Acrylonitrile Copolymers: Synthesis, Characterization, and Formation of Ultrafiltration Membranes

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ABSTRACT: A variety of poly(acrylonitrile-*co*-acrylamide) polymers of different compositions were synthesized by free radical copolymerization. Thin films were cast from polymer solutions, and coagulated into ultrafiltration membranes. The effect of preparative parameters on membrane gel structure was investigated. For nonsupported membranes, concentrated polymer solutions produce fine pore membranes with a lower flux; extending the drying time causes a diminution in membrane thickness, swelling index, and fluxes; the membrane thickness, swelling index, and permeate flux all increased with increasing coagulation bath temperature. For supported membranes, dilute polymer casting solutions, small casting gate opening, and added polyvinylpyrrolidone to the casting solution all increased the permeate flux. The membranes containing acrylamide were more hydrophilic, and had a smaller dispersion force component of the surface free energy than those prepared from the polyacrylonitrile homopolymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1271–1277, 1999

Key words: acrylonitrile copolymer; ultrafiltration; membrane casting; surface characterization

INTRODUCTION

Synthetic ultrafiltration (UF) membranes based upon cellulose acetate and other derivatives were well developed by the mid-1930s. Today, the synthetic membranes' range includes PVDF (polyvinylidine fluoride), PAN (polyacrylonitrile), the nylons and the polysulfones. Despite the many kinds of UF materials available today, the large-scale commercial utilization of UF has been hampered by the costs involved, largely due to the occurrence of membrane fouling, namely the adhesion of dissolved and suspended materials onto the hydrophobic polymer surfaces and the resulting flux decline. This is difficult to reverse except by extensive and often severe cleansing methods that add substantial costs to the process.

Interactions between solute-membrane and solute-solute species can be broadly classified as (1) polar interactions (e.g., H-bonding), (2) interactions due to dispersion forces, and (3) electrostatic interactions. Hydrophilic membrane materials are considered by some to have high surface-free energies, largely due to strong polar interactions; with some hydrophobic materials such as the fluorinated hydrocarbons considered by some to have low surface free energies.[1]

To circumvent membrane fouling problem, we have investigated the use of polymers containing hydrophilic moieties in various forms. By the use of the monomers and the polymers containing the strongly polar amide group of an extremely high

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hydrophilicity UF materials can demonstrate a high degree of nonfouling character.

EXPERIMENTAL

Materials

Acrylonitrile (used after purification by distillation), acrylamide, *N,N*-dimethylformamide (DMF), potassium persulfate, polyvinylpyrrolidone (PVP, MW 55,000), hydroquinone, magnesium chloride, silver nitrate, sodium azide, sodium chloride, potassium hydrogen phosphate, and sodium dihydrogen phosphate were obtained from Aldrich Chemicals. Bovine serum albumin (BSA) and sodium bisulfite were obtained from Sigma Chemicals. Polyacrylonitrile (MW 730,000) was obtained from Monsanto Co. Nonwoven, porous poly(ethylene terephthalate) cloth (Hollytex 3396) was obtained from Eaton-Dikeman Co.

Membrane Preparation

UF and MF membranes are usually prepared by the phase inversion technique,[2,3] where a viscous solution of the membrane polymer is spread out over a glass plate or a sheet of polyester and then coagulated in water.

Synthesis of Polymer

A variety of copolymers based on the different feed compositions of acrylonitrile (AN) and acrylamide (AM) were prepared by free radical polymerization.

The copolymerization of acrylonitrile and acrylamide was carried out in a 5-L three-neck round-bottom flask fitted with a water bath, thermometer, overhead stirrer, gas inlet, and gas outlet. The solution of monomers in water was purged with nitrogen gas for at least 45 min. The initiators were added to the solution at the polymerization temperature (25°C) under a nitrogen atmosphere. Hydroquinone (0.1 g) was added to terminate the polymerization after about 48 h. Magnesium chloride (about 2 wt % of all monomers) was added after the solution was heated to 60°C. The product was filtered and washed with water until the test for chloride with 1 wt % silver nitrate aqueous solution was negative. The product was dried under vacuum to constant weight.

In a typical preparation of poly(acrylonitrile-*co*-acrylamide) (8:2), the polymerization recipe was as follows: 59.7 g of acrylamide; 178.3 g of acrylonitrile; 3600 mL water; 1.422 g of potassium persulfate, and 0.711 g of sodium hydrogen sulfite as initiators.

