Surface Modification of Ultrafiltration Membranes by Low Temperature Plasma. I. Treatment of Polyacrylonitrile

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SYNOPSIS

Excitation with low temperature helium or helium/water plasma and subsequent exposure to air of polyacrylonitrile (PAN) ultrafiltration membranes was used to hydrophilize the surface of these materials. We analyzed the effectiveness of this approach as a function of plasma operating variables including gas phase composition, plasma power, treatment time, and system pressure. Following the changes in physical and chemical composition of the PAN surface resulting from these modifications was a major aspect of this work. Techniques such as the captive bubble contact angle method, ellipsometry, ESCA, and FTIR-ATR were all used. In addition, the formation and lifetime of peroxides during these processes were determined. At low powers (≤ 25 W) and short treatment periods (≤ 30 s), the main chemical conversion of PAN surfaces was simultaneous hydrophilization and stabilization via PAN cyclization. Relatively small water permeability changes were observed as a result of such treatment. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Novel applications and uses of ultrafiltration (UF) are related to the development of membranes with special characteristics. For example, separations with organic solvents or by affinity adsorption require chemically stable or low nonspecific adsorption properties, respectively.[1] For conventional applications of UF, one persistent problem causing performance decline has been "membrane fouling."[2] A widespread example of this phenomenon occurs during filtration of biological solutions where proteins deposit and adsorb onto and within the porous membrane.[3] To extend the potential of UF, an intensive search for new materials and formation methods is currently underway.[1] In addition to new materials and structures, perhaps a less expensive approach is the development of surface modification techniques that will transform the membrane surface chemistry of current commercial polymers

without affecting their transport properties significantly. Thus, for example, nonspecific protein adsorption can be reduced or the desired selective properties could be imparted to the membrane. Several different surface modification techniques have been pursued: one approach involved heterogeneous chemical modifications,[4-6] and others used irradiation methods such as with UV.[7] Low temperature plasma techniques have been used to prepare highly selective composite membranes for reverse osmosis and gas separation (see review by Kramer et al.[8]). A very thin modified selective layer (some nanometers) is obtained by this method. Often, such modified surfaces are undefined and unstable. This technique has been used sparingly with UF membranes. Cho and Ekengren,[9] for example, showed that plasma deposited acrylic acid onto UF and microfiltration (MF) membranes, improved filtration performance with bleach effluents by reducing fouling as compared to the untreated membrane. Thin fluorocarbon films have been deposited onto polysulfone (PSF) membranes to improve their hemocompatibility.[10] However, their filtration properties were not reported in detail. Simple treatment with inert gas, nitrogen, or oxygen plasma enhanced the surface hydrophilicity of asymmetric UF membranes

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made from poly(vinyl chloride), but the pores were also enlarged.[11]

The aim of this work was to optimize plasma excitation conditions to obtain a modified UF membrane with improved permeation behavior and equally good selectivity compared to an unmodified membrane. It is well-known that by increasing surface hydrophilicity with the introduction of hydroxyl groups, membrane fouling can be reduced.[3] This can be accomplished through He/water plasma treatment of various polymeric films.[12,13] He and water plasmas are known to favor radical formation and ablation[7,14] and a highly functionalized surface,[7,12,13] respectively. The effectiveness of plasma modification of polymers depends on reactor design and on operating conditions such as phase composition, plasma power, treatment time, system pressure, and chemical polymer structure and composition.[15-17] Among the numerous reactive species formed during plasma excitation with inert gases, radicals play an important role.[7,13] Polymer radicals can also be formed by plasma excitation of polymeric surfaces. For graft polymerization, the subsequent formation of peroxides and hydroperoxides is advantageous, because these species exhibit a high thermal stability and extended half-life.[14] An assay of these species is expected to provide information about the plasma modification conditions for efficient graft polymerization.

In this study, we have chosen polyacrylonitrile (PAN) because it is widely used commercially as a UF membrane[18,19] and little is known about its low temperature plasma excitation properties. Its thermal stability (up to 130°C) and resistance to many organic solvents makes it an attractive polymer for many applications. This polymer has been modified via its nitrile groups with nucleophiles.[20] An important characteristic during controlled thermal degradation of PAN is its tendency to undergo intramolecular reactions through adjacent nitrile groups forming cyclic structures.[21-26] PAN membranes have been modified by heterogeneous surface reactions[27] and by photoinitiation.[28] However, the use of low temperature plasma excitation has been limited. Porous PAN membranes have been treated by He plasma to form reverse osmosis (RO) membranes.[29,30] Because of this paucity of data, the chemical processes induced by low temperature plasma excitation of PAN are not known in detail.

In this article we report on the low temperature plasma-induced surface modification of PAN UF membranes characterized by different permeabilities and in particular by the treatment with He or He/water plasmas. The influence of gas phase composition, plasma power, treatment time, and system pressure on modifying PAN films and membranes were studied. Several analytical techniques were used to monitor the chemical and physical changes resulting from this treatment. They include ellipsometry, contact angle measurements, electron spectroscopy for chemical analysis (ESCA), Fourier transform infrared spectrometry-attenuated total refraction (FTIR-ATR), and a peroxide assay. Additionally, modified and unmodified PAN UF membranes were compared with respect to their hydraulic permeability.

MATERIALS AND METHODS

Materials

PAN was obtained from BUNA AG (Schkopau, Germany; containing ca. 2% vinyl acetate; M_w = 130,000 g/mol, M_n = 35,000 g/mol[18]). 2,2-Diphenyl 1-picryl hydrazyl hydrate (DPPH, 95%) was purchased from Aldrich Chemical Co. (Milwaukee, WI). Water was purified from Troy, New York tap water by RO, UV irradiation, activated carbon treatment, and passed through a 50-kDa UF membrane. The other solvents such as dimethyl formamide (DMF 99+%), benzene (99+%), and octane (99+%) were received from Aldrich. Helium and nitrogen gas, received from Matheson Co. (Secaucus, NJ) were of ultra-high purity.

PAN UF membranes, made by the phase inversion process from PAN solutions in DMF[18] with water permeabilities of 130, 200, and 1700 $1/(m^2 \, h \, bar)$ at 0.1 MPa (designated as TV3, TV2, and TV1, respectively), were received from the Department of Membrane Research, GKSS Research Center Geesthacht (Teltow, Germany). Thin PAN films were prepared by spin-coating (photoresist spinner, Headway, Co., Garland, TX), with 1-2% PAN solutions in DMF on silicon wafers (Lot No. 1456, Recticon Enterprises Inc., Pottstown, PA). The films were then dried in a convection bake oven at 80°C. Thick PAN films were made by casting a 10% PAN solution in DMF onto a glass plate and allowing solvent to evaporate for 48 h; residual DMF was removed by Soxhlet extraction with water for 48 h.

Plasma Reactor

The system consisted of the following components: a tubular reaction chamber (diameter 50 mm, length 500 mm) with a cold trap, two monomer reservoirs, and connecting tubes (made from glass by Williams Scientific Glassblowing, Montague, MA); an He

supply with flow meter (Type FMA 111: Omega Engineering Inc., Stamford, CT); a radio frequency (RF) power supply RF5S with matching network (AM5 and AMNPS-2A, 13.67 MHz, all made by RF Plasma Products Inc., Marlton, NJ) connected with a copper coil surrounding the reaction chamber; a pressure gauge (120AA-0000IR13 with power supply type 510; MKS Instruments Inc., Andover, MA); and a Welch Duo-Seal vacuum pump (Sargent–Welch Sci. Co., Skokie, IL).

He and He/Water Plasma Treatment

The major parameters that were varied included plasma power, treatment time, and initial gas pressure. Their ranges were between 10 and 50 W, 10 s and 5 min, and 0.1 and 0.2 torr, respectively. Thus, comparatively low and short values were selected. Because polymer deposition was not planned, gas flow rate was only used to manipulate the system pressure.

Membrane or film samples were fixed to a glass plate (500 × 48 mm) resting in the center of the reaction chamber using double-sided tape. The whole system was evacuated for at least 30 min until a final system pressure of ca. 0.030 torr was reached. For He/water plasma, the water was deaerated using two pump freeze–thaw cycles. Then the He flow rate was set to 0.4 or 0.8 cm^3/min, and within the next ~ 30 min, the desired He pressure was adjusted to 0.10 torr (for He/water or He plasma) or 0.20 torr (for He plasma only) using the fine regulation of the gas flow rate. For He/water plasma treatment, the monomer supply valve was opened and the system pressure was adjusted to 0.20 torr. Thereafter, the RF system was turned on with a preprogrammed plasma power setting (between 10 and 50 W) and treatment time (between 10 s and 5 min). After plasma treatment the vacuum was broken either with water vapor (from the monomer reservoir) or with air.

Assay of Peroxides Using DPPH

Attempts to apply the well-established iodometric method[31] to plasma-treated PAN samples failed to give reliable quantitative results, possibly because of the affinity between the reaction product iodine and polymeric nitrile groups.[32] For the assay with DPPH, according to Suzuki et al.,[14] a moderate reaction temperature (50°C) and short reaction time (1 h) were selected, in order to keep the overall conversion of the reagent low (usually between 5 and 25%).

Preweighed samples, either unmodified or treated with He plasma (after various periods of time in air) were placed into a deaerated solution of DPPH in benzene (about 0.1 mM) and kept there for 1 h at 50°C ± 0.5 K. The change of DPPH absorbance at 520 nm was determined spectroscopically. A blank solution without a membrane sample was always studied in parallel to detect any instability of the reagent solution. The consumed amount of DPPH was calculated using absorption coefficients of 1.18 × 10^4 L mol^{-1} cm^{-1} for DPPH[14] and 0 for its product(s). This was normalized to the outer membrane surface area, which was exposed to plasma excitation.

Surface Analytical Methods

Using a Rudolph ellipsometer (Fairfield, NJ) and set at 638 nm and 70°, the film thickness (d) and the refractive index (n) of PAN films on silicon were measured before and after plasma treatment. Data from five different locations on the coated wafers were averaged; the accuracy was better than ±5%.

