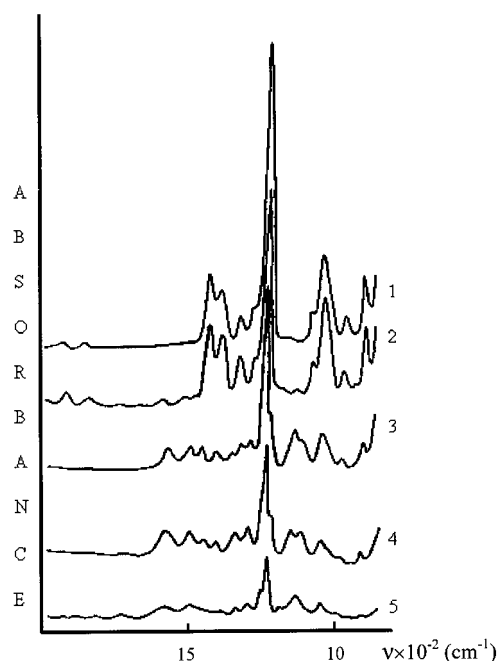


Figure 1 BTIR spectra of composite film surface at various polymerization times: (1) initial PVTMS support; (2) 0.6 h; (3) 1 h; (4) 2 h; (5) 4 h.

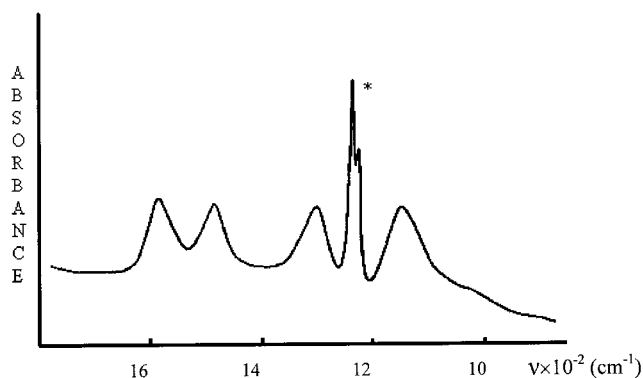


Figure 2 Differential FTIR spectra of composite film surface (excluding initial PVTMS). *, band of modified PVTMS.

of PVTMS, an intermediate layer (2–3 μm) of modified PVTMS, and a dense layer of pure PANI (0.5–1 μm). Formation of an intermediate layer can be explained by assuming that PVTMS does not remain unaffected by reagents and active intermediates forming during the radical reaction of oxidation.

The main characteristic bands of PANI obtained by borderline polymerization (Fig. 2) are 1598 with 1480 cm^{-1} (of almost identical intensity) and 1295 with 1120 cm^{-1} (the latter of which is slightly more intense in this pair). By position and relative intensity of these peaks the reaction product can be identified as the radical cation structure of PANI.^{17,18} No other structures were observed in reaction products on the PVTMS surface.

PANI obtained by borderline polymerization differs from PANI formed in the solution bulk in that there are no defect structures in the former and the fully doped state can be obtained at $[\text{HCl}] = 0.1 \text{ mol/L}$.

As seen from Table II, the main increase in PANI amount on the support surface is observed during the first hour of reaction. As the reaction proceeded, the amount of PANI increased only slightly up to 2 h; at 4 h, the polyaniline amount even decreases. The dynamics of PANI growth on the PVTMS surface is in good agreement with the kinetics of aniline oxidative polymerization in the presence of additionally introduced substrates.^{13,19}

Factors affecting the quality of PANI coating

While finding the optimal conditions of borderline polymerization, the factors affecting the quality of forming PANI coating were established.

