

Reverse osmosis performance of homopolymers and copolymers of poly(amide-sulfonamide)s

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Ten homopolymers and 15 copolymers of poly(amide-sulfonamide)s were synthesized by low-temperature solution polycondensation of five different diamines with isophthaloyl chloride/terephthaloyl chloride in *N,N*-dimethylacetamide. The general reverse osmosis (RO) performance of these new membrane materials were investigated by a systematic screening test with 270 ppm nickel ion industrial waste as the feed solution. A copolymer series based on 2,5-dimethylpiperazine, 1,3-diaminopropane and terephthaloyl chloride emerged as the best polymer system in terms of RO separation characteristics. Optimization of membrane fabrication of one of this series, with a 7:3 ratio of the two diamines was carried out by fixing the evaporation temperature at 65°C and varying the evaporation time and casting solution composition. The RO tests for the membrane were performed at 20 kg cm⁻² operating pressure on three different feed solutions. Membranes showed salt rejection of up to 98.6 and 94.3% at a flux of 13 cm per day for nickel and sodium ion feeds, respectively. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Membrane technology represents one of the most effective and energy saving means amenable to a wide range of separation processes, including reverse osmosis (RO) and pervaporation¹. Because of the unique industrial application value of membranes, the U.S. Department of Energy identified 'reverse osmosis oxidation-resistant membrane' and 'pervaporation membranes for organic-organic separations' as two of the highest-ranking research priorities². As a result, the demand to develop new durable and high performance membrane materials has become a challenge to many synthetic polymer chemists. For the past few years, in searching for new materials for membrane applications, we have engaged in the design and synthesis of poly(amide sulfonamide)s (PASAs). Up to date, PASAs is a new class of polymer which has not been studied extensively³. Based on the synthetic diamino monomers 1A–E (Figure 1) and phthaloyl dichlorides, several series of homopolymers and copolymers of PASAs have been synthesized in our laboratory^{4,5} (Table 1). Most of them possessing high intrinsic viscosity have been proven to be viable materials for membrane applications. In addition, membranes prepared from PASAs also demonstrated chemical resistance to strong acid, alkali and oxidizing agent⁶. We envisage that PASAs have the potential to be developed as viable RO membrane materials for treating

industrial wastewaters. On the other hand, owing to their insolubilities in many common organic solvents, we anticipate that PASAs can also be developed as pervaporation membranes for organic-organic separations. Encouraged by our recent findings on the membrane properties of the newly developed polymers, we have continued our effort on the characterization of new PASA series with a long term goal to establish a polymer system with ideal membrane performance in RO and/or in the pervaporation process.

In this communication, we report the RO performance of several selected PASAs synthesized in our laboratory. Optimization in membrane fabrication was carried out by changing the fabrication parameters. Correlation between the structures and RO properties of the polymers has been investigated.

EXPERIMENTAL

Materials

Solvents and common reagents such as chloroform (Ajax), diethylether (Ajax), ethanol (BDH), methanol (BDH), methylene chloride (Ajax), petroleum ether (Ajax), acetanilide (Fluka), chlorosulfonic acid (Fluka), 2,5-dimethylpiperazine (Redel-de Haën), hydrochloric acid (China National Chemicals), piperazine (Aldrich), pyridine (Fluka), were of analytical grade and were used as received. Dimethylacetamide (DMAc) (Redel-de Haën) was dried by molecular sieve 4 Å (Merck) and phthaloyl chlorides (Fluka) were purified by vacuum distillation before use.

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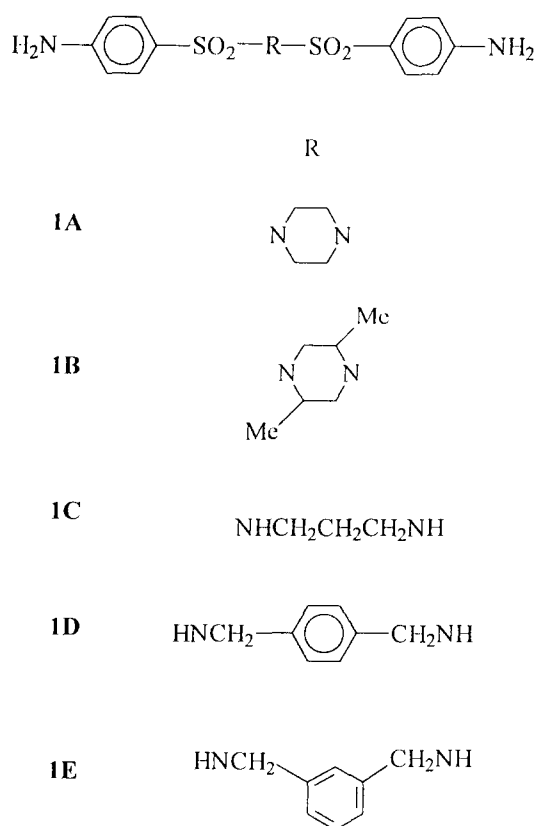


