Polymerization of Aniline on Polyaniline Membranes

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When solutions of aniline hydrochloride and ammonium peroxydisulfate were separated by a semipermeable cellulose membrane, the reactants met at the membrane and produced a polyaniline (PANI) membrane at the interface. The oxidative polymerization of aniline then proceeded in situ on the PANI−cellulose composite membrane. PANI was produced entirely at the monomer side of the membrane; about 80% conversion of aniline to PANI was observed after 24 h. The oxidation of aniline with peroxydisulfate consists in the transfer of electrons from aniline to the oxidant; it is proposed that electrons pass through the PANI membrane, which is conducting, and electroneutrality is maintained by the simultaneous transfer of protons. The reaction between aniline and peroxydisulfate thus takes place without the need for both reactant molecules to be in physical contact. The residual aniline is located only at its original side of the membrane, but the product of ammonium peroxydisulfate conversion, ammonium hydrogen sulfate, was found on both sides of the membrane. Fourier-transform infrared spectroscopy has been used to analyze PANI, the reaction residues and byproducts, and to prove that PANI is protonated with counter-ions of the sulfate type. Using this technique, we have detected only small differences in the molecular structure of PANI prepared with the membrane-separated reactants and in the polymerization when reactants were mixed; also, the molecular weights differed only marginally. The conductivity of both types of PANI was about the same. The repeated polymerization of aniline on the earlier prepared PANI−cellulose membrane yielded similar results, thus confirming the proposed concept of coupled electron- and proton-transfer through the PANI membrane.

Introduction

Studies of membranes comprising conducting polymers, such as polyaniline (PANI) or polypyrrole (PPy), have been reported in many recent papers. PANI membranes have been tested in pervaporation experiments,[1,2] gas separation,[3] metal recovery by electrodialysis,[4,5] analytical ion-selective electrodes,[6,7] pH sensors,[8] enzyme immobilization,[9] improvement of thermal stability,[10] and trans-membrane redox reactions.[11,12] Recent efforts in the design of PANI-modified[13−15] or PPy-containing[16−18] membranes have been aimed at applications in fuel cells.

Membranes cast from PANI solutions, e.g., in *N*-methylpyrrolidone (occasionally containing another polymer,[5,15,20] or an additive, like fullerene[12]), have most frequently been investigated.[1,3,6,11,14,19] Due to the general insolubility of PPy, the solution technique is not applicable to this polymer. Alternatively, the polymer membranes have been modified with colloidal PANI dispersions.[21]

In situ deposition,[22,23] however, seems to be the most promising way to achieve composite membranes containing PANI.[13,24] For example, one of the surfaces of a poly(styrenesulfonic acid) membrane was pretreated with anilinium chloride solution, which was then replaced with ammonium peroxydisulfate (APS) solution. The membrane was coated with PANI preferentially on one side.[13] These asymmetric membranes have been demonstrated to have high selectivity in the separation of alkaline and rare-earth metal cations.[25] The same technique has earlier been used to coat cation-exchange membranes with PANI.[4,24−28] Perfluorinated Nafion membranes have also been modified by the polymerization of aniline or aniline derivatives.[29] The so-called chemical deposition of conducting polymers is preferred due to its simplicity, but the electrochemical preparation of PANI on an alumina membrane modified with gold has also been reported.[30]

Similar experiments have been carried out with the in situ deposition of PPy on various membranes.[9,10,16−18,31−33] Some authors[16,17,31] have used pyrrole and sodium peroxydisulfate solution separated by a Nafion membrane to produce a PPy coating on one side of the membrane. The great interest in the modification of perfluorinated membranes with conducting polymers for applications in fuel cells is connected with the fact that the resulting composite membranes have a lower permeability to liquid fuels, like methanol, and the performance of fuel cells is thus improved.

Kocherginsky et al.[11,12] studied redox processes on the PANI membrane, namely, the reduction of iron(III) salt with ascorbic acid,[11] solutions of the reactants having been separated by a membrane. Such redox reactions are based on the exchange of electrons between reactants. It has been proposed that the electron transfer can be mediated by the PANI membrane, which is *electrically conducting*. The molecules of oxidant and reductant thus react by exchanging electrons through the PANI membrane *without being in any direct contact*.

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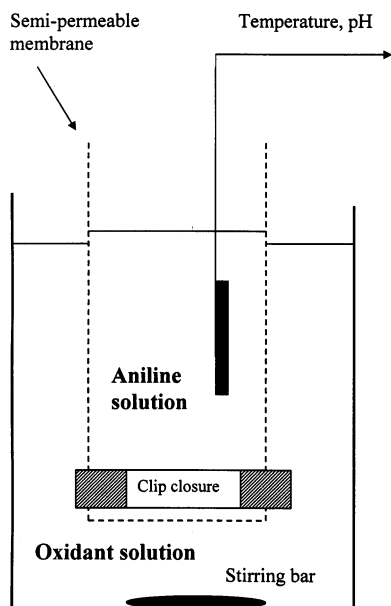[§] Institute of Macromolecular Compounds.

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Figure 1. The aqueous aniline hydrochloride solution in semipermeable dialysis tubing was placed into the oxidant solution, and temperature and pH changes were monitored.

The oxidation of aniline hydrochloride with APS is also a redox process. Aniline provides electrons as it is converted to PANI, and peroxydisulfate accepts these electrons and produces sulfate. The reaction should therefore follow the same principle after the PANI membrane has been produced in situ at the beginning of oxidation. We propose that aniline and oxidant molecules react under such conditions to yield PANI by exchanging electrons through the PANI membrane, without being in direct physical contact, in contrast to common preparations. This concept of PANI preparation is analyzed and discussed in the present paper.

