UV-Assisted Graft Polymerization of *N*-vinyl-2-pyrrolidinone onto Poly(ether sulfone) Ultrafiltration Membranes: Comparison of Dip versus Immersion Modification Techniques

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Two different techniques were used to photochemically modify 50 kDa poly(ether sulfone) (PES) membranes with the monomer *N*-vinyl-2-pyrrolidinone (NVP) to increase surface wettability and decrease adsorptive fouling during the constant volume diafiltration of 0.1 wt % bovine serum albumin (BSA). The filtration performance of the modified membranes was compared to that of a commercially available PES membrane and a regenerated cellulose membrane. Both the dip and immersion modification techniques produced membranes with essentially the same wettability as regenerated cellulose, a wettability increase of 30% over the base PES membrane. There was a substantial decrease in the irreversible adsorptive fouling of the base membrane as measured by the permanent flux drop after water cleaning with respect to the initial buffer flux using either modification (from 0.42 to 0−0.09). The immersion-modified membrane with the best performance exhibited no adsorptive fouling, similar permeability, and higher rejection than the regenerated cellulose membrane. Both modification techniques sharply decreased membrane permeability at high monomer concentrations due to pore blockage by grafted polymer chains. The dip-modified membranes exhibited simultaneous loss of BSA rejection and permeability, which suggested that although radiation cleaved PES bonds and enlarged the pores, the high degree of grafted polymer chains on the surface blocked the pores and decreased the permeability. The immersion-modified membranes retained their rejection because the monomer NVP solution was found to absorb up to 88% of the emitted energy, depending on its concentration, thereby protecting the pore structure from intense irradiation. Thus, the dip and immersion techniques are useful for applications where high protein transmission and retention are desired, respectively.

Introduction

There has been a growing interest in modifying existing synthetic membrane surfaces to develop new membranes. This requires that the membrane surface be modified without substantially changing the membrane bulk properties. UV irradiation and UV-assisted graft polymerization are two techniques that can selectively alter membrane surface properties without affecting the bulk polymer. UV-assisted graft polymerization modifies the membrane surface by grafting polymer chains onto the surface and in the pores. UV irradiation can cross-link polymer chains and cleave polymer bonds, forming functional groups such as hydroxyls, carbonyls, or carboxylic acids on the surface. With this technique, chemical bonds in the membrane polymer can be cleaved directly or through the use of a photoinitiator to form radical sites. When vinyl monomers are present, free radical graft polymerization occurs at these sites, forming polymer chains that are covalently bonded to the surface. UV modification has been used to modify new membrane surfaces for gas separation,[1−6] pervaporation,[7,8] and reverse osmosis.[9−15]

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Other applications include temperature- and pH-sensitive membranes,[16−19] immobilization of proteins and enzymes on membrane surfaces,[20−24] molecularly imprinted membranes,[25,26] and membranes with increased surface hydrophilicity.[27−36]

Our group has used the UV-assisted graft polymerization technique to decrease nonspecific protein adsorption during protein filtration by increasing membrane surface hydrophilicity.[27−30] This is particularly important in the bioseparations area where fouling of membrane surfaces by protein adsorption is a major problem. To decrease protein fouling, Nystrom et al.[31−33] irradiated pure polysulfone (PSf) ultrafiltration membranes in the presence of modifying agents to increase the surface hydrophilicity. Yang et al.[34,35] grafted vinyl pyridine onto styrene-butadiene-styrene (SBS) triblock polymer membranes to decrease albumin and fibrinogen adsorption. Ulbricht et al.[36−38] photografted acrylic acid and various poly(ethylene glycol) methacrylates onto polyacrylonitrile ultrafiltration membranes to increase membrane surface hydrophilicity and decrease protein adsorption. Our past work focused on decreasing fouling during protein filtration using UV grafting of a variety of vinyl monomers onto PSf and PES ultrafiltration membranes.[28,30] It was discovered that PSf and PES membranes are intrinsically photoactive, undergoing bond cleavage upon UV irradiation to produce free radicals without the use of photoinitiators.[27,29] This technique was used to graft several hydrophilic monomers onto 10 kDa PES ultrafiltration membranes, and their fouling during BSA filtration was compared with that of an unmodified PES membrane and a commercial regenerated cellulose membrane.[30] Membranes modified by the monomer *N*-vinyl-2-pyrrolidinone exhibited the best combination of low fouling and high flux. However, membrane permeability was significantly decreased after modification because the grafted polymer chains blocked the membrane pores. It was concluded that NVP grafted PES membranes with the high hydrophilicty and the low fouling behavior of regenerated cellulose membranes might be produced if a sufficiently high degree of grafting was achieved. This would require the use of membranes with greater pore size than the 10 kDa PES membranes.

In this paper, the results of an investigation of the UV-assisted graft polymerization of NVP onto 50 kDa PES ultrafiltration membranes using two different techniques, dip modification and immersion modification, are presented. Large pore size membranes (50 kDa) were selected to effect a greater degree of grafting and to exhibit less relative permeability loss due to the presence of grafted polymer chains blocking or plugging pores. The dip method was used in an effort to find an alternative modification technique which was more suitable for industrial application than immersion modification. The dip method requires less monomer, is more easily adapted to a continuous process, and is more easily controlled. Changes in the surface chemistry and wettability of the unmodified and modified membranes were followed. A new filtration protocol was developed to evaluate and compare the degree of irreversible adsorptive fouling of the modified membranes during the filtration of 0.1 wt % BSA with commercially available PES and regenerated cellulose membranes as standards. The goal of this research was to develop NVP-modified membranes with the high surface wettability and the very low irreversible adsorptive fouling of regenerated cellulose, but with comparable or higher protein retention and permeability. The experimental methods will be discussed first, followed by a summary and discussion of the membrane characterization and filtration results.

Experimental Section

Materials. The base 50 kDa PES UF membrane (lot # 8139B) and the 50 kDa regenerated cellulose (RC) membrane (lot # 8061D) were obtained from Pall-Filtron Corp. (East Hills, NY). The base membrane had been modified by the manufacturer to increase hydrophilicity by an undisclosed process. (Evidence of this modification is presented later using FTIR/ATR; Figure 3). *N*-vinyl-2-pyrrolidinone (NVP) was obtained from Aldrich Chemical Co. (Milwaukee, WI), vacuum distilled to remove inhibitor before use, and dissolved in deionized water. Nitrogen gas, received from Matheson Co. (Secaucus, NJ), was ultrahigh purity. Deionized water was produced from tap water by an in-house deionized water purification system consisting of reverse osmosis (FT-30, FilmTech: Minneapolis, MN), UV irradiation treatment, and a train of polycarbonate, polypropylene, and Teflon micron and submicron membranes (Nucleopore Corp., Pleasanton, CA). Bovine serum albumin (BSA, essentially fatty acid free, >98% lot # 27H1256) was obtained from Sigma Chemical Co. (St. Louis, MO). Protein concentrations were determined spectroscopically at 280 nm using a Hitachi U 2000 double-beam UV/vis spectrophotometer (Hitachi Instruments, Inc., Danbury, CT) and used to prepare a calibration curve.

