

# Evaluation of the Possibility of Utilization of Poly(amidesulfonamide)s (PASAs) in Ultrafiltration Technology

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**ABSTRACT:** Ultrafiltration (UF) membranes of six selected poly(amidesulfonamide)s (PASAs) were prepared and studied. The pure water flux and the retention of albumin (bovine serum) were used to evaluate the quality of the UF performance of the fabricated membrane. Membranes with good mechanical strength were obtained by using the phase inversion method. A comparison of the UF performance of the PASA membranes fabricated from a casting solution containing 12% w/w PASAs and 4% w/w lithium bromide in dimethylacetamide was made. The best retention of albumin (bovine serum) by membranes prepared under the conditions studied from the selected homopolymers of PASAs, and their corresponding pure water flux at 0.207 MPa, ranged from 84.6 to 100% and 120 to 396 L m<sup>-2</sup> h<sup>-1</sup>, respectively. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2087–2093, 1998

**Key words:** poly(amidesulfonamide)s; UF membranes; retention of BSA; lithium bromide as additives; overall mean pore size

## INTRODUCTION

Applications of ultrafiltration (UF) at both laboratory and industrial scale have grown substantially since they were first used.<sup>1</sup> In addition to microfiltration and reverse osmosis technology, UF is a promising technology for industrial pollution abatement<sup>2</sup> and may reduce production cost by recovery of some useful materials from waste water of various industrial processes.<sup>3</sup> Moreover, UF technology is often used in food industry processes.<sup>4</sup> Historically, cellulose acetate (CA) was the major material for preparing separation membranes. Now, many synthetic materials, such as polypropylene, polyethylene, polysulfone, polyvinylalcohol, and polyacrylonitrile, have been used

widely for preparing UF membranes to overcome some weaknesses of the CA membrane, which is biodegradable, susceptible to compaction and flux loss, and hydrolyzable by strong acid, base, and other chemicals. Since 1988, our research group has been committed to developing new synthetic materials for the preparation of separation membranes, and recently, a series of new polymeric materials, poly(amidesulfonamide)s (PASAs), was successfully synthesized in our laboratory.<sup>5–8</sup> PASAs with film-forming viscosities exhibit strong mechanical strength, high hydrophilicity, outstanding thermal stability, and excellent chemical resistance to dilute solutions of hydrochloric acid, sodium hydroxide, and oxidizing agents.<sup>6</sup> Most of these PASAs were found to be good materials for fabrication of tough membranes by using the phase inversion method. Moreover, some of the PASAs membranes gave reasonable flux and over 90% salt rejection in the reverse osmosis process.<sup>9</sup> Preliminary results in the pervaporation process were also encouraging.<sup>10</sup> To fully utilize these polymeric materials, we would

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**Table I The Effect of the Content of PASA Polymer (A<sub>1</sub>) Used in the Casting Solution on Their Membrane Characteristics**

Composition of Casting Solution (%)			Evaporation Time (s)	Membrane Thickness (μm)	Flux at 0.207 MPa (L m <sup>-2</sup> h <sup>-1</sup> )	Retention of BSA (%)	Percent Porosity (%)	<i>d<sub>m</sub></i> <sup>a</sup> (μm)
Polymer A <sub>1</sub>	LiBr	DMAC						
8.0 <sup>b</sup>	4.0	88.0	30	—	1544.6	11.75; 11.57	—	—
			5	—	932.3	7.93; 7.84	—	—
10.0 <sup>b</sup>	4.0	86.0	5	—	1235.7	19.49; 19.06	—	—
			12.0	4.0	84.0	60	87	104.6
12.0	4.0	84.0	45	92	129.5	85.88	60.11	1.80
			30	90	229.0	97.60	69.30	2.21
			0	112	238.2	97.20	68.60	2.60
			14.0	4.0	82.0	45	100	100.6
14.0	4.0	82.0	30	83	76.3	100.0; 100.0	69.82	1.22
			15	95	93.1	97.6; 98.0	70.50	1.46
			16.0	4.0	80.0	45	89	56.4
16.0	4.0	80.0	30	102	67.7	99.32	73.90	1.24
			15	85	72.2	98.81	70.67	1.20

The relative humidity and air temperature during solvent evaporations were 70% and 20.5°C, respectively.