Experimental Section

Polymerization. The dialysis membrane tubing Spectra/Por 1 (Spectrum Medical Instruments Inc., U.S.A.) from the regenerated cellulose (tube diameter 13 mm, molecular-weight cutoff 7000) closed at one end with the clip closure was filled with 50 mL of aqueous solution containing 80 mmol of aniline hydrochloride and immersed in 150 mL of aqueous solution containing 100 mmol of APS (Figure 1). The oxidant-to-monomer ratio was 1.25; the concentrations in the whole 200 mL system were 0.4 M aniline hydrochloride and 0.5 M APS. The polymerizations were started at room temperature, ~20 °C, and temperature and pH have been recorded in the internal aniline compartment or in the external oxidant solution. The reactions were terminated after 2 h or after 24 h. The PANI formed on the monomer side of the membrane (and, if any, also on the oxidant side) have been collected on a filter, and the filtrate was immediately evaporated on a rotary evaporator to yield the water-soluble components of the reaction mixture. In a reference experiment, the oxidation of aniline has been carried out in the absence of the membrane by simply mixing the monomer and oxidant solutions.

The PANI membrane was produced in situ on the cellulose support. Repeated polymerizations have also been carried out by using the PANI membranes prepared in previous polymerizations.

Characterization. Infrared spectra in the range of 400−4000 cm^{-1} were recorded at 64 scans per spectrum at 2 cm^{-1} resolution using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector in the transmission mode after dispersion of the samples in potassium bromide pellets. A Golden Gate Heated Diamond ATR Top-Plate (Specac Ltd.) was applied for the characterization of membrane surfaces. Typically, 256 of scans at 4 cm^{-1} resolution have been recorded. The spectra were corrected for the presence of carbon dioxide and humidity in the optical path.

Molecular weights were assessed with a gel-permeation chromatography/SEC apparatus using a 8×600 mm PLMixedB column (Polymer Laboratories, U.K.) operating with *N*-methylpyrrolidone and calibrated with polystyrene standards using spectrophotometric detection at 650 nm. The samples were dissolved in *N*-methylpyrrolidone containing 0.025 g cm^{-3} triethanolamine (for the deprotonation of the samples) and 0.005 g cm^{-3} lithium bromide (to prevent aggregation of the PANI chains).

The conductivity of the polymers was measured with a four-point Van der Pauw method on pellets compressed at 700 MPa with a manual hydraulic press using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter with a 2000 SCAN 10-channel scanner card. For nonconducting forms, a two-point method using a Keithley 6517 electrometer was applied. Before such measurements, circular gold electrodes were deposited on both sides of the pellets. The density of the PANI was determined with a Sartorius R160P balance by weighing the pellets both in air and immersed in decane.

Results and Discussion

Polymerization of Aniline. PANI is currently prepared by the oxidation of aniline with APS in acidic aqueous medium[34,35] (Figure 2). An aniline salt, e.g., aniline hydrochloride, is oxidized at first to give the aniline cation radical[35,36] (a), which subsequently polymerizes to the protonated pernigraniline intermediate (b), and, finally, converts to a protonated emeraldine form of PANI (c).The electrons removed in steps (a) and (b) are accepted in the reductive step (c), and mainly by APS that reduces to sulfate (d). The PANI formulae in Figure 2 show the delocalized polarons, but they can also be represented by structures containing the localized protonated quinonediimine nitrogens. Hydrogen atoms, which are abstracted from the amino group and the para position on the benzene rings in the aniline molecules, are released as protons. They participate in the protonation of imine sites in the PANI and become a part of the ammonium hydrogen sulfate, which is formed as a byproduct (d). In total (Σ), five molecules of APS are needed to oxidize four aniline molecules to PANI.

Polymerization of Aniline on a PANI Membrane. When we separate the solution of aniline hydrochloride and APS with a membrane permeable to low-molecular-weight species, a composite PANI membrane is produced at the very beginning of oxidation at the interface between the reactant solutions.[22] Aniline molecules can then be oxidized to PANI and APS reduced to ammonium hydrogen sulfate by passing the electrons through the conducting PANI membrane, without the need for direct contact (Figure 3).