Characterization of Polymer

Viscosity measurement were made in a thermostatted water bath at 25 ± 0.1°C by means of a Cannon-Ubbelohde viscometer. A copolymer was dissolved in DMF, which had been exhaustively dried. For each polymer, the viscosity of five concentrations was measured; multiple readings were made at each concentration. Intrinsic viscosity was obtained by extrapolation of a plot of specific viscosity/concentration vs. concentration to infinite dilution using linear least squares; such analysis yield regression coefficients ≥0.999. Estimates of the copolymer molecular weight were obtained from the relationship for PAN in DMF at 25°C[4]:

$$[\eta] = 0.0392 M_v^{0.75}$$

where $[\eta]$ is the intrinsic viscosity, and M_V is the viscosity-average molecular weight.

Glass transition temperatures (T_g) of the polymers were determined by using a Du Pont 910 differential scanning calorimeter. The heating rate was 15°C/min for all samples.

Membrane Casting

The membranes described below were prepared using standard casting techniques. Ultrafiltration membranes were prepared from 3 wt % polymer solutions in DMF by casting the solution onto Hollytex, with a 5 mils (127 μm) gate opening on a casting knife, followed by immediate coagulation in 2–5°C water to minimize skin formation. The membranes were rinsed several times in deionized water and kept at 5°C until used.

A series of unsupported membranes was prepared by casting a polymer solution onto glass plates, followed by immediate coagulation in cold water. Membrane thickness was measured with a Peacock dial gauge.

Membrane Characterization

Determination of Swelling Index

The swelling index was determined according the following equation:

Table I   Properties of the Liquids at 20°C (ergs/cm^2)

Liquid	γ_l^d	γ_l^p	γ_{lv}
Water	21.8	51.0	72.8
Formamide	39.5	18.7	58.2

$$Q = \frac{G_1}{G_0}$$

where G_0 is the dry weight of sample and G_1 is the weight of the equilibrium swollen sample with water at room temperature.[5]

Determination of Membrane Flux

The flux of membranes was usually determined in the Amicon stirred cell 8050.[6] An applied pressure (30 psig) of nitrogen in the pure water feed tank enabled us to measure the flux of water. The flux of water through the membrane was calculated according to the following equation:

$$\text{Flux J } (\mu\text{sa}) = \frac{V \times 10^4}{t \times A \times P}$$

where V (cm^3) is the volume of the permeate water received during the time t (seconds). The area A (cm^2) is the effective filtration area and P (atm) is the pressure applied. Here, flux is given as μsa, which is the abbreviation of micron/s-atm.

Surface Characterization

The surface characterization of each polymer could be done using a dried, clean membrane. The intrinsic hydrophilicity of the membrane materials is determined from the advancing contact angles measured by a goniometer[7] (Model 100-00 Rame-Hart, USA).

Prior to the contact angle measurement, the membrane sample was rinsed three times for 10 min in double-distilled water, and the sample was then cleaned with double-distilled water in an ultrasound bath for two periods of 15 min. The angles were evaluated from photographs using video-enhanced image processing. The values of the contact angles are the average of the 10 air bubbles (two angles per bubble), giving a total of 20 angles for each membrane sample.[8]

The polar and dispersion force components of the surface energy were determined from the fol-

lowing equation[9] using the reported parameters in Table I and measured contact angles for water and formamide.

$$1 + \cos\theta = 2(\gamma_s^d)^{0.5}\lfloor(\gamma_l^d)^{0.5}/\gamma_{lv}\rfloor + 2(\gamma_s^p)^{0.5}\lfloor(\gamma_l^p)^{0.5}/\gamma_{lv}\rfloor$$

where θ is the contact angle, γ_{lv} is the surface free energy of the liquid in equilibrium with the vapor of the liquid, γ_s^d and γ_s^p are the dispersion force component and the polar component of the surface free energies of the solid, γ_l^d and γ_l^p are the dispersion force component and the polar component of the surface free energies of the liquid.

The experimental UF setup has been described in detail elsewhere.[10] A short description, nevertheless, follows here. Each experiment was started with measurement of the steady-state pure water flux (J_1) under a pressure of 30 psig at ambient temperature. Then bovine serum albumin (BSA) solution was ultrafiltrated under the same conditions. The BSA concentration was 1 g/L in phosphate buffer [potassium dihydrogen phosphate (0.025 M)–disodium hydrogen phosphate (0.025 M)] adjusted to various pH values. The BSA concentrations were analyzed using a UV-VIS spectrophotometer (model 2300, CARY).[11] The solute rejections were calculated from the measured values of solute concentration in the permeate C_p and solute concentration in the feed C_f ($R = 1 - C_p/C_f$).

