Preparation and Characterization of Layered Membranes Constructed by Sequential Redox-Initiated Grafting onto Polyacrylonitrile Ultrafiltration Membranes

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ABSTRACT: Layered membranes were prepared by sequential grafting—by means of redox initiators—of water-soluble monomers, with oppositely charged ionic groups, onto ultrafiltration (UF) polyacrylonitrile (PAN) membranes at room temperature. Grafting of a single layer of 2-hydroxyethylmethacrylate (HEMA) onto a PAN membrane gave a highly grafted membrane with a relatively high water flux. Bilayered membranes with various properties containing poly-2-(dimethylamino)ethyl methacrylate (*p*-2DMAEMA) as the bottom layer and polymethacrylic acid or polystyrenesulfonic acid (*p*-SSA) as the upper layer were prepared and compared—by means of infrared spectroscopy and electron microscopy—with single-layered membranes of grafted polyhydroxyethylmethacrylate. Layered membranes exhibited a significant decline in water flux in comparison with the initial UF membranes. The flux could, however, be manipulated by controlling the concentration of monomers, the time of grafting, and the number of layers. When four layers of *p*-2DMAEMA and *p*-SSA were sequentially grafted onto a PAN membrane, pure water fluxes were stable over a wide range of pH values and did not change over long storage times. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 509–520, 2005

Key words: membranes; radical polymerization; graft copolymer; infrared spectroscopy

INTRODUCTION

Polyacrylonitrile (PAN) ultrafiltration (UF) membranes constitute an important family of asymmetric porous membranes whose excellent chemical and mechanical properties facilitate their wide use in separation technologies.[1–3] These membranes, which are prepared by the phase-inversion method, have been chemically modified—primarily to reduce organic fouling—by means of plasma treatment, UV radiation, or free-radical initiation. There are a number of reports in the literature describing both the chemistry and mechanisms of such modifications and the concomitant changes in membrane performance.[4–9] Ulbricht and his group,[4–6] for example, found that surface modification of PAN-UF membranes by plasma treatment or photo-induced graft polymerization of hydrophilic monomers improved membrane stability against proteins but decreased membrane permeability. The loss of permeability was attributed to the blocking of membrane pores by the grafted polymer chains. Jimbo et al.[7–9] attempted to prepare modified amphoteric PAN membranes by free-radical graft-polymerization of 2-(dimethyamino)ethyl methacrylate (2DMAEMA) and methacrylic acid (MA) onto PAN membranes. The surface chemistry of the latter membranes was analyzed by a streaming potential and ATR-FTIR techniques.

The monomers most often used for surface modification are the highly hydrophilic vinyl monomers 2-hydroxyethylmethacrylate (HEMA), acrylic acid (AA), MA, 2DMAEMA, sulfopropylmethacrylate (SPM), and acrylamidopropylsulfonic acid (AMPS). HEMA, in particular, has been used extensively for the improvement or hydrophilization of a variety of surfaces.[10–15] Ozone or redox initiation has been used for simultaneous grafting with HEMA and crosslinking with a number of different dimethacrylate crosslinking agents.[13] The most recent research on the controlled polymerization of HEMA has been conducted using atom-transfer radical polymerization with copper bipyridine chloride or bromide as the catalyst.[16–20] The advantage of this polymerization technology is that it gives a high yield of polymers of low polydispersity due to the suppression of the rate of chain termination relative to the rate of chain propagation.

Our approach to the modification of PAN UF membranes—redox-initiated sequential grafting of oppositely charged monomers[21]—is a continuation of our research and development work on the modification

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of commercial reverse osmosis (RO) and nanofiltration (NF) membranes.[22–24] Contrary to the popular procedure, which involves construction of multilayered assemblies by simple deposition of oppositely charged polyelectrolytes,[25–29] our methodology exploits the advantages of surface-confined grafting[20] for *in situ* modification of existing membranes. In this research effort, PAN membranes were modified by redox-initiated grafting with the water-soluble monomers MA, HEMA, and 2DMAEMA or with styrene sulfonic acid (SSA) Na salt. The major advantage of grafting using redox initiators lies in the greater commercial viability of this procedure over technologies requiring vacuum conditions or nitrogen-purging assemblies and elevated temperatures. Our studies revealed that electrostatic attraction between the graft-polymer and the oppositely charged monomer in the reaction solution surrounding the membrane had a dramatic effect on the extent of grafting. For instance, in PAN grafted with SSA and 2DMAEMA, the grafting of SSA onto PAN was approximately 10 times higher if poly-2 DMAEMA was grafted first.[21] In our procedure, a covalent chemical bond is created between the substrate and the grafted layer as well as between the layers themselves: such covalently bonded layers cannot be obtained by simple deposition. This covalent bonding constitutes the major difference between redox-initiated grafting (our method) and polyelectrolyte deposition, both of which are used to prepare NF membranes. From the extensive literature on the latter subject,[30,31] it is evident that there is a reasonable correlation between the measured thickness of the attached layers and water permeability[30,31]—an important relationship that may be taken as a guideline to simplify the membrane characterization.

In the current work, we set out to modify commercial PAN UF membranes for the construction of layered membranes with potential NF properties. In particular, we sought to determine how sequential graft-polymerization of oppositely charged monomers could indeed be applied to convert a UF membrane to an NF membrane. The changes in the chemical and structural characteristics of the membranes were followed by spectroscopic analysis (ATR-FTIR) and microscopic examination (SEM and TEM) of both the original UF membranes and the new layered membranes. The effect of the main grafting parameters on the degree of grafting and on the pure water flux of the layered membranes was also investigated, and long-term stability testing was performed. The evaluation of important grafting parameters, such as thickness of the grafted layer and swelling, do not fall in the scope of this study, whose aim was primarily to prepare and characterize multilayered UF membranes.

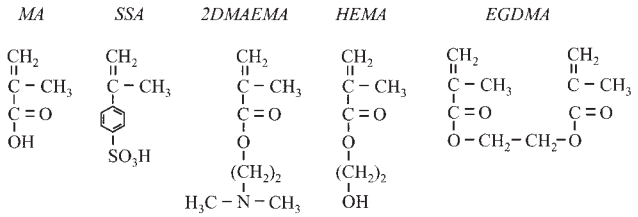


Figure 1 Structural formulae of the monomers and the crosslinking agent used for preparing layered membranes.