One can ask why a metal sheet would not perform like a PANI membrane, because its electron conductivity is obvious. Such a transfer of electrons would not take place through the metal because electroneutrality could not be maintained on both sides of such a sheet, and the electric-potential difference restricting the transport would soon be built up. On the other hand, the protonated PANI is a mixed electron and proton conductor.[14,37,38] The transfer of protons through the PANI membrane is thus feasible. If one electron is transferred through the membrane along with one proton (Figure 3), electroneutrality is preserved on both sides of the membrane.
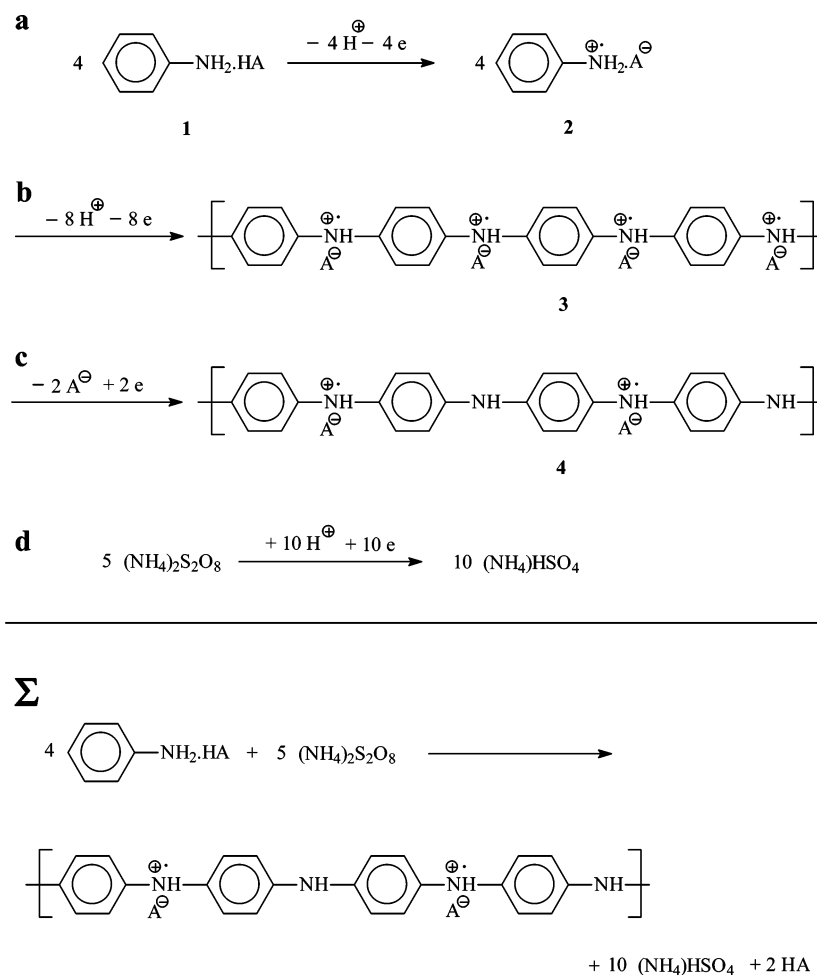
Figure 2. (a) Aniline salt (**1**) is oxidized to the aniline cation radical (**2**) (b), which is polymerized to an intermediate protonated pernigraniline (**3**), and (c) reduced at the end of polymerization to the protonated emeraldine form of polyaniline (**4**). (d) Ammonium peroxydisulfate is reduced at the same time to ammonium hydrogen sulfate. HA is an arbitrary acid, hydrochloric acid in the present study.
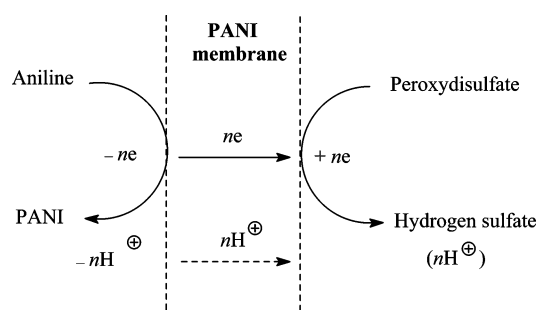

Figure 3. During the oxidation of aniline to PANI (left) with peroxydisulfate (right), the electrons are transferred from aniline molecules to oxidant molecules through the *conducting* PANI membrane. They are accompanied by protons in order to preserve the electroneutrality of the system.

The redox processes between the solutions of reactants separated with a conducting polymer membrane are analogous to trans-membrane transport between the metal electrode coated with a conducting polymer, which is immersed in the solution of the investigated species, and these species. The PANI membrane prepared by the present technique, however, can be used for the generation of large quantities of products without direct contact between the reactants, and not only for the analytical detection purposes.

In the early stages of oxidation, before any PANI formation, the monomer diffuses through the membrane into the oxidant solution, and similarly, the oxidant diffuses to the solution of aniline salt. On the monomer side of the membrane, the oxidant concentration is low and the aniline concentration is high; in this case, the polymerization occurs in a similar manner like when APS is added dropwise to the monomer solution. That is why PANI is produced on the monomer side of the membrane (Table 1). On the oxidant side of the membrane, however, the concentration of APS is much higher than that of the monomer, and anilinium cations on this side are immediately oxidized with APS to aniline nitrenium cations.[35] In the reaction of aniline nitrenium cations with aniline, a 4-aminodiphenylamine dimer is produced, which further undergoes a fast two-electron oxidation with APS to its fully oxidized form, *N*-phenyl-1,4-benzoquinonediimine, which diffuses into the bulk of the oxidant solution. The subsequently formed polycationic PANI membrane restricts the diffusion of anilinium cations into the APS solution[26,27,39] and allows only for the indirect trans-membrane oxidation of aniline with APS via the redox cascade process, APS → PANI (pernigraniline → emeraldine) → aniline. APS oxidizes the PANI membrane, and the oxidized PANI membrane further oxidizes aniline, thus promoting its polymerization. It is proposed that redox mediation of the PANI membrane is much more important for the studied processes than the conductivity of PANI itself.

The oxidation of aniline is exothermic and can be monitored by recording the reaction temperature.[36] Polymerization on the membrane (Figure 4) is considerably slower, compared with

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TABLE 1: Conversion of Aniline Hydrochloride to Polyaniline and Weights (and Weight Fractions) of the Residual Salts on Aniline and Oxidant Sides of the Membrane, Including Total Solids Recovery

		polymer[a]		water-soluble salts		
membrane	reaction time, h	aniline side, g (wt %)	oxidant side, g (wt %)	aniline side,[c] g (wt %)	oxidant side,[d] g (wt %)	solids,[b] wt %
original	2	4.94 (47.7)	∼0	4.28 (41.3)	20.4 (89.4)	89.3
	24	6.76 (65.3)	∼0	2.72 (26.2)	15.9 (69.6)	76.8
PANI-coated	2	4.36 (42.1)	0	5.28 (50.1)	19.2 (84.2)	87.0
	24	7.51 (72.4)	0	2.82 (27.3)	16.7 (73.2)	81.5
none	(4 min)	10.5 (101.3)		12.9 (56.8)		70.6