After ultrafiltration of BSA solution the membrane was simply rinsed with water and the steady-state pure water flux (J_2) was measured under the same conditions. The ratio $J_1/J_2 \times 100$ (%) was defined as flux recovery.

RESULTS AND DISCUSSION

Intrinsic Viscosity Measurement

Polymer solution viscosity is an important consideration for casting flat-sheet membranes. To some

Table II   Results of Intrinsic Viscosity

Copolymer	AM in Feed (mol %)	Intrinsic Viscosity (dL/g)
A-1	10	2.41
A-2	20	2.73
A-3	30	1.58
A-4	40	1.40
A-5	50	1.91
A-6	60	0.78

Table III   DSC Results

Polymer	AM in Feed (mol %)	Glass Transition Temperature (°C)
PAN	0	96
A-1	10	107
A-2	20	113
A-3	30	116
A-4	40	117
A-5	50	120
A-6	60	132
PAM	100	154

extent, this controls the penetration of the casting solution into the backing material.[12] The intrinsic viscosity data are shown in Table II. Because PAM tends to compact in the poor solvents such as DMF, the viscosities are higher with low percentages of AM and substantially lower as AM substitution increases.

The copolymers high in AN are insoluble in water but swell increasingly as AM content increases. Copolymers containing 40% of AM become partially water soluble and entirely water soluble as the percentage of AM increases further.

Glass Transition Temperature Measurement

The glass transition temperatures also vary with copolymer composition as shown in Table III. Each of these polymers was measured in the dry state by DSC. PAN itself has a relatively low glass transition temperature, but this increases sharply as AM substitution in the copolymer increases. It is presumed that strong internal hydrogen bonding in PAM is responsible for its relatively high glass transition temperature.

Effect of Preparative Parameters on Nonsupported Membrane

Polymer molecules will be more highly aggregated in more concentrated solutions, and a higher degree of intermingling will occur between polymer molecules of adjacent coacervate droplets. Consequently, the walls of the open-cell foam structure will be thicker, with the result that a lesser amount of water will be incorporated in the gel network (Table IV).

Extending the drying time after casting and before aqueous coagulation causes a diminution in membrane thickness, swelling index, and flux (Table V). These effects are attributed to the increased droplet compaction that occurs during extensive desolvation and the resultant decrease in the volume of the unit cells and the amount of capillary water contained therein.

Membrane dimensions, swelling indexes, and permeate fluxes all increase with increasing coagulation bath temperatures (Table VI). These effects are explicable on the basis of coagulation occurring in an early phase of the coacervation process. The rapid depletion of the solvent surrounding the polymer droplets ensures contact between adjacent droplets before much compaction has occurred.

The preceding tables show how polymer concentration, drying time, and coagulation bath temperature influence the properties of a given membrane, in this case PAN. The pore volume in the final coagulated membrane is controlled largely by the concentration of polymer in the casting solution. Concentrated polymers solutions produce fine pore membranes with a lower flux; dilute ones give higher flux due to a larger pore volume. This is as anticipated, and is a general rule for virtually all membranes cast and then

Table IV   Polymer Concentration Effects[a]

Polymer Concentration (wt %)	Wet Thickness (mm $\times 10^2$)	Swelling Index (wet wt/dry wt)	Flux (μsa)[b]		BSA Rejection %[b]
			Water	BSA	
4.1	8.2	7.40	79.4	14.9	14.0
6.0	9.3	6.98	66.7	12.8	81.1
7.7	10.0	6.55	55.3	11.9	83.7
10.0	12.5	6.39	54.8	8.6	94.7

[a] Casting solution composition: PAN in DMF (casting gate opening 10 mils).
Dry time: 1 min.
Coagulation at room temperature.
[b] Flux and BSA rejection were measured at room temperature under 30 psig pressure.