EXPERIMENTAL

Materials

Two PAN UF membranes with different properties (designated PAN-HV2 and PAN-HV3), supplied by GKSS, Germany, were produced by phase inversion from a copolymer of PAN and methylmethacrylate. Differences in the conditions of preparation of the PAN-HV2 and PAN-HV3 membranes conferred on the membranes different values for pure water permeability (200 and 130 L/m^{2}h bars, respectively) and porosity (average pore diameter d_{50} = 12 nm, cut off $M_{100} \geq 2.0 \times 10^4$ g/m and d_{50} = 6.7 nm, cut off $M_{100} \geq 9.5 \times 10^3$ g/mol, respectively). The redox system, potassium persulfate-sodium metabisulfite (Merck), was used as the initiator. The monomers HEMA, MA, SSA Na salt, and 2DMAEMA and the crosslinking agent ethylene glycol dimethacrylate (EGDMA), all supplied by Aldrich, were used without purification. The structural formulae of the monomers and the crosslinking agent are given in Figure 1. The solvents ethylene glycol and isopropanol were also supplied by Aldrich. A single-layered membrane was obtained by grafting HEMA onto PAN-HV3. This UF support was also used for construction of three- and four-layered membranes. The bilayered membrane was constructed by sequential grafting of 2DMAEMA and MA or SSA onto PAN-HV2, as described below.

Graft polymerization procedure

Redox-initiated graft polymerization onto the PAN membrane was performed in aqueous solution, as described elsewhere.[21] Briefly, series of single-layered and bilayered membranes were prepared by varying the reaction parameters, as shown in Tables I–III. For each modification procedure, two pieces of membrane, each 128 ×30 mm in size, were placed in a specially designed cell containing an aqueous solution or a water/alcohol solution of the relevant monomer so as to guarantee the grafting exclusively onto the surface facing into monomer solution.[23] The dissolved initiator was then added, and the cell was sealed and allowed to stand for the appropriate time (at about 22°C) without shaking. The membranes were then

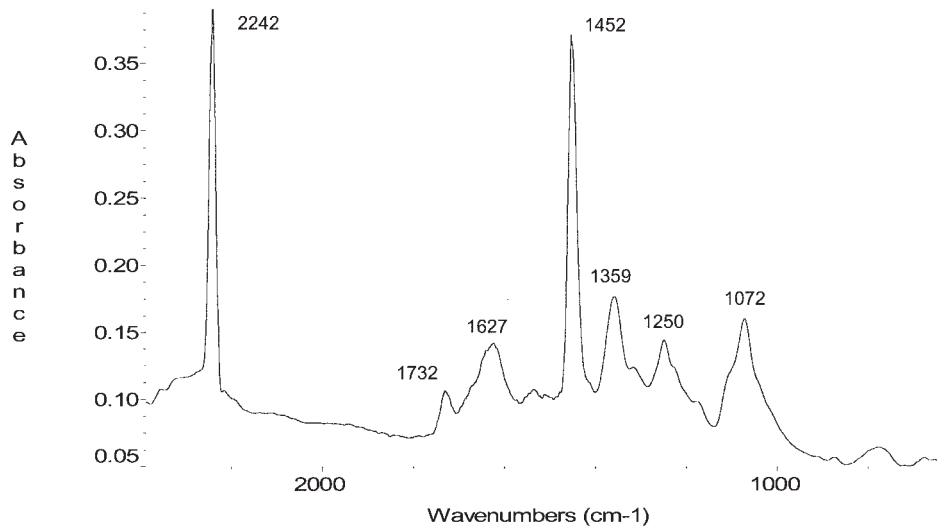


Figure 2 IR spectrum of the PAN-HV3 nonmodified UF membrane.

removed and washed with deionized water for 24 h at 22°C to remove the homopolymer. For sequential grafting, the modified membrane was then brought into contact with an aqueous solution of the second monomer and initiators, in exactly the same manner as that described above, and the procedure was repeated.

Water permeability measurements

Measurements of pure water flux were conducted at 22°C in stirred cells with an active membrane area of 13.4 cm^2. The membranes were subjected to a water pressure of 15 bars for 30 min; thereafter, the pressure was reduced to 3 bars, and water flux was determined by collection of the permeate for a given period. Values of at least three different samples were averaged, giving a maximum error of 15%.

IR spectra

ATR-FTIR spectra were obtained on a Nicolet Fourier transform infrared spectrometer equipped with a mercury cadmium telluride detector. For recording the ATR-FTIR spectrum, a piece of membrane (5 × 2 cm) was stuck to each of the two faces of the internal reflection element; due to the special vertical accession, this set-up provided excellent contact and hence high resolution of the absorbance bands.

Estimation of grafting by means of IR spectroscopy

It is commonly held that IR absorbance (peak height or integrated area) is proportional to the concentration, and this relationship was used as a measure of grafting. [We had also previously shown that the degree of grafting in terms of weight increase (Soxhlet extraction) showed good correlation with the values obtained from spectral analysis[22]]. Thus, the ratio of an analytical peak (absorbance of a new band) to a standard peak (absorbance of the polymer backbone; for instance, the band at 1452 cm^{-1} attributed to CH_2 scissor vibration) was calculated and taken as a measure of grafting.

TABLE I
Preparation of One-Layered Membrane on PAN-HV3

Membrane designation	Monomer concentration (mol/L)	Initiator concentration		Crosslinker concentration (mol/L)	Solvent	Time (min)	A_{1723}/A_{1452}	Flux (L/m^2h)
		$K_2S_2O_8$	$K_2S_2O_5$					
HV3-HEMA-1	0.5	0.01 mol/L	0.01 mol/L	—	H_2O	20	0.38	180
HV3-HEMA-2	0.5	0.01 mol/L	0.01 mol/L	—	H_2O	25	0.70	160
HV3-HEMA-3	0.5	0.01 mol/L	0.01 mol/L	—	H_2O	30	0.98	150
HV3-HEMA-4	1	2% of monomer	1/3 of $K_2S_2O_8$		H_2O:EG	30	0.42	175
HV3-HEMA-5	1	2% of monomer	1/3 of $K_2S_2O_8$	—	H_2O:EG	60	0.82	160
HV3-HEMA-6	1	2% of monomer	1/3 of $K_2S_2O_8$	—	H_2O:EG (50:50)	120	1.08	150
HV3-HEMA-7	1	0.01 mol/L	0.01 mol/L	0.02	H_2O:i-prOH	120	1.05	150
HV3-HEMA-8	1	0.01 mol/L	0.01 mol/L	0.03	H_2O:i-prOH	120	0.89	130
HV3-HEMA-9	1	0.01 mol/L	0.01 mol/L	0.04	H_2O:i-prOH	120	0.95	98
HV3-HEMA-10	1	0.01 mol/L	0.01 mol/L	0.08	H_2O:i-prOH	120	1.04	66

EG, ethylene glycol; *i*-prOH, *iso*-propanol.