Contact angles of PAN films and membranes were measured under water using the captive bubble method (water/air or water/octane).[33] At least five different bubbles (2.5 μm) were applied to the surface of each sample, and then observed using a Intensified Silicon Diode (SIT) camera (SIT66, Dage-MTI, Michigan City, IN), video recorder, and a screen. Angles measured on both sides of the bubbles were averaged.

ESCA spectra of membrane samples were recorded with a Multi Technique System 5500 (Perkin-Elmer Corp., Norwalk, CT) using a Mg Kα source (No. 04-548) at 200 W and 15 kV. The takeoff angle was 60°, nominal resolutions were 0.8 eV for the survey, and 0.125 eV for the high resolution scans, respectively.

FTIR-ATR spectra were recorded using a model 1800 FTIR (Perkin–Elmer) equipped with an ATR unit (germanium or KRS5 crystal, 45°, Perkin–Elmer). Samples of equal size (7 cm^2) were pressed against both sides of the crystal. Usually 60 scans with a nominal resolution of 4 cm^{-1} were obtained. Because the signal intensity for such polymer films depends also on the contact between film and crystal, only qualitative information was obtained from the unmanipulated spectra or difference spectra. To obtain quantitative data, ratioing of absorbance values at different wave numbers was used. The reproducibility of these values, checked either with different samples and by repeated measurement of the sample, was better than ±10%.

UV/Vis spectra were obtained with a UV 2000 spectrophotometer (Hitachi Instr., Danbury, CT).
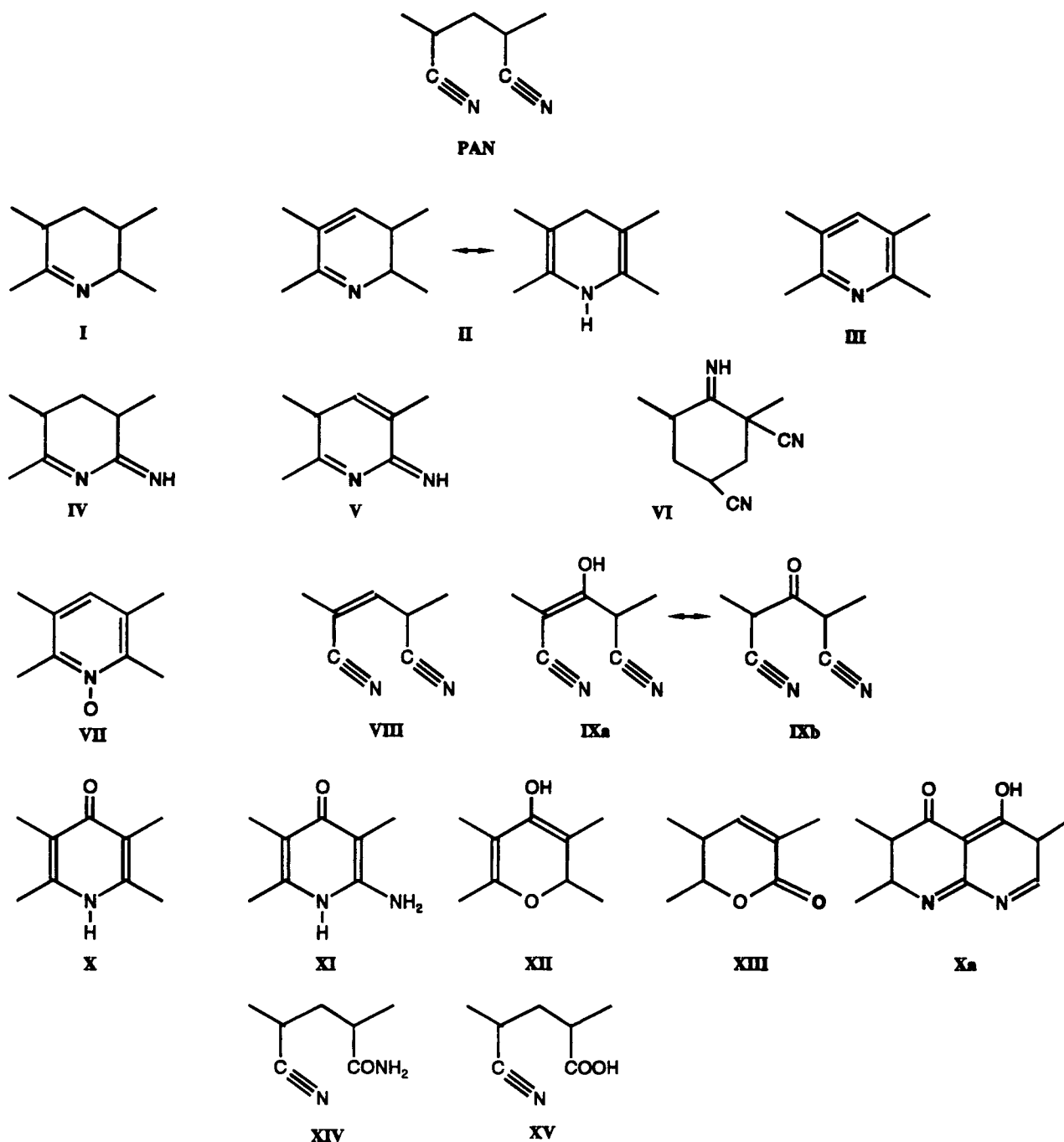
Scheme 1 Structures of PAN degradation products.

Water Permeability of Membranes

Dead-ended stirred UF cells (model 8050, Amicon Div., W. R. Grace Co., Beverly, MA) with a volume of 50 mL and an active membrane area of 12.57 cm^2 were used. Pure water from a reservoir was pressurized through the membranes for at least 0.5 h at 0.3 MPa in order to stabilize the samples; then the water flux was repeatedly measured by collection of the filtrate for given periods until a stable value of the permeation flux, J_w was observed. Values of at least three different samples were averaged, giving a maximum error of ±20%.

RESULTS AND DISCUSSION

There exists a large number of reports about thermal or photochemical degradation of PAN in the pres-

ence or absence of oxygen.[20-26,34-38] Typical proposed products of the degradation of PAN based on spectroscopic studies (UV, IR, ESCA, NMR) and the use of model compounds are shown in Scheme 1. Under all conditions studied so far, the formation of cyclic structures was predominant. This also includes the tendency to form extended cyclic systems (with 2-6 condensed rings, having repeating units as depicted in Scheme 1, called "ladder" structures) along the polymer chain.[20] However, to our knowledge, there are no detailed studies on the effects of low temperature plasma on PAN in the literature. Here, we report on our attempts to study these effects on the surface structure of PAN UF membranes and to interprete them based on previous knowledge.

PAN Removal Due to Plasma Treatment

A major aim of this work was to determine the plasma conditions causing minimal damage of the membrane pore structure as compared with changes of surface chemistry. During He/water plasma treatment, but not with pure He plasma, a quick increase of total system pressure always occurred, approaching a value of about 200% of the initial pressure (max. 0.4-0.5 torr). Pressure increase during plasma is often discussed as indication of material removal.[29] Ablation tendencies of polymers are dependent on their chemical nature.[15-17] However, the same differences between He/water and He plasma were also observed without any sample in the reactor, and with materials as different as PSF and mica. The materials removal due to He/water plasma was investigated using thin PAN films (d = 62 nm) spin-coated onto silicon wafers. The results of ellipsometric film thickness determinations before and after plasma treatment for various times are shown in Figure 1. A nearly linear dependence of material removed on treatment time (7.6 nm min^{-1}) was observed for the 25-W He/water plasma (initial total gas pressure 0.2 torr). For the 50 W He/water plasma, under otherwise similar conditions, a value of 11.9 nm min^{-1} was observed (not shown). With the 25-W He plasma and a known initial pressure of 0.1 torr, only 3.6 nm min^{-1} was removed. These PAN data may be compared with literature values for oxygen plasma (100 W, 0.55 torr).[16] The lowest removal rate of a silicon-free polymer was 16 nm min^{-1} for poly(N-vinyl carbazole).[16] Because ablation rates increased with plasma power and were weakly dependent on pressure,[15] the measured rates for PAN may be extrapolated to be about 20 nm min^{-1} at 100 W. This is relatively low
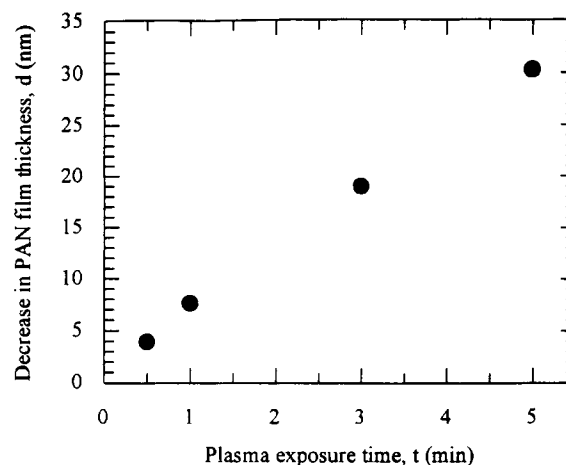

Figure 1 Decrease in film thickness for PAN films, spin-coated on Si [d(0) = 62 nm], as a function of exposure time to He/water plasma (25 W, 0.2 torr; He/water vapor pressure ratio 1 : 1). The thickness was measured with ellipsometry.

compared with other polymers. Similar conclusions result from comparison of the ablation rate in pure He plasma (3.6 nm min^{-1} at 25 W) with data from Yasuda et al.[15] (obtained with He plasma at 30 W). Our PAN data are similar to rates measured for poly(ethylene terephthalate), nylon 6, or polyethylene, and are about 10 times lower than for poly(acrylic acid), or poly(vinyl alcohol). In conclusion, removal rates for PAN are of the same order of magnitude as that for polymers with strong backbones, and/or aromatic or polar functional groups strongly attached to the backbone. They are significantly lower than for other acyclic polymers. This may indicate the formation of ladder structures upon plasma excitation that strongly stabilize the polymer backbone and thus reduces the ablation tendency.