[a] Due to the uncertainty in the type of protonation, 1 g of aniline hydrochloride is assumed to produce 1 g of protonated PANI at full conversion. [b] Solids recovered from initial solids entered (10.36 g aniline hydrochloride + 22.80 g APS = 100%). [c] 10.36 g aniline hydrochloride = 100%. [d] 22.80 g APS = 100%.
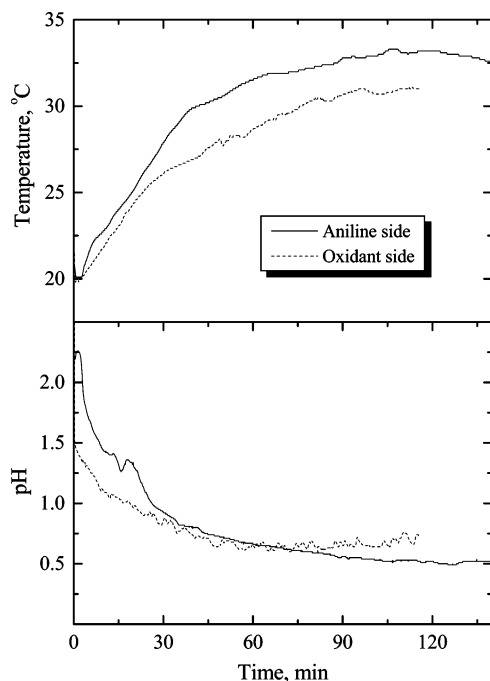

Figure 4. The temperature and acidity profiles in the oxidation of 0.4 M aniline hydrochloride with 0.5 M ammonium peroxydisulfate. Aniline hydrochloride solution (full line) and ammonium peroxydisulfate solution (dashed line) were separated by a semipermeable cellulose membrane.

Figure 5. The temperature and acidity profiles in the oxidation of 0.4 M aniline hydrochloride with 0.5 M ammonium peroxydisulfate in a mixture.

the conventional process in which aniline and oxidant are simply mixed. There is no notable induction period during the oxidation on the membrane (Figure 4), which is typical for the oxidation of aniline in acid media[34] (Figure 5). The course of pH changes shown in Figure 4 reflects the rates of proton transfer through the membrane. In addition, the maximum temperature in the membrane polymerization is lower, because the heat loss is larger during the extended time of the reaction. The temperature in the internal compartment containing aniline was higher (Figure 4), because the polymerization takes place there. This observation may also be affected by the design of the experiment (Figure 1), in which the external oxidant solution dissipates the reaction heat to the ambient atmosphere and thus becomes cooler than the internal monomer solution.

The hydrogen atoms abstracted from aniline molecules in the course of the oxidation are released as protons (Figure 2a, b). The pH of the reaction mixture decreases during the oxidation of aniline (Figure 4). It is expected that protons pass through the PANI membrane to compensate for the electric charge carried by the transfer of electrons (Figure 3). The results reported below suggest that sulfuric acid can penetrate the PANI membrane, and consequently, no marked differences in pH are observed between the monomer and oxidant compartments (Figure
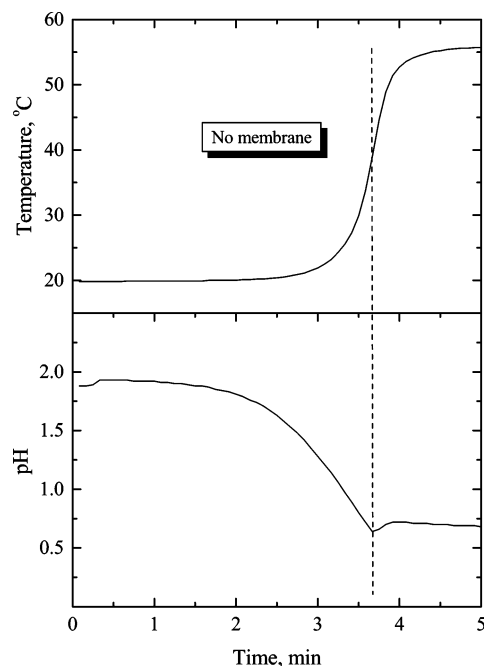
4). It has been reported that proton−anion coupled transport, i.e., acid transport, through the PANI membrane is possible.[11,19]

PANI Membrane. A PANI membrane prepared by in situ polymerization of aniline on a cellulose support is asymmetric; PANI is generated on the aniline side of the membrane. This is illustrated by the morphology of membrane, which shows that the membrane surface exposed to the oxidant solution is smooth (Figure 6a). The typical globular structure of PANI, 1−2 μm in grain size, is observed on the aniline side (Figure 6b). The adhesion of PANI to the supporting cellulose membrane is poor, and PANI peels off easily during drying, leaving exposed areas of the original membrane. This means that the PANI overlayer has been deposited only on the surface of the supporting membrane and does not penetrate to its interior. Another proof of membrane asymmetry is provided by ATR FTIR spectroscopy (Figure 7). The spectrum of the oxidant side of the membrane corresponds to that of the neat cellulose membrane, and the spectrum of the monomer side of the membrane corresponds to PANI. This is well seen after the PANI has been converted to its base form in order to reduce the reflectivity of the coating. The spectra also prove that the coating of the membrane with PANI on the monomer side is complete; the peaks corresponding to the cellulose support are not visible (Figure 7).

Yield of PANI, Residues, and Byproducts. The conversion of aniline to PANI in the membrane-separated solution was about
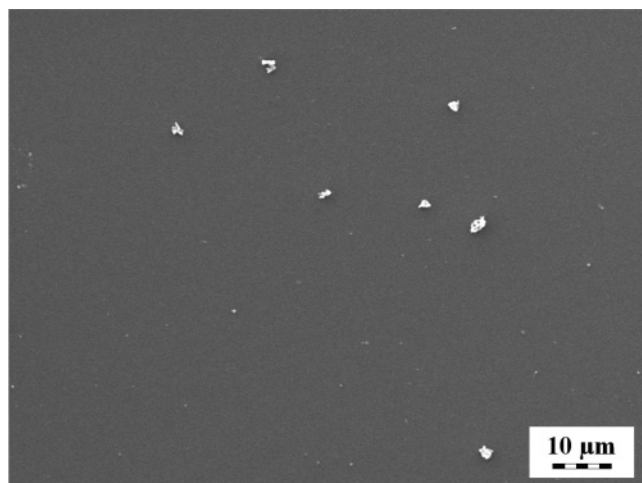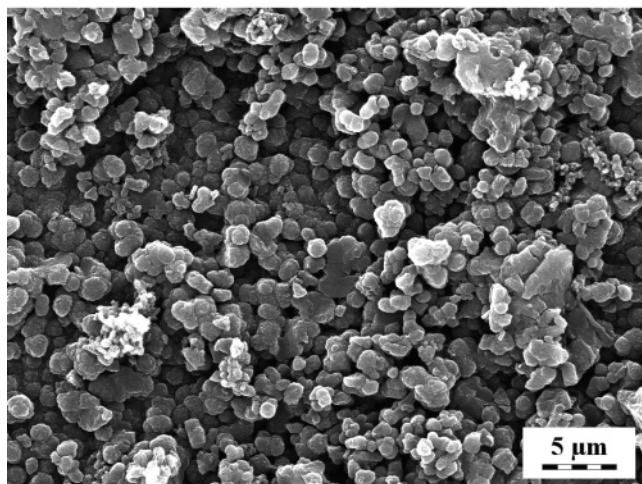
Figure 6. Morphology of (a) the oxidant side and (b) the aniline side of the membrane.