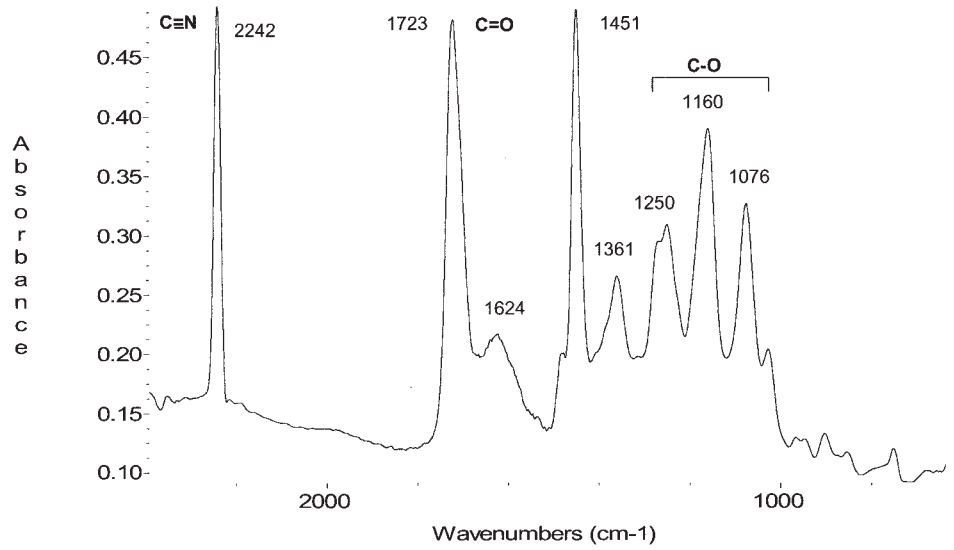


Figure 3 IR spectrum of membrane designated HV3-HEMA-7 (see Table I).

Electron microscopy observations

Modified membranes were detached from the nonwoven support and subjected to scanning electron microscopy (SEM, Leo Stereoscan 440) or to high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2010). Prior to SEM and TEM examinations, the membrane surface (selective layer) and cross sections were coated with a thin layer of gold or carbon, respectively, by means of a sputtering device. For SEM, cross sections were prepared by fracturing the membranes at the temperature of liquid nitrogen. For TEM, ultrathin cross sections were obtained by cutting the membrane with a diamond knife of an ultramicrotome cooled with liquid nitrogen. The membranes were stained by treating them with dilute NaOH solution followed by immersion in excess uranyl nitrate solution (0.1*M*) for about 15 min, thorough washing of the membrane with deionized water, and drying under vacuum at 40°C.

RESULTS AND DISCUSSION

Ir studies of original and modified PAN membranes

The IR spectrum of the PAN-HV3 nonmodified membrane (Figure 2) exhibited prominent peaks at 2243 cm^{-1} (C=N absorbance) and at 1452 cm^{-1} (νCH_2) and peaks at 1731 and 1625 cm^{-1} that may be attributed to traces of remaining DMF or to the presence of a comonomer.[32–34] For grafted polymer the characteristic peaks described below were obtained: Evidence of grafting of MA was provided by the appearance of carbonyl C=O groups at 1730–1700 cm^{-1}.[35] PolySSA was characterized by the symmetric and asymmetric stretch vibrations of SO_3 groups at 1040–1034 cm^{-1} and around 1200 cm^{-1}, respectively. The absorbance at 1008 and 1126 cm^{-1} corresponded to the in-plane bending and in-plane skeleton vibration of a disubstituted benzene ring.[36,37] The appearance of a new absorbance band attributed to tertiary amine groups $–N(CH_3)_2$ at 1152 cm^{-1} was indicative of 2DMAEMA grafting.[38] The ester C=O stretch vibration of this poly-2DMAEMA polymer was positioned at 1728 cm^{-1}. In addition, in the spectra of poly-2DMAEMA-grafted membranes, three small, but distinct, peaks characteristic of methyl derivatives of amines were evident at 2888–2770 cm^{-1} (not shown). Grafting of HEMA was confirmed by the appearance of the characteristic bands of ester carbonyl at 1723 cm^{-1} and of C–O at 1161 cm^{-1}.[35]

Grafting of the HEMA single-layered membrane

In the current study, we initially attempted to graft HEMA in purely aqueous media. At concentrations of

TABLE II
Grafting of MA (Membrane A) and SSA (Membrane B) as a Function of Amount of poly-2DMAEMA Grafted on the PAN-HV2 Membrane

Concentration of first monomer	$A_{1725–1729}/A_{1452}$* for second monomer		A_{1036}/A_{1452}[a] for second monomer	
2DMAEMA (mol/L)	MA (0.1 mol/L)	MA (1 mol/L)	SSA (0.5 mol/L)	SSA (1 mol/L)
0	0.11	0.52	0.04	0.086
0.1	0.57	0.75	0.54	0.77
0.5	0.77	0.97	0.76	0.88
1.0	0.94	—	0.86	1.14

[a] Relative ratio of absorbance of the characteristic band of new graft to the absorbance of characteristic analytical band.

TABLE III
Sequential Grafting of Acidic Monomers on PAN-MV2-*g*-2DMAEMA[a]

	Grafting of first monomer, 2DMAEMA					Grafting of second monomers, MA and SSA					
Membrane	Monomer	Concentration (mol/L)	Time (min)	A_{1723}/A_{1452}	Thickness (mm)	Monomer	Concentration (mol/L)	Time (min)	A_{1036}/A_{1451} or A_{170}/A	Thickness (mm)	Flux[b] (L/m^{2}h)
A	2DMAEMA	1.0	10	0.46	0.24	MA	1.0	60	0.52	0.28	50
B	2DMAEMA	1.0	10	0.46	0.24	SSA	1.0	60	0.76	0.40	20

[a] Flux of the original PAN-HV2 membrane was 530 L/m^{2}h at 3 bars.
[b] Note, the fluxes were measured immediately after synthesis. Further experiments showed that these values changed.