TABLE II
Time Dependency of PANI (Doped Form) Content in Composite Film as Found from IR Spectroscopy Data

Polymerization time, h	0	0.6	1	2	4
Intensity of absorbance band, 1598 cm^{-1} , a.u.	0	0.08	0.18	0.20	0.13

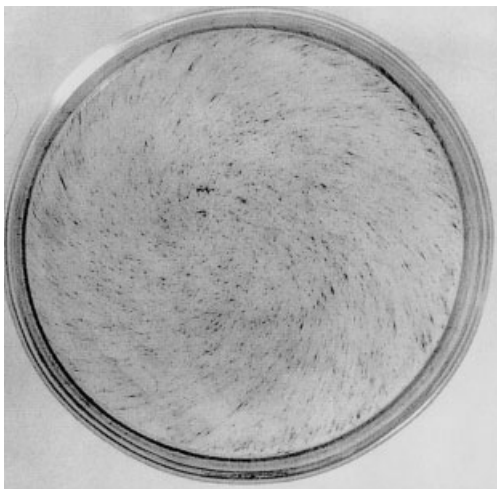


Figure 3 Photograph of composite film surface demonstrating the hearth growth of polyaniline layer.

The first and most important factor is the chemical uniformity of the support surface and the absence of impurities able to catalyze or to inhibit the oxidation reaction. Because oxidative polymerization of aniline is of autocatalytic nature, such impurities lead to the resulting coating having different thickness and not being intact.

The second factor is homogeneity of the reaction mixture. Because it is not possible to eliminate fully various microimpurities on interfacial surface, the autocatalytic nature of the process enhances the difference of borderline polymerization rates along the surface. At low mixing rates (3–10 cycles/min) the hearth growth of the PANI layer on the PVTMS surface was observed, as shown in Figure 3. At reagent concentrations of 0.02 mol/L, the amount of nucleation centers is small (3–5 per 1 cm²), with diameters of 2–3 mm.

At high mixing rates (30–40 cycles/min) and reagent concentrations of 0.02 mol/L, the hearth mechanism of PANI layer growth was not observed. It was found from the measurements of wetting angle that defect-free modification of the PVTMS surface pro-

ceeds in the first few minutes of reaction when the PANI layer thickness was up to 0.1 μm.

The third factor affecting the quality of coating is related to the doping/undoping processes. To measure gas separation properties, the doped form of PANI was transformed into base form, or undoped state. Then, if needed, it was redoped by alternating alkaline (NH₄OH) and acidic (HCl) reagents. During such treatment local tensions can appear in the PANI coating (especially when pH changes sharply), so that the coating is no longer intact. To prevent this, doping and undoping were performed by keeping the samples in distilled water for an extended time, followed by slow adjustment of pH to the required level.

Gas separation properties

The gas permeability of composite PANI–PVTMS films was studied in this work for O₂, N₂, CO₂, CH₄, and He. Table III presents the data on permeability and selectivity coefficients of composite films obtained by borderline polymerization of aniline under conditions described above during 1 h of reaction.

The permeability coefficient P_{eff} is lower for all gases in the case of composite film compared to that of pure PVTMS. Nevertheless, it should be noted that these values exceed those of PANI samples cast from solution by two orders of magnitude.

As to the selectivity of gas separation, the initial doped composite sample behaves very similarly to PVTMS for the O₂/N₂ and CO₂/CH₄ gas pairs. In the case of He/N₂ and He/CH₄, selectivity for the composite film is markedly higher because of the fact that permeability for He decreases only slightly, compared to that for O₂, N₂, CO₂, and CH₄.

In the course of undoping, the dopant (HCl) migrates from polyaniline structure and the free volume grows. Gas permeability for O₂ and CO₂ becomes correspondingly twice as high, whereas that of N₂, CH₄, and He changes only slightly. This phenomenon probably can be explained by the possible interaction or doping of emeraldine structures by O₂ and CO₂.

