

New Composite Reverse Osmosis Membranes Made from Poly-2-vinylimidazoline

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SYNOPSIS

Novel ultra-thin film (UTF) composite reverse osmosis (RO) membranes were fabricated *in situ* by the interfacial polymerization of poly-2-vinylimidazoline (PVI) precursors and aromatic acid chloride crosslinking agents. The syntheses of three different forms of PVI, which were used as precursors, are described. 3-(Chlorosulphonyl)benzoyl chloride, 3,5-di(chlorosulphonyl)benzoyl chloride and 1,3-benzenedicarbonyl dichloride were used as crosslinking agents. Both flat-sheet and tubular membranes were fabricated and tested for their salt retentions and permeate fluxes. The RO performances of the two sets of tubular membranes PVI I and PVI II crosslinked with 3-(chlorosulphonyl)benzoyl chloride, prepared according to optimized fabrication formulations, were recorded. These were $97.1 \pm 0.1\%$ retention; 730 ± 24 lmd flux and $98.2 \pm 0.7\%$ retention; 560 ± 150 L/m²/day (lmd) flux, respectively. The RO performances of initial tubular membranes made from PVI III and 3-(chlorosulphonyl)benzoyl chloride was $97.0 \pm 1.1\%$ retention and 643 ± 74 lmd flux.

BACKGROUND

Since the early days of the reverse osmosis (RO) separation industry, membrane fouling has been recognized as a severe problem;^{1,2} it leads to the blocking of the pores and a reduction in the rate of flow through the membrane. Research on ways to reduce membrane fouling continues. A common approach has been to coat membranes with polymers rich in sulfonate groups.³ According to Gregor and Gregor,¹ the extremely hydrophilic nature of the sulfonate group, and its stability in the salt form, inhibits the absorption of the hydrophobic constituents of a feed stream onto the membrane surface. In addition, since almost all naturally occurring colloidal fouling materials are negatively charged, ionic repulsion occurs between the negatively charged sulfonate groups of the membrane and the natural colloids. Incorporation of sulfonate groups into a desalting membrane structure may, furthermore, offer the following advantages:

1. The fixed charge of a sulfonate group enhances salt rejection by a membrane because

it provides an electrical field in the area of the desalting barrier.

2. The high affinity that a sulfonate group has for water leads to greater water flux through the membrane.

Sulfonate groups can be introduced into an ultra-thin film (UTF) polyamide membrane structure by the hydrolysis of unreacted sulfonic acid chloride groups in a membrane made by the condensation of a polyamine and a sulfonic acid chloride crosslinking agent.

The preparation of polysulfonamides by interfacial polycondensation methods from diamines and aromatic di(sulfonyl chlorides) has been comprehensively described by Morgan.⁴

The following features of homopolymeric poly-2-vinylimidazoline (PVI) make this compound worth investigating as a polymeric precursor in the fabrication of thin-film composite RO membranes by interfacial polycondensation:

1. Water solubility.
2. Apparent ease of preparation from known reagents.
3. Presence of the 2-imidazoline (amidine) group, in which the only reactive hydrogen is

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situated on a nitrogen atom that, after reaction with an acid chloride crosslinking agent, forms a tertiary amide.

4. Functionality in the polymer side chain.

A polymeric precursor material with a secondary amine group (crosslinking site), preferably pendent to the polymer chain, is desired for the fabrication of polyamide membranes with some stability toward chlorinated feedwaters.⁵⁻⁷ This is a most desirable feature for the economic application of RO membranes in the process of desalination.

EXPERIMENTAL

Synthesis of Polymers

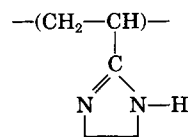
Polyacrylonitrile (PAN) was prepared by a free-radical solution-polymerization method.⁸ A 33% (v/v) solution of acrylonitrile (6.5 mol) in *N,N*-dimethylformamide (DMF) and benzoyl peroxide initiator (0.17 mol) was stirred under a nitrogen atmosphere for 24 h at 70°C, and the product precipitated in water. Several batches of PAN were prepared; their average molecular masses ranged from 11,000 to 23,000, as determined by dilute solution viscometry. One batch had a molecular mass of 46,000.