1*M* of monomer and 0.01*M* of initiator, grafting and homopolymerization took place very rapidly, and phase separation of the solution was observed within 2–3 min at 20°C. The intrinsically high reactivity of HEMA in aqueous media[14,15] is probably due to the low solubility of the polymer in water, which leads to phase separation at a very early stage and consequently to an accelerated rate of radical polymerization. A high concentration of initiator will create many active centers on the surface, thus providing the conditions for high graft density. In contrast, when the reaction was carried out in an ethylene glycol/water or in a propanol/water mixture (50 : 50), phase separation was not observed within as long a time as 2–3 h, evidently because the homopolymer was soluble in the reaction mixture. As was expected, the rate of grafting was significantly lower in the alcohol/water mixture than in pure water. Since there was no precipitation of the newly formed polymer in the organic/water mixtures, a high amount of monomer could be used when there was a need for a high level of grafting.

Table I shows that, when water was used as the solvent, the degree of grafting at a HEMA concentration of 0.5*M* was rather high (0.98) after a relatively short time of 30 min. The first three samples shown in the table were obtained at slightly shorter times (20–30 min), but the other conditions remained the same as those for the other samples. The twofold increase in the degree of grafting from the first to the third sample may indicate very fast grafting of HEMA in an aqueous environment. For the same period of time, grafting was much lower, even at a higher monomer concentration, in water/ethylene glycol as the solvent. It is thus evident that, by varying the oxidant/reductant ratio, the concentration of monomer, and the time (with a certain range), it is possible to control the extent of grafting without a significant decrease of flux.

The spectrum of the membrane designated HV3-HEMA-7 in the range 2260–800 cm^{-1} is presented in Figure 3. If we assume that the new poly-HEMA chains completely covered the surface of the original membrane and created a new layer, it would be reasonable to expect that there would be a decrease in the intensity of the characteristic PAN band (C≡N). However, this was not so: the intensity of the C≡N vibration band at 2243 cm^{-1} (which is attributed to PAN) remained high, while the intensities of the new bands at 1723 and 1161 cm^{-1} were also high. Therefore, we

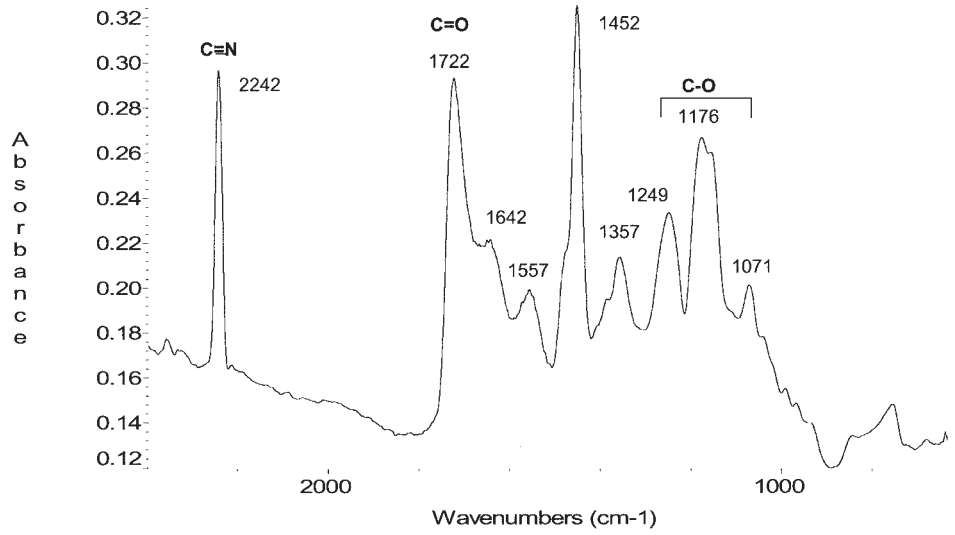


Figure 4 IR spectrum of multilayered PAN-HV2 membrane A (see Table II).

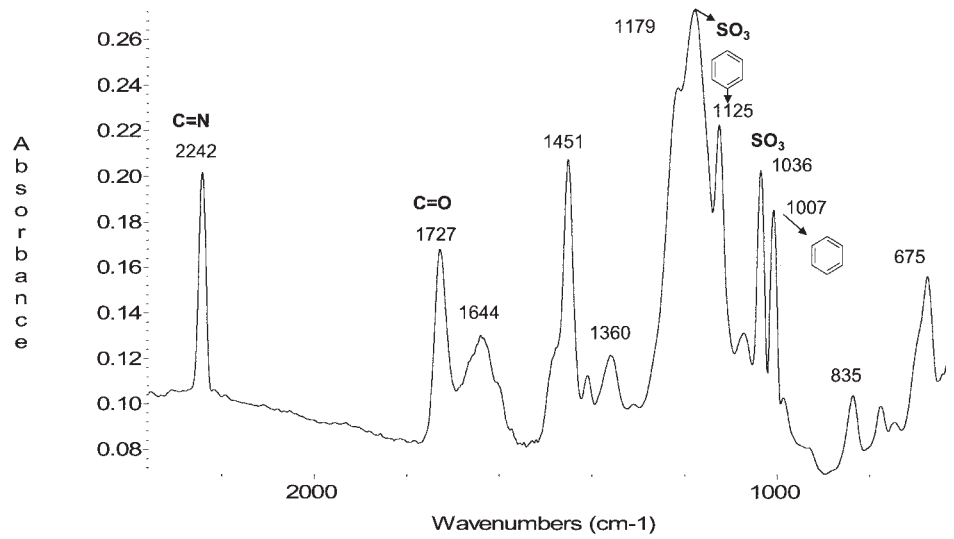


Figure 5 IR spectrum of multilayered PAN-HV2 membrane B (see Table II).

may speculate that the high level of grafting resulted both from surface and inner grafting and that the grafts penetrated inside the membrane and also attached themselves the internal surface of the pores.