Photochemical Modification Technique. A Rayonet photochemical chamber reactor system (Model RPR-100, Southern New England Ultraviolet Co: Branford, CT) was used to modify the membranes (Figure 1). The reactor system and membrane preparation protocol have been described previously.[30]

Two different techniques were employed to modify the membrane surface: a dip modification and an immersion

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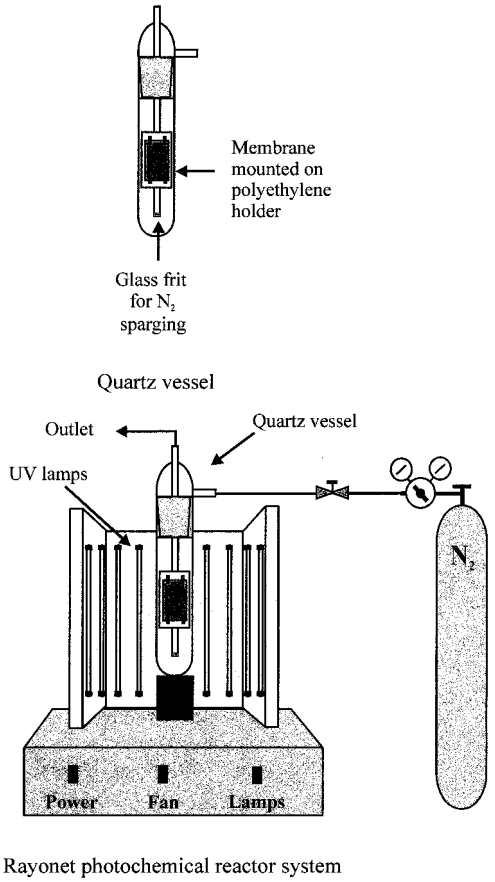

Figure 1. Quartz vessel and UV reactor system. The membrane is fixed on a plastic support and then placed in the quartz vessel, which is positioned in the middle of the UV reactor system.

modification. In the dip method, the membranes were modified by irradiating them in nitrogen after they had been dipped in the monomer solution for 30 min with stirring. After exposure to the monomer solution, the membranes were secured to the polypropylene holder and placed in the quartz vessel. To minimize water evaporation from the monomer solution on the membrane surface, the nitrogen purge was passed through a pool of water (25−30 mL) to ensure saturation of the vapor during irradiation. After a 10 min nitrogen purge, the membranes were irradiated for the specified time. The membranes were washed to remove any unreacted monomer or physically adsorbed polymer by shaking them in bottles of deionized water for 2 h at room temperature. The time needed to wash the modified membranes was determined by monitoring the decrease of the PVP peak absorbance at 1678 cm^{-1} (see below) using FTIR-ATR spectroscopy. An unchanged absorbance peak above 2 h was consider as proof that washing was complete.

In the immersion method, the membranes were modified by irradiating them while they were immersed in the monomer solution. A solution of the monomer was prepared (on a weight basis) in deionized water. The membranes were placed in the quartz vessel, and the vessel was filled with the monomer solution, sealed, and placed in the photochemical reactor. The inlet and outlet nitrogen lines were attached, and a stream of nitrogen (2−5 psig or 13.8−34.5 kPa) was fed at flow rate of 2 L/min into the vessel. The vessel was purged for 30 min and the UV lamps were then turned on for a predetermined time. The membranes were cleaned as described above. The reaction temperature of 22 °C was maintained by cooling fans in the reactor system. This immersion technique was used previously.[30]

Energy Absorbance Measurements. The amount of emitted energy from the UV lamps that reached the membrane surface during dip and immersion modifications was measured using a compact radiometer (UV Process Supply, Inc., Chicago, IL). A quartz vessel filled with air, deionized water, or solutions of varying NVP concentration was secured to the radiometer, and the whole assembly was placed in the center of the UV reactor such that the total path length was 9 cm. The quartz vessel was designed with a path length of 1 cm, which was the distance between the membrane and the wall of the quartz reactor used in both modification techniques. Measurements were taken in duplicate. Full wavelength scans of various solutions were performed using a UV/vis spectrophotometer (Hitachi Instruments, Inc., Danbury, CT).

Surface Analysis. Attenuated total reflection-Fourier transform infrared spectra (FTIR/ATR) of the unmodified PES membrane and the NVP-modified membranes were obtained using a Nicolet Magna-IR 550 Series II spectrometer (Nicolet Instrument Corp., Madison, WI). A total of 256 scans were performed at a resolution of ±4 cm^{-1} using a germanium crystal at an incident angle of 45°. The IR penetration depth for this incident angle is 0.1−1 μm.[39]

Contact Angle Measurements. Static contact angles of the membrane surface were measured using the captive air bubble technique.[40] Membranes were inverted in deionized water and air bubbles were placed in contact with the surface. The static contact angle, θ, was measured using a SIT camera (SIT66, Dage-MTI Inc., Michigan City, IN) connected to a video screen. The contact angles were averages of measurements on 10 different bubbles. The measurement error was ±3°, and cos θ was used as a measure of wettability.

Filtration System. A dead-end stirred cell filtration system was designed to characterize the filtration performance of unmodified and modified membranes and has been described previously.[30] All filtration experiments were conducted at a constant transmembrane pressure between 5 and 25 psig (34.5−172.4 kPa), a stirring rate of 300 rpm, and a system temperature of 21 °C. A 0.1 wt % bovine serum albumin solution (BSA, essentially fatty acid free, >98% Lot # 27H1256, Sigma Chemical Co., St. Louis Mo.) in 10 mM phosphate-buffered saline (PBS) at pH 7.4 was used as the test protein solution.

Constant Volume Diafiltration. A schematic representation of the constant volume diafiltration protocol is presented in Figure 2. Each membrane was first compacted for 30 min at 25 psig (172 kPa). The pressure was lowered to the operating pressure and the water flux was measured by weighing permeate until consecutive recorded values differed by less than 2% (J_o). The filtration was then stopped and the cell emptied. The cell was filled with the BSA solution using a peristaltic pump and the cell repressurized. The flux was then measured after each milliliter of permeate collected. A total of 10 mL of permeate was collected and the flux of the last milliliter was recorded and called J_p, the solution flux during protein filtration. The membrane was cleaned with deionized water by filling and shaking the cell for 1 min three times, and then the deionized water flux was measured (J_1). The membrane was then cleaned with caustic by filtering 0.5 N NaOH at 5 psig (34.5 kPa) for 30 min. The cell was filled with deionized water and shaken three times for 1 min each and then the pure water flux was again measured (J_2). The measurement error for the fluxes was ±2L/m^2 h. All fluxes were converted to permeabilities by dividing the flux by the transmembrane pressure.

The fraction of the initial buffer flux that remains during protein filtration, J_p/J_o, is a measure of the extent of flux loss caused by osmotic effects from concentration polarization, reversible adsorptive fouling, and irreversible adsorptive fouling. A high J_p/J_o fraction corresponds to low transmembrane flux loss. The ratios J_1/J_o and J_2/J_o represent the fraction of the initial buffer flux recovered after water and caustic cleaning, respectively. The fraction of the initial buffer flux lost during protein filtration or the total flux loss, $1 - J_p/J_o$,

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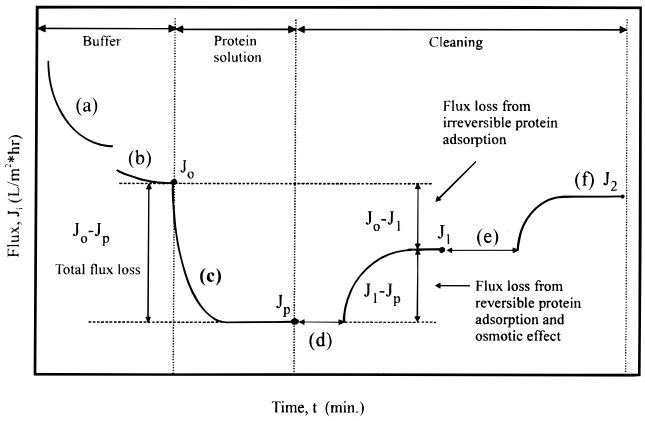