40% after 2 h and 70% after 24 h (Table 1). A similar polymerization in the absence of a membrane was completed within 4 min (Figure 5) with complete conversion of aniline to PANI (Table 1). In the trans-membrane polymerization, PANI was produced on the aniline side. Only traces of a precipitate have been collected on the oxidant side (Table 1) due to the marginal transport of aniline at the beginning of the experiment before the PANI membrane has been produced. These traces of polymer were absent when the PANI-coated cellulose membrane was used in the repeated polymerization, as discussed below.

After the separation of PANI by filtration, the solids obtained after the evaporation of the filtrate in the aniline compartment were about 50% and 30% of the original amount of aniline hydrochloride (Table 1) after 2 and 24 h, respectively. This roughly corresponds to the conversion of aniline to PANI, as expected by the proposed trans-membrane mechanism (Figure 3). On the oxidant side of the membrane, APS is expected to convert to ammonium sulfate and sulfuric acid, in fact to ammonium hydrogen sulfate (Figure 2d). That is why the amount of the solids was about 85% and 70% of the original APS entered in the reaction after 2 and 24 h, respectively (Table 1). Hydrochloric acid, constituting part of the byproducts (Figure 2), evaporates during the collection of solids from the aqueous phase, resulting in a level of solids recovery lower than 100% (Table 1).
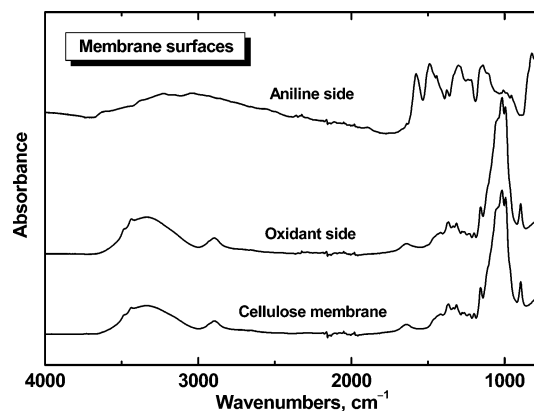

Figure 7. FTIR-ATR spectra of the aniline and oxidant sides of the cellulose membrane and the spectrum of the original uncoated cellulose membrane. PANI coating was converted to the base form prior to the FTIR spectroscopic characterization.
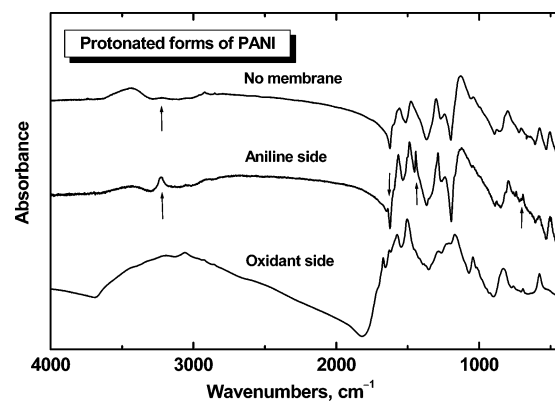

Figure 8. FTIR spectra of PANI powders prepared (a) without any membrane and (b) with membrane-separated reactants on the aniline side of membrane and (c) on the oxidant side of membrane.

Molecular Structure of PANI. In subsequent discussion, we concentrate on PANI prepared after 24 h of polymerization. The FTIR spectrum of PANI powder obtained on the aniline side of the membrane is close to the spectrum of PANI prepared in a conventional way, over the whole region $4000-500$ cm^{-1} (Figures 8 and 9). A broad absorption band observed for protonated PANI, found at wavenumbers higher than 2000 cm^{-1} (Figure 8), is typical of the conducting form of PANI. In both the spectra of protonated PANI, the peaks that belong to hydrogen sulfate ions appear at $\sim$580 and 1041 cm^{-1} (Figure 8); the spectrum of ammonium hydrogen sulfate includes strong peaks at $\sim$584 and 1052 cm^{-1} (cf. NH_4HSO_4 in Figure 10). This means that sulfuric acid participates in the protonation of PANI, along with the hydrochloric acid introduced to the reaction in aniline hydrochloride. The corresponding peaks of hydrogen sulfate disappear after the deprotonation to PANI base, as expected (Figure 9).