Figure 1 Structures of diamino monomers

Apparatus

Metal ion determinations were performed with a Varian Spectra AA-20 atomic absorption spectrometer (AAS). The intrinsic viscosities were measured at a concentration of 0.5 g dl^{-1} in DMAc at $25 \pm 0.05^\circ\text{C}$ in a Ubbelohde viscometer, using the following equation⁵:

$$[\eta]_{\text{intrinsic}} = \frac{1}{C} \sqrt{2(\eta_{\text{sp}} - \ln \eta_r)}$$

A homemade RO testing unit described elsewhere⁶ was used to evaluate the RO performance of new membranes.

Methods

Polymer synthesis. The polymers were synthesized from the diamino monomers and phthaloyl chlorides by low-temperature polycondensation as described elsewhere⁴. To ensure the quality of the products, phthaloyl chlorides were purified by vacuum distillation prior to polymerization.

Asymmetric membrane casting and membrane RO performance evaluation. Flat sheet asymmetric RO membranes of different compositions were prepared by the solution casting technique⁶. Most of the PASAs were soluble in polar aprotic solvents, DMAc was used for the preparation of casting solutions. Because the intrinsic viscosity of the polymers ranged from 0.33 to 1.11, casting solutions of different composition were formulated for membrane fabrication. The three casting solution systems containing 12.5, 15 and 17.5% of polymer, and

Table 1 Composition of PASA homopolymers and copolymers

	Diamino monomer(s) (ratio)	Phthaloyl chloride ^a	Polymer
Homopolymer	1A	a	AT
	1A	b	AI
	1B	a	BT
	1B	b	BI
	1C	a	CT
	1C	b	CI
	1D	a	DT
	1D	b	DI
	1E	a	ET
	1E	b	EI
Copolymer	1B : 1C (9 : 1)	a	BCT-91
	1B : 1C (8 : 2)	a	BCT-82
	1B : 1C (7 : 3)	a	BCT-73
	1B : 1C (6 : 4)	a	BCT-64
	1B : 1C (5 : 5)	a	BCT-55
	1B : 1C (9 : 1)	b	BCI-91
	1B : 1C (8 : 2)	b	BCI-82
	1B : 1C (7 : 3)	b	BCI-73
	1B : 1C (6 : 4)	b	BCI-64
	1B : 1C (5 : 5)	b	BCI-55
	1A : 1C (9 : 1)	b	ACI-91
	1A : 1C (8 : 2)	b	ACI-82
	1A : 1C (7 : 3)	b	ACI-73
	1A : 1C (6 : 4)	b	ACI-64
	1A : 1C (5 : 5)	b	ACI-55

^a a, terephthaloyl chloride; b, isophthaloyl chloride

3.0, 3.5 and 4.0% of pore-forming agent, respectively (Table 2). For polymers with high intrinsic viscosities, it is envisaged that tough RO membrane can be formed from lower polymer concentration of casting solution. For those with lower intrinsic viscosities, higher polymer concentration of casting solution was required for membrane fabrication. Initially, all membranes were fabricated at a temperature of 65°C for an evaporation time of 7 min. Membranes were formed under phase inversion conditions by immersing the polymer film fixed on a glass plate in a cold water bath for several hours before use. The membranes were evaluated with our homemade RO testing unit equipped with a centrifugal pump (Tonkaflo)⁶. In the screen studies, most of the water permeability and salt rejection tests were performed at room temperature for a 270 ppm aqueous nickel rinsing solution obtained from a local electroplating factory. In all RO test experiments, the effective membrane area was kept at 12.56 cm^2 . The operating pressure was maintained constant at 20 kg cm^{-2} . The permeate was collected and measured in ml. The concentration of nickel (II) in the feed and in the permeate were determined by an atomic absorption spectrometer. Permeate fluxes were recorded in metres per day and salt rejections were recorded as per cent salt rejection.