Surface Hydrophilicity Measured with Contact Angles

Contact angle measurements have been frequently used to characterize the hydrophilicity or hydrophobicity of polymer surfaces.[39] The sessile drop technique (with water) has also been used in attempts to characterize the surface porosity of different UF membranes.[40] However, with the captive bubble technique, the sample is studied in the wet state.[33] It has been demonstrated that this is better suited to characterize porous membranes that in the dried state absorbed the water through capillary and other forces.[41-43] Contact angles of PAN films and membranes before and after plasma excitation were

Table I Contact Angles of Unmodified PAN Surfaces Measured with Captive Bubble Technique

Sample	θ (Air/H$_2$O)	θ (Octane/H$_2$O)
PAN film	50.2 ± 3.9	66.0 ± 3.5
PAN UF membrane		
TV3	48.0 ± 4.7	65.4 ± 4.0
TV2	40.5 ± 5.0	51.8 ± 3.6
TV1	36.7 ± 3.5	48.0 ± 2.8

Each value is an average of at least five measurements.

Table II Contact Angles θ (Octane/H$_2$O) Measured with Captive Bubble Technique

Plasma Modified Sample	$\theta_{10\ min}$	$\theta_{3\ days}$	$\theta_{13\ days}$	$\theta_{30\ days}$
PAN film	20	35	38	37
PAN UF membrane				
TV3	23	23	24	25
TV2	24	22	24	25
TV1	20	20	22	20

Each value is an average of at least five measurements; angles are of PAN surfaces after He/water plasma treatment (0.2 torr; 25 W, 30 s) as a function of time in air before immersion into water (relative accuracy ± 10%).

measured; the data for the unmodified samples are presented in Table I. The (static) captive bubble values were between the values of the data from dynamic experiments reported for a Daicel PAN UF membrane (θ_{adv} = 53°; θ_{rec} = 34°; air/water).[42],‡ The octane/water system was chosen to monitor the effect of plasma excitation because, for He/water plasma treated PAN, the air/water contact angle is generally lower than 20°; consequently, differences are hardly detected. For all samples, once immersed and then stored under water, a change of contact angles with time could not be detected (over a period of 6 weeks). The lowest contact angles are observed if the samples are immersed in water immediately after plasma excitation. Exposing the PAN films samples to air causes a partial reversion of the plasma modification effect (Table II). The values for the plasma modified membranes were also generally lower than for analogously treated films. No significant changes of contact angles after plasma treatment could be detected. Even storing He/water plasma treated membranes for 4 weeks under air gave essentially the same low contact angle after immersion in water. Extension of plasma treatment time for PAN films from 0.5 to 5 min did not further reduce the contact angle significantly (Fig. 2). Contact angles θ (octane/water) between 20 and 25° were also measured after treatment of PAN UF membranes with pure He plasma, exposure to air, and immersion in water.

Contact angles of polymer UF membranes were lower when compared with homogeneous polymer films. This has also been observed in other

studies[41,44] and is explained by the roughness caused by the porous surface[43] or by constituents not present in the original membrane polymer.[44] However, for the captive bubble measurements on wet membranes, probably the most important contribution to the improved water wetability was the water content of the exposed surface due to its porosity. For example, contact angles of wet hydrogels are also strongly dependent on their water content.[45] There is a clear correlation between the contact angle (Table I) and the permeability of the unmodified membranes (cf. Materials and Methods): the higher the permeability (due to a larger surface porosity/pore size), the higher the apparent hydrophilicity. Al-
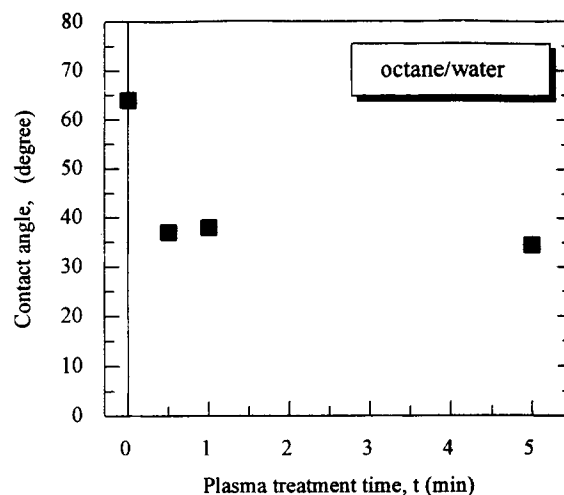
Figure 2 Contact angles (octane/water), measured with the captive bubble method for thin homogeneous PAN films (prepared by spin coating from PAN/DMF solutions onto silicon wafers) as a function of water plasma treatment time [He/water plasma ratio, 1 : 1, 0.2 torr, 25 W]. Data taken after plasma treatment, subsequent storage under air for 13 days and wetting with water.

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‡ Using the captive bubble technique, it is, in principal, possible to determine advancing and receding contact angles. This allows one to distinguish between more hydrophobic and more hydrophilic contributions to the free surface energy.[39] The value obtained for a resting bubble under a surface in water is similar to the receding contact angle.[42] Consequently, we will use this value as an approximation measure of surface hydrophilicity.

though for the sessile drop measurements on dry membranes, no correlation between pore size and contact angle was observed,[40] observations similar to ours were made for PSF membranes, in which the captive bubble technique was used to recover the contact angle.[42,43]

Surface treatment of PAN films and UF membranes with He (followed by oxidation) and He/water plasma, for times as short as 30 s, significantly increased their hydrophilicity (cf. Tables I and II). This is in agreement with literature data for water plasma treatment of a variety of more or less hydrophobic polymers like polyethylene, polypropylene, polyester, polymethyl methacrylate and polystyrene,[12] or membrane materials such as PSF and polyimide.[13] In all these cases, surface hydroxylation[12] or oxidation were considered the mechanism of the plasma reaction. Because the permeability of the plasma modified PAN membranes was not changed much, and was even reduced for longer treatment, the observed decrease of contact angles cannot be explained simply by pore enlargement with consequently higher water content of the exposed surface.

The plasma modification effect for the membranes is relatively permanent as seen in Table II. The increase in contact angle for plasma treated films during storage under air can be explained by a well-known effect: the rearrangement of high energy surfaces in contact with a less hydrophilic environment such as air.[46] Because the chemical modifications of the films and the membranes are similar, the observed higher long-term stability in air for the modified membranes may be attributed to the different surface morphology (microporous structure vs. dense film).

Plasma Induced PAN Conversion

ESCA Studies

The elemental composition of the top layer of a polymer sample (some nanometers thick) can be retrieved from ESCA survey scans and information about the binding state of elements from high resolution spectra via the chemical shift.[47] The method has been used to characterize different commercial UF membranes[40] and also to monitor the surface structural changes of various polymers due to plasma

Table III   ESCA Data for Unmodified and Plasma Treated PAN UF Membranes

	Total (%)	Component Peaks					
		E (eV)	%	E (eV)	%	E (eV)	%
Carbon							
Unmodified	74.0			287	86.3	286	13.7
He/H$_2$O 30″	67.1	288.9	12.3	287.0	71.5	285.7	16.2
He/H$_2$O 3′	64.1	289.6	14.7	287.4	64.3	286.2	21.0
He 30″ + O$_2$	56.4	289.5	21.0	288.0	26.3	286.5	52.7
He 3′ + O$_2$	59.0	289.6	15.5	288.3	22.3	287.0	62.2
He 5′ + O$_2$	40.0	289.3	64.7	287.1	18.1	285.6	17.2
Nitrogen							
Unmodified	23.9			400			
He/H$_2$O 30″	20.3	ND					
He/H$_2$O 3′	22.1	ND					
He 30″ + O$_2$	20.7	402.5	10.1	400.7	89.9		
He 3′ + O$_2$	23.8	402.0	21.2	400.7	78.8		
He 5′ + O$_2$	40.2	400.9	48.1	399.8	51.9		
Oxygen							
Modified	1.8			532			
He/H$_2$O 30″	12.6	ND					
He/H$_2$O 3′	13.8	ND					
He 30″ + O$_2$	22.8	533.7	24.5	532.6	75.7		
He 3′ + O$_2$	17.2	533.9	31.2	532.7	68.8		
He 5′ + O$_2$	19.8	533.6	11.9	531.9	88.1		

Survey (content) and high resolution spectra (binding energy and relative content) from deconvolution assuming Gaussian peaks. ND, Not determined.

modification.[10,12,29] There are very few reported ESCA studies of PAN. These were motivated by the importance of controlled degradation of PAN during the production of carbon fibers.[36-38]

Surface compositions by ESCA of PAN UF membranes before and after He/water plasma treatment are summarized in Table III and shown in Figure 3. The small observed differences from the composition of PAN homopolymer (75% C; 25% N) can be explained via the content of the comonomer vinylacetate (about 2%) in the membrane polymer and also from the surface oxidation. Significant changes were observed due to plasma treatment. After 30-s exposure time, 12.6% oxygen was detected, while both C and N contents decreased. Plasma treatment times longer than 30 s resulted in only minor further changes. Other samples were analyzed about 2 weeks after He plasma treatment and subsequent exposure to air; their surface compositions are shown in Table III. The changes were more pronounced than with the He/water plasma. After 30 s, 22.8% O was detected, but both the C and N content fell to 56.4 and 20.7%, respectively. Again, the changes due to further treatment for 3 min were much less. Interestingly, for 5-min He plasma treatment, a large increase in N content, and a strong C decrease (to 40.0%) were observed.

