Surface Modification of Polypropylene Membrane by Low-Temperature Plasma Treatment

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ABSTRACT: Microporous polypropylene membranes were low temperature plasma treated with acrylic acid and allylamine. Parameters of plasma treatment were examined and optimized for the enhancement of membrane performance properties. Excess power damaged the membrane surface and excess monomer flow rate increased the reactor pressure to interfere with the glow discharge. Longer plasma treatment time resulted in even more plasma coating and micropore blocking. The contact angle with water decreased and wettabilities increased with the increase of plasma treatment time. Deposition of the plasma polymer on the membrane surface was confirmed by FTIR/ATR spectra of the treated surface. In determining the flux, the hydrophilicity of the surface played a role as important as that of the micropore size. Adequate plasma treatment could enhance both water flux and solute removal efficiency. Results from the BSA (bovine serum albumin) solution test confirmed that fouling was greatly reduced after the plasma treatment. The BSA solution flux through the plasma-treated membranes depended on pH, whereas pH variation had no serious effects on the untreated membrane. Modification of the surface charge by the plasma treatment should exert a substantial influence on the adsorption and removal of BSA. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1555–1566, 2001

Key words: plasma treatment; surface modification; polypropylene membrane

INTRODUCTION

Industrial wastewaters have become diversified with the developments of various industries and their treatments have become major issues in environmental processes. The membrane process, which has advantages over the conventional wastewater treatment process, is proposed as a promising treatment in the future.[1] Treatment of industrial waste-water by the membrane process requires thermally and chemically strong membranes for its operation, under the coarse conditions of high temperatures with various chemicals. Polyolefin membranes can satisfy these requirements and some of them were commercialized. Polypropylene (PP) membrane is one of the most widely used membranes in this application. It has good thermal and chemical resistance and can retain its original properties during the operation with wastewater.[2] However, because of the hydrophobicity of the material, it has low water flux and is prone to fouling during the operation. Surface modifications of the membrane with hydrophilic agents have been conducted by using several techniques to solve these problems.

Recently, surface modification of the membrane is regarded to be as important as the membrane material and process development themselves. Surface modification of the membrane can enhance the membrane's performance properties such as flux and selectivity. Moreover, it can reduce the fouling and endow the membrane with various functionalities. Surface modification can be applied to almost every membrane application. The primitive technique of the surface modification was physical application of the surface-active agents to the membrane prior to use, which is a temporary technique whose lasting effect is not guaranteed. Various permanent surface-modification techniques were developed such as UV-grafting and plasma treatments.

Nyström and Järvinen[3] grafted ethanol on the polysulfone membrane surface by UV-irradiation, to hydrophilize it. Rånby et al.[4–6] applied glycidyl acrylate, glycidyl methacrylate, and acrylic acid on the surfaces of polyethylene (PE), PP, and polystyrene (PS) films by the UV-grafting technique. Plasma treatment was initiated by Yasuda, who plasma-coated nitrile-type monomers on the silicone sheet to enhance the hydrogen/methane selectivity. He prepared the various composite membranes by applying the various plasmas to the metal, ceramic, and polymeric supports.[7,8] Belfort and Ulricht[9] enhanced the hydrophilicity of the polyacrylonitrile (PAN) membrane by plasma treatment with helium and water. Uliana et al.[10] enhanced the performance properties of the polyvinyl alcohol (PVA) membrane by plasma treatment with oxygen, nitrogen, water, and helium. Hirotsu and Isayama[11] plasma-treated PP membrane with hydroxyethyl methacrylate (HEMA) for the application to separate water and ethanol by pervaporation. Miyasaka et al.[12] prepared bipolar membrane by plasma treating both surfaces of the PP membrane with acrylic acid and N-(2-methacryloyloxyethyl)-N,N,N-trimethylammonium chloride, and each surface has cation and anion selectivity, respectively. Each surface-modification technique has its own characteristics and further investigations are currently being conducted.

Among the various surface-modification techniques, low temperature plasma treatment is regarded as the most adequate one, in which process gas or organic vapor is deposited on the surface by electrical discharge at low pressure. Most of the polymeric materials including polyolefins have great surface energy and low adhesion force in the absence of the functional groups at the

surface. The plasma-coated layer is quite uniform and has very strong adhesion force to the support, regardless of the structure and reactivity of the surface.[13] Therefore, it has outstanding chemical resistance and mechanical strength. Low temperature plasma treatment, using hydrophilic materials, can increase the hydrophilicity of the membrane, resulting in the enhancement of membrane performance properties while simultaneously reducing the fouling.[14]

In this study PP microfiltration membranes were low temperature plasma treated with hydrophilic materials such as acrylic acid and allylamine. Operation parameters of plasma treatment were investigated in terms of variation of performance properties and sample damage. Changes of membrane characteristics after the plasma treatment, efficiency of removal of organic molecules, and fouling characteristics by proteins were also examined.

EXPERIMENTAL

Materials

Flat-sheet PP membranes were obtained from Hoechst–Celanese Co. (Celgard 2400), which were prepared by a stretching method. Acrylic acid and allylamine were from Aldrich Chemicals (Milwaukee, WI) and bovine serum albumin (BSA) was from Sigma Chemicals (A-2153, fraction V; Sigma, St. Louis, MO). Dextrans of various molecular weights, ranging from 72,600 to 2,000,000, were purchased from Sigma for the determination of molecular weight cutoff of the membrane. Tween 80 (polyoxyethylene sorbitan monooleate) was purchased from Aldrich and used to wet the hydrophobic PP membranes prior to the performance test. Hydrochloric acid and sodium hydroxide (both from Aldrich) were used to control the pH of the BSA solution.

