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FINAL REPORT

Project Duration : March 1, 1990 - February 28, 1994

**PREPARATION AND EVALUATION OF CONDENSATION POLYMERS
FOR MEMBRANE APPLICATIONS**

Submitted to the Office of the Science Advisor
U.S. Agency for International Development

Principal Investigator : Dr. Cholticha Noomhorm
Grantee Institution : Kasetsart University
Bangkok, Thailand
Collaborator : Prof. W. H. Daly
Institution : Louisiana State University
Project Number : 9.367
Grant Number : 493-5542-G-SS-0022-00
A.I.D. Grant Office : Bangkok, THAILAND

Department of Chemistry
Faculty of Science
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cc: BOSTID

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3. EXECUTIVE SUMMARY

The preparation of nine types of polymer and copolymer (arylene ether sulfones) and (arylene ether nitriles) have been achieved. The mechanical strength of these polymer and copolymer have been found satisfactory for membrane applications. The performance of the produced polymer and copolymer were successfully evaluated for the clarification of tangerine juice. The poly and copoly samples were modified further by aminomethylation and quaternization in order to get the proposed membranes. Unfortunately, the new approach to develop effective and reproducible procedures for further membrane modifications by aminomethylation to introduce the $-\text{CH}_2\text{NH}_2$ group and the quaternization to introduce the quaternary ammonium salts in order to produce membrane in large quantity necessary for large scale production could not be accomplished although many investigations related to poly (arylene ether sulfone) membranes have been reported in the literatures.¹⁻⁵

The membrane technology is gaining much recognition in recent years due to its wide range of applications. However, its applications is not progressing as expected in developing countries due to the high cost of membrane materials and its operation. A good membrane has a property of not only with a high flux density and a high selectivity but also it should be cheap and with sufficient mechanical strength. A very selective membrane has a low permeability and a good selectivity membrane is expensive. Therefore, there still is a dire need of a basic research on membrane synthesis in developing countries to have the opportunity to utilize and compete in an equal basis with international producers as most of the membrane materials and manufacturing processes are often secrets and it is hard to obtain information from the literatures.

2. RESEARCH OBJECTIVES:

The wide range of membrane technology applications required for a synthetic membranes with suitable properties and high performance characteristics. The poly (arylene ether sulfone) is an excellent membrane material in terms of thermal, physical and chemical stability and high mechanical strength. This type of membrane is widely used in ultrafiltration and reverse osmosis processes. However, its somewhat hydrophobic nature precludes its use in some aqueous membrane applications that require hydrophilic characteristics. One aspect of enhancing its hydrophilicity is by introducing an aminomethylated functional group for the formation of aminomethylated polymers. A positively charged polymeric quaternary ammonium salts can be obtained by subsequent quaternization of the amino-methylated polymers. Moreover, the charged membranes can show specific separation ability because they unique pore size and charge density. These membrane types can expel solute and colloid particles having the same sign as the membrane charge, thus the effect of fouling, i.e., gel layer formation on the membrane surface⁹, is less than that of the non-charged membrane. The negatively charged membranes which are the most form of sulfonated poly (arylene ether sulfones) are already commercially available and their applications have been extensively studied. Unfortunately, the positively charged quaternary ammonium salts of poly (arylene ether sulfones) are not yet commercially available.

The synthesis of quaternary ammonium polymers can be achieved either by treatment of chloromethylated polymers with various amines, or by addition of an alkyl halides to polymeric amines. Normally, the quaternary salts of poly (arylene ether sulfones) have been prepared via chloromethylation and subsequent amination of poly (arylene ether sulfones) ¹⁰⁻¹⁴. Thus, the objectives of this project are to develop effective and reproducible procedures for a preparation aminomethylated poly (arylene ether sulfones) and the corresponding poly (quaternary ammonium salts) and to evaluate the performance of the developed polymers for membrane applications.

5. METHODS AND RESULTS

5.1 Preparation of the Proposed Polymers

5.1.1 Materials and Methods

5.1.2 Preparation of poly (arylene ether sulfones) and poly (arylene ether nitriles)

There were two procedures followed in the preparation of poly (arylene ether sulfones) and poly (arylene ether nitriles), namely:

i) McGrath et al. procedure

The poly (arylene ether sulfone) and poly (arylene ether nitrile) were synthesized according to the procedure recommended by McGrath et. al.¹⁵ as shown in Figure 5.1 and

Table 5.1 Poly (arylene ether sulfones) and poly (arylene ether nitriles).

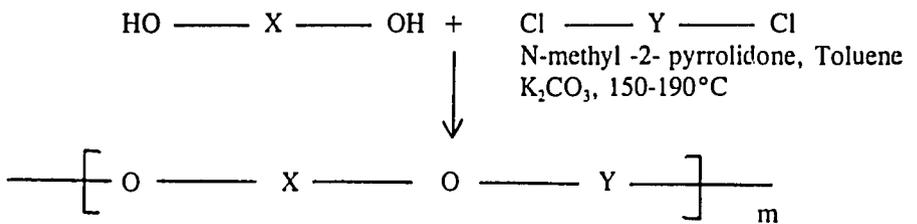
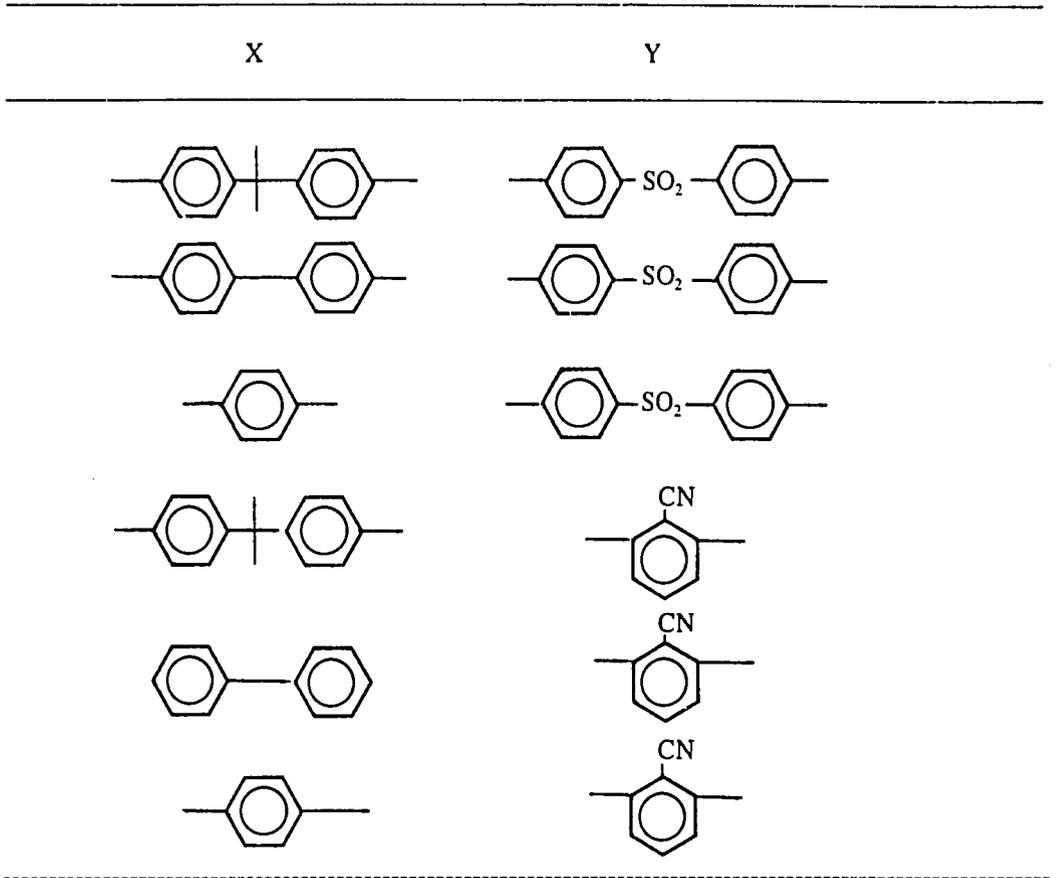


Figure 5.1 Preparation of poly (arylene ether sulfones) and poly (arylene ether nitriles) following the McGrath et al. procedure.