Now let us turn our attention to the results of pure water flux measurements (Table I). When the water/ethylene glycol mixture was used as the solvent, there was no significant decrease in flux (from 175 to 150 L/m^2h) despite the almost twofold increase in grafting (membranes designated HV3-HEMA-4 and HV3-HEMA-6). The most significant loss of flux occurred when a crosslinking agent was added to the monomer (HV3-HEMA-10). Nevertheless, when water alone was used as the solvent, a rather high level of modification could be reached without sacrificing membrane permeability. Water flux through a polymeric hydrophilic membrane is thought to depend largely on the ability of water molecules to approach and penetrate into the membrane and hence to form hydrogen bonds with the hydrophilic groups of the polymer. The exceptional performance of the poly-HEMA-grafted membranes in terms of high water flux at a high level of grafting could be possibly explained by the unique ability of poly-HEMA to attract water and keep it in a state that promotes the fast diffusion of water molecules through the polymer backbone. This unique property of poly-HEMA has indeed been described in a number of publications.[19,20] In this context, it is worth remembering that the conformational profile of HEMA chains plays a significant role in maintaining water "pools" inside the polymer backbone.[20]

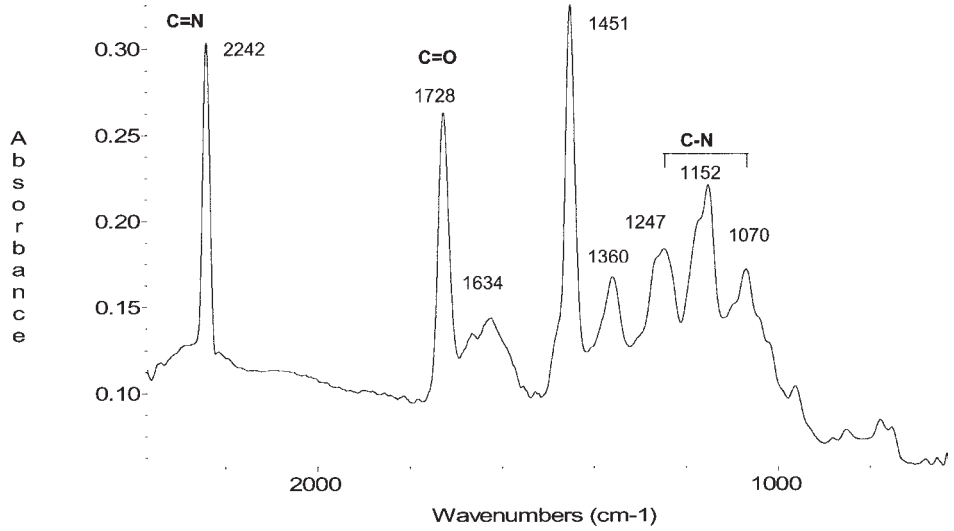


Figure 6 IR spectrum of 2DMAEMA-grafted PAN-HV2 membrane.

TABLE IV
Fluxes of Multilayered Membranes

	First layer			Second layer				Third layer				Fourth layer				Flux[a] after
	Monomer	Concentration (m/L)	Time (min)	Flux (L/m^{2}h)	Monomer	Concentration (m/L)	Time (min)	Flux (L/m^{2}h)	Monomer	Concentration (m/L)	Time (min)	Flux (L/m^{2}h)	Monomer	Concentration (m/L)	Time (min)	Flux (L/m^{2}h)	treatment (L/m^{2}h)
1	MA	1.0	10	215	—				—								270
2	MA	1.0	10		2DMAEMA	1.0	10	18	—								154
3	MA	1.0	10	—	2DMAEMA	1.0	10	—	MA	1.0	10	46					76
4	MA	1.0	10	—	2DMAEMA	1.0	10	—	MA	1.0	10	—	2DMAEMA	1.0	10	15	18
5	2DMAEMA	0.1	10		MA	0.1	20		2DMAEMA	0.1	10		MA	0.1	20	64	88
6	2DMAEMA	1.0	10		MA	1	10		2DMAEMA	1.0	10		MA	1.0	10	8	20
7	2DMAEMA	0.1	10		SSA	0.5	60		2DMAEMA	0.1	10		SSA	0.5	60	6	8
8	2DMAEMA	0.1	10		SSA	0.2	60		2DMAEMA	0.1	10		SSA	0.2	60	41	48

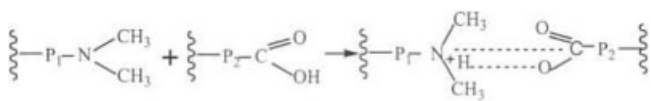
[a] Fluxes were measured after the following treatment (as described in text): 0.001*M* NaOH and 0.001*M* HCl over 24 h for each treatment.

Bilayered membranes

While grafting with nonionic HEMA was used for producing single-layered membranes, covalently bonded multilayered membranes were prepared by sequential grafting of cationic and anionic monomers, i.e., 2DMAEMA and MA or SSA on PAN-HV2. The effect of varying the grafting conditions of 2DMAEMA on the subsequent grafting of MA or SSA is demonstrated in Table II. This table shows that the presence of a polymer with amino groups effectively increased the amount of polyacid grafted subsequently, and the extent of polyacid grafting depended on the amount of poly-2DMAEMA; for instance, grafting of MA (at constant concentration and time) was higher when a higher concentration of 2DMAEMA was used. In the case of SSA grafting, the same relationships were found, but the effect was much more pronounced. These findings are in agreement with the "rules" of surface-initiated grafting of charged monomers, which predict a significant effect of surface charge density on the rate of subsequent polymerization and consequently on the extent of grafting.[39,40] Some of the relevant properties of two representative bilayered membranes, designated A and B, are summarized in Table III. These two membranes were obtained by grafting first 2DMAEMA and then MA or SSA, respectively, onto the PAN membrane. The spectra of membranes A and B are given in Figures 4 and 5, respectively. (Spectral analysis of the grafting of the first monomer, 2DMAEMA, has been reported previously.[31])

For membrane A, the grafting of the poly-MA led to the following changes in the spectrum of PAN-HV2-*g*-2DMAEMA (Figure 6): The band around 1727 cm^{-1} became broader, with a shoulder at 1642 cm^{-1}, and a band of medium intensity appeared at 1557 cm^{-1}. These two changes may be explained by the known effect of acid transfer from an associated to a dissociated form as the polyamine layer begins to approach and exert an influence on the acidic underlayer.[27] Alternatively, the changes may be associated with different vibrational modes of the carboxylate ion:[41] the transition from one mode to another occurs when conditions are favorable for the formation of an acid–base complex. A possible reaction is shown in Scheme 1.