Table 2 Composition of casting solutions on the screening studies

Casting solution	Polymer (%)	Pore-forming agent LiNO ₃ (%)	DMAc (%)
System 1	12.5	3.0	84.5
System 2	15.0	3.5	81.5
System 3	17.5	4.0	78.5

RESULTS AND DISCUSSION

Polymer preparation

By using the new diamino monomers **1A–E** synthesized in our laboratory and phthaloyl chlorides, both homopolymers and copolymers of PASAs were obtained under the low temperature polycondensation conditions. The chemical and physical characterization of these polymers were reported elsewhere^{4,5}. The composition of the polymers are shown in *Table 1*. After adequate purification of the diamino monomers by reprecipitation and phthaloyl chlorides by vacuum distillation, successful polymerization reaction could be carried out in 10 g scale to provide sufficient materials for subsequent RO studies. It is our intent to synthesize as many structurally closely related PASAs as possible and to compare their RO properties. Eventually, a superior RO materials may emerge from this investigation.

Membrane evaluation

Screen studies. To compare the RO performance of several series of PASAs, our first task was to design

and unify the membrane fabrication conditions for the preparation of RO membrane from each of the PASAs. Most of the PASAs were only soluble in aprotic polar solvents, DMAc was selected as the casting solvent for membrane fabrication. Previous findings indicated that 65°C and 7 min would be a reasonable evaporation temperature and evaporation time for preparing viable RO membranes from this class of polymeric materials. To shed light on the industrial application of this separation technique, rinsing water which consisted of 270 ppm nickel ion obtained from a local electroplating factory was used as the feed solution. Prepared membranes were subjected to RO tests, using a homemade tester. Membrane characteristics in terms of salt rejection and flux rate for each of the membrane materials were obtained as an average of at least two measurements. Results of this systematic screening study are summarized in *Table 3*. Because of their low solubility in common organic solvents including DMAc, **AT** and **DT** cannot be used for fabricating membranes. For a similar reason, only 8.8% polymer concentration casting solution can be prepared from **BT**. In addition, for some of the materials, viable RO membranes can only

Table 3 General RO performance of PASAs^a

Entry	Polymer	[η] (dl g ⁻¹) ^b	Casting solution ^c					
			System 1		System 2		System 3	
			Salt rejection (%)	Flux (m day ⁻¹)	Salt rejection (%)	Flux (m day ⁻¹)	Salt rejection (%)	Flux (m day ⁻¹)
1	AT	0.04 ^f	— ^d	—	— ^d	—	—	—
2	AI	1.04	92.9	0.0243	97.9	0.0370	86.0	0.0370
3	BT	0.89	79.8	0.0323	— ^d	—	—	—
4	BI	1.07	82.3	0.0370	42.6	0.0323	—	—
5	CT	1.11	— ^e	—	< 10	0.1200	—	—
6	CI	0.86	— ^e	—	< 10	1.16	—	—
7	DT	—	— ^d	—	— ^d	—	—	—
8	DI	0.86	— ^e	—	49.7	0.0296	87.6	0.0499
9	ET	1.09	34.4	0.240	< 10	0.468	—	—
10	EI	0.64	— ^e	—	19.5	0.0530	—	—
11	BCT-91	0.91	96.2	0.0832	— ^d	—	—	—
12	BCT-82	0.79	92.3	0.0416	68.5	0.0305	—	—
13	BCT-73	0.92	96.9	0.0506	96.2	0.0347	—	—
14	BCT-64	0.70	96.9	0.0712	98.5	0.0451	—	—
15	BCT-55	0.75	96.6	0.0418	98.5	0.0532	—	—
16	BCI-91	0.44	— ^c	—	— ^e	—	58.9	0.0971
17	BCI-82	0.36	— ^c	—	— ^e	—	73.3	0.0555
18	BCI-73	0.48	— ^c	—	78.6	0.0770	45.8	0.0670
19	BCI-64	0.49	— ^e	—	— ^e	—	56.8	0.0578
20	BCI-55	0.33	— ^c	—	— ^e	—	< 10	0.0343
21	ACI-91	0.51	— ^c	—	88.5	0.0303	92.6	0.0508
22	ACI-82	0.52	— ^c	—	66.7	0.0485	92.1	0.0555
23	ACI-73	0.61	— ^c	—	85.6	0.0763	89.5	0.0629
24	ACI-64	0.56	— ^c	—	— ^c	—	91.3	0.0721
25	ACI-55	0.72	— ^e	—	88.5	0.0409	93.7	0.0693

^a 270 ppm nickel rinsing solution was used as the feed and operation pressure of 20 kg cm⁻²

^b Intrinsic viscosity in DMAc solution at 25.00 ± 0.05°C

^c Composition of casting solutions are shown in *Table 2*

^d Casting solution of this composition cannot be prepared because of the low solubility of the polymers