Table 5.1. This procedure used a mixture of 0.05 mol of HO-X-OH, 0.05 mol of Cl-Y-Cl, 83 ml of N-methyl-2-pyrrolidone and 37.5 ml of toluene. The mixture was placed in a 250 ml 3 neck-round bottom flask fitted with a nitrogen inlet, a Dean-Stark trap fitted with a condenser and a thermometer. A 7.26 g (0.0525) mol) of powdered anhydrous potassium carbonate was used to form the bisphenolate salt. The nitrogen sparged reaction mixture was heated to 170°C under reflux until water was removed completely from the system by toluene-water azeotropic distillation. The polymerization was completed in 3-5 hours. The viscous solution was allowed to cool at room temperature and neutralized with glacial acetic acid. The solution was precipitated into 1 liter 1:1 volume mixture of water and methanol using a high speed blender. Then, the obtained polymer was reprecipitated from chloroform into methanol and dried in vacuum.

ii) Scholl Reaction

The alternative procedure for preparation of poly (arylene ether sulfone) has also been tried using Scholl reaction¹⁰ as shown in Figure 5.2. Phenol or phenol derivatives (61.6 mmol) was dissolved in a mixture containing 85 ml DMSO and 28.5 ml toluene and K_2CO_3 (74 mmol) was added. The reaction flask was equipped with a nitrogen inlet, a thermometer, and a Dean-Stark trap equipped with a condenser. The reaction mixture was heated at 155°C until the theoretical amount of water was collected. Then, the mixture was allowed to cool at 70°C and a solution of 4,4'-dichlorodiphenyl sulfone (28.4 mmol) in 14.5 ml toluene was added. The mixture was heated up again to 155°C until all the toluene was collected in the Dean-Stark trap. Afterwards, the reaction mixture was stirred at 155°C for 6 hours. The reaction mixture was cooled, poured into 2 l cold water, and neutralized with diluted HCl. The resulting precipitate was filtered and the precipitate was dissolved in 100 ml toluene, washed three times with 2N NaOH and then with water until it became neutral. The toluene layer was dried over anhydrous $MgSO_4$, and the toluene was removed in a rotavapor. After purified twice by column chromatography (basic aluminum, dichloromethane as eluent) the residue obtained (1 mmol) was dissolved in 2 ml dry nitrobenzene, to which a solution of anhydrous $FeCl_3$ (4 mmol) in 1.5 ml dry nitrobenzene was added dropwise. The reaction mixture was stirred at room temperature for 17 hours and then precipitated into 200 ml methanol acidified with 2% HCl. The precipitate was filtered, washed with boiling methanol and dried in vacuum.

5.1.3 Preparation of aminomethylated poly (arylene ether)

The preparations of aminomethylated poly (arylene ether) were carried out according to the procedures presented by Daly et al.¹⁷⁻¹⁸ as shown in Figures 5.3 and 5.4, respectively.

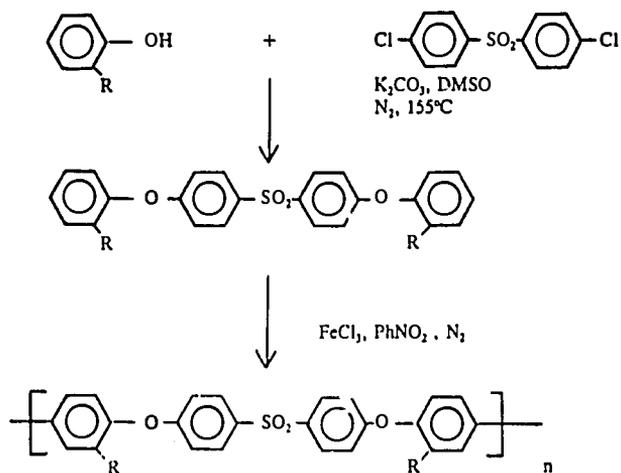


Figure 5.2 Preparation of poly (arylene ether sulfone) via Scholl reaction.

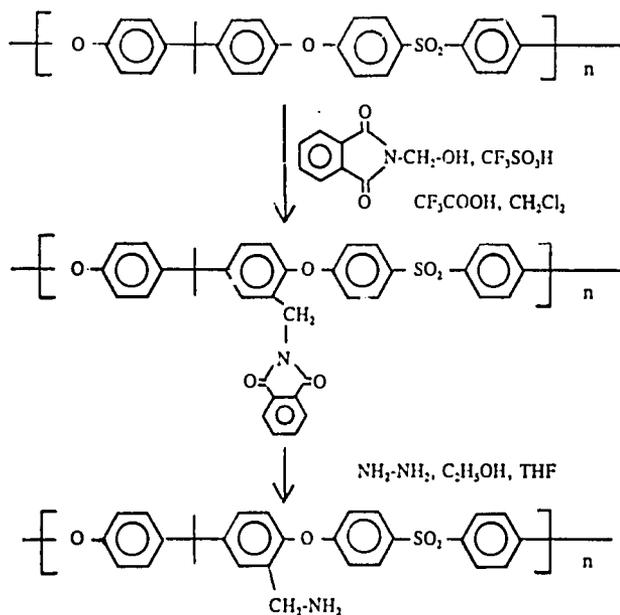


Figure 5.3 Preparation of aminomethylated polymer using poly (arylene ether sulfone) as starting polymer.

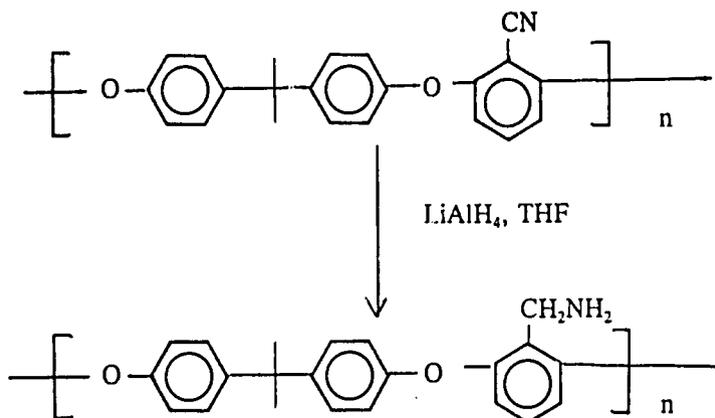


Figure 5.4 Preparation of aminomethylated polymer using poly (arylene ether nitrile) as starting polymer.

5.1.3.1 Aminomethylation of poly (arylene ether sulfone)

A solution of 0.025 mol of N-hydroxy-methylphthalimide and 2.5 g of trichloromethanesulfonic acid in 100 ml of trifluoroacetic acid was added dropwise to a mechanical stirred solution of 0.025 g of poly (arylene ether sulfone) in 100 ml of dichloromethane. The addition process required 30 minutes. During this time, the mixture became deep brown. After stirring for 4 hours at room temperature, the polymer was precipitated in 1 l of methanol and washed sequentially with 200 ml solution of concentrated ammonium hydroxide, 12 l of water and 1 l of methanol. A white powder of poly (phthalimidomethyl arylene ether sulfone) was isolated.