PVI I was prepared by the reaction of PAN with 1,2-diaminoethane (molar ratio 1 : 2) in DMF with elemental sulfur as catalyst, by a method based on that described by Hurwitz.⁹ The reaction was carried out at 110°C for 6 h in an atmosphere of nitrogen. The pendent nitrile groups were converted to 2-imidazoline groups, with the liberation of ammonia. The crude product was precipitated in acetone and oven-dried at 40°C under reduced pressure to yield the product PVI I in an 80% yield. This was characterized by elemental analysis and ¹³C NMR spectroscopy.

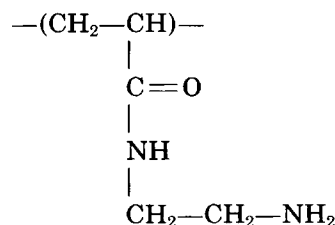
PVI II was prepared by the reaction of PAN and an excess of 1,2-diaminoethane (molar ratio 1 : 5). In this reaction, 1,2-diaminoethane was both reagent and solvent, reaction conditions being otherwise similar to those used for the preparation of PVI I. The crude product was dried on a freeze-dryer to a fine, light-brown powder. Several batches were made in essentially quantitative yields and the products were characterized by ¹³C NMR spectroscopy. Selected batches were also characterized by elemental analysis.

Poly-2-vinylimidazoline hydrolyses to form poly-*N*-aminoethylacrylamide. Because water forms one

phase in the interfacial polycondensation reaction by which thin-film membranes were made from poly-2-vinylimidazoline, strictly anhydrous conditions were not used in the synthesis of PVI I and PVI II. The PVI products contained repeat units with intact groups



and repeat units with aminoethylamide groups



The content of hydrolyzed repeat units in batches of PVI II was quantified by ¹³C NMR spectroscopy.¹⁰ The content of 1,2-diaminoethane impurity in PVI II was also determined by ¹³C NMR spectroscopy. ¹³C NMR analysis of a batch of PVI I revealed traces of DMF solvent in the product, and there was evidence of 22% hydrolyzed repeat units present. Table I lists the contents of hydrolyzed repeat units and 1,2-diaminoethane in batches of PVI II.

These calculations were made from spectra recorded under the experimental conditions used for the routine characterization of all batches of PVI II and not from fully relaxed spectra. The figures for the contents of hydrolyzed repeat units are considered accurate because the relaxation time of the carbon atom of the ---C=N group (1.63 ± 0.39 s) is

Table I Percentages of Hydrolyzed Repeat Units and 1,2-Diaminoethane Calculated To Be Present in Batches of Poly-2-Vinylimidazoline (PVI II)^a

PVI II Batch No.	Hydrolyzed Repeat Units (%)	1,2-Diaminoethane (%)
8	11.4	13.9
16	14.6	11.4
18	10.3	21.1
19	11.4	22.2
24	19.5	9.8
25	15.5	14.5
34	11.0	14.0
36	9.7	15.5

^a Calculations based on ¹³C NMR data.

close to that of the amide group of the hydrolyzed form (1.73 ± 0.1 s). The relaxation time of 2.7 ± 0.12 s for the carbon atoms of 1,2-diaminoethane is not close; the figures in Table I for the percentages of 1,2-diaminoethane are only relative. Calculations based on data for a fully relaxed spectrum of PVI II (batch 16) revealed the presence of 17.2% 1,2-diaminoethane, about 50% more than originally calculated from data for the ^{13}C NMR spectrum of PVI II 16 recorded under routine experimental conditions.

The chain lengths of the PVI products were assumed to be the same as those of their PAN precursors.

PVI III was obtained by the partial extraction of 1,2-diaminoethane from PVI II. A sample of PVI II (batch 24) was washed with a threefold volume of acetone, filtered, and dried. The percentage of 1,2-diaminoethane was determined by ^{13}C NMR to be 4.8%; a reduction of about 50%.

Synthesis of Crosslinking Agents

3-(Chlorosulphonyl)benzoyl chloride was prepared as described by Imai and Okunoyama¹¹ and characterized by mass spectroscopy.