Plasma Reactor and Treatment

A tube-type Pyrex reactor was manufactured (Fig. 1) [190 × 7000 mm (inside diameter × length)], to each end of which a duralumin flange was assembled with a silicone O-ring. A rotary vacuum pump from Edward Co. (E2M8, A362-01-981) was used to evacuate the reactor. A power supply (RFX 600 generator) and matching network (ATX600) from Advanced Energy Industry Co. were installed to the system. A metering valve
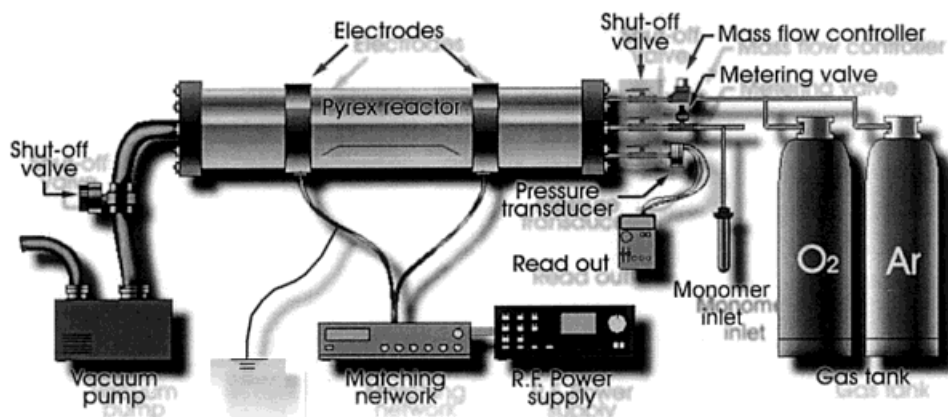
Figure 1 Schematic diagram of the plasma reactor system.

and mass-flow controller were installed for controlling the molar flow rate of monomer. A pressure transducer from MKS (type 622) was used to monitor the pressure in the reactor. Copper electrodes were installed at the outside of the Pyrex tube in the ring form, and their location was adjusted to attain the optimum discharge conditions.

Plasma treatment formed an active layer on the membrane surface, which modified the surface properties. A flat-sheet membrane was placed in the reactor before it was evacuated. When the pressure inside the reactor reached to below 2.666 Pa, the monomer vapor was introduced into the reactor by adjusting the microvalve to maintain the steady state at 5.332 Pa. The RF power supply was switched on to initiate the glow discharge for the plasma polymerization.

Membrane Characterization

Plasma-treated membranes were characterized by several techniques. The contact angle of each membrane surface with water was measured to quantify its hydrophilicity. A 1-g aliquot of water was dropped onto the leveled surface of the membrane to make a single drop. A CCD camera installed at a right angle to the surface captured the image of the drop and was processed by the image analyzer system (ImagePro; Mediacybernetics Co.). The structure of the membrane was examined by a scanning electron microscope (Hitachi S-4200; Hitachi, Japan). Surface analyses of the plasma-treated membranes were performed by FTIR/ATR (Perkin–Elmer System-2000; Perkin–Elmer, Foster City, CA). A batch-type stirred membrane test cell (Amicon 8050; Amicon, Dan-

vers, MA) was used for the performance test of the membrane. The volume of the test cell was 50 mL, the membrane area was 13.4 cm^2, and the transmembrane pressure was 2 kg$_f$/cm^2. Dextran solutions of various molecular weights (72,600; 162,000; 503,000; and 2,000,000) were used at a concentration of 5 g/L. The concentration of each permeate was determined by using an RI detector (RI-930; Jasco Co.) for the calculation of rejection. Because the PP membrane is very hydrophobic it should be hydrophilized before testing, so it was wetted by 10% Tween 80 solution for 10 min and was rinsed with pure water for 10 min.

The membrane fouling test was performed for 2 h with BSA solution at a concentration of 1 g/L. Membrane fouling was quantified by measuring the amount of BSA deposited on the membrane after the test. The membrane saved from the test cell was then vacuum dried and its weight was compared with that before the test. Effects of pH of solution on the flux were examined by adjusting the pH of solution with hydrochloric acid and sodium hydroxide.

RESULTS AND DISCUSSION

Effects of Plasma-Treatment Conditions

The most important factor in the plasma-treatment process is $(W/FM)t$, as proposed by Yasuda, where W is the supplied power in watts, F is the molar flow rate of gas or monomer fed to the reactor in mol/min, M is the molecular weight of gas or monomer, and t is the time of treatment in minutes.[7,8] The reactor pressure was reduced to 2.666 Pa and the vacuum pump was shut off. F

was calculated for each gas or monomer by measuring the pressure increase rate caused by the introduction of gas or monomer into the reactor. Effects of kind of monomer, power, monomer flow rate, and treatment time were examined.

Oxygen, ammonia solution, water, acrylic acid, and allylamine were tested under the conditions of $W = 5$ W, reactor pressure $= 5.332$ Pa, and treatment time $= 10$ min. As shown in Figure 2 the membranes treated with oxygen, ammonia solution, and water plasma were seriously damaged, although the contact angle decreased and hydrophilicity increased. Membranes treated with acrylic acid and allylamine were well coated with little damage. Therefore, acrylic acid and allylamine were selected for further experiments.

At a reactor pressure maintained at 5.332 Pa, the membrane was plasma-treated with acrylic acid for 10 min at various powers. As shown in Figure 3, with the increase of the power, the sample was more coated until 10 W and was damaged at 15 W. An increase of power resulted in the increase of $(W/FM)t$ and caused more reaction of acrylic acid until 10 W. However, excess power damaged the surface of the membranes, as shown in the sample treated at 15 W. A similar trend was observed for the allylamine treatment.

The effect of monomer flow rate was examined using allylamine plasma, under a power of 5 W and treatment time of 10 min. An increase of monomer flow rate resulted in an increase of reactor pressure. More monomer flow rate decreased the $(W/FM)t$, which represents the energy received per unit mass of monomer. The glow discharge was not induced at low $(W/FM)t$ value, and plasma treatment was not properly performed. As shown in Figure 4, with the increase of reactor pressure, the membrane is less plasma coated and slightly damaged at the 13.330 Pa condition.