To a solution of 4.94 meq of poly (phthalimidomethyl arylene ether sulfone) in 150 ml of THF and 150 ml of ethanol was added 51.6 mmol of hydrazine hydrate at 70°C. After stirring for 18 hours at 70°C, the precipitate was recovered by filtration, and extracted with 300 ml of THF. The filtrate was evaporated and the residue was extracted with 50 ml of THF. The extracts were combined, the volume was reduced to 50 ml and the product was precipitated by pouring the solution into 500 ml of methanol. The polymer was washed sequentially with 50 ml of saturated aqueous NaHCO₃, 200 ml of water and 200 ml of methanol and dried in vacuum. Aminomethylated poly (arylene ether sulfone) was obtained.

5.1.3.2 Aminomethylation of poly (arylene ether nitrile)

Twenty-five ml of a 1.0 M solution of lithium aluminum hydride (LAH) in THF was cooled to 0°C before adding a solution of 5.0 meq of poly (arylene ether nitrile) in 120 ml of THF. The resultant slurry was stirred for 24 hours at 0°C, reflux for 1 hours, recooled at 5°C and the excess LAH was decomposed with 2 ml of water. The volume of the solution was reduced to 25 ml before pouring the mixture into 500 ml of 5% HCl to dissociate the amine aluminum salt complex and precipitate the polymer. The polymer was recovered by filtration, reslurried in 20 ml of water and the pH was adjusted to 9.0 with NaOH. After recovery of the neutralized polymer, it was dried in vacuum, redissolved in CHCl₃, and reprecipitated using water as the nonsolvent, Aminomethylated poly (arylene ether) was obtained.

5.1.4 Preparation of Aminomethylated poly (arylene ether sulfone) via chloromethylation

Chloromethylations of poly (arylene ether sulfones) were carried out using procedures suggested by Hodge¹⁹ and Itsuno²⁰ to avoid contact with highly carcinogen chloromethyl methyl ether.

- i) Using methoxy acetyl chloride (MAC) as shown in Figure 5.5.

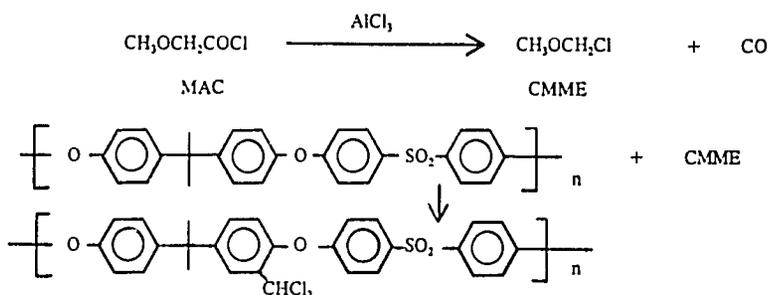


Figure 5.5 Chloromethylation of poly (arylene ether sulfone) using methoxy acetyl chloride

A mixture of MAC (47 mmol) and AlCl₃ (0.9 mmol) in dichloromethane (DCM) (50 ml) was stirred and heated under reflux for 5 hours to give a solution of chloromethyl methyl ether (CMME). The solution was cooled and diluted with DCM (50 ml), then stannic chloride (0.9 mmol) was added followed by a solution of poly (arylene ether sulfone, 0.09 mol) in 300 ml DCM. The reaction mixture was stirred at 20°C under nitrogen for 20 hours, recooled and 5 ml of water was added, followed with 2N NaOH (10 ml) to destroy unreacted CMME. The solution was reduced to 100 ml and precipitated in methanol. Then, the obtained polymer was reprecipitated from chloroform into methanol and dried in vacuum.

ii) Using trioxane and chlorotrimethylsilane as shown in Figure 5.6.

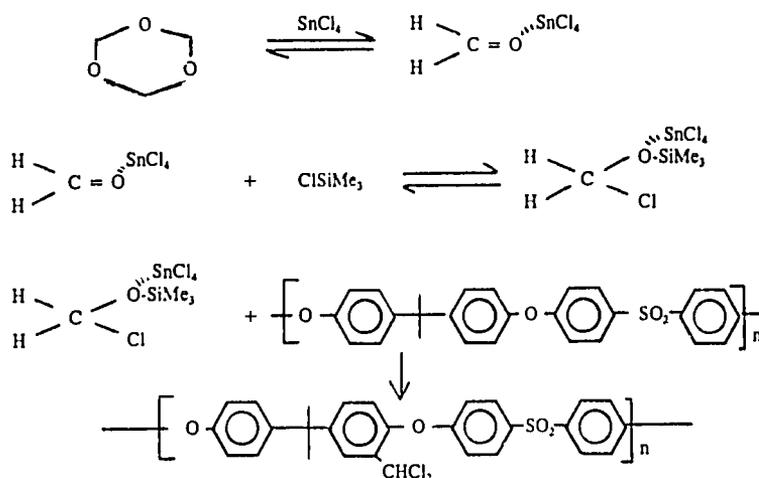
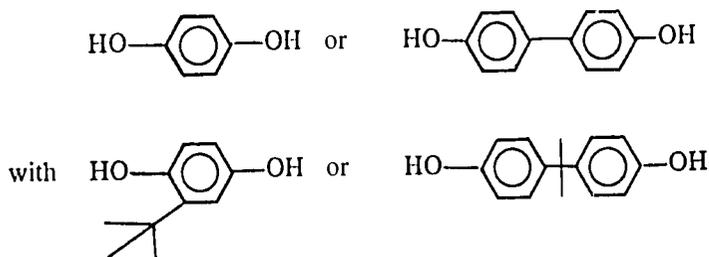


Figure 5.6 Chloromethylation of poly (arylene ether sulfone) using trioxane and chlorotrimethylsilane.

Trioxane (10 mmol) and chlorotrimethylsilane (30 mmol) were dissolved in chloroform (20 ml) and 4.3 mmol of SnCl_4 was added at 0°C . Then a solution of 2.25 mmol of poly (arylene ether sulfone) in 30 ml CHCl_3 was added dropwise. The mixture was stirred at 0°C for 30 min and for another 5 hours at room temperature. The reaction was quenched by addition of methanolic water.

5.2 Results and Discussions

The poly (arylene ether sulfone) and poly (arylene ether nitrile) were successfully synthesized using a McGrath procedure. It was found out that it very difficult to obtain a high molecular weight polymers using the McGrath method when hydroquinone and biphenol were used as one of the monomer pairs. This was probably due to the crystallization occurred before high conversion took place and there was a solubility problems. The membrane produced was not used for further studies. A modification on the process was made by copolymerization with 2-tert-butylhydroquinone and bisphenol-A as shown below:



The synthesis of poly (arylene ether sulfones) and poly (arylene ether nitriles) by condensation of 4,4'- dichlorophenylsulfone or 2,6-dichlorobenzonitrile with hydroquinone or 4,4'-biphenol together with 2-tert-butylhydroquinone or bisphenol-A were not satisfactory since the casted membrane has poor mechanical strength. Dissolving the developed polymers having undesirable characteristics with commercially available poly (ether sulfone) (Aldrich Chemicals) was done to improve the mechanical strength of the membrane¹. However, different tests with different parameter combinations such as concentration of the casting solution, solvent preevaporation period, gel formation conditions, etc. did not improve the strength of the membranes.

An alternative procedure for preparation of poly (arylene ether sulfones) were carried out using Scholl reaction. Several trials have been made using a 2-tert-butylphenol or phenol as starting monomers, but there was a difficulty in the separation of products from 4,4'-dichlorophenylsulfone using column chromatography. As a result, the yield (%) of poly (arylene ether sulfones) obtained from this procedure was very low. Hence, evaluation of the membrane was not made.