^e Casting solution was too dilute to obtain tough polymer membrane

^f Viscosity in conc. sulfuric acid at 25.00 ± 0.05°C

be furnished from a relatively high polymer concentration casting solution. Thus, the solubility of the polymers was our first concern in the study. To provide insight into the diverse RO properties of different PASAs listed in Table 3 is not a simple task. Judging from the fact that homopolymers derived from diamino monomers **1A** or **B** exhibited more superior RO properties to those of polymers from **1C**, we believe that rigidity in the polymer backbone may contribute to the improved RO performance (entries 2–4 vs 5 and 6). Furthermore, all 15 copolymers (entries 11–25) containing a structural moiety from the diamino monomer **1C** plus some rigid subunit **1A** and **B** demonstrated improved RO properties as compared with homopolymer **CT** and **CI** derived solely from **1C**. On the other hand, the RO tests revealed that the performance of copolymers was superior to that most of the homopolymers, even though the latter in general possessed higher intrinsic viscosities (third column, Table 3). In contrast, the RO performance of the three series of copolymers appeared to have some correlation with their viscosities. Conceivably, in order to have acceptable RO performance, the copolymers should possess a reasonably high viscosity (i.e. $\eta > 0.50$). Thus we had made a great effort to optimize polymerization conditions to produce polymers with the highest possible viscosity. Once the viscosity requirement was met, without optimization in the membrane fabrication parameters, high salt rejection and reasonably large flux rate could be ensured in the case of the **BCT** series. For fabricating viable membranes with acceptable RO properties, the copolymer **ACI** series which had a lower intrinsic viscosity required a higher polymer concentration casting solution (i.e. system 3). Membranes fabricated from copolymer **BCI** which possessed the lowest intrinsic viscosities demonstrated a moderate salt rejection and flux rate comparable to their copolymer counterparts. Presumably, if the viscosity of copolymers of **BCI** could be raised further, they may be a good RO material as well. In summary, the copolymer **BCT** series emerged as the best RO membrane materials from this screening study. In fact, all **BCTs** possess the potential to be further developed as commercial membrane materials. To determine the optimal conditions for membrane fabrication, **BCT-73** (entry 13) was chosen for the subsequent indepth investigation.

Effect of evaporation time. Our previous studies unambiguously established that a good compromise between salt reject and flux rate for RO separation occurred by using PASA membrane materials fabricated at high evaporation temperature. However, the practical highest temperature for fabricating membrane on a glass plate was around 70°C. Without repeating the study of effect of evaporation temperature on RO performance, 65°C was chosen for investigating the effect of evaporation time. Thus, several membranes derived from **BCT-73** casting solution were fabricated at 65°C for periods of 5, 7, 9 and 11 min. The effect of evaporation time on the RO performance of **BCT-73** is shown in Figure 2. Results revealed that the flux rate of the membrane appeared to be insensitive to the change of evaporation time. At 20 kg cm⁻² operating pressure, the flux reached a common value of around 0.065 m per day. On the other hand, excellent salt rejection (> 99%) was observed for membranes with an evaporation time greater than

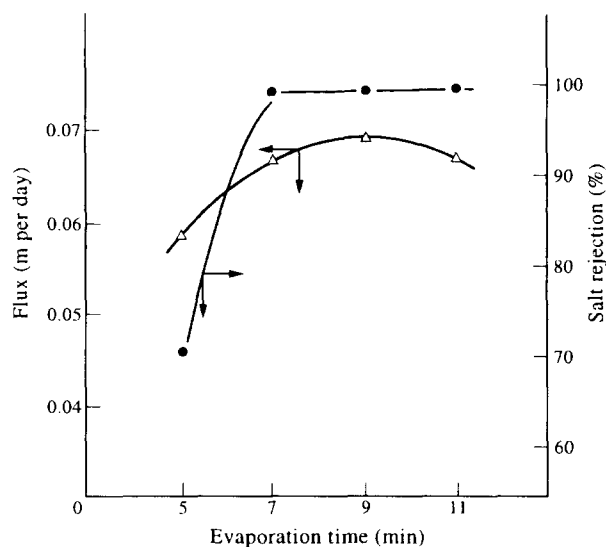


Figure 2 Effect of evaporation period on flux and salt rejection of **BCT-73**

7 min. Apparently, too short an evaporation time discourages the formation of asymmetric membrane with good separation characteristics. Incidentally, under the optimum evaporation temperature and time, the RO performance of **BCT-73** was much improved as compared to our previously reported PASAs materials⁶.