Figure 2. Constant volume diafiltration protocol: (a) To minimize compaction effects, 10 mM phosphate-buffered saline (PBS) was passed through the membrane for 30 min at a transmembrane pressure (TMP) of 25 psig (172.4 kPa), (b) TMP was lowered to the operating pressure and flux (J_o) noted when the difference between consecutive measurements was less than 2%, (c) 0.1 wt % BSA solution was pumped into the cell using a secondary pump, the operating pressure was reapplied, and the filtration was continued until 10 mL of permeate was collected (J_p), (d) the cell was rinsed with distilled, deionized H_2O three times for 1 min each and the flux measured (J_1), (e) 0.5 N NaOH was filtered for 30 min at a TMP of 5 psig (34.5 kPa), (f) the flux was again measured (J_2). All filtration steps were operated at 21 °C. $J_o - J_p$ was the total flux loss, $J_1 - J_p$ was the flux loss to reversible protein adsorption and osmotic effects from concentration polarization, and $J_o - J_1$ was the flux loss to irreversible protein adsorption.

is the sum of (i) the flux lost to reversible adsorptive fouling and osmotic effects from concentration polarization, $(J_1 - J_p)/J_o$, and (ii) fouling due to irreversible protein adsorption and aggregation, $(J_o - J_1)/J_o$. A high value of $(1 - J_p/J_o)$ corresponds to a large reduction in flux. The fraction of the initial buffer flux recovered after water cleaning, $(J_1 - J_p)/J_o$, is a measure of the degree to which the osmotic effects from concentration polarization and reversibly adsorbed protein have decreased the flux. The remaining unrecovered initial buffer flux, $(J_o - J_1)/J_o$, is a measure of the irreversibly adsorbed protein fouling and can, in principle, be regained by treatment with caustic (when $J_2 \cong J_o$). The rejection of BSA, *R*, indicates both the effect of photochemical grafting on the membrane pore structure and the protein fouling of the membrane. It is desirable to modify the membrane surface without severely compromising the pore structure of the base membrane.

Since these experiments were of very short duration, care should be taken in extending them for longer periods. However, since BSA adsorption is a fast process,[41] the protocol for fouling by BSA described above during filtration is likely a good representation of longer operation.

Results and Discussion

A summary of the modification conditions, degree of grafting, wettability, and membrane ultrafiltration performance is given in Table 1.

FTIR/ATR. Modification of 50 kDa PES membranes was conducted using the monomer *N*-vinyl-2-pyrrolidinone (NVP). Modification technique (dip or immersion), monomer concentration, and irradiation time were varied in these experiments.

FTIR/ATR verified that NVP was photochemically grafted onto the PES membrane surface (Figure 3). The most significant change in the spectra of NVP-modified PES membranes was the appearance of an absorbance band at ~1678 cm^{-1} representing the amide I carbonyl stretch of the NVP five-membered ring. As previously described,[30] the ratio of the peak height of the amide I carbonyl stretch found in the five-membered ring of the NVP molecule (~1687 cm^{-1}) to that of the benzene ring carbon−carbon double bond stretch (~1487 cm^{-1}) of the PES membrane was used to determine the degree to which NVP was grafted onto the surface as poly(vinylpyrrolidinone) (PVP) polymer chains. The latter was selected because this band did not vary during modification. Notice that the base 50 kDa PES membrane, which was obtained directly from the manufacturer and was not modified here, exhibited a small peak at about 1680 cm^{-1}. It was also more wettable than the unmodified PES membrane (Table 1; cos θ of 0.75 versus 0.62).

Dip-Modified 50 kDa Membranes. The degree of grafting (DG) achieved through the dip-modification technique as a function of irradiation time is shown in Figure 4a. High degrees of grafting were achieved even at short irradiation times (30−60 s). Several phenomena could support these observations. They include increased monomer concentration at the solution−membrane interface due to preferential adsorption/absorption, evaporative concentration due to water loss from the solution on the surface, and a large fraction of emitted energy received by the surface. Figure 5 shows the amount of energy transmitted through a quartz vessel filled with air, deionized water, or NVP solutions and received by the membrane surface during irradiation. The energy transmitted through the empty quartz vessel simulated conditions during dip modification (the light path length was identical in both cases). A large fraction (80−90%) of the emitted energy was received by the membrane surface during dip modification in air. This large amount of transmitted energy could cause extensive bond cleavage and free radical production at which graft polymerization could occur, resulting in a high degree of grafting. Varying the monomer concentration affected the rate and extent of grafting. High NVP concentrations (5 wt %) led to very high degrees of grafting that appeared to level off after 600 s of irradiation. The polymerization rate was highest in the first 30 s of irradiation. As a result, high degrees of grafting (DG > 1.00) were achieved after only 30 s of irradiation. Low monomer concentrations (1 wt %) led to lower degrees of grafting. This was probably due to lower amounts of monomer available for polymerization. The degree of grafting reached a maximum between 30 and 60 s and then decreased with irradiation time. This suggests that the small amount of monomer available at the surface and in the pores was most likely exhausted after 60 s and further irradiation may have caused trunk polymer scission with loss of grafted polymer.

Immersion-Modified 50 kDa Membranes. The results of the immersion modification are shown in Figure 4b. High degrees of grafting were achieved with high monomer concentrations (5 wt %), but long irradiation times were required (>300 s). However, the degree of grafting achieved was 2−3 times lower than through dip modification. At low monomer concentrations (1 wt %), a small increase in grafting was observed, but only

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Table 1. Comparison of Modification Conditions and Degree of Grafting, Wettability, and membrane ultrafiltration performance

membrane	modification conditions	degree of grafting[c]	wettability (cos θ)[d]	L_{p_o}[e] (lmh/kPa)	L_p[f] (lmh/kPa)	% rejection[g] (R_{bsa})	total flux loss[h]	flux loss due to adsorptive fouling[i]
50 kDa PES membrane[a]		0.254	0.75	5.29	1.60	98.3	0.70	0.42
50 kDa regenerated cellulose		0	0.90	1.80	0.85	94.2	0.53	0.0
NVP-modified (D)[b]	1 wt %/10 s	0.421	0.80	5.45	1.86	71.6	0.66	0.296
NVP-modified (D)	1 wt %/30 s	0.550	0.83	5.21	3.20	2.8	0.39	0.286
NVP-modified (D)	1 wt %/60 s	0.549	0.83	9.45	7.81	5.1	0.17	0.076
NVP-modified (D)	1 wt %/300 s	0.473	0.81	24.58	23.41	8.4	0.05	0.008
NVP-modified (D)	1 wt %/600 s	0.373	0.79	26.95	25.94	8.8	0.04	0.0
NVP-modified (D)	2 wt %/5 s	0.518	0.82	5.12	1.67	89.7	0.67	0.298
NVP-modified (D)	2 wt %/10 s	0.501	0.82	3.44	1.76	61.8	0.49	0.128
NVP-modified (D)	2 wt %/30 s	0.732	0.86	2.70	2.14	3.1	0.21	0.097
NVP-modified (D)	5 wt %/5 s	0.445	0.81	3.30	1.56	93.9	0.53	0.192
NVP-modified (D)	5 wt %/10 s	0.626	0.84	0.97	0.65	71.1	0.32	0.087
NVP-modified (D)	5 wt %/30 s	1.032	0.87	0.60	0.54	51.1	0.10	0.0
NVP-modified (D)	5 wt %/60 s	1.177	0.87	0.59	0.59	47.2	0.11	0.0
NVP-modified (I)[b]	1 wt %/60 s	0.265	0.75	4.51	1.50	99.1	0.66	0.412
NVP-modified (I)	1 wt %/180 s	0.380	0.79	3.41	1.50	99.1	0.56	0.289
NVP-modified (I)	1 wt %/300 s	0.424	0.80	3.04	1.22	98.0	0.59	0.258
NVP-modified (I)	1 wt %/420 s	0.483	0.81	2.18	0.73	98.7	0.66	0.227
NVP-modified (I)	1 wt %/600 s	0.490	0.82	2.64	1.14	99.3	0.58	0.255
NVP-modified (I)	5 wt %/60 s	0.283	0.76	5.72	1.70	98.7	0.69	0.484
NVP-modified (I)	5 wt %/180 s	0.703	0.86	0.78	0.55	99.7	0.28	0.0