The preparation of poly (arylene ether sulfones) and poly (arylene ether nitriles) using McGrath procedure was reinvestigated to overcome the failures. Various poly and copoly (arylene ether sulfones) and poly (arylene ether nitriles) have been synthesized successfully by varying the molar ratio of monomers, temperature and reaction time (Table 5.2). Since the polymers 1, 2, 4, 5, 6, 7, 8, 9, and 14 showed desirable characteristics, these polymers were modified further. Poly 1, 2, 4, 5, 6, 7, 8, 9, and 14 were modified by introducing the $-CH_2NH_2$ groups but the yields were rather low and the processes were stopped. Introducing the $-CH_2Cl$ group was made instead of $-CH_2NH_2$. Several processes were chosen in order to figure out the best procedure for chloromethylation without a contact with chloromethyl methyl ether because the chemicals were highly carcinogenic. Chloromethylation using trioxane and chlorotrimethylsilane produced a gel-like polymers which cannot be dissolved in any solvent. The chloromethylation did not take place when methoxyacetyl chloride was used. Therefore, further modification by quaternization as proposed in this project could not be accomplished because introducing either a $-CH_2NH_2$ or a $-CH_2Cl$ group as an intermediate step could not be achieved.

Table 5.2 The prepared polymers.

Polymer		m:n	$[\eta]$
1	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$	1.0:0.6	0.73
2	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$	1.0:0.0	0.93
3	$\left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$	1.0:0.0	--- ^a
4	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$ $\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$	0.5:0.5	0.33
5	"	0.6:0.4	0.52
6	"	0.7:0.3	0.32
7	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$ $\left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$	0.5:0.5	0.42
8	"	0.6:0.4	0.15
9	"	0.7:0.3	0.39
10	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$ $\left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$	0.5:0.5	--- ^b
11	"	0.6:0.4	--- ^b
12	$\left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_m$ $\left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4 \right]_n$	0.75:0.25	--- ^b
13	"	0.5:0.5	--- ^b
14	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4(\text{CN}) \right]_m$	1.0:0.0	0.50
15	$\left[\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4(\text{CN}) \right]_m$	1.0:0.0	--- ^b
16	$\left[\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4(\text{CN}) \right]_m$	1.0:0.0	--- ^b

Note:

^a = could not soluble in any solvents

^b = too small to measure

5.3 Evaluation of Developed Polymers for Membrane Applications

5.3.1 Materials and Methods

Figure 5.7 shows a schematic diagram for preparation of flat sheet membranes from the developed polymers. Firstly, the developed polymer was combined with one of the high boiling water miscible solvents from the group of N,N-dimethyl-formamide (DMF), N-methylpyrrolidone (NMP) and N,N-dimethylacetamide (DMAC) using 2-methoxyethanol (ME) and/or water as nonsolvent to form the casting solution. Secondly, the casting solution was poured over a glass plate at room temperature. Membrane casting was accomplished with a glass rod and the required thickness was controlled with the aid of an appropriate spacers provided on both ends of the glass plate. Thirdly, casted membranes were evaporated or annealed before immersing into a 15% NaCl solution bath in which solvent was exchanged with a precipitation agent and a gel was formed. The membrane formed was then cut into the required sizes, put into deionized water and stored in the refrigerator at 4°C.

5.3.2 Results and Discussions

The polymer concentration in the casting solution using the commercially available poly (arylene ether sulfone) (Aldrich Chemicals) was studied. The results are shown in Figure 5.8 and Table 5.3.

The performances of the resulting membranes were studied using a RO/UF flat sheet membrane test cell supplied by Nitto Denko Corporation. A schematic diagram of the set up is given in Figure 5.9. Pure water permeability of the resulting membranes with satisfactory characteristics as shown in Table 5.3 were determined. The results showed that the resulting membranes was too dense to be used because there was no permeate.

A composite membranes was produced by casting from the developed polymer 1, 2, 4, 5, 6, 7, 8, and 9 on porous substrate were investigated. A series of developed membranes were casted into 0.40 mm 100% non woven polyester substrate stuck onto a glass plate with the use of casting solution concentration having the ratio of polymers: N-methylpyrrolidone: 2-methoxyethanol = 12.5 g: 75.0 g: 12.5 g except that the casting solution concentration of polymer 2 and 8 was reduced to 8.0 g: 79.5 g: 12.5 g and 10.0 g: 77.5 g: 12.5 g, respectively because resulting membrane with the above concentration shown was too thick characteristics as shown in Table 5.4. The composite membrane form was preevaporated at room temperature for 5 and 20 minutes and then immersed into 15% NaCl solution bath to allow a gelation to occur. The performance of the composite membranes was evaluated to produce a clarified tangerine juice.

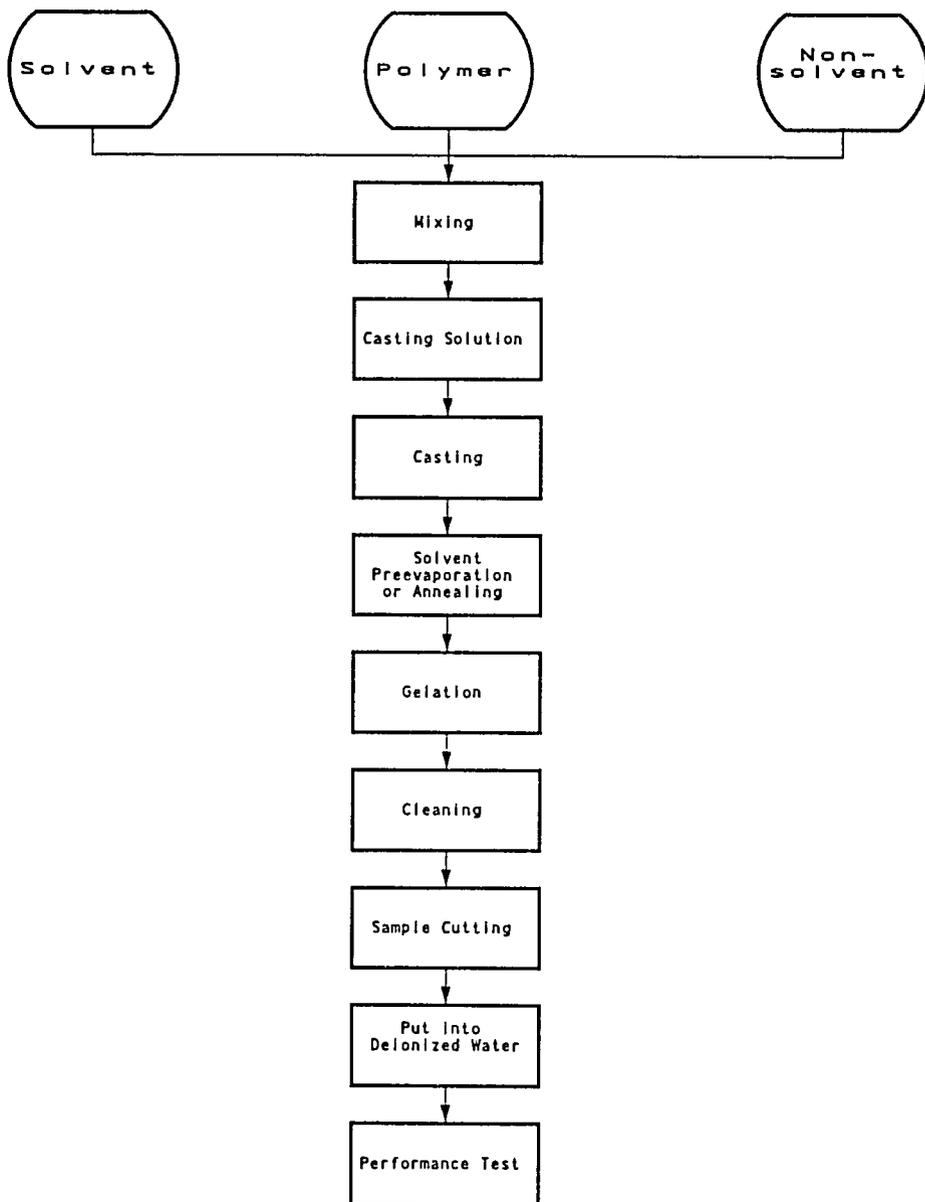


Figure 5.7 Procedure for the preparation of flat sheet membrane.