TABLE III
Effect of the PANI Layer Form on Gas-Transport Properties of the Studied Composite Film

Sample	Permeability coefficient P_{eff} , barrier (10 ⁻¹⁰ [cm ³ (STP) cm]/[cm ² s ⁻¹ cmHg])					Selectivity coefficient			
	O ₂	N ₂	CO ₂	CH ₄	He	O ₂ /N ₂	CO ₂ /CH ₄	He/N ₂	He/CH ₄
PVTMS	50	12	190	22	263	4.2	8.6	22	12
Initial sample, doped by 0.1M HCl	8.0	2.0	27.7	2.6	136	4.0	10.7	68.0	52.3
Undoped	19.2	2.35	62.9	2.35	159	8.2	26.8	67.7	67.7
Redoped by 0.1M HCl	6.03	1.0	24.2	1.61	153	6.0	15.0	153	95.0
Reundoped	20.0	3.0	—	—	—	6.7	—	—	—
Redoped by 0.1M p-toluenesulfonic acid	8.72	1.49	32.1	1.84	152	5.9	17.4	102	82.6

TABLE IV
Dependency of Gas-Transport Parameters of Composite Film (Undoped Form) on Polymerization Conditions

[aniline] ^a (mol/L)	[HCl] (mol/L)	Time (min)	Permeability coefficient P_{eff} , barrier (10^{-10} [cm ³ (STP) cm]/[cm ² s ⁻¹ cmHg])					Selectivity coefficient			
			O ₂	N ₂	CO ₂	CH ₄	He	O ₂ /N ₂	CO ₂ /CH ₄	He/N ₂	He/CH ₄
0.01	0.1	60	31	5.7	129	8.9	176	5.4	14.5	30.9	19.8
0.02	0.1	60	19.2	2.35	62.9	2.35	159	8.2	26.8	67.7	67.7
0.03	0.1	60	19.0	3.15	81.7	5.36	163	6.0	15.3	51.7	30.4
0.04	0.1	60	15.1	2.73	60.6	3.6	116	5.5	17.1	42.5	32.7
0.02	0.5	90	33.6	6.88	—	—	—	4.9	—	—	—
0.02	2	90	58	13.4	181	—	—	4.3	—	—	—
0.01	0.1	90	31.7	5.34	118.0	6.07	192	4.9	19.4	36.0	31.6
0.01	0.1	120	44.5	9.17	164.0	16.1	202	7.6	10.2	22.0	12.5
0.02 ^b	0.1	60	11.8	1.55	36.3	1.0	155	—	36.3	100	155

^a [aniline]/[NH₄S₂O₈] = 1.

^b Double polyaniline layer.

The corresponding significant growth of gas separation selectivity also occurs, up to 8.2 for O₂/N₂ and to 26.8 for CO₂/CH₄. Thus, it is shown that the prepared composite film is only slightly less permeable than PVTMS, whereas its gas separation selectivity is 2–5 times higher.

Redoping of composite film by the same acid of the same concentration as in the preparation (0.1M HCl) would have allowed the film to regain the structure and gas-transport properties of the initial film. In reality, the gas permeability of redoped samples is even lower than that of the initial films. Gas permeability for He stays on the level of undoped samples. Selectivity coefficients for He/N₂ and He/CH₄ are 153 and 95, respectively. Selectivities for O₂/N₂ and CO₂/CH₄ are slightly higher than those of initial films but lower than those of undoped samples.

Repeated undoping of redoped samples of composite material yields almost the same permeability value as that for undoped film obtained in the first cycle. Selectivity of gas separation was degraded (see Table III). The latter result can be ascribed to tensions in the two-layered film, leading to the appearance of microdefects.

In addition to HCl, *p*-toluenesulfonic acid was used as the redoping agent (Table III). It is seen that there is no marked difference in gas permeation characteristics.

In discussing the mechanism of gas transfer in PANI membranes, the preference is given to the diffusion mechanism. The dependency of the gas permeability coefficients on the kinetic diameter of the gas for composite film in initial, undoped, and redoped forms corroborates the diffusion mechanism of gas transfer. Moreover, somewhat underestimated values of permeability for O₂ compared to those for CO₂ of the film in undoped form suggest only slight solubility of oxygen in the PANI coating.