At a power of 5 W and reactor pressure maintained at 5.332 Pa, the plasma-treatment time was varied for acrylic acid and allylamine plasma treatment. Because the power and reactor pressure were already optimized in this work, each sample was well plasma coated without any damage to the surface. As expected, more plasma-treatment time resulted in even more plasma coating, as shown in Figures 5 and 6 for both cases. With the increase of treatment time, the deposit covered the micropores to reduce its size. The sample surface treated with allylamine for 30 min was completely covered and the micropores disappeared.
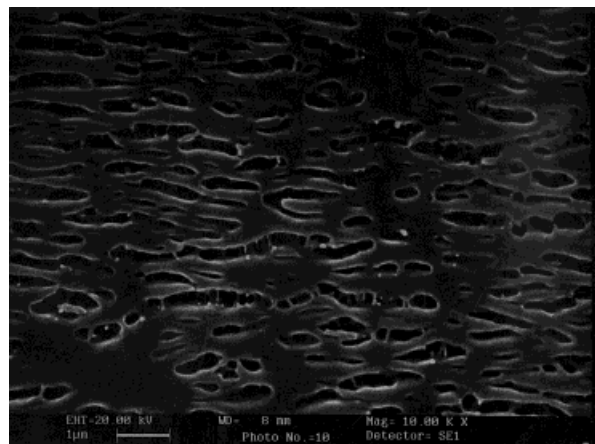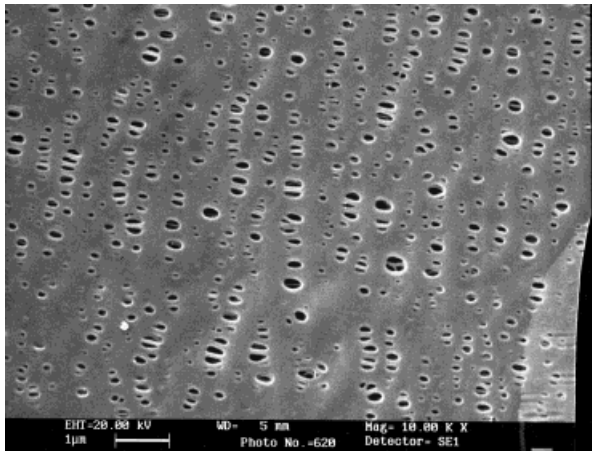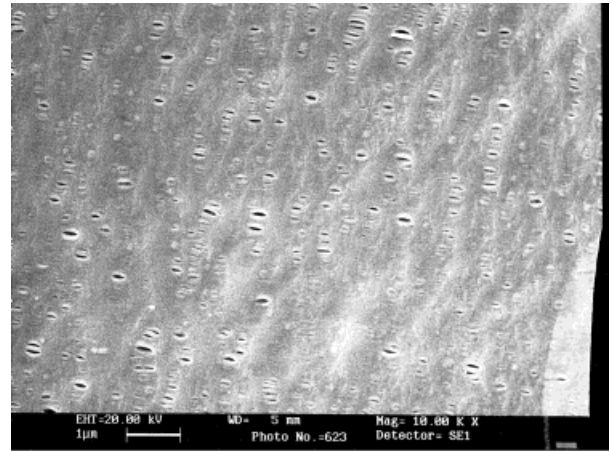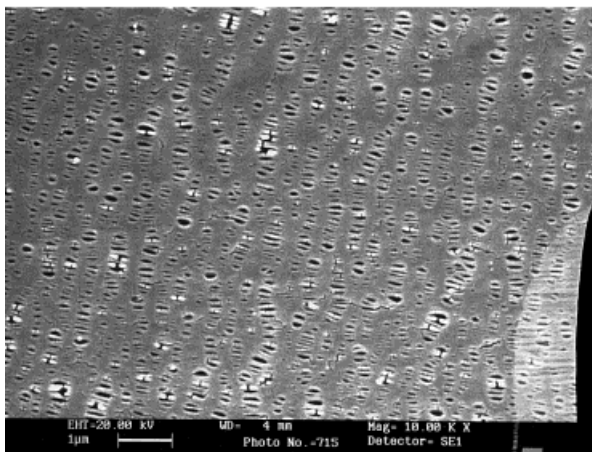

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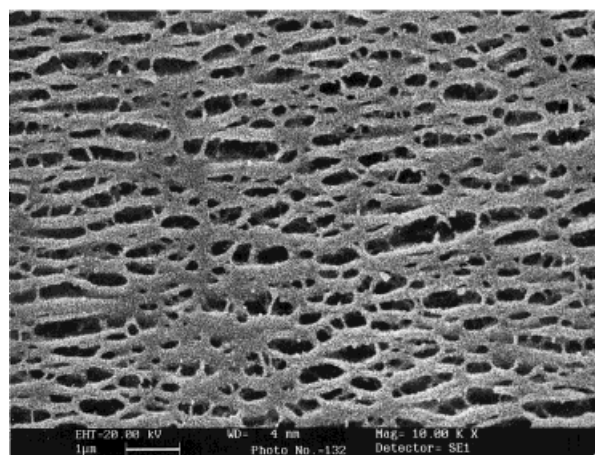
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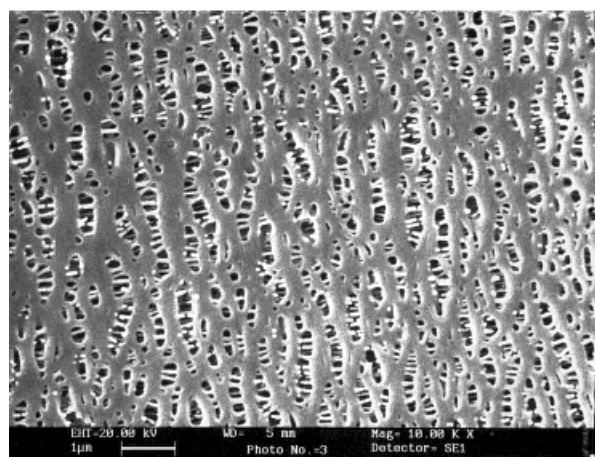
(c)

Figure 2 Surface images after various plasma treatments: (a) oxygen; (b) ammonia; (c) water.

(a)