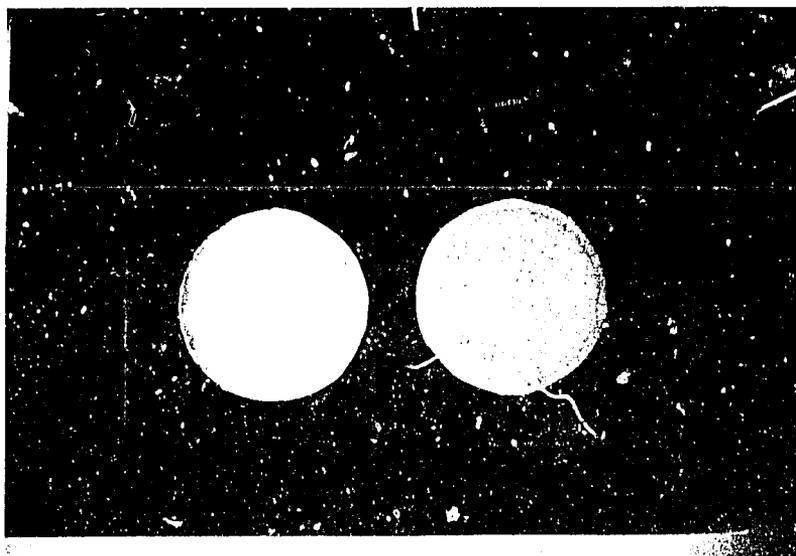


Figure 5.8 Formation of resulting membranes (left) poly (arylene ether sulfone) membrane and (right) is the composite membrane.

Table 5.3. Effect of polymer concentration in the casting solution on the resulting membranes'.

% Wt. of Casting Solution							Characteristics of Membranes
PS	NMP	PS	DMAC	PS	NMP	ME	
2.5	97.5	2.5	97.5	2.5	87.5	10.0	Imperfect
5.0	95.0	5.0	95.0	5.0	85.0	10.0	Imperfect
10.0	90.0	10.0	90.0	10.0	80.0	10.0	Satisfactory
12.5	87.5	12.5	87.5	12.5	77.5	10.0	Satisfactory
15.0	85.0	15.0	85.0	15.0	75.0	10.0	Too thick

Note:

PS = poly (arylene ether sulfone)

• = Cast polymers were immediately immersed in gelation bath without solvent preevaporation.

Table 5.4 Conditions of Making Developed Polymeric Membranes

Polymer	Casting solution composition (%w/w)			Membrane casting conditions		Clarifications performance at 2 bars
	P	S	NS	Preevaporation period at t, (min)	Annealed temp (°C)	% Transmittance
1	12.5	75.0	12.5	5	--	73
	12.5	75.0	12.5	20	--	72
2	8.0	79.5	12.5	5	--	57
	8.0	79.5	12.5	20	--	80
4	12.5	75.0	12.5	5	--	87
	12.5	75.0	12.5	20	--	80
5	12.5	75.0	12.5	5	--	98
	12.5	75.0	12.5	20	--	78
6	12.5	75.0	12.5	5	--	42
	12.5	75.0	12.5	20	--	80
7	12.5	75.0	12.5	5	--	87
	12.5	75.0	12.5	20	--	85
8	10.0	77.5	12.5	5	--	21
	10.0	77.5	12.5	20	--	83
	10.0	77.5	12.5	15	65	100
	10.0	77.5	12.5	30	65	88
9	12.5	75.0	12.5	5	--	85
	12.5	75.0	12.5	20	--	85

Note:

Casting atmosphere = 30-32°C, gelation temperature = 4°C

P = polymer, S = N-methylpyrrolidone, NS = 2-methoxyethanol

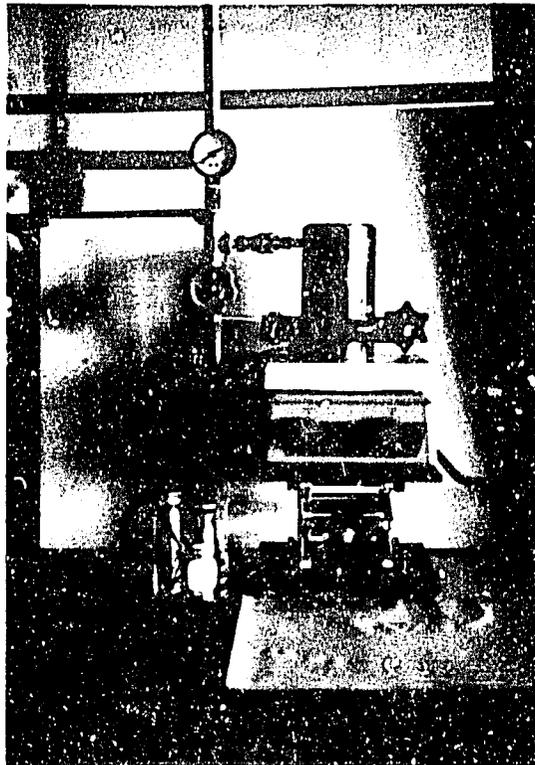
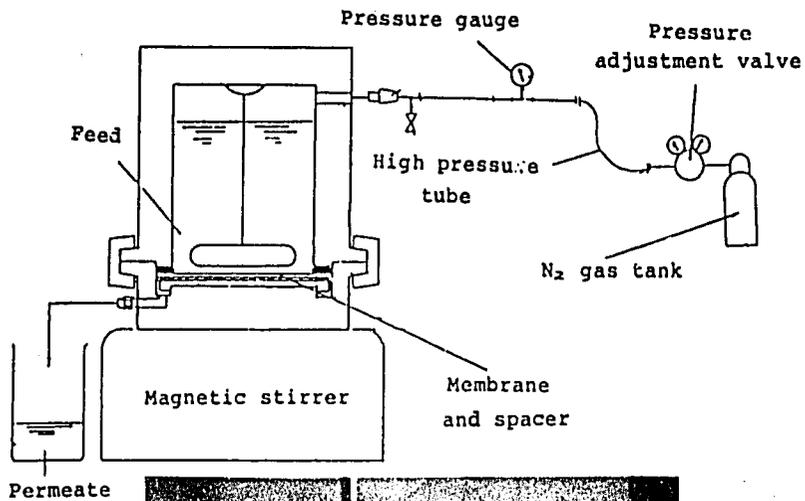


Figure 5.9 Schematic diagram of the test cell used.

Tangerine (*Citrus reticulata*, Blanco) juice for clarification studies were passed through a sieve (mesh = 0.18 mm) to remove physical impurities such as seeds, rag and pulp (Figure 5.10). Before running the experiments, all membranes were subjected with deionized water as feed so as to minimize the compaction effects during runs with tangerine juice at operating pressure of 200 kPa. The pure water permeability flux for all membranes with preevaporation at room temperature for 5 min. was shown in Figure 5.11. With all membranes, there was an initial rapid drop in flux in the first 10 min., followed by relatively steady flux as shown in Figure 5.12. Membranes with higher steady water flux might be due to having larger pore size but pure water flux for membranes with preevaporation at room temperature for 20 min could not be obtained due to the permeate rate was too fast to measure.