3,5-Di(chlorosulphonyl)benzoyl chloride was prepared by conversion of the disodium salt of 1,3-di(sulpho)benzoic acid¹² with thionyl chloride to the acid halide form and subsequent recrystallization from benzene. The product was characterized by mass spectroscopy.

1,3-Benzenedicarbonyl dichloride is commercially available and was recrystallized from petroleum ether.

Membrane Fabrication and Testing

The membranes were prepared by depositing a thin layer of a dilute aqueous solution (0.5–1.5% m/m) of PVI on the finely porous surface of a polysulfone support membrane and subsequently contacting the polymer layer with a dilute hexane solution (1–3% m/m) of a crosslinking agent to form a thin semi-permeable film of crosslinked polymer, followed by drying at elevated temperature (80–100°C, 10 min). Membranes were made either in flat-sheet form or by the manual dip-coating of 1.2-m-long tubes. The internal diameter of the tubes was 13 mm.

Membranes were tested in a closed-loop system for salt retention and water permeability. The standard conditions employed during testing are given in Table II.

The average salt retentions and water permeabilities (fluxes) of a set of tubular membranes (six

Table II Conditions for Testing of UTF Membranes

	Flat-sheet Membranes	Tubular Membranes
Operating pressure	4.1 MPa	2 MPa
Feed water temperature	25°C	20°C
Feed solution composition (NaCl in distilled water)	5000 mg/L	2000 mg/L
Test time	> 24 h	> 18 h
pH	6.4–6.8	6.4–6.8
Linear flow velocity	—	1.0 m/s

membranes per set) were determined and then used in the calculation of the overall membrane performance, given by the figure of merit, that is, A^2/B .¹³ The product A^2/B is proposed as an empirical, but useful, figure of merit. It combines into a single value both water flux and salt retention; the value is independent of the concentration of the feed solution and operating pressure. The water permeability constant (A) and salt permeability constant (B) are characteristic of a particular membrane. (Water flux = $A \times$ net operating pressure and salt flux = $B \times$ concentration gradient across membrane.) This figure of merit was used to compare the overall performance of each batch of tubular membranes made.

RESULTS AND DISCUSSION

Flat-Sheet Membranes

Numerous sets of membranes were made under various combinations of fabrication conditions. The RO performances reported here are those for the batches that gave the best results. The results for flat-sheet membranes are the average of four membranes per set and the results for tubular membranes are the average obtained for six membranes per set. Results given include standard deviations.

Sets of flat-sheet membranes were made with the PVI I precursor and crosslinked with the three various crosslinking agents. These membranes were tested for their RO performance; the results are presented in Table III.

Membranes formed from crosslinking agents containing sulfonyl chloride functionality showed better salt retention than membranes made from the crosslinking agent with only carboxylic acid functionality. This may be ascribed to a greater depth of crosslinking through the thickness of the membrane, due to the lower reactivity of sulfonic

Table III Comparison of RO Performances of PVI I UTF Flat-Sheet Membranes Fabricated with Various Crosslinking Agents

Membrane composition	PAN Reagent mol mass	RO Membrane Performance	
		Salt retention (%)	Flux (lmd) ^a
PVI I + 1,3-benzenedicarbonyl dichloride	8,000	72.7 ± 0.4	1760 ± 58
	46,000	65.2 ± 4.8	2174 ± 235
PVI I + 3-(chlorosulphonyl) benzoyl chloride	8,000	84.8 ± 1.9	680 ± 58
	46,000	86.1 ± 3.0	881 ± 65
PVI I + 3,5-di(chlorosulphonyl) benzoyl chloride	8,000	96.4 ± 0.6	797 ± 86
	46,000	93.9 ± 1.8	1394 ± 50
Membrane Fabrication Conditions			
Polysulfone support cast from DMF solution (13%)			
Concentration PVI I precursor (mass %)			3
Precursor contact time (min)			60
Precursor drainage time (min)			2
Concentration crosslinking reagent (mass %)			2
Crosslinking reagent contact time (min)			5
Post-crosslink drain time (min)			2
Oven temperature (°C)			100
Oven residence time (min)			10

^a lmd = liters/m²/day.