[a] 50 kDa base poly(ether sulfone) base membrane. [b] D = dip modification and I = immersion modification. [c] Degree of NVP grafting (DG) = ratio of the peak height of the amide I carbonyl stretch in the five-membered ring of NVPmolecule (~1687 cm^{-1}) to that of the benzene ring carbon−carbon double bond stretch (~1487 cm^{-1}). The average estimated error was ±2%. [d] cos θ = 0.62 ± 0.02 for an unmodified PES membrane. The cos θ for the immersion modified membranes were estimated from Figure 6. The average estimated error for cos θ was ±0.02. [e] Initial pure buffer permeability flux of 10 mM PBS, pH 7.4 at 21 °C. The average estimated error was ±7%. [f] Solution permeability flux during filtration of 0.1 wt % BSA in 10 mM PBS, pH 7.4 at 21 °C. The average estimated error was ±10%. [g] Percentage of rejection of bovine serum albumin, $R_{bsa} = (1 - C_p/C_b)100\%$. The average estimated error was ±5%. [h] Total flux loss = $1 - J_p/J_o$; J_p was the final solution flux during BSA filtration. The average estimated error was ±9%. [i] Irreversible adsorptive fouling of membrane = $1 - J_1/J_o$; J_1 was the final buffer flux after BSA fouling and water cleaning. The average estimated error was ±11%.

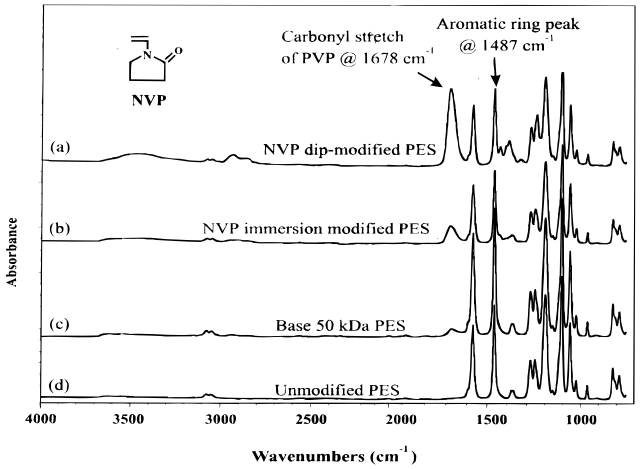

Figure 3. FTIR/ATR spectra of the surface (a) unmodified PES, (b) base 50 kDa PES, (c) base PES membrane immersion-modified with 1 wt % NVP and 10 min of irradiation, and (d) base PES membrane dip-modified with 5 wt % NVP and 1 min of irradiation. All reactions were conducted in an oxygen free monomer solution at 22 °C.

after long irradiation times (>300 s). This result is similar to that observed during dip modification; the reaction appears to be concentration-limited due to the low amount of monomer available at the membrane surface or from depletion by competing processes such as homopolymerization. In contrast to the dip modification in which the polymerization proceeded immediately upon irradiation, essentially no grafting took place for at least the first 60 s of irradiation at both high and low monomer concentrations. We speculate that the induction period could be explained by initial insufficient wetting of the membrane surface by the monomer. As grafting proceeds, the surface wettability is increased, enhancing the degree of grafting (see below). The lower degrees of grafting attained during immersion modification were likely the result of the NVP monomer shielding the membrane from the UV irradiation. Figure 6 shows the UV absorbance of pure PSf, pure PES, the skin layer (PES) of the base 50 kDa membrane stripped off the membrane support and dissolved in methylene chloride, and the NVP monomer dissolved in deionized water at various concentrations. It is clear that NVP absorbs very strongly in the UV, even at low NVP concentrations (0.001 wt % NVP, absorbance of 1.4 relative units). The emission maximum of the UV reactor used was 254 nm (83% of emitted light was at this frequency according to the manufacturer).[42] Even at low monomer concentrations (0.001 wt %), the absorbance at 254 nm was extremely high. As the concentration of NVP was increased above 0.01 wt % NVP, the absorbance at 254 nm leveled off, but the higher wavelengths were absorbed more strongly. Since the absorbance of light at a wavelength of 254 nm by the monomer solution was very high at all NVP concentrations, most of the emitted energy was likely absorbed by the NVP solution during immersion modification. Direct measurements of the energy transmitted through NVP solutions are shown in Figure 5. At NVP concentrations above 0.01 wt %, only 12−18% of the emitted energy was received by the membrane surface (Figure 5). It is only at very low NVP concentrations (0.001 wt %) that the transmitted energy (46−76%) approached that of the energy emitted by the lamps. Since a high NVP concentration (1 and 5 wt %) was used during

(42) Operation Manual of Rayonet Photochemical Chamber Reactor System, Model RPR-100, Southern New England Ultraviolet Co., CT, 1992.

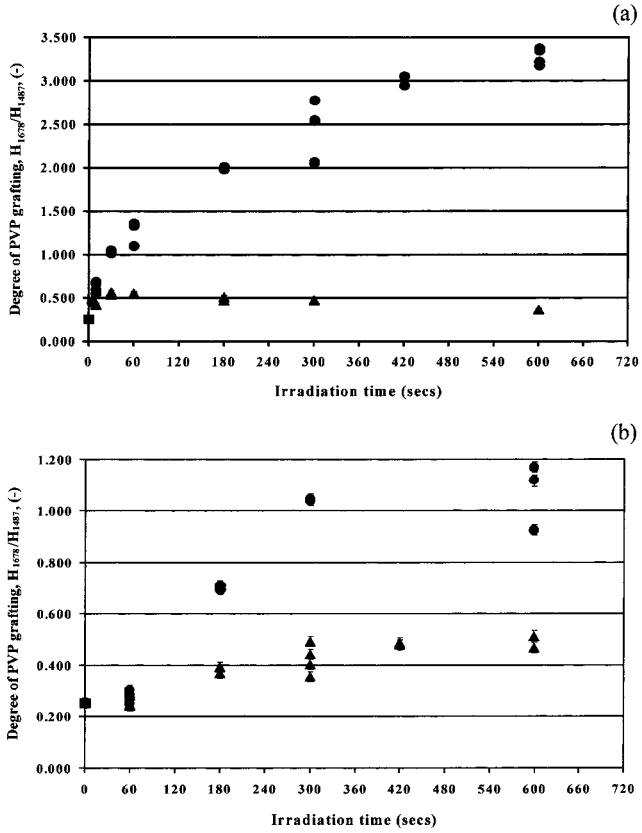

Figure 4. The effect of irradiation time exposure on the amount of NVP grafted during the modification of PES membrane using the (a) dip and (b) immersion techniques. The degree of PVP grafting is the ratio of the absorbance peak height at 1678 cm^{-1} of the amide I carbonyl group found in the NVP five-membered ring to that of the height of the benzene carbon−carbon double bond absorbent peak at 1487 cm^{-1}. (■) Base 50 kDa PES membrane and base membrane modified with (▲) 1 wt % NVP; (●) 5 wt % NVP.