The permeate flux of tangerine juice was subsequently investigated. Permeated quality (% transmittance) was measured in % transmittance at 660 nm wavelength on a spectrophotometer with distilled water as blank²². Permeate quality improved with filtration time for all membranes as shown in Figures 5.13, 5.14, 5.15 and 5.16. Membranes with preevaporation of 5 min at room temperature showed lower pure water influx and gave better permeate quality, but the permeate quality of all membranes with preevaporation 20 min at room temperature showed a relatively value of 72-85% after within an hour. In membranes subjected to 5 and 20 min preevaporation, there was an initial rapid drop in permeate flux of the clarified tangerine juice in the first 20 min, followed by relatively steady flux. From there onwards, it was observed that all membranes filters gave approximately the same flux (3-6 l/m².h) as shown in Figures 5.17 and 5.18 which was probably affected by concentration polarization and gel formation.

The membranes obtained from polymer 8 which showed the worst clarification properties (21% transmittance) was further studied to improve its performance. Instead of having the composite membrane form to preevaporate, it was annealed at 65°C for 15 and 30 min. There was not much difference in pure water flux of the annealed membranes for 15 or 30 min but pure water flux of the annealed membranes were decreasing as shown in Figure 5.19 due to pore size shrinkage. The permeate flux and quality were also improve as shown in Figures 5.20 and 5.21.

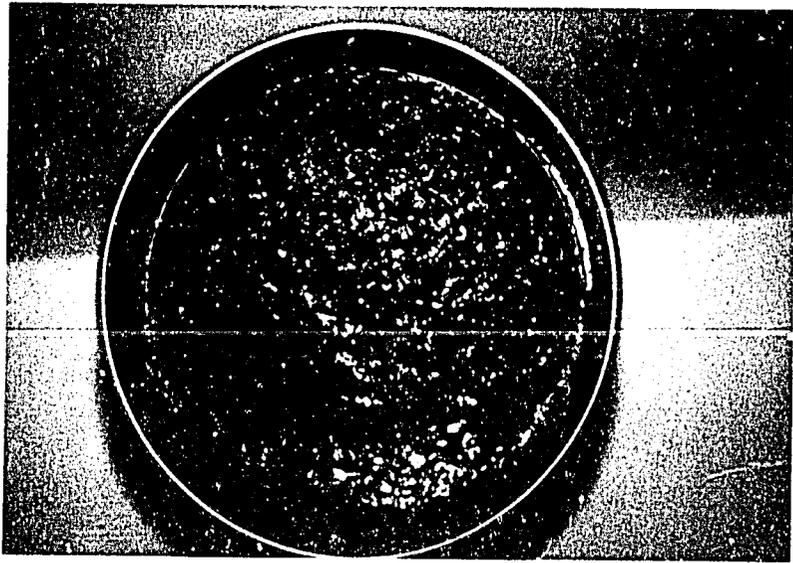


Figure 5.10 Physical components removal by sieve (mesh = 0.18 mm) in juice preparation.

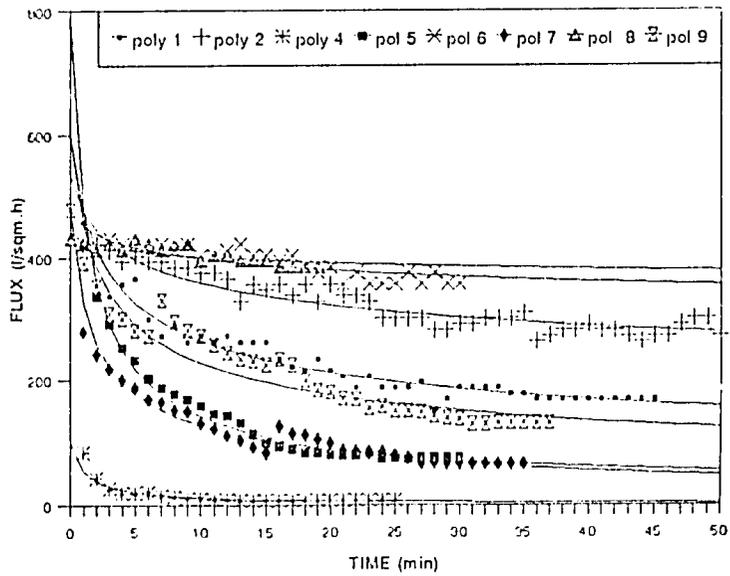


Figure 5.11 Pure water flux of composite membranes with preevaporation at room temperature for 5 min.

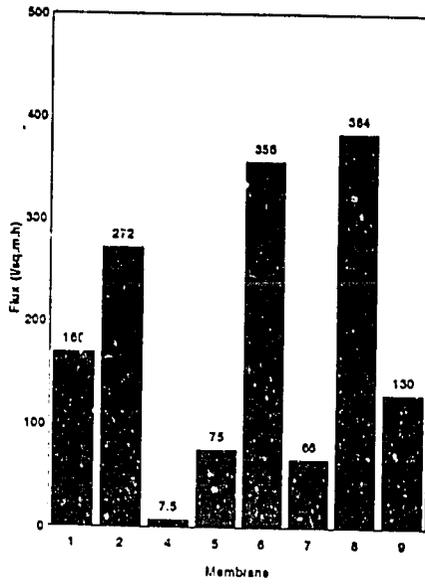


Figure 5.12 Steady-state pure water flux from membranes with preevaporation at room temperature for 5 min.



Figure 5.13 Physical appearance of tangerine juice before the filtration.

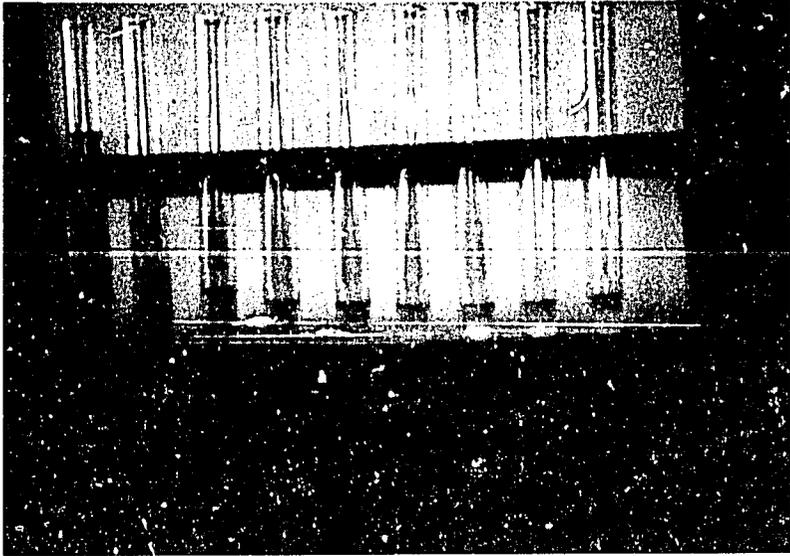


Figure 5.14 Clarity of permeate of tangerine juice improved with filtration time.

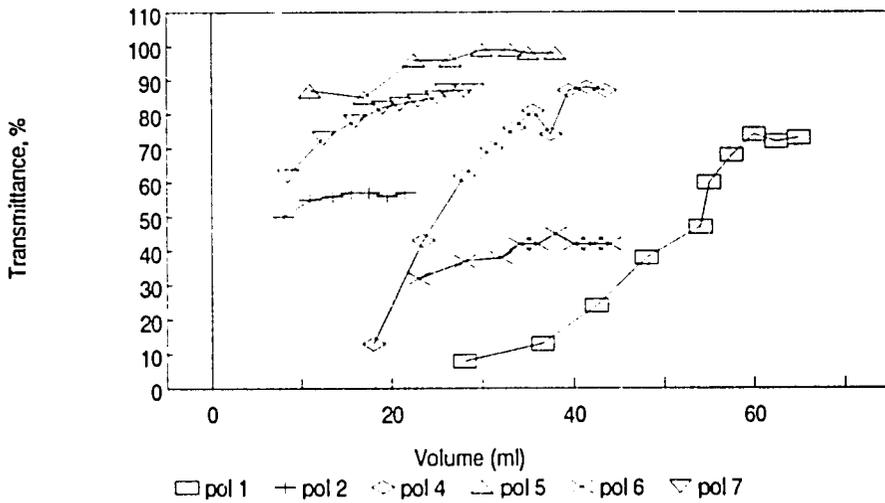


Figure 5.15 Permeate quality with filtration time for membranes with preevaporation at room temperature for 5 min.