acid chloride groups with amines, thus resulting in an increase in retention. The formation of carboxylate and sulfonate groups in the desalting barrier (from the hydrolysis of unreacted acid chloride

groups) leads to an increase in water permeability.¹⁴ In membranes crosslinked with 3-(chlorosulphonyl)benzoylchloride or 3,5-di(chlorosulphonyl)-benzoyl chloride these groups are predominantly

Table IV Optimized PVI I Tubular Membrane Fabrication Formulation and RO Performance

Concentration of PVI I precursor (mass %)	5.0
Concentration of triethylamine (mass %)	1.1
Concentration of trisodiumphosphate (mass %)	0.14
Precursor contact time (min)	43.00
Precursor draining time (min)	1.50
Concentration crosslinking agent (mass %)	4.50
3-(chlorosulphonyl)benzoyl chloride	
Crosslinking reagent contact time (min)	3.00
Post-crosslink air drying time (min)	10.00
Oven temperature (°C)	95.00
Oven residence time (min)	5.40
RO performance	
Salt retention	97.1 ± 0.1%
Permeate flux	730 ± 24.1 lmd
A ² /B value	8.89 × 10 ⁻⁵

sulfonate as the carboxylic acid chloride groups react faster during the polycondensation reaction because of their greater reactivity with amines.¹⁵ The poorer performance of membranes made with 1,3-benzenedicarbonyl dichloride is probably because a thinner desalting barrier is formed. The gradient of crosslinking density in an ultra-thin film composite membrane will be discussed in a future study.

Tubular Membranes

Reaction conditions for the fabrication of PVI I + 3-(chlorosulphonyl)benzoyl chloride and PVI II + 3-(chlorosulphonyl)benzoyl chloride membranes were optimized for high retention and flux¹⁶ by means of the Simplex approach.¹⁷

The optimized fabrication formulations and the resulting membrane RO performances are shown in Tables IV and V, respectively.

Moderately high salt retentions were obtained with tubular membranes prepared with the PVI I precursor material. The maximum retention obtained during this study for a PVI I UTF membrane was 98%.

PVI II is superior to PVI I as a precursor; the first UTF membrane to exhibit 99% salt rejection was a PVI II membrane. The optimum formulation for membranes made from PVI I and PVI II differed (see Tables IV and V). When the optimum formulation for PVI I membrane fabrication was applied to fabrication of a PVI II membrane, the resultant membrane showed very low permeate flux. Only after the polymer content had been reduced considerably could satisfactory membranes be fabricated.

Two sets of membranes were made with PVI III precursor and crosslinked with 3-(chlorosulphonyl)benzoyl chloride. These membranes were made under the optimized fabrication conditions established for the PVI I and the PVI II membranes (see Tables IV and V), and their RO performances were compared with those of the optimized membranes. In this experiment all the PVI precursors [PVI I, PVI II (batch 24) and PVI III] were made from the same batch of PAN reagent; viscosity average molecular mass 18,000. Results are presented in Table VI.

Membranes prepared with the PVI III precursor, using the optimum formulation for PVI II membranes, showed the best RO performance. Membrane flux was higher than that of PVI II membranes and retention was as good as PVI II membranes.

Reverse osmosis membrane research and development has centered on achieving, among other goals (e.g., chlorine resistance and stability over a wide pH range), the ideal of high productivity coupled with high selectivity. The development of adequate medium-to-low pressure desalination membranes was of specific importance due to the many advantages associated with the operation of RO membranes at lower pressure (pressures lower than those of at least 5.5 MPa required for seawater membranes). Target goals recommended for the medium-to-low pressure desalination of brackish water were membranes with fluxes in the range of 600–800 L/m²/day (lmd) and with a minimum salt retention of 95%, tested at an operating pressure of 1.7 MPa with a feed solution of 3200 mg/L total dissolved solids (TDS) content.¹⁸

The development of the commercial FT-30 thin-

Table V Optimized PVI II Tubular Membrane Fabrication Formulation and RO Performance

Concentration of PVI II (batch 3) (mass %)	1.2
Concentration of triethylamine (mass %)	0.2
Concentration of trisodiumphosphate (mass %)	0.5
Precursor contact time (min)	15.0
Precursor draining time (min)	4.0
Concentration crosslinking reagent (mass %)	3.0
3-(chlorosulphonyl)benzoyl chloride	
Crosslinking reagent contact time (min)	6.0
Post-crosslink air drying time (min)	16.00
Oven temperature (°C)	95.00
Oven residence time (min)	4.0
RO performance	
Salt retention	98.2 ± 0.7%
Permeate flux	560 ± 150 lmd
A ² /B value	10.9 × 10 ⁻⁵