(b)
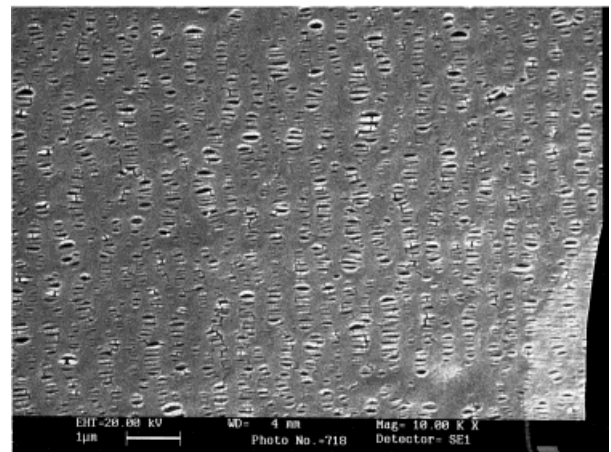
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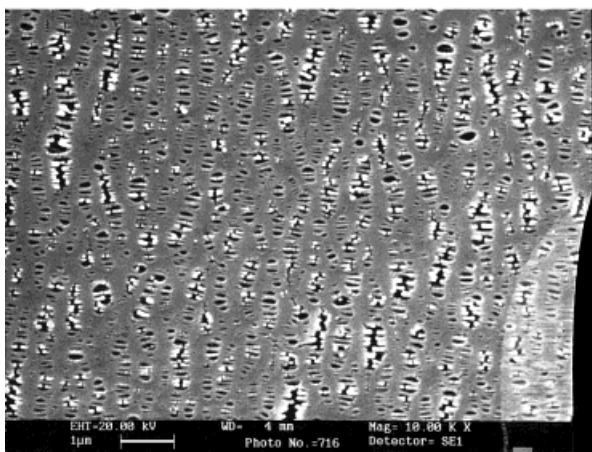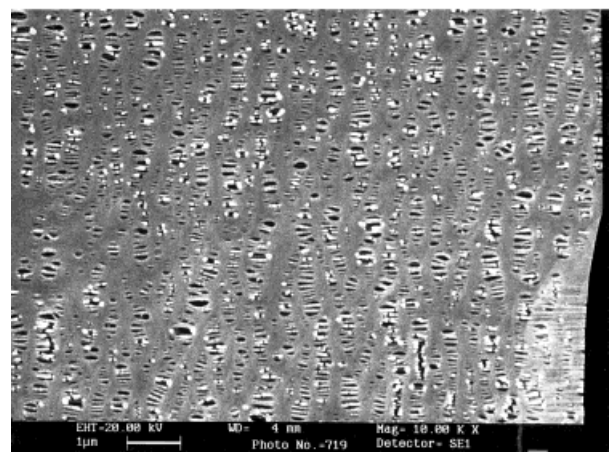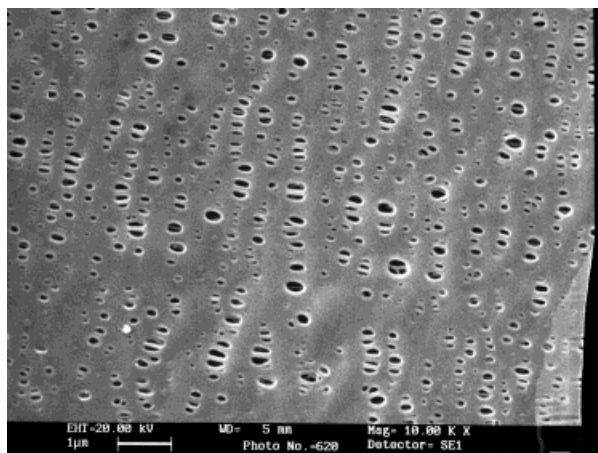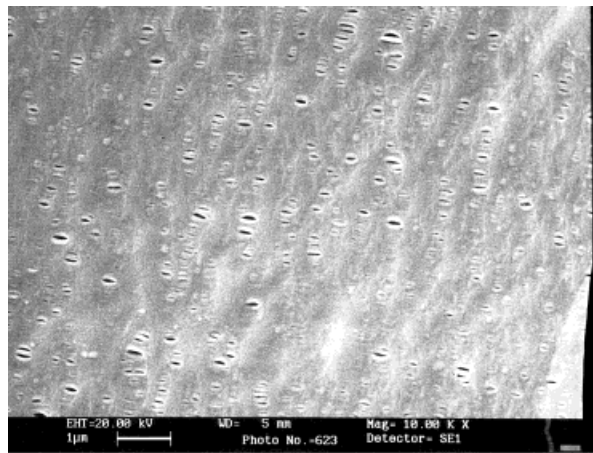**Figure 3** Surface images after acrylic acid plasma treatment at different powers: (a) 5 W; (b) 10 W; (c) 15 W.
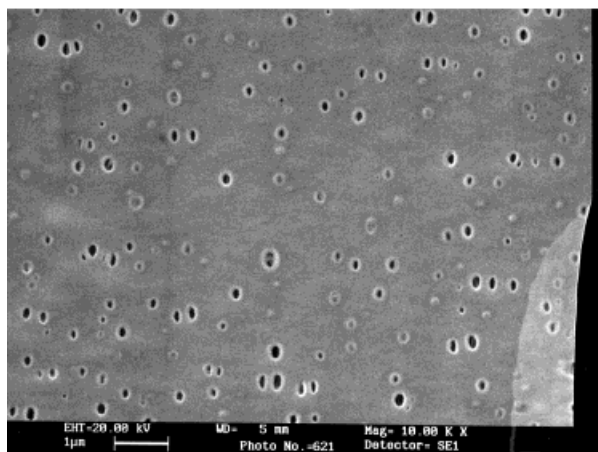

(a)

(b)

(c)

Figure 4 Surface images after allylamine plasma treatment at different monomer flow rates and reactor pressures: (a) 5.332 Pa; (b) 9.331 Pa; (c) 13.330 Pa.
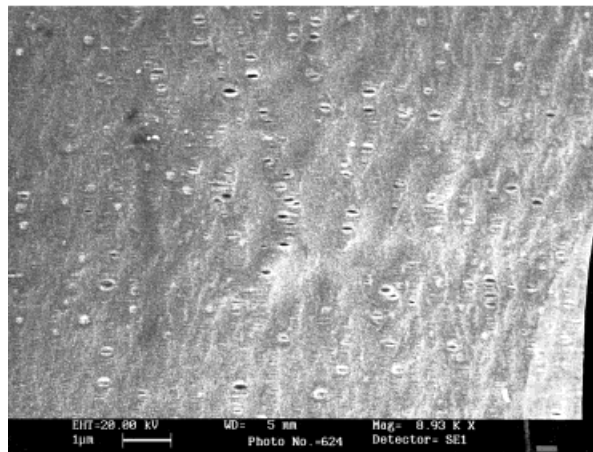
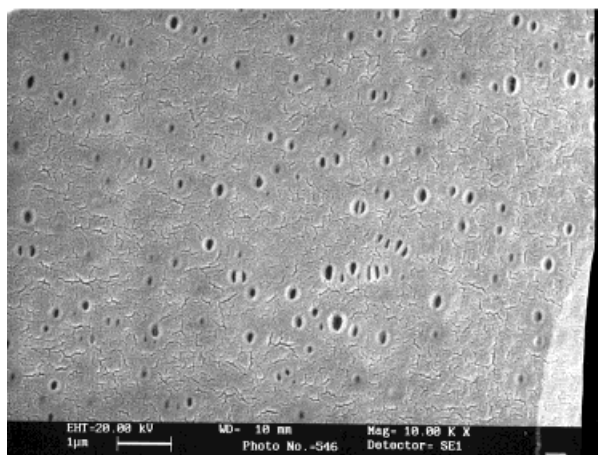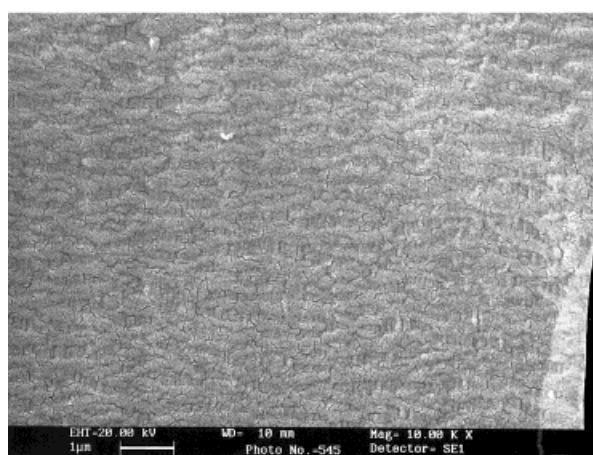**Figure 5** Surface images after acrylic acid plasma treatment for different treatment times: (a) 10 min; (b) 20 min; (c) 30 min.