The C signal in the high resolution spectra of unmodified samples could be deconvoluted into two peaks [Fig. 4(a)]. Clark and Harrison[47] found two peaks for PAN at 286.4 and 285.0 eV with an intensity ratio of 2 : 1. These were assigned to a nitrile and the backbone carbon in the α-position, and a β-backbone C atom, respectively. After plasma

Binding Energy (ev)

Figure 4 High resolution ESCA spectra of carbon of the surface of a PAN membrane (TV1): (a) for the unmodified membrane, (b) after 30 s, and (c) 5 min of helium plasma treatment. The dashed and dotted lines are calculated best-fit contributions of different carbon binding states to the measured spectra assuming Gaussian peaks.

treatment, C binding energies higher than 289 eV were detected [Table III, cf. Fig. 4 (b,c)]. Signals from C in carboxylic acid or analogous structures (e.g. **XII, XIV, XV,** Scheme 1) are found in this region. Keto structures appear in the 287-eV region, and can consequently not be separated from signals of PAN. After He/water plasma relative intensities of the high energy peak were 12.3 and 13.5% of the total C content after 0.5 and 3 min, respectively. This was 8.3 and 8.7% of the total surface composition of the plasma treated samples (while the O content of these samples was 12.6 and 13.8%). This means that O was also bound in keto structures. For samples after He plasma treatment and subsequent exposure to air, changes in C, N, and O binding states are also easily detected (see Table III). An example is shown in Figure 4(a-c). With extended
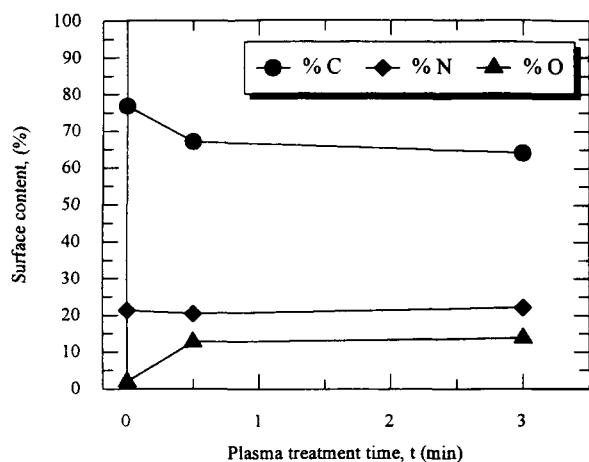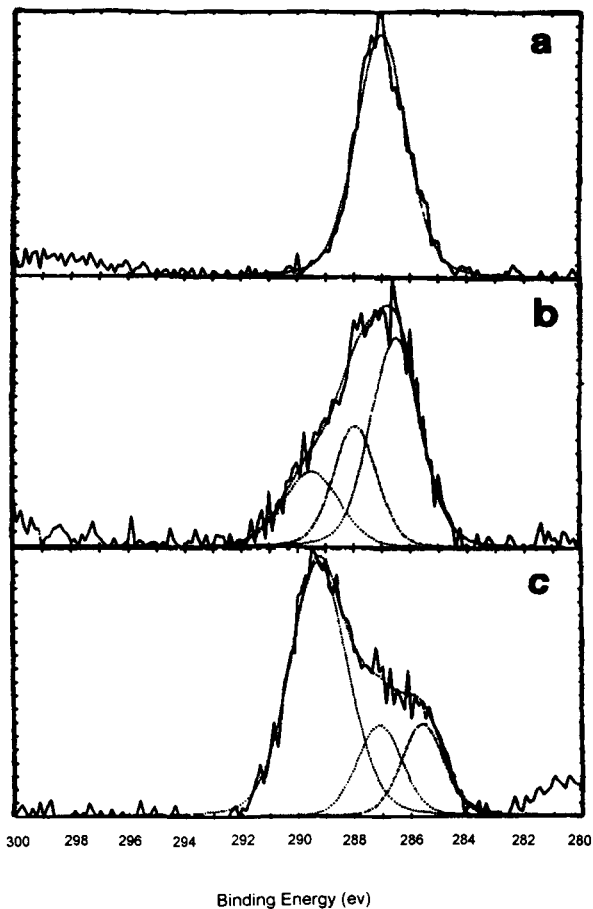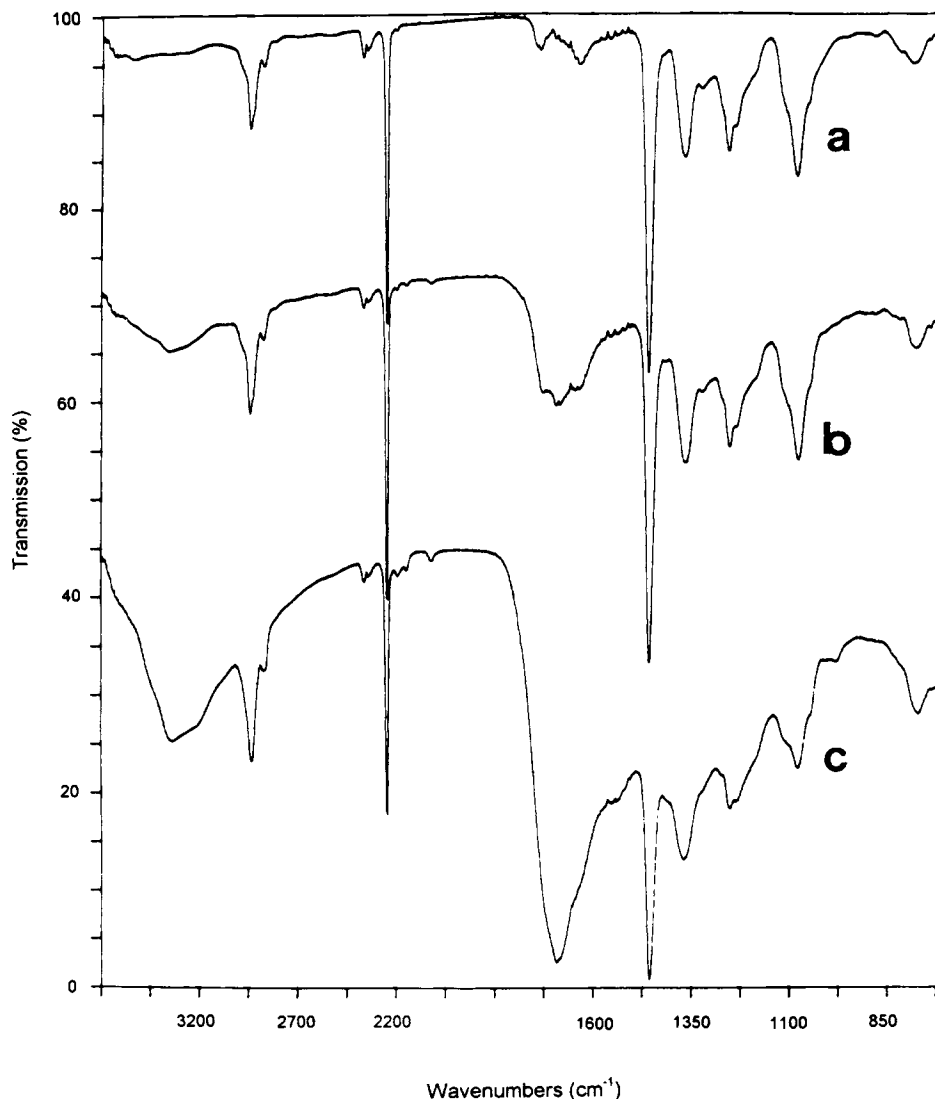

Figure 3 Surface chemical composition of PAN UF membranes (TV3) from ESCA as a function of water plasma treatment time (0.2 torr; 25 W).

Figure 5   FTIR-ATR spectra with a KRS5 crystal (45°) of the surface of a PAN membrane (TV1): (a) for the unmodified membrane, (b) after 30 s, and (c) 5 min of helium plasma treatment.

plasma treatment time, the percentages of those peaks that indicate the highest degree of surface oxidation (for C and O) or nitrile conversion (for N) increased too.

We observed after plasma excitation of PAN membranes, that the nitrogen content was only slightly changed with plasma time, while reductions in surface C content were significant (Fig. 3, Table III). There was a moderate oxygen uptake due to He/water plasma treatment (ca. 13%), more for He plasma with subsequent exposure to air (18–23%). However, both values were much lower than 40 wt %, reported for 30-s. He plasma treatment of porous PAN films to produce RO membranes.[29] The major difference between others and our experiments is

that they used much higher plasma power (350 W instead of 25 W), but the gas (He) and pressure (0.1 torr) were the same. In other articles,[36–38] the surface composition from ESCA analysis was not given. However, it has been reported by elemental analysis that heating PAN fibers in air yielded an increase in O content, accompanied by a strong decrease in H content, but the relative amount of N remained nearly unchanged (C data was not presented).[36] These results for bulk modification agree with our data for plasma induced surface modification of PAN.

The high resolution C, N, and O spectra (Fig. 4, Table III) are qualitatively in agreement with nitrile group conversion (which also contributed to the in-

creased content of C in a higher oxidized state, cf. Scheme 1), and surface oxidation due to plasma. Because of charge effects, it is not possible to compare absolute energy values from different ESCA spectra; however, all maxima in our spectra (Table III) are about 1.5 eV higher than the values reported in Takahagi et al.[36] This is an indication that analogous compositions were being monitored. Similar ESCA results were obtained by Hiraoka and Lee[37] for PAN thermally treated *in vacuo*. Takahagi et al.[36] described the structure of optimally stabilized PAN as comprised of 40% acridone ring (dimer of **X**), 30% naphtyridine ring (dimer of **III**), 20% hydronaphtyridine ring (dimer of **I**), and 10% others (cf. Scheme 1). Qualitatively, this is relevant to plasma treated PAN in our study, too. For extended He plasma treatment (5 min) highly oxidized carbon (63%, presumably also including e.g., carboxylic acid, **XV**) became dominant; the spectrum is analogous to the one reported by Ishitani[38] for "extensively oxidized" PAN surfaces. The entire composition cannot be fully interpreted. Complications to obtain completely conclusive data from a surface selective method such as ESCA, may partially be explained by the observed material ablation from the surface.

FTIR-ATR Studies

In order to obtain more detailed information about the structural changes of PAN, after plasma treatment, IR spectra of the surface region of the membrane samples were recorded using the ATR technique.[40] The sampling depths with the Ge crystal (45°) were 131 nm at 4000 cm^{-1} and 615 nm at 850 cm^{-1} (calculated according to Oldani and Schock[40] with a refractive index of PAN, $n = 1.51$). Some spectra were also recorded using a KRS 5 crystal, (sampling depths were 224 nm at 4000 cm^{-1} and 1058 nm at 850 cm^{-1}). IR spectra of the unmodified membranes exhibited small absorbances at 1720 cm^{-1}, and around 1630 cm^{-1} [Fig. 5 (a)]. Because these bands were also observed in spectra of dense films made from the same polymer as the membrane, they can be explained by the presence of the comonomer vinyl acetate, and minor structural defects formed during polymer synthesis or degradation.[24–26,34] A peak at 1670 cm^{-1}, which indicates the presence of residual solvent (DMF) used for casting membrane and film preparations, is not detected.