Proton transfer and the formation of the carboxylate ion may be responsible for the carboxylate ion vibration band at 1557 cm^{-1}. The band at 1152 cm^{-1} assigned to NH vibration also developed a new shape due to the contribution of the absorbance at 1171 cm^{-1} related to acid.



Scheme 1

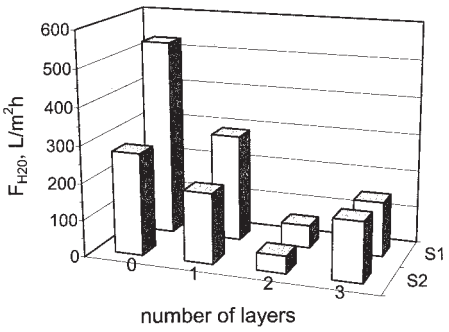


Figure 7 Pure water flux of membranes measured just after synthesis (S1) and after storage in deionized water for 6 months (S2). The PAN-HV2 support corresponds to layer 0; membrane A corresponds to two layers (see Table II).

The prominent features of the spectrum of membrane B (Figure 6) are the extremely intense broad band in the region of 1200 cm^{-1} and the appearance of new sharp bands at 1126, 1035, 1008, and 675 cm^{-1}. The band at 1179 cm^{-1} might be a complex band of symmetric SO_3 and N–C vibrations, the band at 1036 cm^{-1} corresponds to asymmetric SO_3 vibrations, and the two other bands may be attributed to benzene ring absorbance.[36,42] The complete absence of the bands at 987 and 910 cm^{-1}, which are characteristic of C=C vibrations of the vinyl group of SSA,[42] indicates complete grafting of SSA. The extremely high intensities of the bands at 1214 and 1035 cm^{-1} provide evidence for the high degree of grafting. An important feature of the spectrum of this membrane is the marked reduction of intensity of the band at 2242 cm^{-1} (C≡N), in direct contrast to the findings for HEMA grafting.

Multilayered membranes

Three- and four-layered membranes were obtained by further grafting of 2DMAEMA and MA or SSA onto the bilayered membrane. The obtained membranes were characterized in terms of the water flux measured immediately after synthesis and after exposure to NaOH and HCl (Table IV). Water flux was used as the main indicator for characterizing the membranes because the flux is not only the most important membrane performance parameter but it also provides a good picture of the structural aspects of membrane polymer material (hydrophilicity, chain packing, and polyelectrolytes interaction).

The first three membrane samples presented in Table IV underwent an increased level of grafting as the number of layers increased. As a result, the magnitudes of the fluxes measured immediately after synthesis were not constant because the grafted macromolecules were not crosslinked and were therefore able to relax and swell. There was, however, no decline in flux as the level of grafting increased, as would be expected on the assumption of some kind of gradual "closing" of the surface and interior pores following deposition of each layer. After an insignificant decrease in flux (20%) resulting from the grafting of MA, the grafting of the second layer led to a dramatic flux drop from 215 to 18 L/m^{2}h (Table IV, column 5 versus 9). This drop may be explained by the formation of an acid–base complex between the polycation and the polyanion and consequently by the formation of very dense skin that decreased the permeability. (In analogy, the formation of the polyelectrolyte complex in the solution resulted in a drastic increase in solvent viscosity and complex precipitation.) An additional explanation for the dense layer formation may be taken from the modern theory of polyelectrolyte adsorption from solution, which starts from the flattened conformation of the first layer (dense layer) of polyelectrolytes adsorbed on the surface of substrate. As the mass of adsorbed (or grafted) macromolecules grows with concentration or time, the flattened conformation vanishes, and the loops and tails become dominant. Returning to our membranes, we see that, after deposition of the third layer, there was some restoration of flux. A possible, albeit simplified, explanation may be that the segments of polyamine layer became swollen as the new layer of polyacid approached and the effect of the dense skin was thus negated, since swelling caused chain expansion.

Stability of multilayered membranes

The theory of grafted polyelectrolytes predicts a strong dependence of the permeability of membranes modified by grafting on the pH, ionic strength, and solute concentration of the solution being filtered. When pure water was filtered through the membrane,

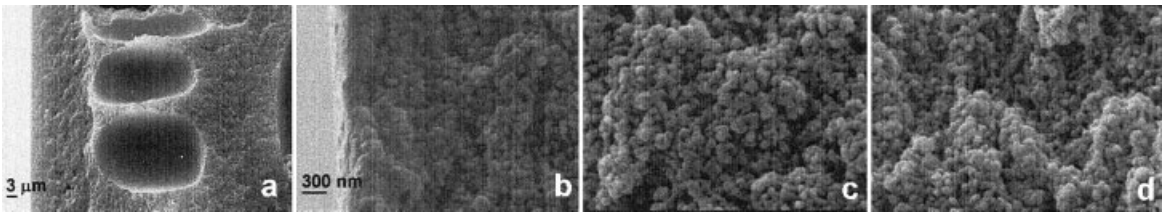


Figure 8 SEM micrographs of cross section of PAN-HV2 unmodified UF membrane.

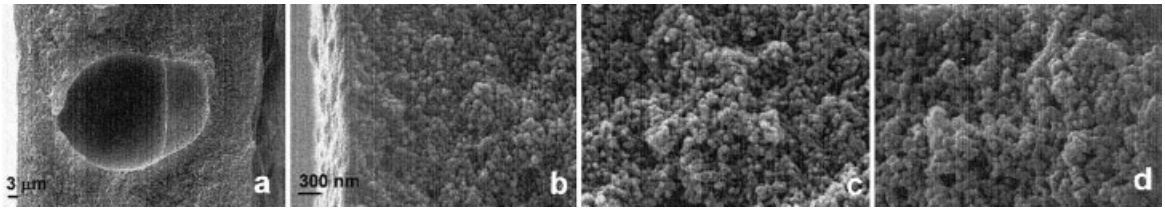


Figure 9 SEM micrographs of cross section of multilayered PAN-HV2 membrane A (see Table II).

the flux could be easily measured. Pure water flux therefore served as a tool for evaluating membrane characteristics. It is well known that the permeability of a membrane modified by grafting is influenced by the hydrophilicity and amounts of the attached grafts and by the order of the macromolecule arrangements.