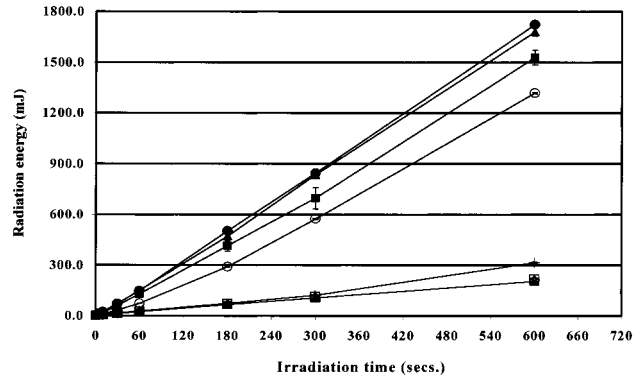

Figure 5. The radiation energy received by the membrane surface during UV irradiation: (●) without quartz cell; with quartz cell filled with (■) air; (▲) water; (○) 0.001 wt % NVP; (+) 0.005 wt % NVP; (△) 0.01 wt % NVP; (□) 0.1 wt % NVP; (◇) 1 wt % NVP; (×) 5 wt % NVP.

immersion modification, it is likely that only a small fraction of energy reached the membrane surface. This would have resulted in a lower extent of bond cleavage and radical formation and hence lower degrees of grafting relative to the dip modification.

Wettability Measurements. The cos θ of the contact angles of the air−water−solid triphase line of the dip-modified membranes, the base 50 kDa PES membrane, an unmodified 10 kDa PES membrane, and a 50 kDa

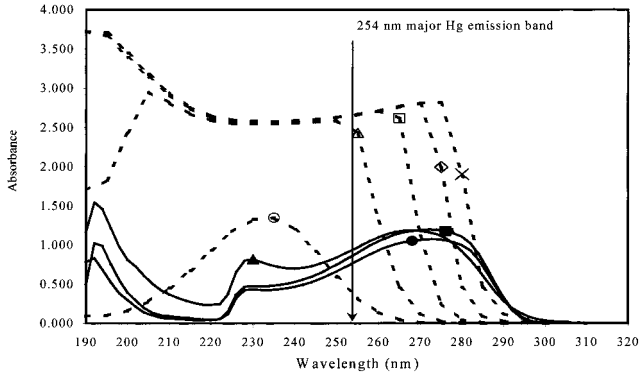

Figure 6. The UV absorbance of NVP and membrane polymers in solution. NVP was dissolved in deionized water. Pure poly(sulfone) (PSf) and PES were dissolved in methylene chloride. The skin layer of the base 50 kDa PES membrane was selectively dissolved in methylene chloride. (-) monomer solutions; (—) membranes; (○) 0.001 wt % NVP; (△) 0.01 wt % NVP; (□) 0.1 wt % NVP; (◇) 1 wt % NVP; (×) 5 wt % NVP; (●) pure PES; (▲) Pure PSf; (■) 50 kDa base PES membrane.

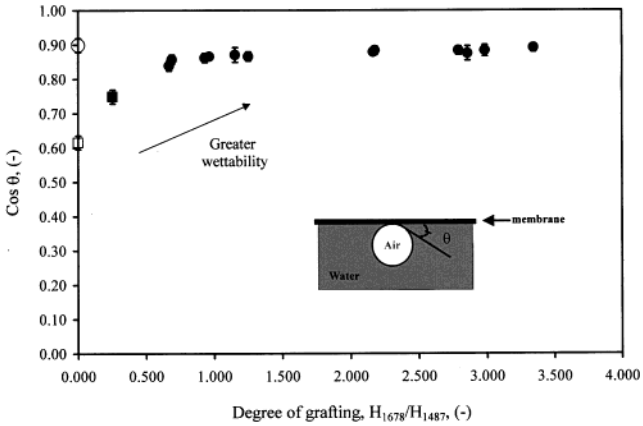

Figure 7. The surface wettability of membranes as measured by cos θ versus degree of grafting. Static contact angles of the membrane surface were measured using the captive air bubble technique (inset). Membranes were inverted and submersed in deionized water, and air bubbles were placed in contact with the surface. The contact angles were averages of measurements on 10 different bubbles. The measurement error was ±3°. (■) Base 50 kDa PES membrane; (□) unmodified 10 kDa PES membrane; (○) regenerated cellulose membrane; (●) NVP dip-modified membranes.

regenerated cellulose membrane are shown in Figure 7. The cos θ of the contact angle has been termed the wettability of a membrane surface;[43] the higher the cos θ, the greater the wettability of that surface to the solvent (water). As expected, the unmodified PES membrane had the lowest wettability (0.62 ± 0.02, Table 1). The base 50 kDa membrane, modified by the manufacturer to decrease protein adsorption, had a higher wettability (0.75 ± 0.03) than the unmodified PES membrane. However, the surface wettability was still substantially lower than that of regenerated cellulose (0.90 ± 0.02), the membrane with the highest surface wettability tested here. Modifying the base 50 kDa PES membrane led to considerable increases in surface wettability over that of the base membrane. Nearly all the increase in surface wettability (cos θ from 0.75 to ~0.86) was achieved by increasing the DG from 0.254 (base

(43) Sigal, G.; Mrksich, M.; Whitesides, G. *J. Am. Chem. Soc.* **1998**, *120*, 3464.

membrane) to 0.68, a factor of 2.7. Above a DG of 0.68, the cos θ increased only slightly, leveling off at a value of 0.87 ± 0.01 at high DG values. These modified membrane surfaces had a wettability close to that of the regenerated cellulose membrane (0.90 ± 0.02). The contact angles for the immersion-modified membranes were not measured. The cos θ values for the immersion-modified membranes listed in Table 1 were estimated from the data in Figure 7. However, they should be similar to those of the dip-modified membranes at the same degree of grafting because the identical base membrane surface and monomer were used.

The contact angle values of the NVP dip-modified membranes were significantly lower than those measured previously[30] because a much higher level of modification was achieved in the present work.

Ultrafiltration Experiments. *Membrane Filtration Parameters.* The performance of the base membrane, the modified membranes, and the regenerated cellulose membrane during filtration of a 0.1 wt % BSA solution was compared using several filtration parameters. The pure buffer permeability, L_{po}, is a measure of the effect of photochemical grafting on the membrane flux. The goal was to reduce fouling through membrane surface modification while maintaining the (i) membrane flux and (ii) solute retention as high as possible. The absolute value of the protein solution flux, L_p, for any modified membrane should be higher than that of the unmodified membrane or else the practical advantage in using modified membranes is diminished.