Figure 5 shows the FTIR-ATR spectra of PAN membranes after different plasma treatment times. Qualitatively, similar changes were observed for all three different PAN membrane types and the dense PAN film (cf. below) for He/water and He plasma

exposure and also for different plasma powers or system pressures. The predominant product absorption was observed as a broad peak with a maximum around 1670 cm^{-1}, which extended throughout the entire carboxylic and aromatic region of the IR spectrum. Other large increases occurred between 3000 and 3600 cm^{-1}, where NH and OH absorptions are expected. Other new bands with lower intensity, characteristic for the plasma treatment products of PAN, were also detected [cf. Fig. 5 (b,c) and following discussion].

Modified PAN structures, shown in Scheme 1, can be identified from their IR spectra. During thermal or photochemical degradation in the absence of oxygen, bands around 1610 and 1570 cm^{-1} were formed. These have been attributed to isolated and conjugated C=C and C=N bonds[25,26,34] (present in all structures except **IXb**, **XIV**, and **XV**, Scheme 1), including aromatic structures (**III**). All (except **VIII** and **IX**) indicate PAN cyclization. Absorptions of amide bonds (e.g. in **XIV**) were also found in this region.[25,26] Consequently, it is hard to obtain specific information from this part of the spectrum. Absorptions at higher wave numbers have been explained by the presence of oxygen during degradation, yielding different carbonylic structures (around 1720 cm^{-1}), carboxylic acid derivatives (**XIII**, **XIV**, **XV**) at ca. 1700 cm^{-1} ketones (**IXb**) at ca. 1670 cm^{-1} ketones in conjugation (**X**, **Xa**, **XI**).[27,28,30,35] The major changes (cf. Fig. 5) agree qualitatively with IR spectra obtained from PAN after extended thermal or photochemical degradation in the presence of oxygen.[25,26,34,35] The broad intense IR band centered at 1670 cm^{-1}, always observed after plasma treatment, is assigned to oxidation and cyclization products. This was additionally confirmed by increases in the region between 3100 and 3600 cm^{-1}, resulting from NH (e.g., in "end groups" **IV–VI**, or **X**, **XI**, and **XIV**) and OH (e.g. in **IXa**, **XII**, and **XV**) absorptions. The oxygen uptake, seen in the ESCA spectra [cf. Fig. 3 (a)] can be explained with these structures. Such OH or NH containing structures (and the nitron **VII**[24]), are also expected to increase the hydrophilicity of the surface significantly. This was indeed observed. The IR spectrum reported for an RO membrane made via plasma treatment of PAN films, is similar to ours, but a detailed interpretation was not given.[29]

More specific information about the conversion of nitrile can be drawn from the IR region between 2300 and 1900 cm^{-1} (Fig. 6). At least three new bands were observed with PAN conversion. One of them (at 2190 cm^{-1}) was already previously assigned to an imino-nitrile (**VI**, Scheme 1).[25,26] Interestingly,
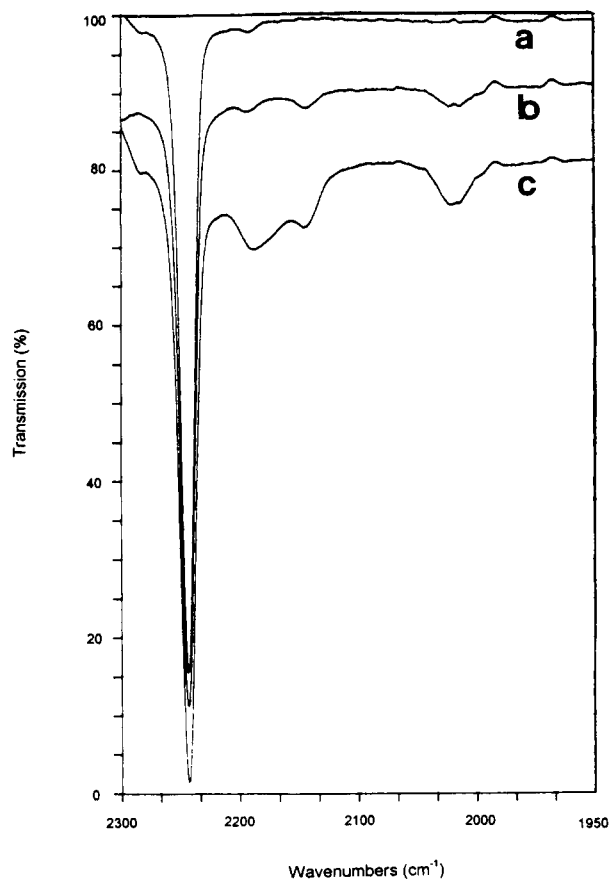
Figure 6 FTIR-ATR spectra with a Ge crystal (45°) in the kumulene region of the surface of a PAN membrane (TV1): (a) for the unmodified membrane, (b) after 30 s, and (c) 5 min of helium plasma treatment.

two more bands were observed at even lower wave numbers. One band was at about 2140 cm^{-1} and the other band was clearly visible in the spectra of all plasma treated PAN membranes at 2020 cm^{-1}. We do not have a reasonable explanation for the former absorption, for example, kumulenes such as ketenes are observed in this region. The latter product maximum decreased very slowly during the storage of the plasma treated samples under air at room temperature, and disappeared quickly and completely when the membranes were exposed to acid, for example, 10 mM HCl. This 2020 cm^{-1} absorption (in a region where not many alternatives exist) will be assigned to a valence bond of polymeric ketene-imine (Scheme 2). These valence isomers of alkyl nitriles are usually not very stable[48] but their IR maxima are observed exactly in this IR region (e.g., 2016 cm^{-1} for 1,1-dimethyl N-(1-cyano-isopropyl) ketene imine.[49] The observed thermal and especially the hydrolytic instability was expected: hydrolysis of

ketene imines yielded amides[49] (see Scheme 2). Principally, two different structures are possible, deriving from different processes (Scheme 2): the "true" valence isomer KI-1 and an N-alkyl derivative KI-2, dimer of two polymer radicals formed analogously to the primary "cage" dimerization product after thermolysis of N,N'-azo(bis-isobutyronitrile).[49] Structure KI-1 should be less stable than KI-2; PAN radical formation is easily possible under plasma conditions, but the dimerization to KI-2 may be less probable, however. A decision between these alternatives is not possible with our data. However, the formation of such an unusual structure, presumably stabilized by the solid-state polymeric backbone as "substituent" is a specific indication of the extreme reactivity of the low temperature plasma environment.

Within 1 week after plasma treatment, no spectroscopic evidence was found for the formation and thermal decomposition of hydroperoxides (at around 3400 cm^{-1} for H-bonded hydroperoxide or 3550 cm^{-1} for free hydroperoxide.[31])

Short plasma treatment time caused very large effects. This is surprising considering the expected low penetration depth of the plasma excitation into the membrane film sample (in the lower nanometer range) and the sampling depth of the surface spectroscopic method (cf. above).[§] Spectra of the same samples taken with a KRS 5 crystal (larger sampling depth) indicated significantly lower apparent conversion that demonstrated that the plasma induced reactions are indeed surface selective. In order to clarify whether the observed large conversion was caused by a plasma reaction within the microporous surface layer of the membranes, or by an especially high reactivity of the polymer material, IR spectra of homogenous, dense PAN films (about 10-μm thick) before and after plasma exposure were also recorded. Changes due to plasma modification were also easily detected but with less conversion compared with membrane samples treated under identical conditions. Lower conversions, measured with FTIR-ATR for a dense PAN film may be explained by the higher polymer density of the films in the sampled region. Accordingly, absolute signal intensities in PAN film spectra were much higher as compared to the membrane spectra. Because a contribution of surface porosity to the exposed surface can be excluded in this case, the important conclu-

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[§] Conversion of nitrile in 30 s was estimated to be 10%. Thus, with PSF UF membranes, hardly any changes in FTIR-ATR spectra could be detected after plasma treatment for 3 or 5 min under the same conditions.
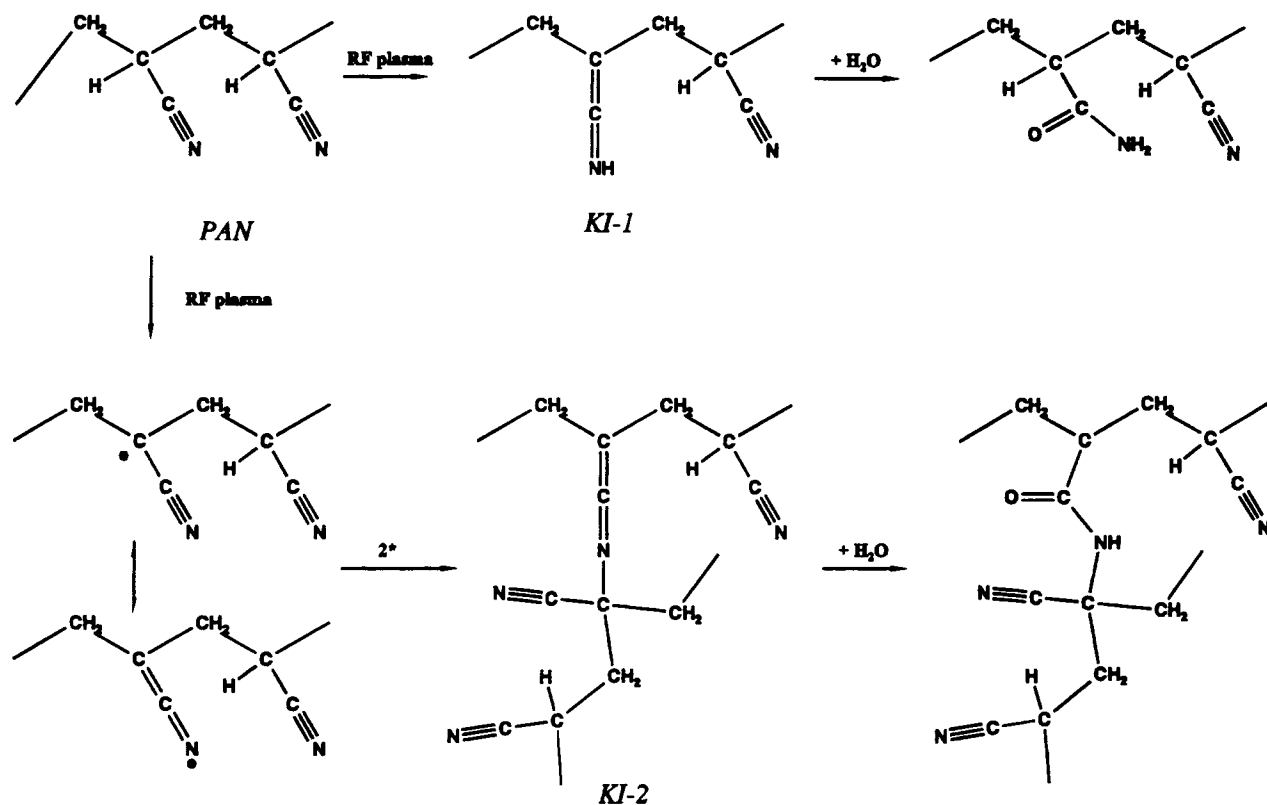
Scheme 2 Formation and hydrolysis of PAN-derived ketene imines.