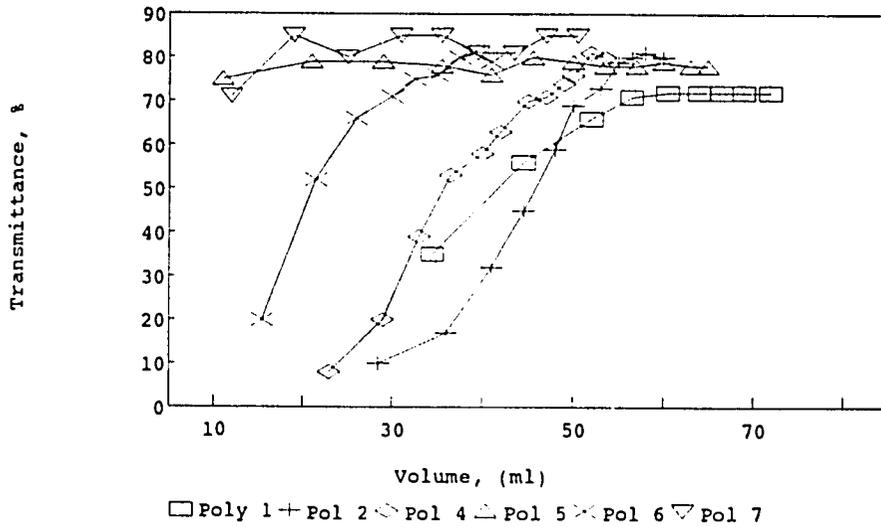


Figure 5.16 Permeate quality with filtration time for membranes with preevaporation at room temperature for 20 min.

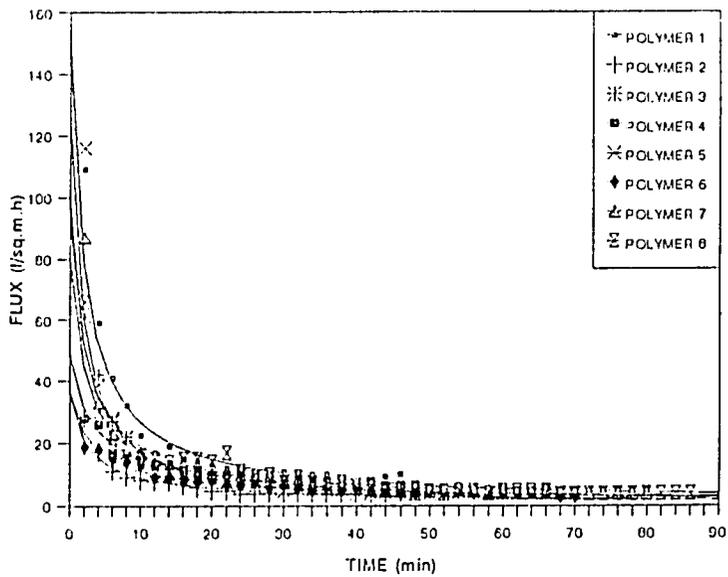


Figure 5.17 Permeate flux of the clarified tangerine juice from membranes with preevaporation at room temperature for 5 min.

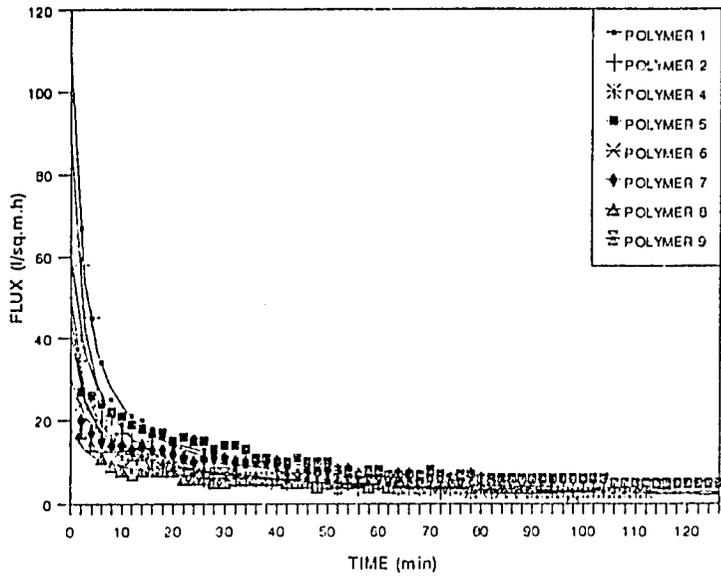


Figure 5.18 Permeate flux of the clarified tangerine juice from membranes with preevaporation at room temperature for 20 min.

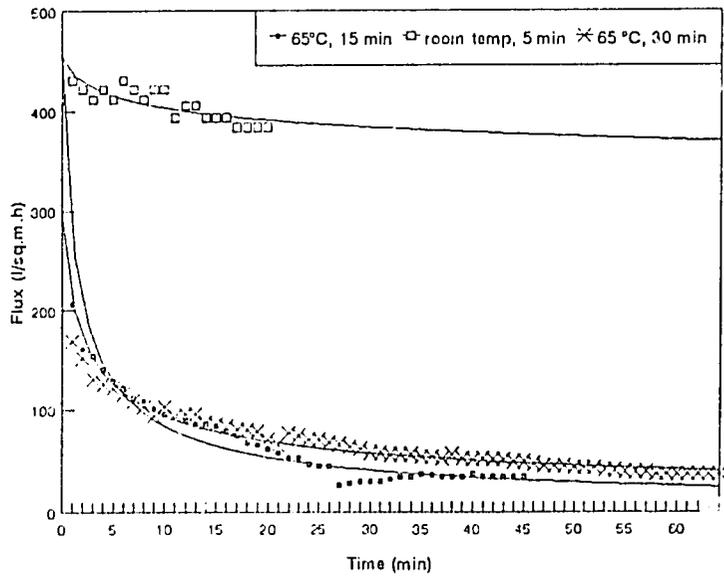


Figure 5.19 Comparison of pure water flux from polymer 8 membranes with different casting conditions.

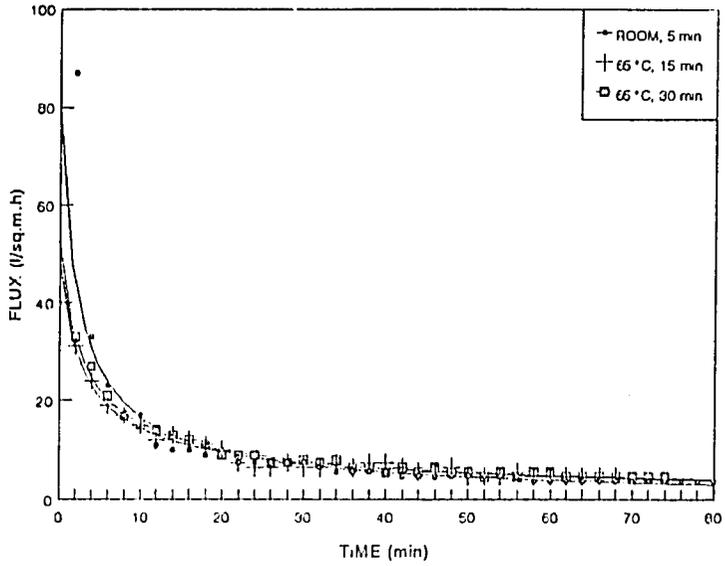


Figure 5.20 Comparison of permeate flux in clarified tangerine juice from polymer 8 membranes with different casting conditions.