The main peaks corresponding to quinonoid and benzenoid ring-stretching vibrations in the spectrum of conducting protonated PANI prepared in the conventional way are blue-shifted from 1557 and 1476 to 1564 and 1489 cm^{-1}, and they are narrower in the spectrum of PANI obtained on the aniline side of the membrane (Figure 8). The absorption band at 1301 cm^{-1}, corresponding to π-electron delocalization induced in the polymer by protonation,[41] is sharper and shifted to 1288 cm^{-1}. The band characteristic of the conducting protonated form, observed at 1242 cm^{-1}, has been assigned to the C$-$N$^{+\bullet}$ stretching vibration in the polaron structure,[42] and the prominent band located at 1130 cm^{-1} to a vibration mode of the $-$NH^{+}=

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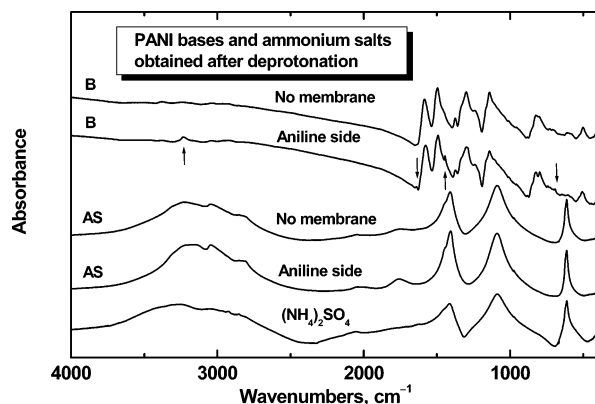*J. Phys. Chem. B, Vol. 111, No. 10, 2007* **2445**

Figure 9. FTIR spectra of PANI bases (B) and ammonium salts (AS) obtained after deprotonation of the protonated PANI with ammonium hydroxide. Ammonium salts correspond to the original counter-ions in the protonated PANI, which was prepared without a membrane or produced on the aniline side of a PANI membrane when membrane was used.
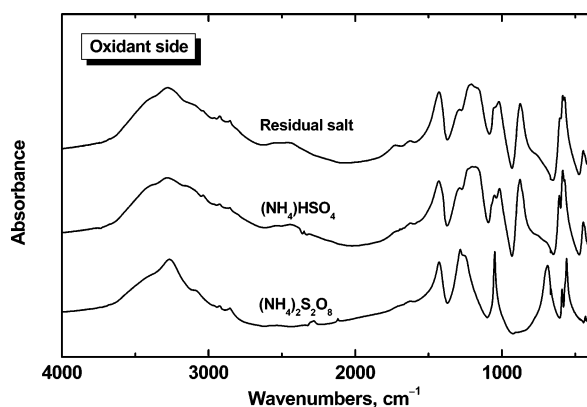

Figure 10. FTIR spectrum of a residual salt obtained on the oxidant side of a membrane and comparison with the spectra of ammonium hydrogen sulfate and ammonium peroxydisulfate.

TABLE 2: Conductivity, Density, Weight-Average Molecular Weights, M_w, and the Weight-to-Number Average Molecular Weight Ratio, M_w/M_n, for PANI Prepared on Neat or PANI-Coated Membranes after 2 or 24 h

membrane	reaction time, h	conductivity, S cm^{-1}	density, g cm^{-3}	M_w	M_w/M_n
original	2	7.3	1.35	47400	6.3
	24	6.5	1.34	35500	5.4
PANI-coated	2	7.8	1.35	47700	9.7
	24	7.0	1.33	41700	6.3
none	(4 min)	9.4	1.42	30500	3.9

Protonation of PANI. The density of PANI prepared in the absence of a membrane, 1.42 g cm^{-3}, is higher than that of the PANI prepared on the membrane, $\sim$1.34 g cm^{-3} (Table 2). This may suggest a difference in the type of protonation; PANI sulfate has been reported[48] to have a density 1.40 g cm^{-3} and PANI hydrochloride[34] 1.33 g cm^{-3}. The PANI prepared on the membrane thus may contain the majority of chloride counter-ions. This is logical, because the polymerization was initiated with aniline *hydrochloride*. Yet, the presence of hydrogen sulfate counter-ions in PANI was proved by FTIR spectra (Figure 8); the spectra of ammonium salts obtained after the deprotonation of PANI prepared with and without the membrane are identical to the spectrum of ammonium sulfate (Figure 9). This means that sulfuric acid has always protonated PANI, to various extents, in the form of sulfate or hydrogen sulfate counter-ions. In contrast to ammonium sulfate, the presence of ammonium chloride, corresponding to chloride counter-ions, cannot be detected by this method; there are no bonds active in the FTIR spectra.

Molecular Weights. The weight-average molecular weights of PANI prepared on the membrane is $M_w \sim 40\,000$ (Table 2), with a broad molecular-weight distribution. PANI produced in the early stages of polymerization, after 2 h, has a slightly higher molecular weight, and PANI of lower molecular weight is obviously produced in the advanced stages of polymerization. All the distributions were monomodal. The molecular weight of PANI prepared by mixing the reactants is only slightly lower, $M_w = 30\,500$, and the distribution of molecular weights is narrower (Table 2). It is quite surprising that the PANI produced on completely different time scales, minutes after mixing of components or tens of hours on the membrane, are essentially identical products with respect to molecular weight.

Conductivity. The conductivity of the PANI prepared on the membrane was on average 6.9 S cm^{-1}, regardless of the reaction time (Table 2), only slightly lower than conductivity of PANI prepared by mixing the solutions in the absence of a membrane. This difference is on the verge of the experimental error of conductivity determination.[34] It has recently been suggested that the molecular structure of PANI can be improved,[49] and conductivity exceeding 600 S cm^{-1} attained,[49,50] if the PANI produced has been separated from the oxidant in the course of preparation. This has been achieved by performing a dispersion-like polymerization in chloroform/water, and the success has been assigned to the fact that the oxidant was present in the aqueous phase while the aniline was preferentially in the organic phase. In the present experiments, the oxidant and the PANI produced are also separated; no accompanying marked improvement of the structure or properties, however, has been observed (Table 1).