Figure 6 Surface images after allylamine plasma treatment for different treatment times: (a) 10 min; (b) 20 min; (c) 30 min.

**Table I   Contact Angle Variation by the Plasma Treatment at 5 W and 5.332 Pa**

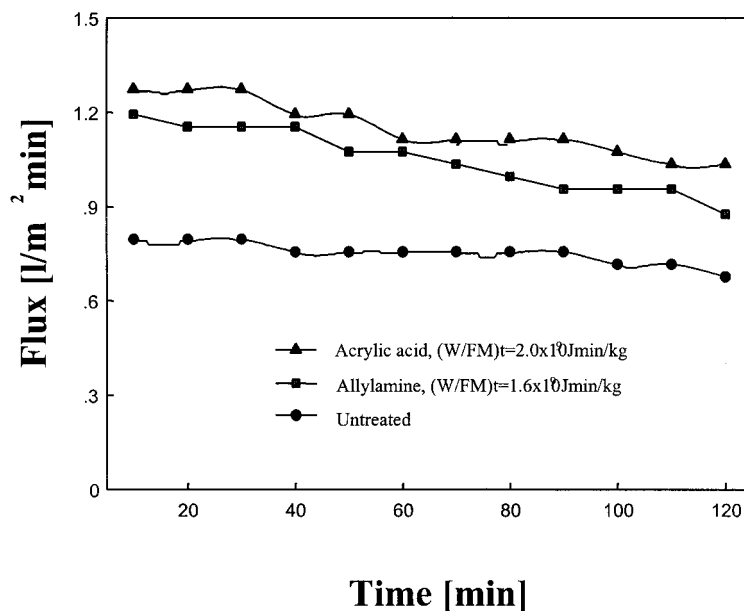| Membrane	Treatment Time (min)		
	10	20	30
Untreated		108°	
Treated with acrylic acid	69°	35°	25°
Treated with allylamine	65°	49°	38°

Performance Test

The hydrophilicity of the polymer surface can be partly represented by the contact angle with water on it. The original PP membrane has a contact angle of 108°, which was remarkably reduced after the plasma treatment with hydrophilic monomers such as acrylic acid and allylamine. As shown in Table I, the contact angle decreased with the increase of plasma-treatment time, and acrylic acid reduced the contact angle more than did allylamine.

FTIR/ATR spectra of the acrylic acid– and allylamine-treated surfaces are compared with that of untreated sample in Figure 7. Carbonyl stretching at 1704 cm^{-1} was found for the acrylic acid–treated sample and a N—H bending peak was observed at 1636 cm^{-1} for the allylamine-treated sample. Therefore, it was confirmed that the plasma polymer from each monomer was deposited on the membrane surface. However, exact reaction mechanisms were not yet clearly revealed.

Pure water fluxes through the plasma-treated membranes with acrylic acid and allylamine were greater than that through the untreated membrane, as shown in Figure 9. The acrylic acid–treated membrane had a slightly greater flux than that of the allylamine-treated membrane because the former had greater hydrophilicity than the latter, as proved by the contact angle measurement. The (W/FM)t value of the acrylic acid–treated membrane was greater than that of the allylamine-treated membrane, although they were treated under the same conditions: W = 5 W,
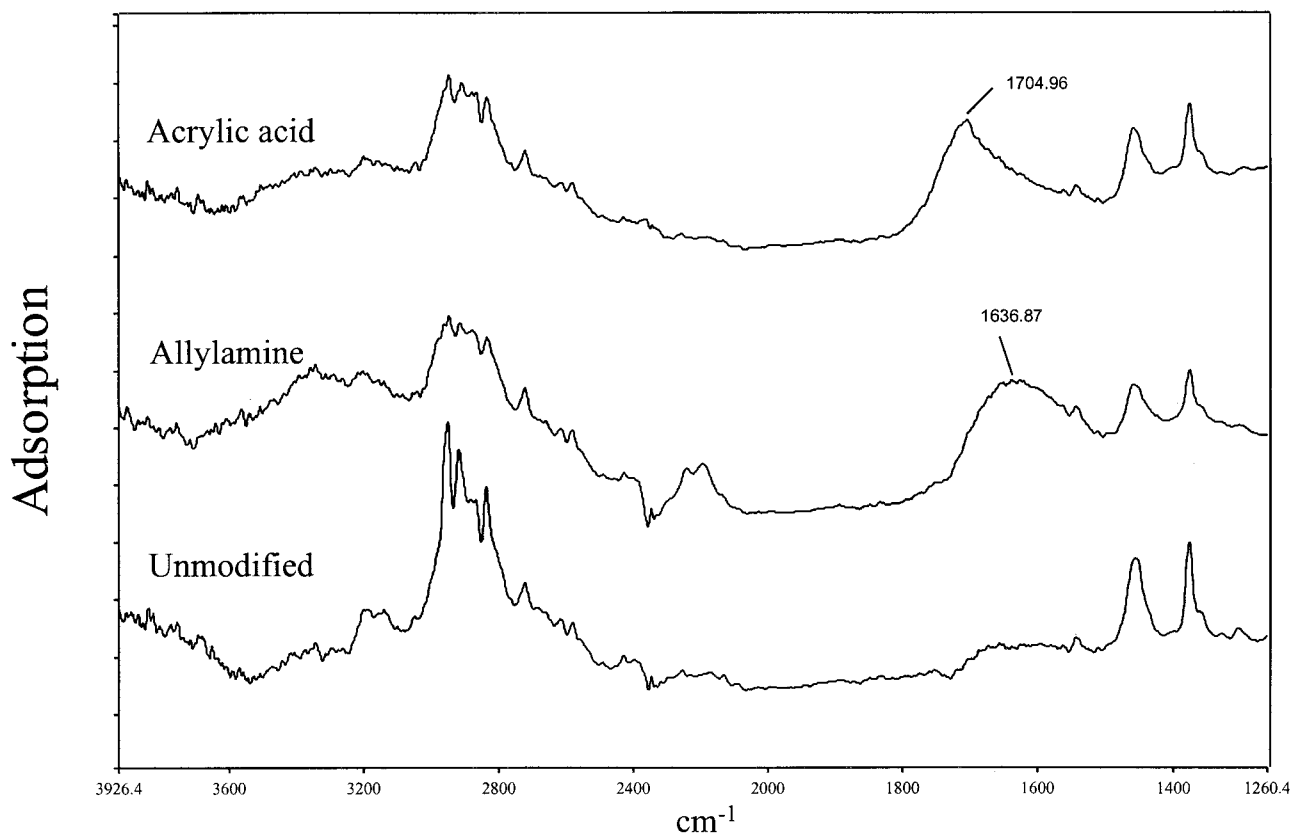
Figure 7   Comparison of FTIR/ATR spectra of the membranes before and after the plasma treatment at 5 W and 5.332 Pa for 10 min.