Effect of casting solution composition. For actual industrial applications, RO membranes with large flux rate are highly desirable. Normally, this can be achieved by either elevating the operating pressure in the separation process or increasing the concentration of pore-forming agent in the casting solution. The effect of lithium nitrate concentration in the casting solution on the RO performance of the membrane is shown in Table 4. For testing nickel plating rinsing solution, RO membranes with an increase in lithium nitrate concentration from 3 to 5%, an almost 50% increase in the flux and without any change in salt rejection (> 99.4%) was observed. On further increasing the pore-forming agent content in the membrane casting solution from 5 to 9%, a slight decrease in salt rejection and a further increase in flux resulted. The relative high polymer concentration in casting solution (i.e. solution **V**) imposed some difficulties in fabricating uniform RO membranes. To obtain further insight into the RO performance of the new materials, **BCT-73** membrane was further assessed with aqueous sodium chloride solution at two different concentrations. At 135 ppm NaCl feeding solution, the general performance of the membrane was very similar to that of the nickel rinsing solution except with a slightly lower salt rejection. The findings were in agreement with the fact that monovalent Na⁺ ion is more difficult to separate than the divalent Ni²⁺ ion by the RO technique. The impressive separation characteristics of the membrane can be sustained when 10-fold increase in concentration of the feed solution was used. After this series of optimization in fabrication parameters, the potential of **BCTs** exemplified by **BCT-73** as excellent membrane materials was explored and demonstrated.

Table 4 Effect of casting solution composition on the RO performance of **BCT-73**^a

Casting solution	Polymer (%)	LiNO ₃ (%)	DMAc (%)	Feed solution					
				Ni ²⁺ (270 ppm)		Na ⁺ (135 ppm)		Na ⁻ (1150 ppm)	
				Salt rejection (%)	Flux (m per day)	Salt rejection (%)	Flux (m per day)	Salt rejection (%)	Flux (m per day)
I	12.5	2	85.5	99.55	0.0703	94.78	0.0651	95.42	0.0475
II	12.5	4	83.5	99.45	0.0944	97.00	0.0882	96.58	0.0673
III	12.5	5	82.5	99.55	0.0988	96.45	0.0843	93.62	0.0667
IV	12.5	7	80.5	98.64	0.1326	92.42	0.1225	94.29	0.1307
V	12.5	9	78.5	98.56	0.1220	87.72	0.1277	–	–

^a Operating pressure of 20 kg cm⁻²**Table 5** The RO performance comparison of PASAs with common commercial membrane products

Membrane materials ^a (commercial name)	Manufacturer	Test conditions	Flux (m per day)	Salt rejection (%)
Cellulose acetate (CA 990)	DDS	2500 ppm NaCl 25°C, 4 mPa	1.68	90–92 ^b
Polyamide (HR 95)	DDS	2500 ppm NaCl 25°C, 4 mPa	1.80	95–97 ^b
Cross-linked polyethylenimine (NS 100)	UOP	5000 ppm NaCl 25°C, 4.1 mPa	0.39	99 ^b
HAI	our laboratory	1000 ppm NaCl 25°C, 4 mPa	0.12	98 ^c
BCT-73	our laboratory	1150 ppm NaCl 25°C, 2 mPa	0.13	95 ^d

^a Flat-sheet membranes were used^b Taken from ref. 1, pp. 283–285^c Taken from ref. 6^d Results of this work

Comparison of the RO performance of PASAs with that of some commercial membrane products

In order to make a sensible assessment on the viability of using PASAs as membrane materials for RO applications, the RO performance of PCT-73, together with that of some commercial products, is shown in Table 5. Although the test conditions for different materials were a bit varied, the salt rejection of PASAs were clearly comparable with that of the commercial products (~95%). After correcting for the pressure effect, the **BCT-7** flux was estimated to be 20% that of cellulose acetate and polyamide. It should be mentioned that PASAs proved to be highly chemical resistant, and can be used under harsh conditions. They worked well in a wide pH range (1–13) and withstand attack by dilute chromic acid⁶. Evidently, the relatively small in flux rate of PASA membranes can be favourably compensated for by their stability characteristics.

CONCLUSIONS

Both homopolymers and copolymers of poly(amide-sulfonamide)s of film-forming viscosities were synthesized for RO membrane preparation. In the screening and comparative studies, copolymers with relatively high viscosity possessed superior RO separation properties.

By optimizing membrane fabrication parameters including casting solution composition, evaporation time and evaporation temperature, the improved RO performance of a representative copolymer of PASAs was demonstrated.

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