sion from this experiment is that the membrane material, polyacrylonitrile, is very reactive under the plasma conditions studied.

Intensities of both characteristic PAN peaks (νCN at 2240 cm^{-1} and δCH$_2$ at 1450 cm^{-1}) decreased with product formation. This has previously been observed for thermally degraded PAN, too.[26] Functional groups and the polymer backbone are influenced by conversion (Scheme 1). To obtain a quantitative measure of conversion, the nitrile band was chosen as a reference for ratioing, because in PAN degradation products, nitrile is either completely

reacted, or its chemical environment is changed (cf. Fig. 6). Figure 7 shows ratios of plasma oxidation products (v_{max} = 1670 cm^{-1}) vs. unmodified PAN (v_{max} = 2240 cm^{-1}) as function of previous He plasma treatment time. Although a linear dependence with time was initially observed, the rate of change in composition decreased with extended treatment. The effect of plasma power, presented in Figure 7 (b) showed an increase with a slight tendency to level off at high powers. Comparison of He plasma with subsequent exposure to air and He/water plasma treatment, and the effects onto the three dif-

Table IV   Dependence of Overall Composition Changes

Set	Plasma Conditions 25 W Plasma Power	PAN Membrane	A (1670 cm^{-1}/2240 cm^{-1}) 0.5 min	A (1670 cm^{-1}/2240 cm^{-1}) 5 min
1	He, 0.1 torr	TV1	1.20	5.02
2	He, 0.2 torr	TV1	0.57	nd[a]
3	He/H$_2$O, 0.2 torr	TV1	0.74	4.43
4	He/H$_2$O, 0.2 torr	TV2	0.43	3.06
5	He/H$_2$O, 0.2 torr	TV3	0.40	2.89

Values measured with the absorbance ratio for the plasma product(s) (v_{max} = 1670 cm^{-1}) and the original PAN UF membrane (v_{max} = 2240 cm^{-1}) as a function of plasma conditions and membrane type.

a

IR Absorbance ratio (A[1670]/A[2240]) from ATR spectra of PAN membranes

He plasma treatment time, t (sec)

b

IR absorbance ratio (A[1670]/A[2240]) from ATR spectra of PAN membranes
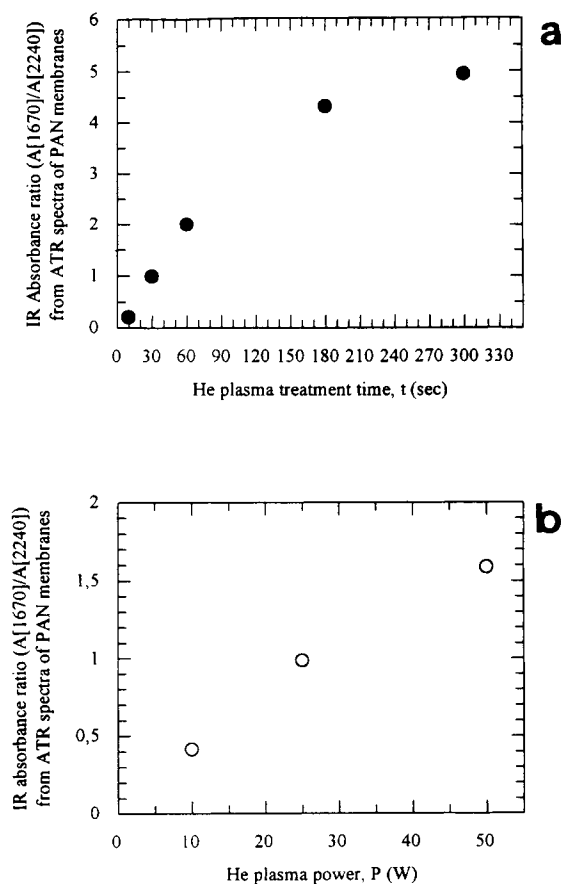
He plasma power, P (W)

Figure 7 Chemical conversion of PAN measured by the absorbance ratio of plasma products (1670 1 cm^{-1}) to PAN (2240 1 cm^{-1}) (from IR-ATR spectroscopy, cf. Fig. 6) on the surface of UF membranes (TV1) as a function of: (a) He plasma excitation time (0.1 torr, 25 W; immediately exposed to air) and (b) plasma power (He plasma, 0.1 torr, 30 s; immediately exposed to air).

ferent membrane types are summarized in Table IV. For He plasma, an increase in the system pressure resulted in less polymer conversion (cf. sets 1 and 2, Table IV). He/water instead of He plasma treatment, starting with the same total pressure, gave higher conversion (however lower than for set 1; cf. sets 2 and 3, Table IV). The influence of surface pore size on conversion due to He/water plasma is clearly illustrated: the smaller the pore size, the lower the conversion after the same treatment time (cf. sets 3–5, Table IV).

Qualitative differences between short and long time plasma treatment effects (cf. Fig. 5) become clear with difference IR-ATR spectra obtained by subtracting spectra of the parent membranes from that recorded after 30 s treatment, and that obtained by subtracting spectra of samples after 3 min from

that after 5 min treatment, respectively (Fig. 8). For the early phase of plasma modification, the maximum of a broad product band lay at 1670 cm^{-1} (together with strong bands in the 3100–3600 cm^{-1} region; for assignment cf. above). However, for the later phase of plasma induced conversion, a much broader peak was observed in the difference spectrum, and was divided into two broad bands with maxima at 1700 cm^{-1} ("isolated" ketone **IXb**; also other oxidation products (e.g. **XV**) and ca. 1640 cm^{-1}, respectively (Fig. 8). High intensities were also observed below 1600 cm^{-1}, indicating completion of "aromatization." This is supported by product bands at 810 and 765 cm^{-1}. Two conclusions from these results can be made. First, with longer plasma treatment time "stabilization" via formation of aromatic structures (**III**) becomes more important. This is understandable because aromatization is a multistep process. Second, with extended plasma treatment, more oxygen containing structures (e.g., carboxylic acid groups, **XV**) are formed that will again destabilize the polymer backbone. Note that the same conclusions were drawn from the ESCA spectra.

Assay of Peroxides after Plasma Treatment and Subsequent Exposure to Air

There are several methods for detecting peroxides; most of them use their decomposition of derivatization properties.[31,50] The application of direct spectroscopic methods is limited because of the instability of the target structures (using ESCA[14]) or the low sensitivity of the technique (using IR[31]). We were unsuccessful in using IR in this regard. Finally, a method proposed by Suzuki et al.[14] using conversion of the free radical DPPH by thermally decomposed polymeric peroxides,[†] was used in our studies.

Figure 9 shows the consumption of DPPH in deaerated benzene solutions at 50°C after immersion of unmodified and He plasma-treated membrane samples. Both parent PAN membrane types caused similar changes of solution composition and DPPH concentration with time. The plasma treated samples induced much higher DPPH conversion with rates dependent on membrane type. From the differences between plasma treated and unmodified samples, DPPH conversion due to surface reactive species can be calculated: for example, for plasma treated PAN TV1, 4.62 × 10^{-9} mol cm^{-2} appeared