The above-described relationships between the conditions of modification and membrane performance have been studied by many researchers.[4–6,28,30,31] Much less attention has been paid to the stability—in terms of long-term operation and cleaning—of multilayered membranes, particularly NF membranes comprising multilayered assemblies.[43,44] The use of alkaline and acidic chemicals is unavoidable for membrane cleaning, and therefore stability is a crucial consideration in the actual application of these membranes in water treatment. This problem of membranes having coatings or adsorbed layers has long been recognized in the membrane world.[45,46] From Table IV, it is evident that the fluxes of single and bilayered membranes treated with 0.001*N* NaOH or 0.001*N* HCl increased after the treatment. The greater the number of layers comprising the membranes, the less marked their response to changes in pH: The flux of the four-layered membrane designated N4 changed only insignificantly in response to a pH change. The most stable flux values were obtained for the series of membranes constructed from 2DMAEMA and SSA. It appears that a strong polyanion gives a strong ion-pair interaction, which improves the stability of the membrane. This latter finding is in agreement with pH-independent polyelectrolyte layers with an outer strong polyacid layer.[44] It is also likely that thermal treatment would improve the stability, and such stability studies are currently in progress.

Finally, we determined the fluxes after the above-mentioned membranes had been stored in deionized water for 6 months. The results of this study are shown schematically in Figure 7. Note that the conditions of this "test" are less severe than the previous one, in which acid and alkaline treatments were employed. The most significant drop in flux was obtained for the initial nonmodified membrane, while the modified membranes exhibited smaller losses. The three-layered membranes, in particular, showed no loss of flux. This "stability" may be attributed to the antifouling effect of polyelectrolyte grafting, which is in good agreement with the literature results for deposited polyelectrolyte membranes.[26]

Electron microscope studies

SEM micrographs of cross sections of the nonmodified PAN-HV2 UF membrane are shown in Figure 8. Inspection of the overall cross section [Figure 8(a)] reveals the presence, in the intermediate part of the membrane, of voids whose length is about 40–50% of the membrane thickness. High-magnification micrographs taken in different areas of the membrane cross section (b, upper part, near the selective layer; c, intermediate part; d, lower part, near the nonwoven support) show a structure formed by polymer globules and/or their agglomerates. The globules are more closely packed at the membrane surface [Figure 8(b)], but their size does not differ from area to area of the membrane cross section.

SEM micrographs of the cross section of modified membranes prepared by sequential grafting of oppositely charged monomers 2DMAEMA + MA (membrane A) and 2DMAEMA + SSA (membrane B) on the PAN-HV2 UF membrane are shown in Figures 9 and 10, respectively. It is evident that the grafting did not affect the membrane structure or the size and packing

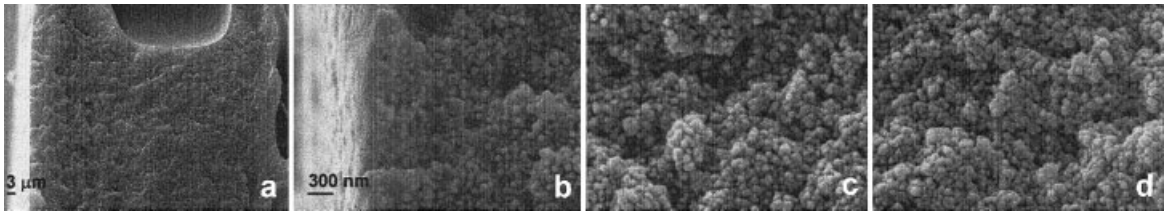


Figure 10 SEM micrographs of cross section of multilayered PAN-HV2 membrane B (see Table II).

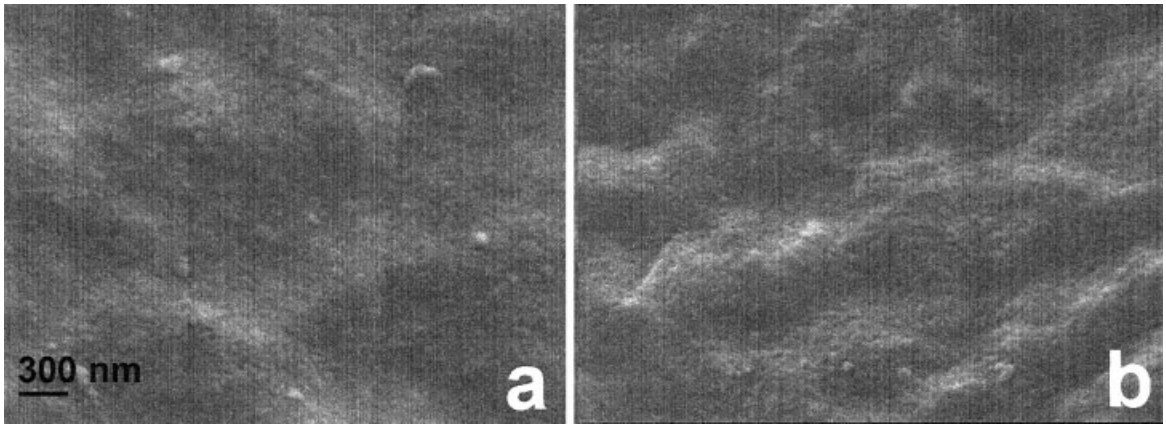


Figure 11 SEM micrographs of surface of multilayered PAN-HV2 membranes (a, membrane A; b, membrane B) (see Table II).

density of the globules and/or their agglomerates. Similarly, there were no changes in the morphology of the selective layer surface, as demonstrated by inspection of the high-magnification SEM micrographs (Figure 11). We may speculate that, since the size of the separate globules was only slightly increased, it is likely that grafted chains simply adopt the dimensions and shapes of already existing globules.