Figure 8 Comparison of pure water fluxes through the membranes before and after the plasma treatment at 5 W and 5.332 Pa for 10 min.

reactor pressure = 40 mTorr, and treatment time = 10 min. The monomer property and the (W/FM)t value influenced the hydrophilicity of the membrane surface and water flux.

Micropore size variations with treatment time were examined by using the image analyzer system, the results of which are plotted in Figure 9. With the increase of treatment time micropore size linearly decreased, and 30 min of allylamine plasma treatment resulted in complete covering of the sur-

face, that is, all the micropores disappeared. In Figures 10 and 11 dextran removal efficiencies were compared for plasma-treated samples with various treatment times. In both acrylic acid and allylamine, removal efficiencies increased after the plasma treatments as a result of the pore size reduction. Removal efficiency increased by more deposition with the increase of treatment time.

Even though the plasma-treated membranes had smaller micropore sizes than that of the un-
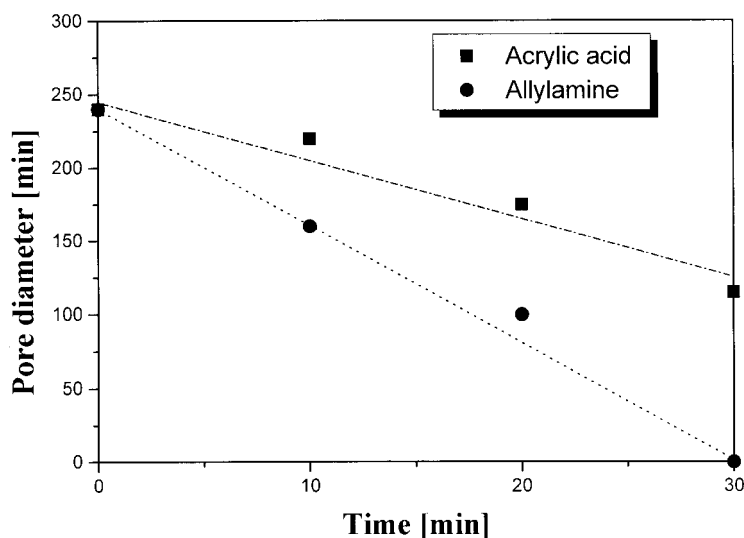
Figure 9 Pore size reduction with plasma treatment time at 5 W and 5.332 Pa.
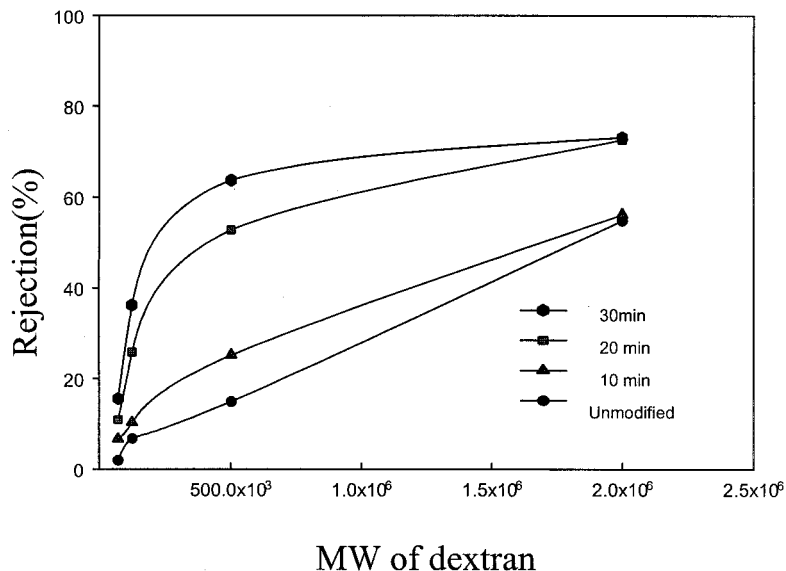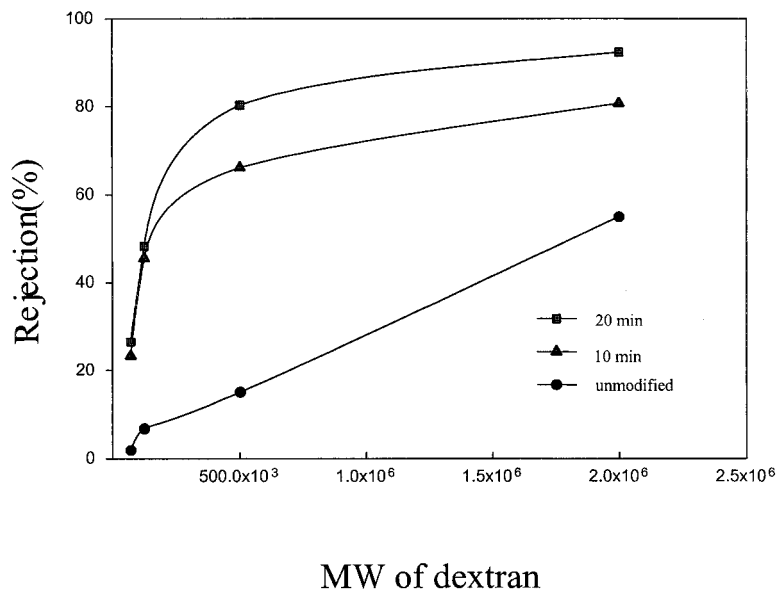
Figure 10   Dextran removal efficiencies of acrylic acid plasma–treated membranes at 5 W and 5.332 Pa.