<sup>a</sup> Mean value calculated from the pure water flux obtained at 0.207 and 0.250 MPa.

<sup>b</sup> Incomplete data obtained for the membranes fabricated from casting solution containing polymer content 10% or less due to membrane broken.

8–16% w/w of the chosen polymer and 4% w/w of LiBr in DMAc solution with the evaporation time ranging from 5 to 60 s at room temperature. A second series of PASA membranes were fabricated from a casting solution containing 3.0 to 7.2% w/w of LiBr and 12% w/w of polymer A<sub>1</sub> or B<sub>2</sub> with the evaporation time of 0, 30, or 45 s at room temperature. The gelating medium was D.I. water and the gelating period was 24 h at room temperature.

After a steady permeate rate of water at 0.300 MPa was observed, the pure water flux at 0.207 MPa, the overall mean pore size (*d<sub>m</sub>*) and also the retention of the serum albumin (bovine) (BSA) in 0.1% w/w solution for each of the studied membranes were then measured.

### Membrane Characterization

The pure water flux at a particular pressure was calculated by using the equation<sup>11</sup> given below.

$$J = Q / A \Delta t$$

where *J* is the pure water flux, L m<sup>-2</sup> h<sup>-1</sup>; *Q* is the permeate amount, L; *t* is the sampling time, h; and *A* is the effective area of membrane, m<sup>2</sup>.

The retention ability or the rejection coefficient (*σ*) was obtained by measuring the initial concen-

tration of bovine serum albumin in the ultrafiltration cell and the BSA concentration in the filtrate after 25 mL of the collection. The rejection coefficient was calculated by using the equation<sup>11</sup> given below.

$$\sigma = 1 - \frac{C_f}{C_o}$$

where *C<sub>o</sub>* is the initial concentration of the solute and *C<sub>f</sub>* is the solute concentration in the filtrate.

The pure water flux of each studied membrane, measured at 0.207 and 0.250 MPa, was used to determine the overall mean pore size by the water flux method. By assuming an uniform pore size and a laminar flow through these pores, the overall mean pore size (*d<sub>m</sub>*) of the studied membrane was calculated by using the Hagen–Poiseuille equation<sup>12</sup> as shown below.

$$d_m = 2[(8\eta J l / Pr \Delta p) 1/2]$$

where *J* is the pure water flux, L m<sup>-2</sup> h<sup>-1</sup>; *l* is the thickness of the membrane, m; *η* is the viscosity of water at room temperature, 0.8937; *Pr* is the percent porosity of the membrane or [(the weight of the wet membrane – the weight of the dry membrane)/density of water]/the volume of the

**Table II The Effect of the Content of PASA Polymer (B<sub>2</sub>) Used in the Casting Solution on Their Membrane Characteristics**

Composition of Casting Solution (%)			Evaporation Time (s)	Membrane Thickness ( $\mu\text{m}$ )	Flux at 0.207 MPa ( $\text{L m}^{-2} \text{h}^{-1}$ )	Retention of BSA (%)	Percent Porosity (%)	$d_m^a$ ( $\mu\text{m}$ )
Polymer B <sub>2</sub>	LiBr	DMAC						
8.0 <sup>b</sup>	4.0	88.0	30	64	1162.1	15.36; 15.00	—	—
			5		3931.7	11.97; 11.46	45.45	10.11
10.0 <sup>b</sup>	4.0	86.0	30	100	378.9	55.69	—	—
			5		1920.3	40.17; 30.57	72.95	6.61
12.0	4.0	84.0	60	85	172.2 <sup>c</sup>	82.20; 81.72	83.09	1.53
			45	105	191.4 <sup>c</sup>	99.50; 99.70	73.03	1.91
			30	94	525.2	98.59; 98.58	64.08	1.52
			15	79	879.5	95.99; 94.87	74.63	3.16
14.0	4.0	82.0	5	53	1909.0	70.00; 65.80	—	—
			45	101	141.6 <sup>c</sup>	98.20	68.45	1.67
			30	105	198.4 <sup>c</sup>	99.89	67.16	2.03
			15	84	134.7 <sup>c</sup>	97.80	69.54	1.47
16.0	4.0	80.0	45	97	122.0	99.50	71.16	1.49
			30	105	126.2	100.00	62.84	1.67
			15	110	67.8	93.10	76.66	1.14

The relative humidity and air temperature during solvent evaporation were 70 to 74% and 20.5 and 22.5°C, respectively.