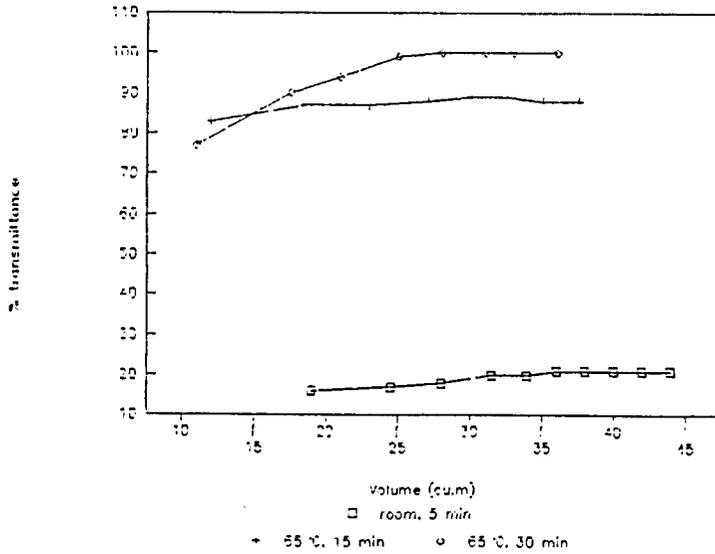


Figure 5.21 Comparison of permeate quality in clarified tangerine juice with membranes from polymer 8 at different casting conditions.

6. IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER:

The potentials of the membrane technology applications in developing countries including ASEAN is tremendous and very encouraging considering the emergence of novel agro-industries especially on fruit and beverage industries aim to produce high quality products intended for domestic consumption and for export. The polymeric membranes obtained from this project are very promising but more experiments will be conducted to obtain more reliable data so that the results will be useful. This project is the first of kind at Kasetsart University hence this serves as a pioneer research work carried out on membrane technology at the University. The equipment purchased from this grant are absolutely useful for further research activities on membrane technology and other related researches to be conducted in the future.

7. PROJECT ACTIVITIES/OUTPUTS

The principal investigator has attended two meetings related to membrane technology:

1) The IUPAC International Symposium on " Speciality Polymers " on November 7-9, 1990 held at Singapore.

2) The 3rd SPJS International Polymer Conference on " Membranes and Interfacial Phenomena of Polymers" on November 26-29, 1990 held at Nagoya, Japan.

There was no action taken on the request to AID or BOSTID to arrange a training program for the principal investigator in order to help resolve some problems encountered during the processing and application of prepared polymeric membranes.

8. PROJECT PRODUCTIVITY

The project did not accomplish some of the proposed goals. Only the first part of the project which is the preparation of poly (arylene ether sulfones) having good mechanical strength in large scale usable for membrane applications has been achieved. The problems encountered were:

8.1 Management Impact

i) There were no input from the collaborator since his first visit to Thailand between August 1-11, 1990. The collaborator has never replied to any communication sent. Two inquiries were sent to the collaborator. The first inquiry was to request him to nominate or designate another US scientist to take his place and the second inquiry was to ask for a possibility of conducting some experiments at the collaborator's University due to the delay of equipment for the project.

ii) The biggest problem encountered in the project was the hiring of skilled personnel. The research assistants hired for the project worked only for a short period and then transferred to the private sectors because of the lucrative incentives plus other fringe benefits and longer employment duration. The personnel hired under the project were on a temporary basis only and has to follow government regulations for salary standard. The personnel problem has caused considerable delay on the project and hence could not be accomplished on time.

8.2 Scientific Impact

i) Considerable effort has been devoted to overcome the problems encountered in the scale up production of the proposed polymeric materials with sufficient mechanical strength.

ii) It very difficult to obtain the desired membrane properties due to the inadequate experience and skills in membrane processing of the principal investigator.

iii) Modifications by chloromethylation and quaterization to produce enough quantity of polymer materials have not been overcome. As a consequence, intensive membrane performance testing was not carried out.

9. FUTURE WORK

The results of this study indicated that the proposed objectives could be achieved if the study will be extended. The only unfinished part of this project is the modification of poly (arylene ether sulfones) by introducing a positively charged quaternary ammonium salts on the polymeric membranes. The problems on the precasting has already been solved and the experience gained on membrane casting processes will definitely be useful to complete the project.

10. REFERENCES

1. M. Nyström and P. Jarvinen, J. Membrane Sci., 1991, 60, 275-296.
2. H. Jihua, W. Wentong, Y. Puchen and Z. Qingshuang, Desalination, 1991, 83, 361-371.
3. J. D. Le Roux and D. R. Paul, J. Membrane Sci., 1992, 74, 233-252.
4. T. Liu, D. Zhang, S. Xu and S. Sourirajan, Sep. Sci. Technol., 1992, 27, 161-172.
5. C. L. Radiman, H. Sangkanparan, V. S. Praptowidodo and O. B. Liang, Desalination, 1993, 93, 273-286.

6. I. Jitsuharu and S. Kimura, J. Chem. Eng. Japan, 1983, 116, 389-393.
7. W. M. Deen, B. Satvat and J.M. Jamieson, Am. J. Physiol., 1980, 238, F126-F139.
8. I. Jitsuhara and S. Kimura, J. Chem. Eng. Japan, 1983, 16, 394-399.
9. S. Kimura and A. Tamano, "Separation of Amino Acids by Charged Ultrafiltration Membranes" in Membranes and Membrane Processes, E. Driori and M. Nakgaki (Eds). Plenum Press, New York, 1986, 191-197.
10. W. H. Daly and S. J. Wu, in New Monomers and Polymers, B. M. Culbertson, and C. U. Pittman (Eds)., Plenum Press, New York, 1984, 201-222.
11. P. T. McGrail, P. D. MacKenzie and I. W. Parsons, EP 373, 783 (June 20, 1990).
12. S. A. Berger, R. Stewart and R. B. Wuchter, EP 327, 255 (August 9, 1989).
13. A. Warshawsky, N. Kahano, A. Deshe, H.E. Gottlieb and R. Arad-Yellin, J. Polym. Sci., Part A: Polym. Chem., 1990, 28, 2885-2905.
14. E. Hinke and E. Staude, J. Appl. Polym. Sci., 1991, 42, 2951-2958.
15. D. K. Mohanty, J. L. Hedrick, K. Gobertz, B. C. Johnson, I. Yilgor, E. Yilgor, R. Yang and J. E. McGrath, Polymer Preprint, 1982, 23, 284-286.
16. V. Percee, J. H. Wang and Y. Oishi, J. Polym. Sci. Part A: Polym. Chem., 1991, 29, 949-964.
17. W. H. Daly, S. Lee and C. Rungaroonthaikul, "Modifications of Condensation Polymers, Challenges and Opportunities" in Chemical Reactions on Polymers, J. L. Benham and J. F. Kinstle (Eds). ACS Symposium Series 364, Washington, 1988, 4-23.
18. W. H. Daly and C. Rungaroonthaikul, Polymer Preprint, 1985, 26, 148-149.
19. F. Abassi, P. Hodge and E. Khoshdel, Polym. Commun., 1988, 29, 368-370.
20. S. Itsuno, K. Uchikoshi and K. Ito, J. Am. Chem. Soc., 1990, 112, 8187-8188.
21. E. Stande and E. Breitach, J. Appl. Polym. Sci., 1991, 43, 559-566.
22. M. Chamchong and A. Noomhorm, J. Food Process Engineering, 1991, 14, 21-34