Table V   Drying Time Effects[a]

Drying Time (min)[b]	Wet Thickness (mm × 10²)	Swelling Index (wet wt/dry wt)	Flux (μsa)[c]		BSA Rejection %[c]
			Water	BSA	
1	10.1	6.55	55.3	11.9	41.9
5	9.2	6.08	40.0	8.2	71.4
10	8.5	5.44	39.2	7.2	83.7
30	7.4	5.31	34.6	6.1	87.1

[a] Casting solution composition: 7.7 wt % PAN in DMF (casting gate opening 10 mils).
[b] Dry time = interval between casting and immersion into coagulation bath (room temperature).
[c] Flux and BSA rejection were measured at room temperature under 30 psig pressure.

coagulated in the nonsolvent. Indeed, the best and sometimes the only way to set the pore size or MW cutoff points for a given membrane is to use more concentrated or more dilute polymer casting solution. Of course, this applies only to the use of good solvents wherein the polymer chain is highly extended. Poor polymer solvents, i.e., ones that have low viscosity in the casting solution do not result in satisfactory and uniform membranes.

The thickness of the freshly cast membrane affected the flux, but only to a minor extent, with the flux falling off with increasing membrane thickness, but not linearly. On the other hand, the solid content of the casting solution is much more controlling than the membrane flux. This is observed in Table IV. Both water and BSA fluxes fall off as the percentage of solids in the casting solution increases. With the most concentrated solutions there is much stronger rejection of the solute than with more dilute casting solutions.

Drying the membrane after casting reduces the overall thickness of membrane and pore size, but not very dramatically. For example, the thickness of membrane after some 30 min of drying time is about 75% the thickness of the membrane, coag-

ulated almost immediately after casting. Interesting enough, the flux of water decrease only slightly, and this suggests that the average pore size is not be strongly affected, but because the BSA flux drop is in the same range, there is apparently no change in pore size distribution. Obviously, because BSA rejection increases as the result of more drying, a substantial change in average pore diameter was produced.

It is known that slowing down the coagulation process makes a more uniform pore size distribution. The data of Table VI shows that as the coagulation bath temperature was increased from 3 to 40°C, the rejection of BSA fell substantially, and the flux of water and BSA did not change significantly. We assume the pore diameter is considerably more uniform when using cold water in the coagulation bath.[13]

Effect of Preparative Parameters on Supported Membrane

Almost all data correlate the properties of membranes that are supported with those not supported. Here, the membrane solution is cast onto

Table VI   Coagulation-Bath Temperature Effects[a]

Coagulation-bath Temperature (°C)	Wet Thickness (mm × 10²)	Swelling Index (Wet wt/dry wt)	Flux (μsa)[b]		BSA Rejection %[b]
			Water	BSA	
3	8.4	5.97	53.9	10.7	100
10	8.9	6.09	54.4	10.7	98.5
23	10.1	6.55	55.3	11.9	83.7
40	14.0	6.67	57.5	14.6	83.1

[a] Casting solution composition: 7.7 wt % PAN in DMF (casting gate opening 10 mils).
Drying time: 1 min.
[b] Flux and BSA rejection were measured at room temperature under 30 psig pressure.
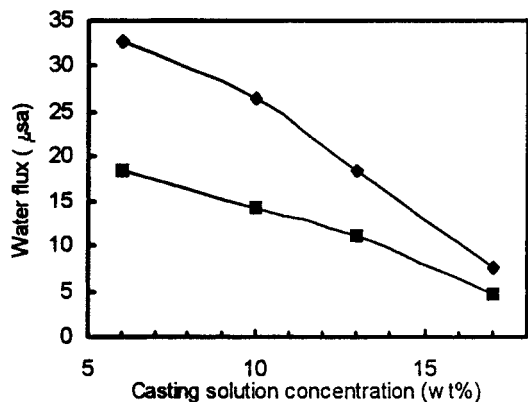
Figure 1 Effect of casting solution concentration on membrane water flux. Casting gate opening = 8 mil. ■: A-1; ◆: A-2.

a nonwoven or woven cloth of polymer such as polyester. Spun-bonded polyester is probably the most common membrane support material. Large-scale membrane manufacture usually requires a continuous casting of a solution film onto nonwoven fabric that acts as a mechanical support.[14] Because the nature of the casting procedure, especially the coagulation procedure, differs for supported or nonsupported membranes, different results are obtained, but the same general trends are observed. For example, Figure 1 shows that the water flux is a function of casting solution concentration for two hydrophilic copolymers, with the upper line representing a membrane with a higher AM content. A substantial change in the water flux is observed as the percent of solid in the casting solution is varied from 6 to 17. The effect of casting gate size upon water flux is also approximately linear, but the difference is not as pronounced as with a change of the percentage of solid (Fig. 2).