<sup>a</sup> Values calculated from the pure water flux measured at 0.250 MPa.

<sup>b</sup> Incomplete data obtained for the membranes fabricated from casting solution containing polymer content 10% or less due to membrane being broken.

<sup>c</sup> Permeate rate at 0.250 MPa.

membrane; and  $\Delta p$  is the loaded pressure on the membrane, MPa.

The thickness of each of the studied membranes was measured by using a 25-mm micrometer (Mitutoyo) graduated in 0.01 mm divisions.

The morphology of some selected PASA-UF membranes was observed by using the JOEL scanning electron microscope (SEM).

#### UF Performance of Membranes Fabricated from Different PASAs

A comparison of the UF performance of each fabricated membrane of all selected polymers, namely A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub>, C<sub>1</sub>, and C<sub>2</sub> was studied. The composition of the casting solution was 12.0% w/w of the chosen polymer with 4.0% w/w of lithium bromide as the pore-forming agent dissolved in DMAC. The pure water flux, the overall mean pore size, and the retention of the BSA in 0.1% solution were studied for each prepared UF membrane.

## RESULTS AND DISCUSSION

The data given in Tables I and II report the water flux ( $\text{L m}^{-2} \text{h}^{-1}$ ), the molecular weight cutoff (%),

the percent porosity (%), and the overall mean pore size ( $\mu\text{m}$ ) of the PASA membranes fabricated from casting solutions with various contents of polymers, A<sub>1</sub> and B<sub>2</sub>, respectively. The UF performance and also the toughness of the membranes, fabricated from the casting solution with polymer A<sub>1</sub> and B<sub>2</sub> content of 12% w/w or more, were found to be satisfactory. In addition, the permeate rate and retention ability of the membranes fabricated from the same casting solution were greatly affected by the evaporation time and also other operational conditions, such as the relative humidity and the cleanliness of the glass plate and rod used for spreading the casting solution and the operation skill of an individual. The permeate rates and retention abilities of the studied membranes were not significantly related to their thickness. Tables III and IV show the characteristics of the membranes fabricated from casting solutions with various PASA-polymer-to-lithium bromide ratio for A<sub>1</sub> and B<sub>2</sub>, respectively. Excellent pure water fluxes (ranging from  $\sim 230$  to  $350 \text{ L m}^{-2} \text{h}^{-1}$ ) and high molecular weight cutoff ( $>90\%$ ) were observed at least once for the PASAs membranes fabricated from each studied composition of the casting solution. Again, the permeate rates of the studied membranes were mainly af-

**Table III The Characteristics of the Membranes Fabricated from Casting Solutions with Various PASA-Polymer (A<sub>1</sub>)-to-LiBr Ratios**

Polymer-to-LiBr Ratio	Evaporation Time (s)	Membrane Thickness ( $\mu\text{m}$ )	Flux at 0.207 MPa ( $\text{L m}^{-2} \text{h}^{-1}$ )	Retention of BSA (%)	Percent Porosity (%)	$d_m^a$ ( $\mu\text{m}$ )
12.0 : 3.0	0	85	372.0	80.32	55.70	3.11
	30	100	301.8	95.43	71.40	2.71
	45	70	356.9	95.85	58.80	2.72
12.0 : 3.5	0	103	304.8	90.89; 87.86	72.80	2.67
	30	75	315.0	98.71; 100.00	65.70 <sup>b</sup>	2.47
	45	50	352.4	54.80 <sup>c</sup>	81.90	1.86
12.0 : 4.0	0	112	238.2	97.12	68.60	2.60
	30	90	229.0	97.60	69.30	2.21
	45	105	342.8	69.00	74.80	2.85
12.0 : 7.2	0	92	247.2	79.06	84.06	2.23
	30	113	313.6	98.16	79.31	2.79
	45	90	278.3	100.00	79.10	2.27

The relative humidity and air temperature during solvent evaporation were 67% and 20.2°C, respectively.

<sup>a</sup> Mean value calculated from the pure water flux measured at 0.207 and 0.250 MPa.

<sup>b</sup> Micrographs of this membrane are given in Figures 1–3.