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[†] For simplicity, we call all the thermally labile peroxy radicals, hydroperoxides, and alkyl peroxides formed in polymers "peroxides."
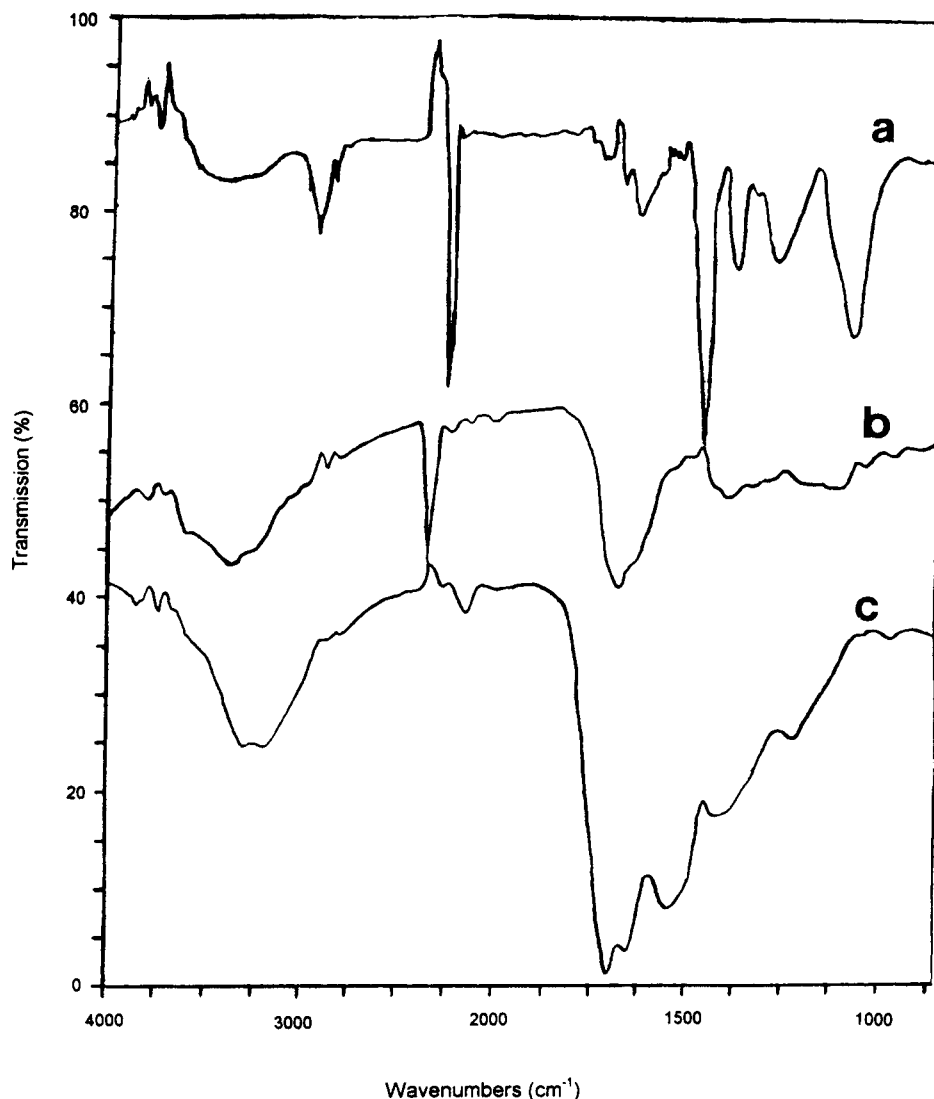
Figure 8 FTIR-ATR difference spectra for PAN membranes (TV1) after exposure to He plasma: (a) unmodified membrane, (b) spectrum obtained by subtracting the spectrum shown in (a) from the one obtained after 30 s, and (c) the spectrum obtained by subtracting the spectrum obtained after 5 min from that obtained after 3 min.

in the first hour (cf. Table V) and (12.31 ± 0.76) × 10^{-9} mol cm^{-2} appeared after 24 h at 50°C, respectively. We consider these DPPH conversion values proportional to the total amount of thermally labile surface reactive species, presumable peroxides, created by plasma modification. The method probably has a systematic error; for example, for the same ozone treated samples, iodometric determination (which failed in our study) yielded about 25 times higher peroxide values than the DPPH assay, explained by diffusion limitations for DPPH.[50] Table V summarizes the amounts of DPPH reacted as a

function of membrane type and plasma conditions for samples with equal treatment time and posttreatment history. Higher peroxide amounts on the membrane surface under otherwise similar conditions were observed: for the higher permeability membrane (TV1) compared with the less permeable membranes (TV2 and 3); by increasing the power from 10 to 25 to 50 W; and due to higher pressures. The dependence of the amount of DPPH conversion on plasma treatment time is presented in Figure 10 (a). After an initial lag, the DPPH conversion increased linearly with time until 120 s when its rate
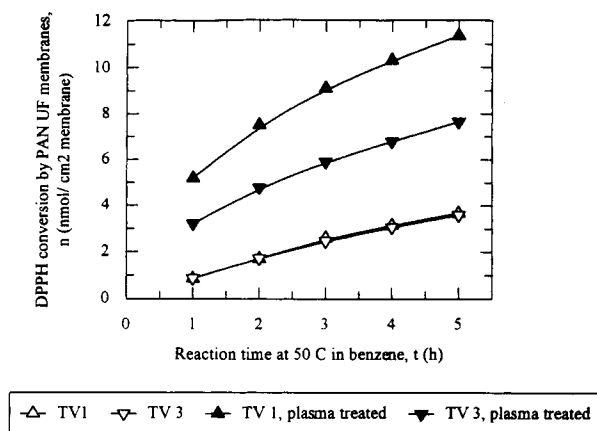
Figure 9 Conversion of DPPH by PAN UF membranes as a function of reaction time at 50°C in benzene for the original and He-plasma treated samples (0.1 torr, 25 W, 30 s; immediately exposed to air, assay after 10 min).

decreased. At 180 s, the DPPH conversion reached a maximum and declined thereafter. In addition, the dependence of the amount of peroxides on exposure time to air at room temperature after plasma excitation is shown in Figure 10 (b). The first measurement was obtained after 10 min (cf. Table V); a continuous decay was observed, within about the first 5 h the decrease was nearly linear with time. However, after 24 h, about 42% of the initially observed amount of peroxide on the membranes remained.

After plasma excitation and subsequent exposure

to air, the PAN membranes were chemically activated. In the DPPH assay, plasma treated samples caused faster and more total conversion of the free radical upon thermal activation than the unmodified material (Fig. 9). The response of the DPPH assay depended directly on the plasma and post-plasma conditions [Fig. 10 (a,b); Table V]. The reactivity of plasma activated and air-exposed samples decreased with time at room temperature, which is complementary to the thermally stimulated DPPH decomposition by the plasma activated samples [Figs. 9, 10 (b)]. There are other possible reactions of DPPH, for example, with amines.[51] However, the fast reaction rate and the decay of reactivity with time support the notion that thermal decomposition of peroxide species occurred. Besides the formation of peroxides via reaction of polymer radicals with oxygen, a commonly accepted mechanism for other polymers,[7,14] there is an alternative route for plasma modified PAN. Cyclic imines (e.g., **I**, cf. Scheme 1) can add oxygen under formation of hydroperoxides, which then slowly rearrange to alcohols.[26,52] This could be a PAN specific way to increase peroxide yields. The total peroxide amounts, determined with the DPPH assay, were $(12.31 \pm 0.76) \times 10^{-9}$ mol cm^{-2} and $(5.83 \pm 0.54) \times 10^{-9}$ mol cm^{-2}, for PAN TV1 and TV3, respectively, and are about two orders of magnitude higher than the DPPH values found after Ar plasma treatment of a dense polyethylene.[14] Also, they are about 5–2 times higher, respectively, than for plasma treated dense polyurethane film.[50]

Table V   DPPH Assay for Peroxides for Different Membrane Types and Plasma Parameters

Plasma Modification of Membrane Samples[a]	Amount of DPPH Conversion in 1 h at 50°C, n (nmol/cm^2 Membrane Area)[b]
Plasma: He, 0.1 torr, 25 W variation of membrane type	
TV3	2.00
TV2	1.26
TV1	4.62 ± 0.71 ($n = 13$)
Membrane TV1, variation of plasma conditions	
He, 0.1 torr; 10 W	4.34
He, 0.1 torr; 25 W	4.62 ± 0.71 ($n = 13$)
He, 0.1 torr, 50 W	11.29
He, 0.2 torr, 25 W	6.55
He/water, 0.2 torr, 25 W	13.26 ± 2.58 ($n = 5$)

Plasma treatment time was 30 s; samples immediately exposed to air, DPPH assay after 10 min and for 1 h at 50°C.
[a] Conditions: plasma gas, pressure, power.
[b] All determinations were at least duplicated; in cases where more than three independent samples were analyzed, the standard deviation is also given (n is the number of samples).
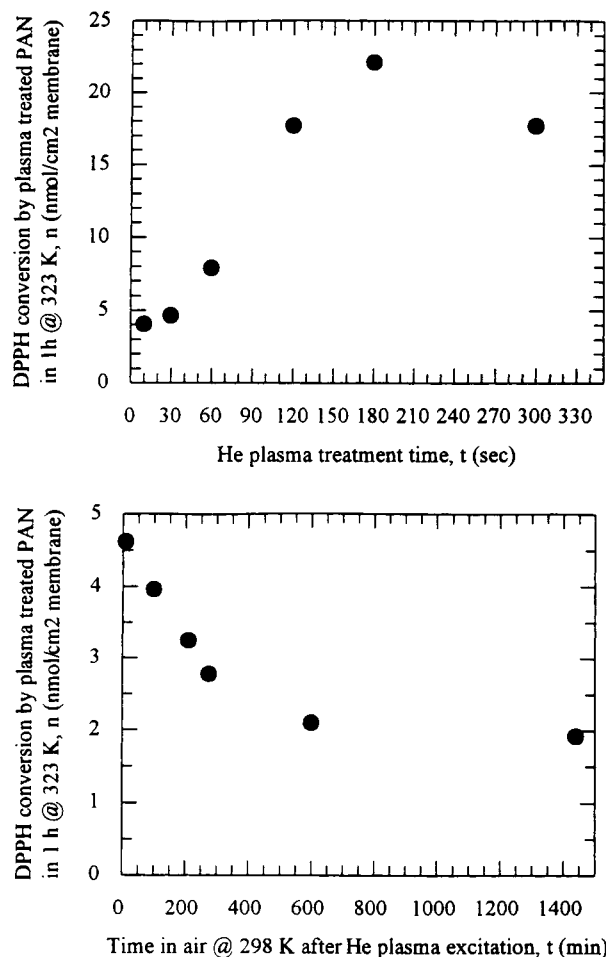
Figure 10 Amounts of DPPH conversion: (a) after 1 h at 50°C (benzene), induced by He plasma excitation of PAN UF membranes (TV1) as a function of plasma treatment time (He; 0.1 torr; 25 W; immediately exposed to air; assay after 10 min) and (b) by He plasma treated PAN UF membranes as a function of time in air at room temperature after plasma excitation (He, 0.1 torr, 25 W). All values were corrected with the DPPH conversion due to the unmodified membranes.

This may be an indication that PAN conversion was not completely restricted to only the exposed surface of the membrane, but that also the porous structure was involved.