TEM micrographs of the PAN-HV3 UF membrane before [Figure 12(a and c)] and after [Figure 12(b and d)] HEMA modification demonstrated marked differences between the modified and nonmodified membranes: The latter membrane had a clearly heterogeneous morphology with phase-separated domains, whereas there is no such phase separation in the structure of the modified membrane, which has a highly

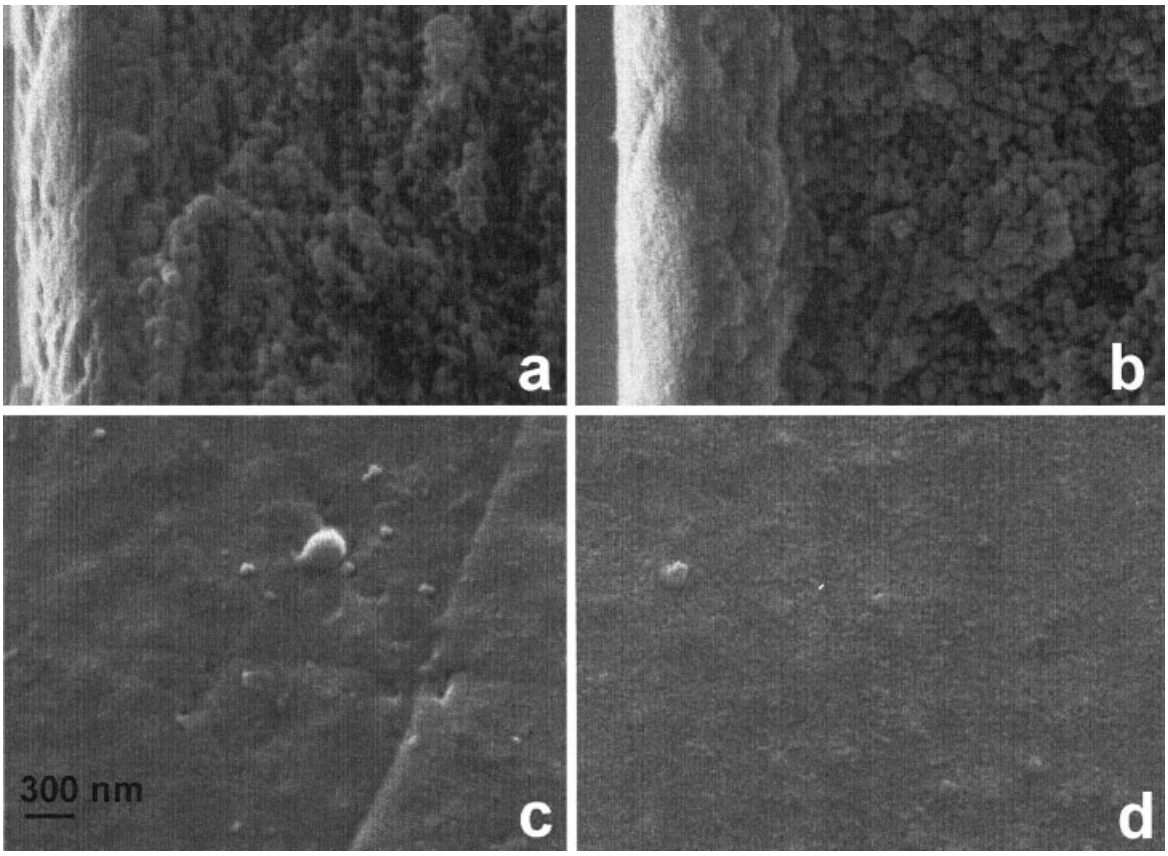


Figure 12 SEM micrographs of cross section and surface of PAN-HV3 unmodified membrane membranes (a and c) and HEMA-grafted PAN-HV3 membrane (b and d).

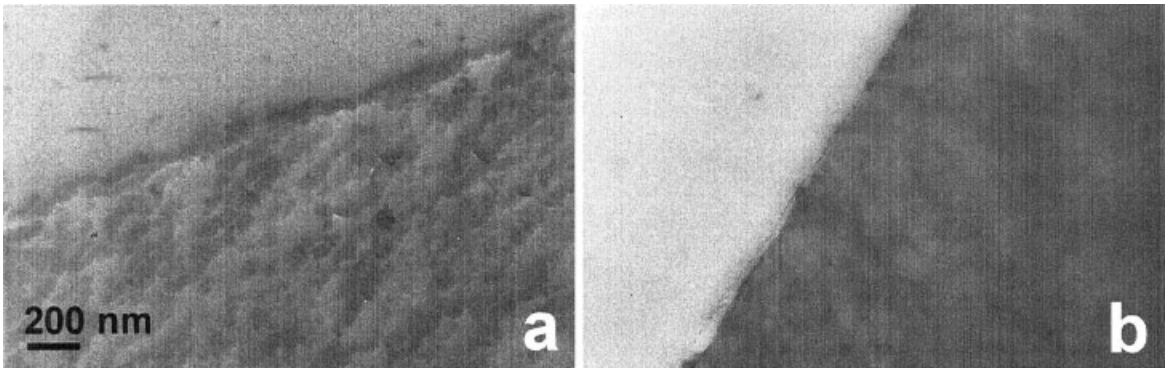


Figure 13 TEM micrographs of cross section PAN-HV3 unmodified membrane membranes (a) and HEMA-grafted PAN HV3 membrane (b).

homogeneous less open structure. The more homogeneous structure of the modified membrane is probably due to the impregnation of the open spaces between the globules by the graft polymer (Figure 13). The absence of outwardly visible changes may interpreted as an absence of regions of high electron density in the modified polymer, and consequently, as a sign of good compatibility between the HEMA grafts and the original membrane. Homogeneous distribution of the grafted polymer may also be manifested as a slight decrease of flux: This specific influence of grafted HEMA on the flux holds true up to a certain degree of grafting, but within these limits it is sufficient to have a very positive effect on the low-fouling behavior of the modified membranes, as has been shown in our patent application.[47] This fouling resistance was also demonstrated in the performance of the modified NF-90 element manufactured by DOW, which is in operation at the waste water treatment plant of Mekorot, Israel.[48]

CONCLUSIONS

In HEMA grafting, varying the composition of the aqueous solution of reagents produces a wide range of values for water fluxes of the grafted membranes. Free-radical grafting produced membranes with covalently bonded layers that exhibited reasonable stability in aqueous solutions of various pH values, unlike membranes made up of deposited polyelectrolytes. Sequential grafting of water-soluble monomers with opposite charges gave stable multilayered membranes. The layered membranes will be suitable for use as NF membranes if the desirable retention of bivalent ions or of low-molecular-weight organic solutes can be accomplished. It should be stressed that manipulation of the conditions of grafting enables control not only of the flux but also of the surface-specific properties of the membrane, such as antifouling properties.

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