<sup>c</sup> Measured at nonsteady flux.

fectured by the evaporation time. A suitable composition of the casting solution contains 3–7% lithium bromide and 12% of the studied polymer. The characteristics of UF membranes fabricated from different homopolymers of PASAs are given in Table V. The rejection coefficients of albumin (bovine serum) of all studied membranes of PASAs homopolymers, except polymer C<sub>1</sub>, were found to be very good (>0.90) if fabricated under suitable conditions. In general, a high water flux was ob-

served for most of the prepared PASA membranes. The permeate rates of the studied PASA membrane are much higher than those of the PS membrane (Dalian),  $\sim 100 \text{ L m}^{-2} \text{h}^{-1}$  at 0.207 MPa. The percent porosities and the overall mean pore size of the PASA membranes prepared under the conditions studied were found to range from 18.2 to 84.1% and 1.09 to 3.63  $\mu\text{m}$ , respectively. The percent porosities, found in 51 out of 63 of the studied PASA membranes, were higher than

**Table IV The Characteristics of the Membranes Fabricated from Casting Solutions with Various PASA-Polymer (B<sub>2</sub>)-to-LiBr Ratios**

Polymer-to-LiBr Ratio	Evaporation Time (s)	Membrane Thickness ( $\mu\text{m}$ )	Flux at 0.207 MPa ( $\text{L m}^{-2} \text{h}^{-1}$ )	Retention of BSA (%)	Percent Porosity (%)	$d_m^a$ ( $\mu\text{m}$ )
12.0 : 3.0	0	65	273.0	99.50	73.1	2.03
	30	78	353.5	99.65	66.1	2.67
12.0 : 3.5	0	68	175.3	99.80	58.3	3.63
	30	60	237.7	95.30	18.2	3.65
	45	62	242.9	99.50	45.9	2.31
12.0 : 4.0	0	80	265.0	94.99	48.1	2.41
	30	75	141.5	96.30	35.5	2.22
	45	72	175.2	99.60	28.2	2.15
12.0 : 7.2	0	115	227.9	99.21	68.39	1.93
	30	140	196.4	99.84	70.15	2.61
	45	144	118.2	100.00	63.09	2.87

The relative humidity and the air temperature during solvent evaporation were 58% and 20.5°C, respectively.

<sup>a</sup> Mean value calculated from the pure water flux measured at 0.207 and 0.250 MPa.

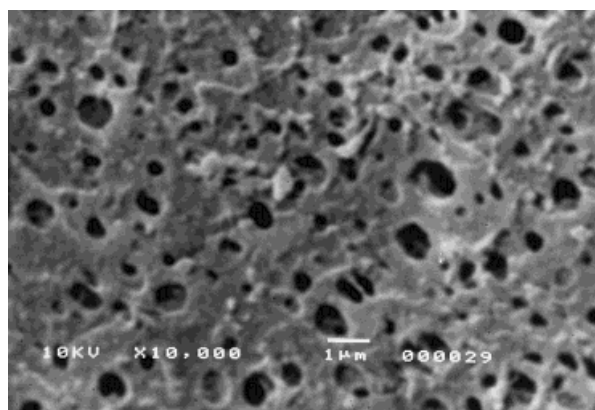
**Table V** The Characteristics of the Membranes Fabricated from the Casting Solution Consisting 12.0% of Six Studied PASA Polymers and 4.0% of LiBr as the Pore-Forming Agent

Polymer Used	$[\eta]$ (dL g <sup>-1</sup> )	Evaporation Time (s)	Membrane Thickness ( $\mu\text{m}$ )	Flux at 0.207 MPa (L m <sup>-2</sup> h <sup>-1</sup> )	Retention of BSA (%)	Percent Porosity (%)	$d_m^a$ ( $\mu\text{m}$ )	RH/Air Temp. (%/°C)
A <sub>1</sub>	1.17	0	112	238.20	97.12	68.60	2.60	67/20.2
		30	90	229.00	97.60	69.30	2.21	
		45	105	342.80	69.00	74.80	2.85	
A <sub>2</sub>	0.98	0	100	286.70	92.37	56.42	2.96	42/20.0
		30	75	396.30	97.97	65.69	2.76	
		45	89	320.30	90.03	70.99	2.61	
B <sub>1</sub>	0.79	0	142	22.10	96.09	65.73	0.91	42/20.0
		30	69	222.10	99.51	66.19	1.93	
		45	126	157.20	98.00	64.40	2.53	
B <sub>2</sub>	0.78	0	85	168.50	99.14	67.30	1.09	58/20.5
		30	75	141.50	96.30	35.50	2.22	
		45	72	374.80	100.00	45.60	1.87	
C <sub>1</sub>	1.18	0	61	170.50	16.40	81.35	1.47	68/20.5
		30	70	162.00	64.15	74.99	1.62	
		45	68	130.60	84.63	71.11	1.47	
C <sub>2</sub>	1.82	0	92	130.20	67.82	78.15	1.63	68/20.5
		30	74	147.30	72.20	78.04	1.55	
		45	93	120.80	94.83	74.04	1.62	