Summary of Effects of Plasma Parameters on PAN Conversion

He/water and He plasma excitation was chosen in order to study two different types of plasma modifications: direct surface functionalization (hydroxylation) and subsequent graft polymerization (via peroxides), respectively. However, the data show

many similarities between the effects of He/water and He plasma, thus, ESCA and IR product spectra were very similar, both kinds of treatment yielded presumably peroxide species, similar surface hydrophilicity was observed, and ablation rates were very similar. Major reaction products can be identified with help of Scheme 1, where extended plasma action favors aromatization of cyclic structures, but also further oxidation. The differences between these two plasma gases were evident only with respect to quantitative results on their time dependence.

Plasma effects on the PAN samples showed fair reproducibility. This can be seen, for example, from the relatively low error of DPPH assay results (cf. Table V), or from the time or power dependences (measured with film thickness, IR, or DPPH assay) where pronounced discontinuities were not observed [Figs. 1, 7(a, b), 10(a)]. Minor exceptions were observed for very short treatment times [10 compared with 30 s, cf. Fig. 10(a)] or low power (10 compared with 25 W, cf. Table V) in the DPPH assay. This may indicate that comparatively larger effects (e.g., formation of radical sites) were induced before stable plasma conditions were reached. The pressure increase, exclusively for He/water plasma treatment, also indicated unsteady plasma conditions, especially for short treatment times. This is not an indication for PAN ablation, as stated by Shinomura et al.[29] Two possible explanations should be considered: it is known that water dissociates in plasma, forming hydroxyl radicals that have been characterized spectroscopically[13] and that could cause an increase in the total pressure; water, adsorbed on the reactor walls during the preadjustment of system pressure may have evaporated due to plasma excitation. In both cases, the total amount of reactive species in He/water plasma was higher than estimated from the preplasma pressure.

Increased system pressure resulted in less PAN conversion due to He plasma (cf., Table IV), but more surface peroxides were detected with the DPPH assay (cf. Table V). However, He/water instead of pure He plasma gave higher conversion (cf. Table IV). Exposing He/water plasma treated samples to air immediately after plasma gave very large amounts of surface peroxides. With the He/water plasma, the system pressure drastically increases with time, while remaining nearly unchanged with the He plasma. Thus, the system pressure alone (a measure of the number of reactive species in the plasma) continuously increased the yield of peroxide species formed from polymer radicals by subsequent exposure to air. On the other hand, He/water plasma yielded less intense PAN cyclization (measured with

FTIR-ATR; cf. Table IV) under otherwise same conditions, as pure He plasma. In the same way, the top layer composition measured with ESCA was influenced more by the pure He plasma and subsequent oxidation than by the He/water plasma.

Longer water plasma treatment times did not significantly increase the surface hydrophilicity, as measured by contact angles (Fig. 2). With ESCA, some further changes were detected for the same samples (Fig. 3); with FTIR-ATR a decrease, but not to zero, in conversion rate with plasma time was observed [Figs. 5, 7(a)]. Using less surface selective methods, conversion was detected for longer treatment times. Consequently, the dependence of conversion on plasma time, measured with IR [Fig. 7(a)] indicated significant chemical conversion in the membrane surface layer thicker than a few nanometers.[||] Similar conclusions can be drawn from the DPPH assays where, within the first 3 min, an increase in peroxide produced by plasma excitation was observed. The decrease in DPPH values for longer treatment time is similar to findings by Suzuki et al.[14] and can be interpreted as a consequence of in situ destruction of previously formed polymer radical sites by continuing plasma excitation.

Increasing the plasma power yielded higher PAN conversion [from IR, cf. Fig. 7(b)] and more peroxide formation (cf. Table V). Comparing Figure 7(a, b) supported by DPPH data (Table V) leads to the conclusion that the effect of time (for short treatment periods up to 2–3 min) and of power (up to 50 W) on the magnitude of plasma induced changes were similar: doubling of either time or power yielded about a twofold modification effect.

The influence of the surface pore size on conversion due to He/water plasma was clearly illustrated with IR and DPPH results: the smaller the pore size,[#] the smaller the conversion after the same short plasma treatment time (cf. Tables IV, V). For extended treatment, observed conversions are more similar, indicating that the reaction was not restricted to the outer specific surface of the pore structure.

From a comparison of ESCA, FTIR-ATR spectroscopy, the failed attempt to detect peroxide species directly, and the DPPH results it follows that

the chemical conversion of nitrile groups was the major reaction path, and the formation of peroxides from polymer radicals was a side reaction. Also, there is no doubt that peroxides were partially responsible for the observed PAN oxidation. Nevertheless, this side reaction could yield high peroxide surface concentrations and its use under appropriate reaction conditions seems very promising.

Pure Water Permeability of Plasma Treated PAN Membranes

The influence of He/water plasma modification time on the permeability of the three types of PAN UF membranes is presented in Figure 11. It is obvious that short treatment periods do not change the permeability very much. After longer times, however, in all cases, a decrease of permeability was observed. Also, there was no indication that the time period and environment after plasma treatment influenced the water permeability. The effects of He plasma treatment on permeability were only checked for 0.5-min treatment time; no significant differences were observed. This is not surprising considering the strong similarities between the two plasma types.

Polymer removal due to plasma was observed for PAN, but compared with other polymers, the rate is relatively low. This was explained by the efficient formation of ladder structures upon plasma excitation, which strongly stabilized the polymer backbone. During longer treatment, chemical conversion
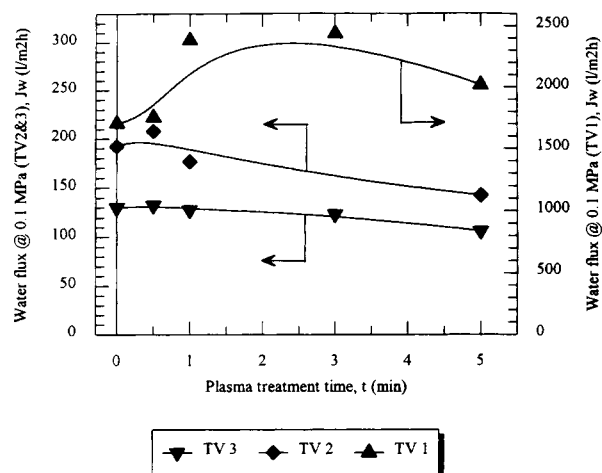
Figure 11 Water permeation flux of PAN UF membranes as a function of water plasma treatment time (He/water plasma, 0.2 torr; 25 W). After plasma treatment membranes were exposed to water vapor, then left in air for about 16 h, then wetted with water.

[||] Using the absorbance values from the original FTIR-ATR spectra, a rough estimate gives about 20–40% nitrile conversion for 5-min plasma treatment, for the different membranes under different plasma conditions; the sampling depth of the method was about 500 nm at the absorbance maximum of nitrile.

[#] The ratio of permeabilities as a measure of the surface pore size for the membranes TV1, TV2, and TV3 was about 10 : 2 : 1 (cf. Materials and Methods).

along with ablation/redeposition seemed to form outer surface layers with about the same composition and hydrophilicity. Consequently, with the highly selective surface methods, such as contact angle measurement and ESCA, large changes were observed only within the first 30 s. For modifications of UF membranes with an asymmetric pore structure (thin active layer, d = 50–100 nm), the observed ablation rate may be acceptable if the plasma treatment time does not exceed 1 min. In this range, the stability of the remaining polymer structure is high enough to provide the dimensional support of the active layer of the membrane.

With the exception of the high-permeability membrane TV1 at medium treatment time, no flux increase due to plasma was observed. This increase is an indication of plasma induced etching through the active layer of the membrane or pore enlargement due to an otherwise changed polymer structure.[8,11] The reduced permeability after extended treatment could also be caused by material deposition onto a porous structure that had not been changed significantly during the previous treatment period. This corresponds to earlier findings with PAN membranes.[29,30] Under our conditions, especially because of the low plasma power, at the most, the very first degree of porous PAN film densification was obtained. In general, the behavior of the UF membranes upon plasma excitation seemed to be determined by the specific properties of PAN, enabling surface hydrophilization via chemical conversion and structure stabilization via controlled degradation, as outlined in the previous sections.

CONCLUSIONS

The main result of this study is that treatment of PAN UF membranes with He/water plasma or He plasma followed by exposure to air significantly increases their surface hydrophilicity with only minor changes in permeability. Using He plasma followed by exposure to air, high surface concentrations of peroxide species (in the range of about 10 nmol cm^{-2}) were created, which could be decomposed at higher temperature. These interesting modification effects can be explained with surface analysis. The surface structure of polyacrylonitrile underwent fast and intensive chemical changes after excitation with He/water plasma or He plasma, followed by exposure to air:

1. the conversion of nitrile groups yielded predominantly cyclic (ladder) structures, which

finally (via dehydration) formed aromatic structures;
2. oxidation products were formed during plasma and partially formed via peroxides by exposure to air after plasma.

The structures formed within seconds by plasma excitation were similar to the well-known, complex products of the slow oxidative degradation of PAN films or fiber. Changes were similar to those occurring during the fabrication of carbon fibers. This surface selective stabilization could explain the relatively low ablation rates and the small changes in membrane permeability along with a remarkable stability of the surface hydrophilization effect. The highly reactive plasma also caused the formation of unusual products such as ketene imines in minor amounts. Longer treatment periods (e.g., 5 min, He plasma at 25 W) caused completion of aromatization together with extensive oxidation.

The plasma modification effects were not restricted to the outer layer of the polymer surface:

1. there was significant conversion of homogeneous nonporous PAN films;
2. the microporous structure beneath the active layer of PAN UF membrane increased the surface area exposed to plasma. Consequently, plasma modification also occurred within this region of the membranes.

The impact of dominant plasma parameters (power and treatment time) on PAN has been carefully studied. This information can be used to adjust the extent of chemical surface modification of PAN membranes. For a surface hydrophilization without permeability changes, low plasma power (10–25 W) and short treatment time (30 s) are recommended.

The development of a graft polymerization modification method, based on the results obtained in this study, will be described in a companion article.[53] The positive effects of changed membrane surface hydrophilicity on protein adsorption and UF performance will also be shown in another article.[54]

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