Residues and Byproducts. It is of fundamental importance to decide what are the low-molecular-weight residues and byproducts and on which side of membrane they are located. The salt collected at the oxidant side of the membrane is ammonium hydrogen sulfate, which is produced from am-
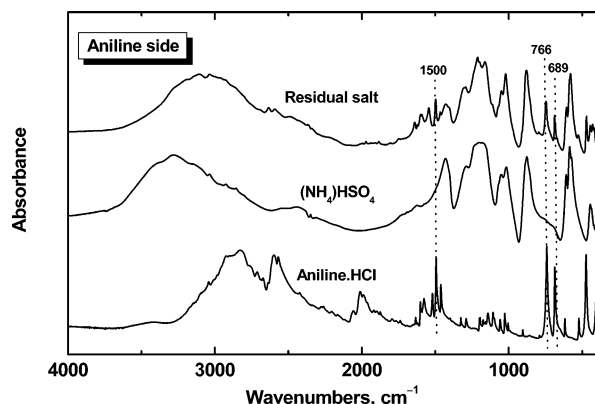
structure, which is formed during protonation.[43,44] These are found at 1240 and 1123 cm^{-1} in the spectrum of the product on the aniline side of the membrane. The last band is much more pronounced in the spectrum of conventional PANI due to the higher proportion of sulfate anions in the structure.

In addition, however, a sharp peak at 3228 cm^{-1}, a small but well-defined peak at 1644 cm^{-1}, a pronounced peak located at 1444 cm^{-1}, and a sharp peak at 693 cm^{-1} have been observed in PANI prepared on the membrane (they are marked by arrows in Figure 8). They were assigned to aniline oligomers and are well recognized in the spectra of PANI prepared in solutions of weak acids.[44-46] In the spectra of standard PANI, these peaks are overlapped by the spectrum of the polymer component. There is practically no PANI produced on the oxidant side of the membrane (Table 1). The traces of material (milligram quantities) that could be collected have a completely different spectrum (Figure 8) and can probably be related to over-oxidized intermediates in the aniline oxidation.

The FTIR spectra of PANI bases obtained after deprotonation (Figure 9) show closer similarity in the molecular structure of PANI prepared with and without the membrane over the whole region 4000−500 cm^{-1} than in the case of the protonated forms (Figure 8). The peaks at 1644, 1444, 695 cm^{-1}, and the sharp peak observed at 3228 cm^{-1}, are still present in the spectrum of the PANI base. They are thus inherent to the PANI structure and not connected with the protonation or the spectral features of the counter-ions.

Figure 11. FTIR spectrum of residual salt obtained after the separation of the sample prepared on the aniline side of membrane and the comparison with the spectra of ammonium hydrogen sulfate and aniline hydrochloride.
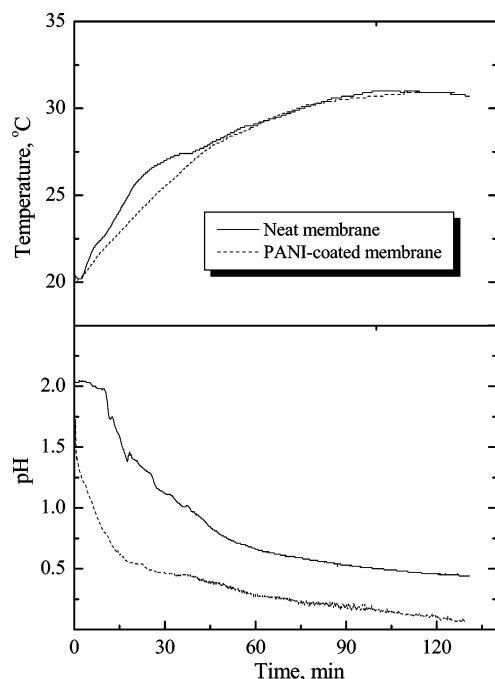

Figure 12. The temperature and acidity profiles in the oxidation of aniline hydrochloride with ammonium peroxydisulfate separated by (a) a neat cellulose membrane (full line) and (b) a membrane that had already been coated with PANI (dashed line) and recorded on the aniline side of the membrane.

monium sulfate at reduced pH. This is clearly demonstrated by the FTIR spectra of this salt and of commercial ammonium hydrogen sulfate (Fluka, Switzerland) (Figure 10). The presence of ammonium hydrogen sulfate on the aniline side of the membrane is indeed obvious from the FTIR spectra (Figure 11). In addition, the residual aniline salt is also present on this side of membrane; the peaks located at 1500, 746, and 689 cm^{-1} clearly demonstrate this fact. The aniline monomer is, however, completely missing in the solids isolated on the oxidant side of the membrane (Figure 10).

Repeated Polymerization on the Membrane. The use of the PANI-coated cellulose membrane for the repeated polymerization experiments gave analogous results. There is no substantial difference between these two cases (Table 1), i.e. whether the PANI membrane was produced in situ or in advance. The reaction proceeded at the same rate (Figure 12), only the pH was lower when the PANI-coated membrane was used instead of a neat cellulose one. This may mean that the
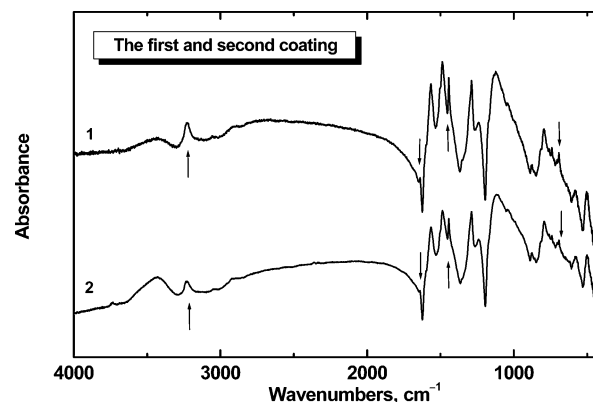