Dip-Modified 50 kDa Membranes. The effect of irradiation time on the buffer permeability is shown in Figure 8a. Modifying the base membrane surface caused a severe decline in the permeability from 5.3 to 0.6 lmh/kPa above a DG ~ 0.50 (5 s of irradiation). Grafting of PVP chains onto the membrane surface blocked pores and resulted in a decline in permeability. At a low NVP concentration (1 wt %), the buffer flux increased when an irradiation time of longer than 30 s was used. This suggested that the monomer on the membrane surface was exhausted after 30 s and longer irradiation times opened up the pore structure. This corroborated the FTIR/ATR results which showed a DG maximum at 30 s of irradiation and a decline thereafter (Figure 4a). Up to 30 s of irradiation, the monomer was grafted onto the surface. During this period of irradiation, the monomer was completely consumed. Further irradiation only opened up the pore structure, enlarging pores and increasing the flux. At higher monomer concentrations (>2 wt %), the flux decreased sharply because of the high degrees of grafting attained at short irradiation times (<10 s). The flux decline was so severe that above a DG = 1.40, the buffer flux ($L_{po} \ll 0.5$ lmh/kPa) was not high enough to perform the entire filtration protocol. However, the large decreases in buffer flux did not necessarily translate into a smaller membrane pore size, since the solute rejection was found to decrease with increasing degree of grafting (see below).

A plot of BSA rejection as a function of the irradiation time (Figure 9a) reveals that rejection decreased sharply with irradiation time at all monomer concentrations. Surface modification using high monomer concentrations (5 wt %) and increasing irradiation times caused severe rejection losses, despite the fact that a high degree of grafting was achieved (Figure 4a) which led to a sharp decline in permeability (Figure 8a). At low monomer concentrations (1 wt %) and high irradiation times (>30 s), the rejection dropped to below 15% while the permeability was greatly increased. This low value of the rejection coefficient supports the theory that the monomer supply was consumed and further irradiation only enlarged the pores through trunk polymer scission. It is possible that at high monomer concentrations, the photochemical modification enlarges pores while simultaneously creating a layer of polymer chains that obstructs a significant number of pores and lowers the flux. We speculate that protein diffusion through this layer would explain the loss of rejection. However, when a low monomer concentration was used, pore enlargement dominated because the monomer supply was too low to create a layer and rejection decreased while the permeability increased. Overall, regardless of the monomer concentration, irradiation times should be restricted to less than 10 s or the emitted energy from the UV lamps should be reduced to prevent serious pore enlargement.

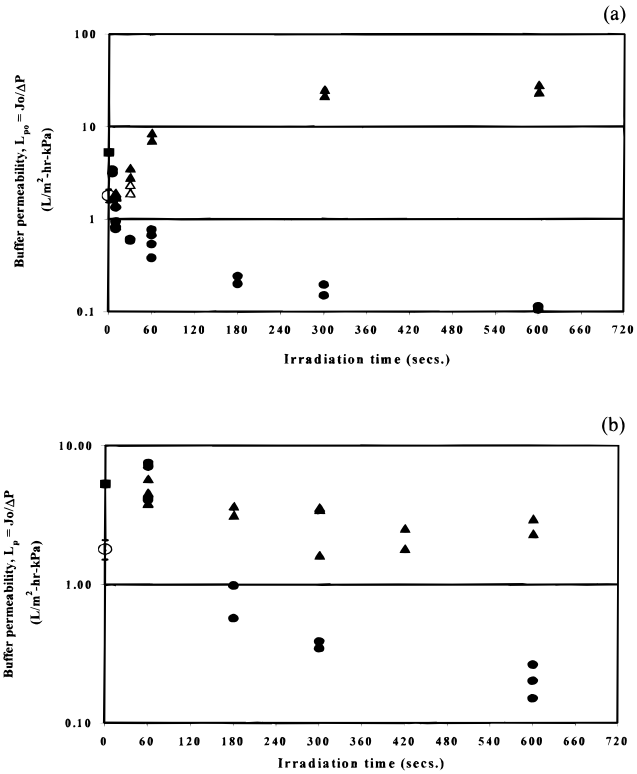

Figure 8. Membrane buffer permeability as a function of irradiation exposure at various NVP concentrations after (a) dip modification and (b) immersion modification. The buffer was 10 mM PBS at pH = 7.4 and 22 °C. (■) Base 50 kDa PES membrane; (○) regenerated cellulose membrane; base membrane modified with (▲) 1 wt % NVP; (△) 2 wt %; (●) 5 wt % NVP.

The filtration results for BSA solutions are shown in Table 1. As the degree of grafting was increased, the total membrane flux loss (J_p/J_o) decreased. Almost all the modified membranes showed decreased total flux loss in comparison with the unmodified base membrane. The total membrane flux loss decreased from the base membrane value of 0.70 down to 0.28 for the best modified membranes. Most of the modified membranes had lower total flux loss than regenerated cellulose

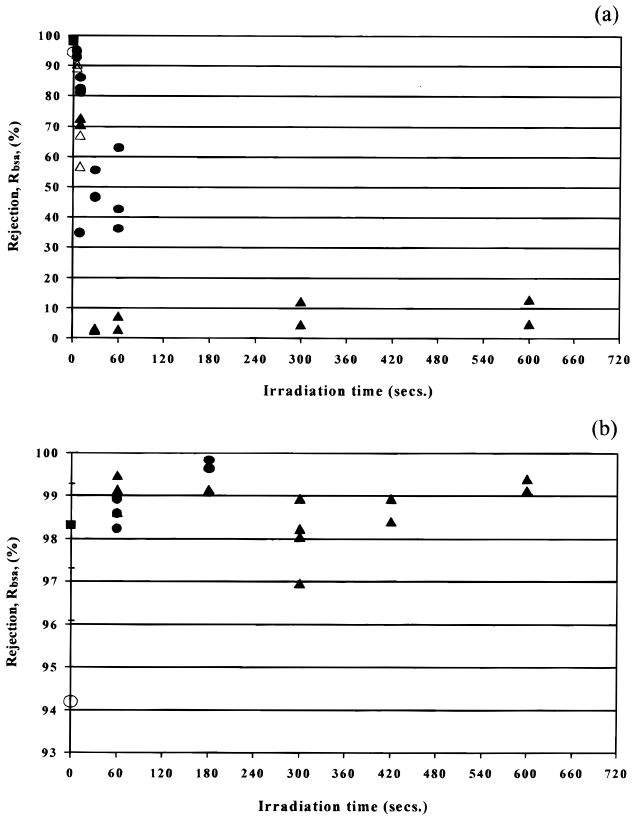

Figure 9. Bovine serum albumin rejection as a function of irradiation exposure at various NVP concentrations after (a) dip modification and (b) immersion modification. A solution of 0.1 wt % BSA in 10 mM PBS at pH 7.4 and 22 °C was filtered according to the constant volume diafiltration protocol shown in Figure 1. (■) Base 50 kDa PES membrane; (○) regenerated cellulose membrane; base membrane modified with (▲) 1 wt % NVP; (△) 2 wt %; (●) 5 wt % NVP.