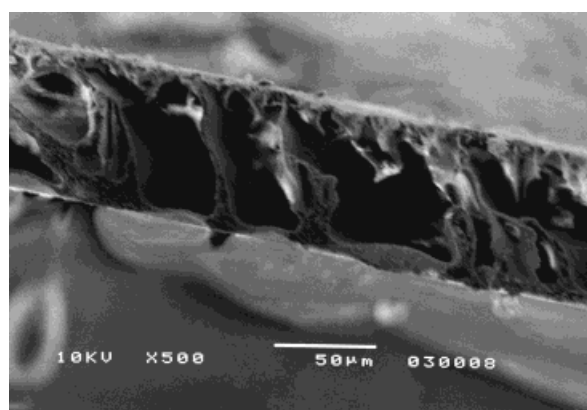
<sup>a</sup> Mean value calculated from the pure water flux measured at 0.207 and 0.250 MPa.

60%. The mixed relationship between the water flux and the percent porosity or the overall mean pore size of the prepared PASA membrane was found. The electron micrographs of UF membrane of polymer A<sub>1</sub> of PASAs are shown in Figures 1, 2, and 3. From Figures 2 and 3 high density of pores and large finger pores were observed in the lower surface and the support layer of the UF membrane fabricated from polymer A<sub>1</sub>, respectively. A comparison of the UF performance of two

selected PASA-UF membranes with some common commercial UF membranes is given in Table VI. In conclusion, the results of this study show that most of the PASA polymers have the potential to be used to prepare good-quality UF membranes. We believe that PASA-UF membranes with excellent flux and MWCO might be obtained if fabricated under optimized condition(s). Additional research work on the UF application of



**Figure 2** Electron micrograph of the lower surface ( $\times 6300$ ) of the UF membrane fabricated from polymer A<sub>1</sub> of PASAs.



**Figure 3** Electron micrographs of the cross section ( $\times 315$ ) of the UF membranes fabricated from polymer A<sub>1</sub> of PASAs.

**Table VI A Comparison of the UF Performance of Two Selected PASA Membranes with Some Common Commercially Available Membranes**

Membrane Material <sup>a</sup> (Commercial Name)	Manufacturer	Flux (L m <sup>-2</sup> h <sup>-1</sup> )	MWCO
Cellulose acetate (CA 500)	DDS	350 (at 0.5 MPa and 20°C)	65 K (>90%) <sup>b</sup>
Polysulfone (PS-60P)	DDS	200 (at 0.5 MPa and 20°C)	30 K (>90%) <sup>b</sup>
Polyethersulfone (UF-PES-50/PP-100)	NADIR	150–250 (at 0.3 MPa and 20°C)	50 K (75%) <sup>b</sup>
PASA-polymer A <sub>1</sub>	Our laboratory	238–357 (at 0.207 MPa and 20°C)	66 K (95.0 to 100%) <sup>c</sup>
PASA-polymer B <sub>2</sub>	Our laboratory	227–273 (at 0.207 MPa and 20°C)	66 K (95.0 to 99.8%) <sup>d</sup>

<sup>a</sup> Flat-sheet membranes were used.

<sup>b</sup> Taken from ref. 12, pp. 411–414.

<sup>c</sup> Data of the best UF performances of some A<sub>1</sub>-UF membranes fabricated under the studied condition in Table III.

<sup>d</sup> Data of the best UF performance of some B<sub>2</sub>-UF membranes fabricated under the studied condition in Table IV.

PASA polymers will be worth investigation in the future.

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