The change in conditions of borderline polymerization (reagent concentrations, acidity of medium, du-

ration of reaction) was shown in this work to affect not only the quality of PANI coating in composite films, but also gas separation properties. Gas separation characteristics of undoped composite films are presented in Table IV, depending on preparation conditions. Attention is drawn to the fact that selectivity of gas separation is deteriorated for the films obtained by borderline polymerization of aniline at reagent concentrations other than the optimal value (0.02 mol/L). By decreasing the aniline concentration to 0.01 mol/L, a decrease in the reaction rate was observed, as well as an increase in the induction period. The same effect was achieved by increasing the HCl concentration. As the result, the PANI layer becomes less homogeneous, its thickness decreases, and various microdefects appears. Although permeability increases in this process for all gases, selectivity of gas separation was degraded.

At concentrations of monomer and oxidant >0.02 mol/L, the gas permeability of the samples essentially did not decrease, despite the growth of polymerization rate, which demonstrates that there is no correlation between the thickness of the PANI barrier layer and the reaction rate. As the UV-visible spectroscopy data show, even though there is an increase of PANI amount in the composite film, a certain part of this polymer does not seem to be affecting the gas-transfer process. As mentioned above, the increase in monomer concentration during growth of the PANI layer > 0.02 mol/L gives rise to adsorption polymerization. This process facilitates the formation of the layer of loose polymer adsorbed from solution bulk on the surface of the PANI coating formed by borderline polymerization. This layer, which essentially does not participate in the gas separation process, only degrades the quality of the PANI layer, and gas separation selectivity is adversely affected. Thus, in a succession of concentrations, 0.02, 0.03, and 0.04 mol/L, selectivity for O₂/N₂ decreases from 8.2 to 6.0 and 5.5.

As mentioned above, polymerization times > 2 h favor destruction processes in PANI that deteriorate its quality and make the coating thinner; thus, gas permeability increases, whereas separation selectivity worsens.

Data from Table IV attest to the sharp decrease in gas permeability for the sample containing a double PANI layer on the PVTMS support. After aniline borderline polymerization under optimal conditions the sample was again subjected to the same procedure followed by undoping. For a number of gases, permeability values are close to those of doped samples. At the same time, permeability for He remained essentially the same, thus giving the double-layered composite film high selectivity for He/CH₄ (155). Because of the sharp decrease in permeability for CH₄, selectivity for CO₂/CH₄ is also high (36.3).

CONCLUSIONS

The method of borderline oxidative polymerization of aniline allows the direct preparation of composite membrane materials (PANI coating supported by PVTMS) in the course of synthesis, without any additional steps. The coating is a uniform, strongly adhering film of thickness up to 1 μm , which differs in both morphology and chemical structure from polymer that forms in solution bulk. The foremost differences are the absence of faulty repeat groups in the polymer chain and mainly radical cation structure in the doped state, as well as the dense, finely structured texture of its morphology. It is shown that in the course of PANI synthesis the changes also occur in the borderline PVTMS layer.

To obtain a quality polyaniline coating during borderline polymerization, optimal reagent concentrations and reaction time, as well as increased requirements to homogeneity of support surface, must be observed. Otherwise, either the hearth growth of the coating layer occurs or adsorption polymerization starts to prevail. In both cases, the end result is deterioration in the quality of the PANI layer.

Study of gas separation properties of composite films has shown that these films have greater permeability than that of monolayer PANI films cast from solution, by two orders of magnitude. For certain gases, their permeability is only insignificantly smaller than that of PVTMS, whereas selectivities of gas separation for O₂/N₂, He/CH₄, He/N₂, and CO₂/CH₄ are higher than those of PVTMS.

In the undoped state, these samples have better selectivities of gas separation for O₂/N₂ and CO₂/CH₄ than those of PANI films cast from solution. We have not succeeded in increasing the selectivity to any significant degree by redoping the samples with the same or different dopant. The change in process conditions also has not improved gas-transport characteristics. Any deviation from the optimal mode of borderline polymerization leads to deterioration of coating quality and gas separation selectivity.

Comparing gas separation characteristics of our samples with those of a large number of polymer materials,²⁰ it can be concluded that the composite PANI-PVTMS films have an appropriate combination of gas separation selectivity and permeability for most gases. In the case of O₂/N₂, He/CH₄, He/N₂, and CO₂/CH₄, characteristics of composite material significantly exceed those of most known polymer materials.

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