Figure 13. FTIR spectra of PANI prepared on a neat cellulose membrane (1) and on a membrane, which had already been coated with PANI during a preceding polymerization (2).
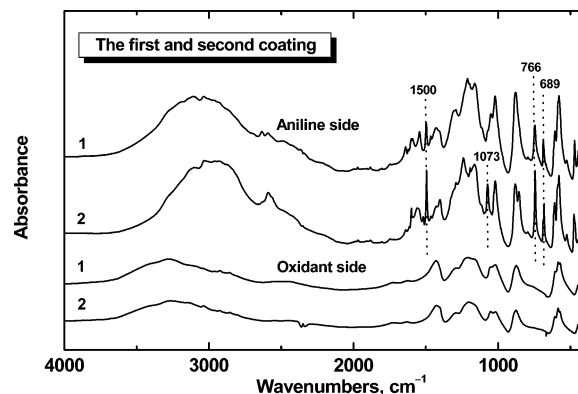

Figure 14. FTIR spectra of residual salts in samples prepared on a neat cellulose membrane (1) and on a membrane, which had already been coated with PANI during the preceding polymerization (2).

transport of sulfuric acid through the membrane is restricted. The PANI membrane produced in the first experiment becomes once more coated with PANI, and thus thicker, during the second polymerization.[51] The PANI samples produced in both experiments are practically identical, as reflected by their FTIR spectra (Figure 13), and confirmed by observing the same molecular weight and conductivity (Table 2). The residues after polymerization are also similar in the two cases (Figure 14). We conclude that, in the present experiments, a PANI membrane can be prepared in situ on a neutral polymer support and does not need to be produced separately in advance.

Different Levels of Reactant Solutions. An additional test has been made in support of the present concept of redox mediation by the PANI membrane. The aniline and oxidant solutions were separated by a cellulose membrane, but the solution levels were different (Figure 15). The membrane became coated with PANI over the whole membrane interface with the aniline solution, not only on the part of the membrane where solutions of aniline and an oxidant faced each other. This experiment proves that the polymerization of the aniline molecule does not require the oxidant molecules to be present as such, but only the electrons provided by the oxidant, and transported through the growing or the PANI deposited on the cellulose membrane.

The Concept of Trans-Membrane Polymerization of Aniline. On the basis of the experimental evidence discussed above, we summarize the features of the trans-membrane polymerization of aniline as follows:

The reactants, anilinium cation and peroxydisulfate anion, diffuse through the semipermeable cellulose membrane and meet
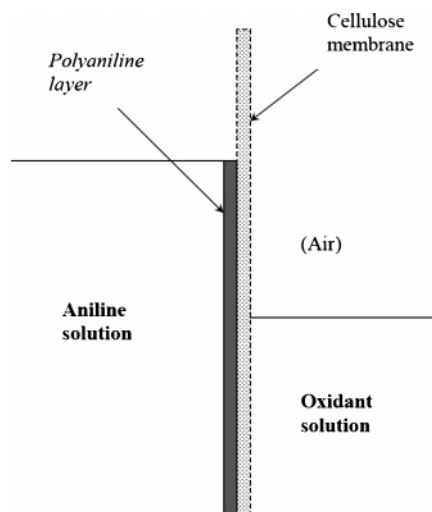
Polymerization of Aniline on Polyaniline Membranes

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Figure 15. When aniline and oxidant solutions were separated by a cellulose membrane, PANI was produced at the entire membrane surface in contact with the aniline solution and not only in the area where aniline and oxidant solution faced each other.

each other. The first oxidation products are produced on the aniline side of the membrane. A composite membrane is produced in situ on this side of the membrane by the growth of PANI on the cellulose template. The neutral template membrane converts to an actively conducting polymer membrane.

Under the acidic conditions of the experiment, pH ~ 2, PANI is protonated and represents a polycation with uniformly distributed protonated imine sites. Such a positively charged membrane is hardly permeable to a protonated monomer, the anilinium cation, due to the electrostatic repulsive interactions. Monomer diffusion through the membrane is thus suppressed. On the other hand, the imine nitrogen in the PANI forms a salt with the acid present in the medium. The protonated PANI is a mixed electron and proton conductor. The membrane composed by the PANI can thus mediate the transfer of both electrons and protons between the reactants separated by the membrane and thus also preserve electroneutrality on both sides of the membrane. The PANI membrane thus can act as a mediator of various redox processes, which are based on the exchange of electrons. The oxidant and the reductant, although physically separated, can, in this way, interact.

The oxidative polymerization of aniline on the PANI membrane proceeds by the transfer of electrons from aniline molecules to the peroxydisulfate through the conducting PANI membrane, and it exploits the ability of the PANI to be both oxidized and reduced. The monomer and oxidant are separated; the polymer is produced exclusively on the aniline side of the PANI membrane. The protons generated in this process penetrate the membrane easily, and the pH is maintained at a comparable level at both sides of the membrane. The membrane is also permeable to anionic species, chloride counter-ions from the aniline hydrochloride, and hydrogen sulfate anions generated from the peroxydisulfate.

Conclusions

A new method for the preparation of PANI, using aniline and oxidant solutions separated by a non-ionic semipermeable cellulose membrane is reported. PANI was produced entirely on the aniline side of membrane. This is explained by the formation of a thin layer of PANI on the cellulose membrane, which converts a cellulose membrane to a composite PANI−cellulose membrane. An in situ produced PANI membrane

possesses both electron and proton conductivity and also redox ability. The positively charged composite membrane restricts the diffusion of aniline cations to the oxidant side. On the other hand, it serves as a mediator of the oxidative polymerization of aniline; electrons are transferred from aniline to oxidant through the PANI membrane. The transfer of electrons is accompanied by the simultaneous transfer of protons in order to maintain electroneutrality on both sides of the membrane. The aniline is thus oxidized to PANI without the need to be in direct contact with oxidant molecules.

The preparation of PANI on the membrane is slower compared with the case when the reactants are simply mixed. Yet, the properties of PANI prepared by trans-membrane process are strikingly similar to the features of PANI prepared by simply mixing the reactants. These experiments demonstrate that redox reactions in general and aniline oxidation in particular take place between reactants separated by a conducting PANI membrane. The reaction products remain separated by the membrane after the reaction. This principle could be exploited generally in redox reactions, leading to the simplification of the separation of reaction products.

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