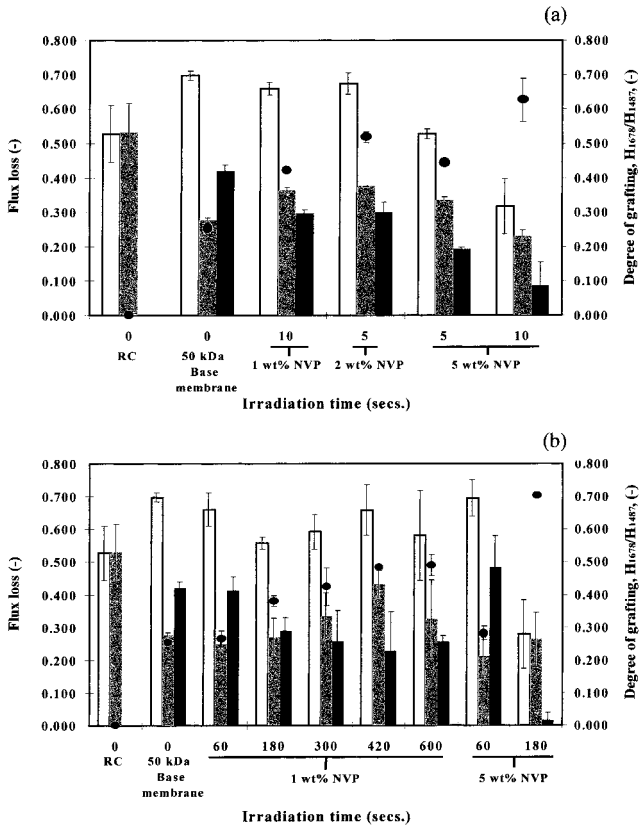

Figure 10. A summary of the sources of flux loss during the filtration of 0.1 wt % BSA versus irradiation time for (a) dip-modified membranes and (b) immersion-modified membranes. The white bars represent the fraction of the initial buffer flux lost during the filtration of 0.1 wt % BSA, $(J_o - J_p)/J_o$; the gray bars represent the fraction of the initial buffer flux lost due to the reversible adsorptive fouling and osmotic effects from concentration polarization, $(J_1 - J_p)/J_o$; and the black bars are the difference between these quantities and represents the fraction of the initial buffer flux lost due to irreversible adsorptive fouling, $(J_o - J_1)/J_o$. The total flux loss (white bars) is the sum of the flux loss caused by reversible adsorptive fouling and the osmotic effects from concentration polarization (gray bars) and by irreversible adsorptive fouling (black bars). The points (●) are the degree of grafting for the membranes modified with the listed reaction conditions (abscissa). The data shown are averages of at least two runs.

(0.53). However, these dip-modified membranes possessed lower rejection, which might explain some of the fouling improvement. Lower protein rejection or higher sieving led to less concentration polarization and hence lower osmotic effects. Lower concentration polarization may also have led to lower flux loss caused by reversible and irreversible adsorptive fouling because there was less protein near the membrane surface. Therefore, significant rejection loss may be correlated with lower total flux loss. This was the case for dip-modified membranes with flux loss values below 0.20 in which the BSA rejection was lower than 50%. This is illustrated by the flux loss of dip-modified membranes modified by 1 wt % NVP/300 s. and 2 wt % NVP/10 s. The membranes had vastly different initial water permeabilities, similar wettability and degrees of grafting, but different total flux loss and flux loss due to adsorptive fouling (columns 8 and 9). These results could be explained by the different pore structure of these membranes as indicated by their permeability (columns 5 and 6) and the rejection values (column 7). The more open pore structure of the membrane modified by 1 wt %NVP/300 s might explain the total flux loss differences as described above. This indicates that both the membrane porous structure and hydrophilicity must be considered when comparing the total flux loss of membranes.

A summary of the membrane flux loss and flux recovery through membrane cleaning for the lowest fouling modified membranes as a function of the degree of grafting is shown in Figures 10a and 11a. The bars represent the flux loss during the filtration of BSA and the points are the degree of grafting of the tested membranes. The total flux loss (white bars) is the sum of the flux loss due to reversible adsorptive fouling and osmotic effects from concentration polarization (gray bars) and the flux loss due to irreversible adsorptive fouling (black bars). Figure 10a shows that the modified membranes not only had lower total flux loss (white bars) than the base 50 kDa membrane but most of the flux loss was caused by osmotic effects from concentration polarization (gray bars). Membranes that were modified with irradiation times longer than 10 s were not included in the figure because the rejection was below 70% (see above). As the degree of grafting was increased, the flux loss due to irreversible adsorptive fouling (black bars) of the base membrane (0.42) decreased to 0.30−0.09 for the modified membranes. This indicated that fouling due to irreversible protein adsorption was lower for the modified membranes than

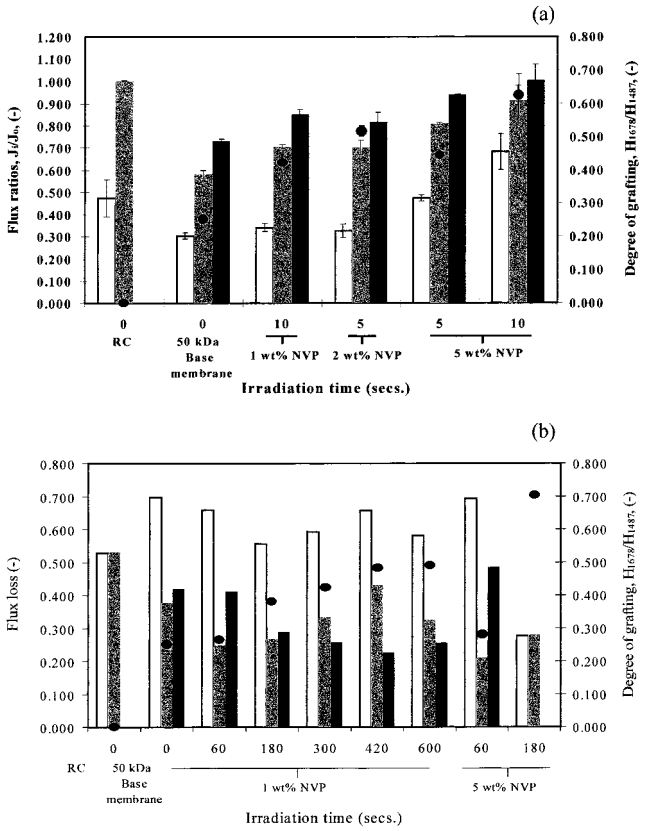

Figure 11. Flux ratio changes during filtration and after cleaning with water and caustic versus irradiation time for (a) dip-modified membranes and (b) immersion modified membranes. The white bars represent the fraction of the initial buffer flux that exists during filtration of 0.1 wt % BSA, J_p/J_o; the gray bars represent the fraction of the initial buffer flux that exists after water cleaning, J_1/J_o; and the black bars represent the fraction of the initial buffer flux that exists after caustic cleaning, J_2/J_o. The points (●) are the degree of grafting for the membranes modified with the listed reaction conditions. The data shown are averages of at least two runs. The cleaning procedure is described in Figure 2.

for the base membrane. Therefore, the higher surface wettability of the modified membranes decreased the flux loss by reducing protein adsorption. However, the higher initial permeability of the base membrane (Table 1) may result in shorter processing times than the modified membranes for short runs (few hours) and at lower protein concentrations despite the higher irreversible adsorptive fouling. The modified membrane with the highest DG (0.626) had significantly lower total flux loss (0.32) than the base membrane (0.70) and lower flux loss due to irreversible adsorptive fouling (0.09 compared with 0.42). However, the regenerated cellulose membrane outperformed all the dip-modified membranes because it had no measureable adsorptive fouling; the flux loss was entirely caused by reversible adsorptive fouling, and osmotic effects from concentration polarization and flux were recovered by water washing alone. In addition, the lower rejection of the dip-modified membranes would make the regenerated cellulose membranes more attractive for applications in which high protein retention is desired. In uses in which high protein transmission is desired, such as the separation of proteins from the lysis products of *Escherichia coli* or yeast cells or the separation of monoclonal antibodies from transgenic sources, these modified membranes could be very attractive. The membranes would allow proteins to pass through while the larger cellular material is retained.