treated membrane, plasma-treated membranes had a greater flux than that of the untreated membrane, as shown in Figure 8. Plasma treatment resulted in the increase of hydrophilicity of the membrane surface, which can be represented as a decrease of contact angle with water and an increase of surface tension of the membrane surface. Referring to the equation for determining the maximum pore size by ASTM F316-80 and E12-61, as shown below, the decrease of contact angle and the increase of surface tension resulted in the decrease of pressure required to cause permeation. Therefore, hydrophilic surface after plasma treatment showed greater flux than an untreated one.

$$D = 4\gamma \cos \theta / \Delta P$$

Figure 11   Dextran removal efficiencies of allyl amine plasma–treated membranes at 5 W and 5.332 Pa.

Table II Adsorption Amount of BSA on the Membrane Surface After 2-h Test

Membrane	Adsorption Amount (mg/cm^2)
Untreated	0.57
Treated with acrylic acid	0.21
Treated with allylamine	0.32

From these results we can conclude that the increased surface hydrophilicity played a more important role than that of the micropore size, in terms of pure water flux. However, excessively longer plasma treatment could cause micropore
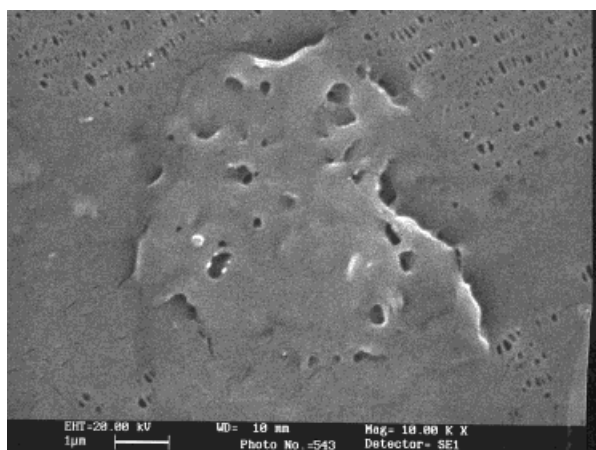
(a)
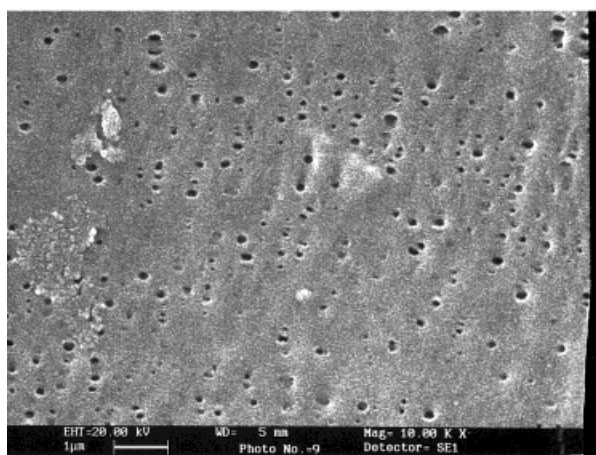
(b)

Figure 12 Membrane surface images after the BSA solution test at 5 W and 5.332 Pa for 10 min: (a) untreated; (b) acrylic acid plasma–treated.

Table III BSA Removal by Each Membrane at Different pH

Membrane	pH	Rejection (%)
Untreated	2	19.7
	4.5	6.1
	7	39.4
Treated with acrylic acid	2	12.1
	4.5	39.4
	7	96.2
Treated with allylamine	2	35.6
	4.5	53.6
	7	89.8

covering and decrease of water flux, which were proved by the test using 20- and 30-min-treated samples, although any systematic relationships could not be drawn. Adequate plasma treatment could enhance both water flux and solute removal efficiency.

For application to industrial wastewater treatment, the membrane should be free from fouling. In this work the fouling test was performed by using 1 g/L BSA solution for each membrane. After testing with BSA solution for 2 h, the amount of BSA deposited on the membrane surface was measured for each membrane. As shown in Table II, fouling was greatly reduced after the plasma treatment. Plasma treatment with acrylic acid reduced the fouling to less than half. Because acrylic acid–treated membrane has greater hydrophilicity and flux than that of the allylamine-treated membrane, the former had less fouling than the latter. In Figure 12 SEM images of fouling at the membrane surfaces were revealed for untreated membrane, whereas acrylic acid plasma–treated membrane has less fouling, which is in good agreement with the results in Table II. It was proved that plasma treatment with hydrophilic material could enhance the general performance properties of the membrane, such as flux, removal efficiency, and fouling.