Table VI RO Performances of Tubular Membranes Made with Precursors: PVI I, PVI II, and PVI III Crosslinked with 3-(Chlorosulphonyl)benzoyl Chloride

Fabrication Formulation	Polymeric Precursor	Test Time (h)	Retention (%)	Flux (lmd)
For fabrication formulation see Table IV	PVI I	22.4	96.8 ± 0.7	256 ± 5
		48.1	97.4 ± 0.5	296 ± 5
	PVI II ^a	22.4	60.5 ± 16.5	47 ± 8
		48.1	62.6 ± 15.0	24 ± 5
	PVI III	22.4	78.1 ± 6.9	32 ± 5
		48.1	80.3 ± 6.1	25 ± 5.5
For fabrication formulation see Table V	PVI I	23.8	94.1 ± 0.7	463 ± 24
		47.4	94.5 ± 0.3	491 ± 33
	PV II ^a	23.8	97.3 ± 1.2	340 ± 39
		47.4	97.4 ± 1.6	417 ± 41
	PVI III	23.8	96.5 ± 1.1	566 ± 50
		47.4	97.0 ± 1.1	643 ± 74

^a Batch 24.

film composite membrane for brackish water desalination has been described by Larson et al.¹⁹ These membranes have routinely exhibited retentions of 98% and fluxes of 800 lmd, when operated at an applied pressure of 1.3 MPa (200 psi) with a 2000 mg/L NaCl solution. The commercial poly(ether/amide) thin-film composite membranes, designated PA-300, have also exhibited retentions of greater than 98% and fluxes in the order of 800 lmd when tested with simulated brackish water (5530 mg/L NaCl) at a pressure of 2.7 MPa (400 psi).²⁰

The RO performances of the thin-film composite polyamide membranes MSI-400 and TFC-202 have been reported to be greater than the recommended target goals for medium-to-low pressure membranes.¹⁸

The RO performances exhibited by the membranes prepared from PVI precursors, as described in this study, are well within the recommended range for adequate medium-to-low pressure desalination membranes, although the PVI membranes were tested at a slightly higher pressure.

CONCLUSIONS

New thin-film composite reverse osmosis membranes were fabricated under various conditions and tested for their RO performances. The three different aqueous precursor solutions used contained vinyl copolymers with repeat units with 2-imidazolinylolethyl and 2-aminoethylamidoethyl pendent groups. The crosslinking agents used were 3-(chlorosulphonyl)benzoyl chloride, 3,5-di(chlorosul-

phonyl)benzoyl chloride, and 1,3-benzenedicarbonyl dichloride. Use of the crosslinking agents containing sulfonic acid chloride functionality resulted in the fabrication of membranes with improved RO performances. Optimized fabrication formulations were determined for the PVI I and PVI II tubular membranes crosslinked with 3-(chlorosulphonyl)benzoyl chloride, and the RO performances of these membranes were recorded. These were 97.1 ± 0.1% retention; 730 ± 24 lmd flux and 98.2 ± 0.7% retention; 560 ± 150 lmd flux, respectively. Tubular membranes were prepared from PVI III and 3-(chlorosulphonyl)benzoyl chloride, according to unoptimized fabrication conditions, and their RO performance recorded. The average flux of these membranes was much higher, by about 30%, than that exhibited by the membranes prepared from PVI I and PVI II (in the case where the PVI II precursor is the same product as the mother material from which PVI III precursor was obtained).

PVI II contained an amount of 1,2-diaminoethane impurity whereas PVI III contained about half this amount; PVI I contained no 1,2-diaminoethane, but there was evidence of the presence of traces of DMF solvent and a higher concentration of hydrolyzed repeat units, about 22%, compared with between 9.7 and 19.5% in batches of PVI II.

The financial support of the Water Research Commission is gratefully acknowledged.

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Received August 28, 1991

Accepted November 26, 1991