Finally for the dip modification approach, the buffer fluxes after water and caustic cleaning (Figure 11a) showed that the modified membranes recovered more of their flux after cleaning than the base membrane. While the base membrane recovered only 0.73 of the initial flux after the water and caustic cleaning procedure, all the modified membranes recovered between 0.82 and 1.00 of the flux. The modified membranes with the highest DG (0.626) recovered 0.91 of the initial flux after water cleaning and all of its original flux after both water and caustic cleaning. The regenerated cellulose membrane recovered all of its flux after water cleaning alone because very little irreversible adsorbed protein fouled its surface, while the best performing modified membrane needed the extra caustic cleaning step to remove the remaining irreversibly adsorbed protein on its surface.

Immersion-Modified 50 kDa Membranes. Modification of PES membranes via the immersion technique resulted in lower degrees of grafting than the dip method (Figure 4a,b) because of the protection afforded to the surface by the monomer in the solution during irradiation. This led to striking differences in membrane characteristics. Figure 8b shows the effect of irradiation on membrane buffer permeability after immersion modification. The permeability decreased with irradiation when either low (1 wt %) or high (5 wt %) monomer concentration was used. At low monomer concentrations, the permeability decreased and leveled off at about 3.5 lmh/kPa after 300 s at $\Delta P = 70$ kPa. This mirrored the degree of grafting which also leveled off after 300 s (Figure 4b). The observed permeability at high monomer concentration (5 wt %) decreased more slowly as compared with dip modification (Figure 8a). This was a direct result of a lower observed degree of grafting for the immersed versus the dip method (cf. the *y*-axes in Figure 4a,b) because a high proportion of the UV light (81−88%) was absorbed by the monomer in solution. This reduced the energy received by the membrane surface and hence the degree of grafting. Above an irradiation time of 180 s, a relatively high degree of grafting was achieved (Figure 4b). However, the permeability was too low ($\ll$0.5 lmh/kPa) to perform the entire filtration run. Modification with 1 wt % NVP caused a decrease in permeability after immersion modification while it *increased* after dip modification (Figure 8a,b). This indicates that during dip modification the effect of polymer chain scission was more important than that of NVP grafting because a large fraction of emitted energy reached the surface, resulting in overall pore enlargement. However, during immersion modification, the reverse was observed because less energy reached the membrane surface due to monomer shielding. Although there was a significant decrease in the permeability after immersion modification, the modified membrane permeabilities (2.2−5.7 lmh/kPa) were higher than that of regenerated cellulose (1.8 lmh/kPa).

The BSA rejection results further supported the monomer shielding argument (Figure 9b), where it can be seen that the BSA rejection at two monomer concentrations remained constant and high even after 600 s

of irradiation. The dip modification, however, led to large drops in rejection (20−70%) after only 10−60 s of irradiation. This strongly supports the contention that membrane screening occurred in solution during the immersion method but was less effective with the dip method when the monomer alone wetted the membrane surface. It is also interesting to note that the base and the higher permeable modified membranes had a higher rejection (98−99%) than the regenerated cellulose membrane (∼94%).

Immersion-modified membranes exhibited lower total flux loss than the base membrane during protein filtration, although they had slightly lower permeability (Table 1). Despite their lower permeability than the base membrane (Table 1, columns 5 and 6), the immersion-modified membranes could be chosen over the base membrane if lower protein loss (higher yield) due to irreversible adsorptive fouling outweighed the lower permeability. As the degree of grafting was increased through increased irradiation time, the flux loss *decreased* from approximately 5−40% below that of the unmodified base membrane. These results were lower than the flux decreases (5−60%) achieved through dip modification. However, since these membranes had no loss in rejection, the decreased flux loss was not due to changes in the rejection and hence the convective flux. The membrane with the highest degree of grafting (∼0.703) exhibited a lower total flux loss than regenerated cellulose and an equivalent buffer permeability to the regenerated cellulose membrane (Table 1, columns 8 and 6).

A summary of the sources of flux loss and the flux recovery after cleaning are shown in Figures 10b and 11b. Modified membranes with DG values close to that of the base membrane (DG = 0.254−0.283) had similar irreversible adsorptive fouling (Figure 10b) and recovered about the same fraction of the initial buffer flux after cleaning (Figure 11b). This clearly showed that a sufficient amount of monomer was not grafted to the surface to produce a low-fouling membrane. Those membranes with higher degrees of grafting (>0.38) not only had lower flux losses but also had significantly lower irreversible adsorptive fouling (0.02−0.29) than the base membrane (0.42). These membranes also recovered more of their initial buffer flux after cleaning than the base membrane (Figure 11b). These results were nearly the same as those of the dip-modified membranes (Figure 10a). The modified membranes with a DG > 0.38 recovered greater than 0.84 of the initial flux after the full cleaning. The membrane with the highest degree of grafting (0.703) had no flux loss due to irreversible adsorptive fouling. All the flux loss was caused by reversible adsorptive fouling and osmotic effects from concentration polarization, which was completely recovered by rinsing the membrane with water. The regenerated cellulose membrane also experienced no adsorptive fouling. However, the best immersion modified membrane (DG = 0.703) performed better than the regenerated cellulose because it had lower overall flux loss during BSA filtration (Figure 10b or Table 1, column 8). However, this membrane had a lower initial buffer permeability (0.8 lmh/kPa) than the regenerated cellulose (1.8 lmh/kPa). Nevertheless, because of their higher rejection, these membranes could replace regenerated cellulose in applications in which product loss was undesirable.

Conclusions

UV-assisted graft polymerization of *N*-vinyl-2-pyrrolidinone onto 50 kDa PES membranes using two different techniques created highly wettable PES membrane surfaces with superior fouling resistance compared with the base membrane. High degrees of grafting were achieved with 30% increased wettability (cos θ) values over that of the base PES membrane. These values are nearly equal to those of regenerated cellulose. The adsorptive fouling of the base membrane was decreased significantly from 0.42 to 0.0 using either dip or immersion modification. The immersion technique created the best performing modified membranes for applications in which high protein retention is required, while the dip-modified membranes performed best for applications in which high protein transmission is preferred. The best performing immersion-modified membrane had the same adsorptive fouling, similar permeability, and higher rejection than regenerated cellulose, the so-called "gold-standard" membrane. The use of either modification technique sharply decreased the base membrane permeability at high monomer concentrations because the grafted polymer chains obstructed pores. The dip-modified membranes also exhibited severe rejection loss with increased irradiation due to pore enlargement. The simultaneous loss of BSA rejection and permeability during the dip modification of membranes at high NVP concentrations suggests that as radiation cleaved PES bonds and enlarged the pores, a high density of long chains was created on the surface. This might have caused the buffer permeability to decrease, yet the rejection might still decrease because the protein was able to permeate this layer and easily pass through the enlarged pores. The lower rejection of the dip-modified membranes caused by radiation-induced pore enlargement could lead to unacceptably high protein loss and render these membranes less desirable for use in the processing of expensive proteins. Yet, in uses in which high protein transmission is desired, these membranes could be very attractive. The immersion-modified membranes retained their rejection after modification because a large fraction (81−88%) of the emitted UV energy was absorbed by the NVP monomer in solution before it reached the membrane surface. The NVP in solution shielded most of the UV light, even at very low concentrations (0.001 wt %), thereby protecting the membrane surface from severe pore enlargement.

The wettability and fouling data indicated that the irreversible adsorptive fouling can be eliminated by modifying the base membrane with NVP at a DG ∼ 0.700, at the expense of the permeability. Higher degrees of grafting resulted in only further loss of permeability. Further work should be performed to determine how to maintain membrane permeability. Also, further investigation is needed to determine the density of chains on the surface and the polymer chain length. A high density of polymer chains must be created on the surface to increase wettability and decrease fouling. However, a short polymer chain length is necessary to minimize pore blockage and maintain membrane permeability. Work on these and other related topics are currently underway.

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