Figure 3 shows the effect of added water-soluble PVP to the 8% casting solution of copolymer on membrane water fluxes. Here, the water flux increases strongly by a factor of about 6 when the PVP is added to two different copolymers. The percentage of PVP varied from 0 to 4%. Obviously, PVP functions not only to increase the pore size of finer membranes, but probably also causes a highly pronounced local swelling of the membrane, and its removal from the pores by subsequent elution makes for a major change in the water flux.

Surface Characterization and UF Experiments

As would be expected from the chemical modification, Table VII shows that the polymer/water
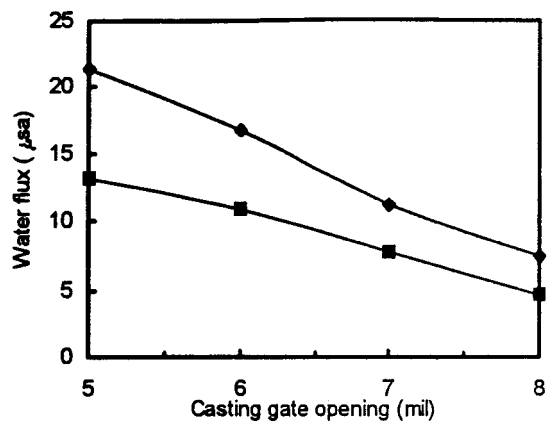
Figure 2 Effect of casting gate opening on membrane water flux. Casting solution concentration = 17% wt. ■: A-1; ◆: A-2.

contact angles decrease with an increasing acrylamide content. The polar component of the surface energy increases with increasing acrylamide content; while the dispersion force component of all acrylamide containing membranes is less than that of the PAN membrane.

Table VII compares the contact angles of four clean membranes with their UF flux recovery. It is noted that the three hydrophilic membranes, A-1, A-2, and A-3, have a better flux recovery than the less hydrophilic PAN membrane.

SUMMARY

A variety of poly(acrylonitrile-*co*-acrylamide) polymers of different composition were synthesized by free radical copolymerization. The intrin-
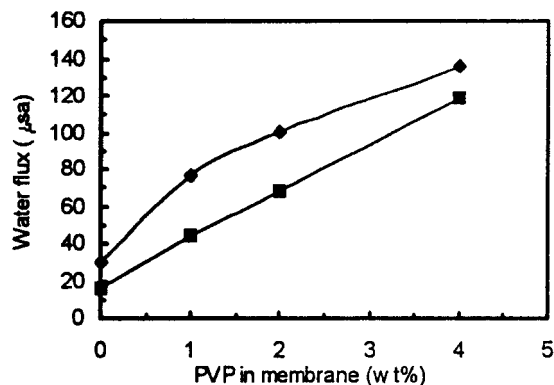
Figure 3 Effect of addition of PVP on membrane water flux. Casting gate opening = 8 mil; casting solution concentration = 8 wt %. ■: A-1; ◆: A-2.

Table VII   Correlation of Contact Angle of Clean UF Membranes with UF Performance

Membrane	AM in Feed (mol %)	Contact Angle (°)		Surface Energy (erg/cm^2)			UF Flux Recovery (%)
		Water	Formamide	γ_s^P	γ_s^d	γ_s	
PAN	0	72	47	8	34	42	44
A-1	10	68	44	11	33	44	81
A-2	20	61	37	15	32	47	94
A-3	30	54	35	22	27	49	100

sic viscosities in DMF were higher with low percentages of AM and substantially lower as AM substitution increased. The glass transition temperature increased sharply as AM substitution in the copolymer increased.

The effect of preparative parameters on membrane gel structure was investigated. For nonsupported membranes, concentrated polymer solutions produce fine pore membranes with a lower flux; extending the drying time causes a diminution in membrane thickness, swelling index, and fluxes; the membrane thickness, swelling index, and permeate flux all increased with increasing coagulation bath temperature. For supported membranes, dilute polymer casting solutions, small casting-gate opening, and added PVP to the casting solution all increased the permeate flux.

Contact angle measurements on dry samples were used to determine relative hydrophilicities of membranes. Due to heterogeneity of technical surfaces a larger number of readings were averaged resulting in smaller uncertainties. In comparison with PAN, the AM containing copolymers yield membranes with higher polarity/hydrophilicity and smaller dispersive surface energy.

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