BSA, a kind of protein, was well removed by the membrane, as shown in Table III. Plasma-treated membranes had greater removal efficiency than that of the untreated membrane for the same reason as discussed earlier at Figures 9 and 10. BSA removal efficiencies by the plasma-treated membranes were more influenced by pH than were those by the untreated membrane. Isoelectric point of BSA solution is pH = 4.5, and at higher pH values than this, BSA removal effi-
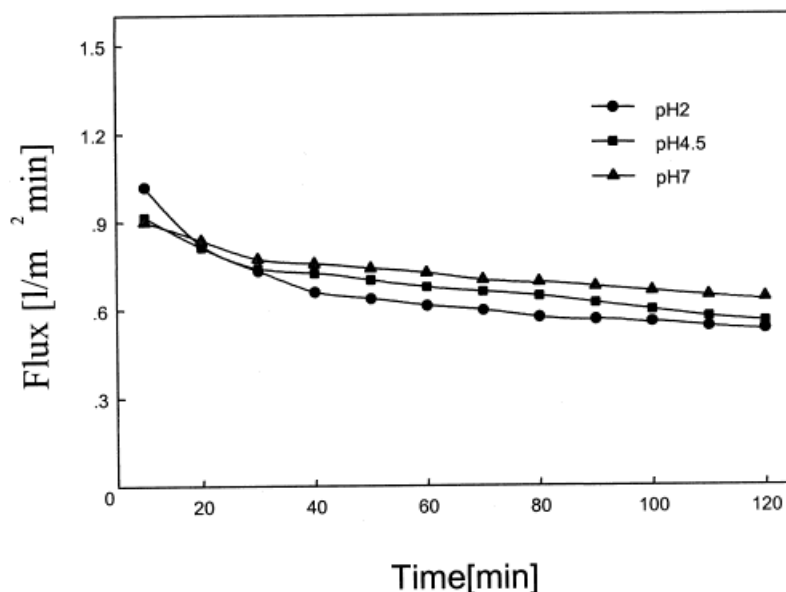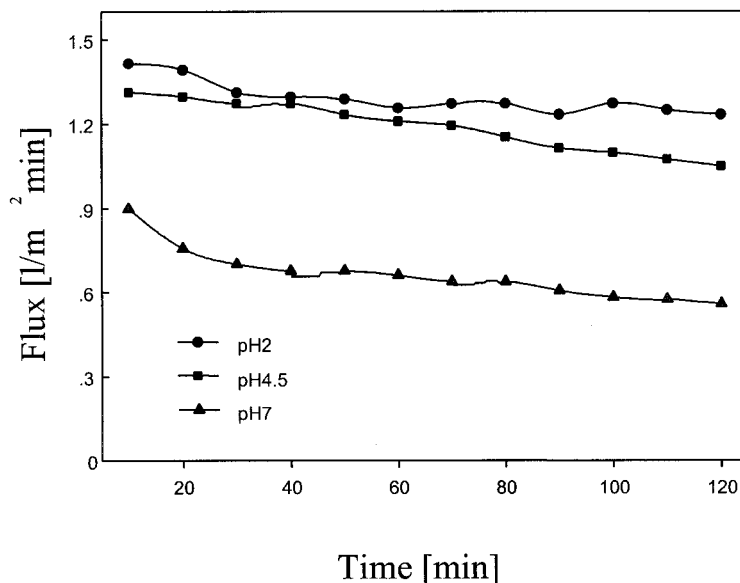
Figure 13 BSA solution flux through the untreated membrane at various solution pHs.

ciency by the plasma-treated membrane remarkably increased up to 95%.

Solution flux through the untreated membrane did not depend on the pH of the BSA solution (Fig. 13), whereas fluxes through the plasma-treated membranes were greatly influenced by pH (Figs. 14 and 15). Acrylic acid plasma–treated membrane retained its solution flux at a pH below the

isoelectric point, and it was remarkably reduced at higher pH values. Solution flux through allylamine plasma–treated membrane was gradually reduced with the increase of solution pH. At higher pH values most of the BSA was rejected and the rejected BSA reduced the solution flux. The surface charge of the membrane should have been changed by the plasma treatment with

Figure 14 BSA solution flux through the acrylic acid plasma-treated membrane (5 W and 5.332 Pa for 10 min) at various solution pHs.
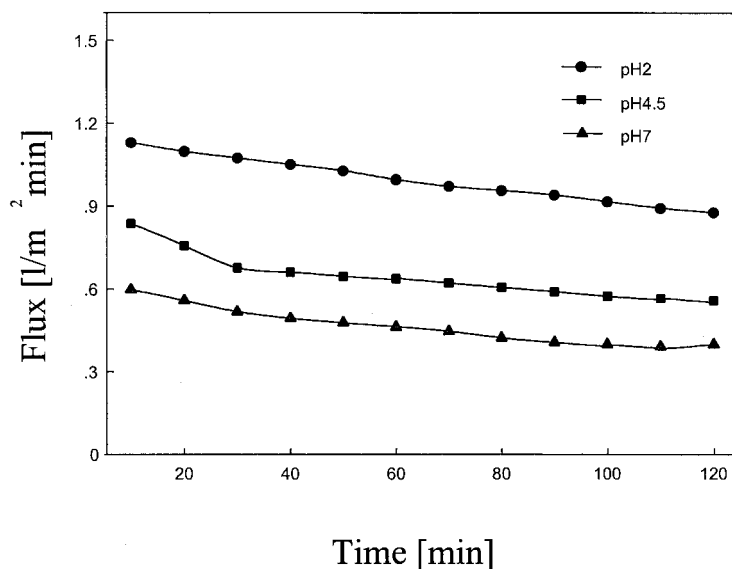
Figure 15 BSA solution flux through the allylamine plasma-treated membrane (5 W and 5.332 Pa for 10 min) at various solution pHs.

acrylic acid and allylamine, whereas the untreated membrane has no surface charge at all. At this point the exact mechanisms of BSA behavior at modified surfaces were not clearly revealed. However, surface charge modification by acid or base should exert great influences on the adsorption and removal of BSA. More systematic investigations on the effects of pH will be reported in the future.

REFERENCES

1. Cheryan, M. Ultrafiltration Handbook; Technomic Publishing: Lancaster, PA, 1986.
2. Kim, S. S.; Lloyd, D. R. J Membr Sci 1991, 64, 13.
3. Nyström, M.; Järvinen, P. J Membr Sci 1991, 60, 275.
4. Allmér, K.; Hult, A.; Rånby, B. J Polym Sci 1989, 27, 3419.
5. Allmér, K.; Hult, A.; Rånby, B. J Membr Sci 1988, 26, 2099.
6. Allmér, K.; Hult, A.; Rånby, B. J Membr Sci 1989, 27, 1641.
7. Yasuda, H. J Membr Sci 1984, 18, 273.
8. Yasuda, H. Plasma Polymerization; Academic Press: New York, 1985.
9. Ulbricht, M.; Belfort, G. J Appl Polym Sci 1995, 56, 325.
10. Vigo, F.; Nicchia, M.; Uliana, C. J Membr Sci 1988, 36, 187.
11. Hirotsu, T.; Isayama, M. J Membr Sci 1989, 45, 137.
12. Yokoyama, Y.; Tanioka, A.; Miyasaka, K. J Membr Sci 1989, 43, 165.
13. Chan, C.-M. Polymer Surface Modification and Characterization; Hanser Publishers: New York, 1994.
14. Mittal, K. L. Polymer Surface Modification: Relevance to Adhesion; Utrecht: The Netherlands, 1996.