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# 역삼투막 재료

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(중앙대 화공과)

# Content

1. Aromatic Polyamides
2. Aromatic Polyesters
3. Polystyrene amides
4. Blend for RO membranes
5. Summary

# Factors Affect on The Performance in RO

## 1. Chemical Structure of The Performance in RO

- monomer structure

## 2. The High Structure of Polymer Chains

- Amorphous or Crystalline Structure
- Degree of Cross-linking
- Physical bonding
- Skin and Core Structure

# Materials for Active Skin Layer of RO Membranes

## 1. Aromatic Polyamides

( Aromatic Amine + Acyl Halide )

## 2. Aromatic Polyesters

( Bisphenol + Acyl Halide)

## ✓ 3. Flexible Main Chain with Amide Cross-linking

( Poly(p-aminostyrene) + Acyl Halide )

( Poly(m-aminostyrene) + Acyl Halide)

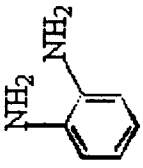
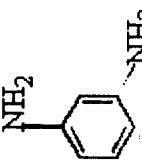
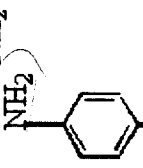
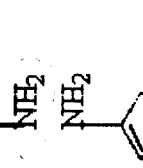
## ✓ 4. Polymer Prepared from Monomer Blend

{ Aromatic amine } + Acyl halide  
{ Polyaminostyrene }

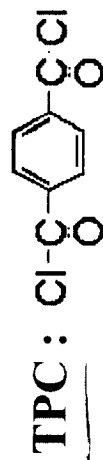
{ Aromatic amine } + Acyl halide  
{ Bisphenol }

# 1. Aromatic Polyamide

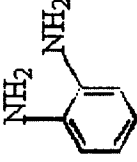
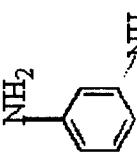
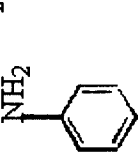
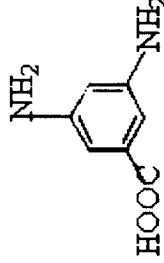
Table 1. Performance of RO Membranes Prepared from TPC and Various Diamines diaminebenzene

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	<b>OPDA</b>	10	1.24
	<b>MPDA</b>	12	0.47
	<b>PPDA</b>	40	0.82
	<b>DABA</b>	7	2.97

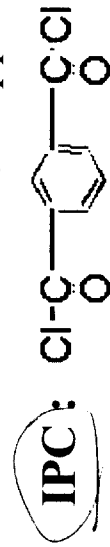
<sup>a</sup> Test condition : 2,000ppm NaCl, 30 atm, 25° C



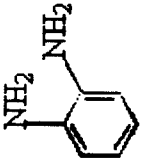
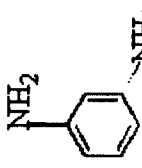
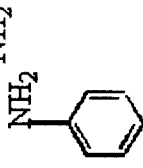
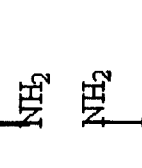
**Table 2. Performance of RO Membranes Prepared from IPC and Various Diamines**

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	<b>OPDA</b>	20	1.24
	<b>MPDA</b>	45	0.47
	<b>PPDA</b>	22	0.82
	<b>DABA</b>	17	2.97

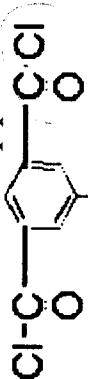
<sup>a</sup> Test condition : 2,000ppm NaCl, 30 atm, 25° C



**Table 3. Performance of RO Membranes Prepared from TMC and Various Diamines**

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	<b>OPDA</b>	86	1.24
	<b>MPDA</b>	98	0.47
	<b>PPDA</b>	91	0.82
	<b>DABA</b>	24	2.97

<sup>a</sup> Test condition : 2,000ppm NaCl, 30 atm, 25° C



**TMC:**

*2,4-dichloro-6-(chlorocarbonyl)benzoic acid*

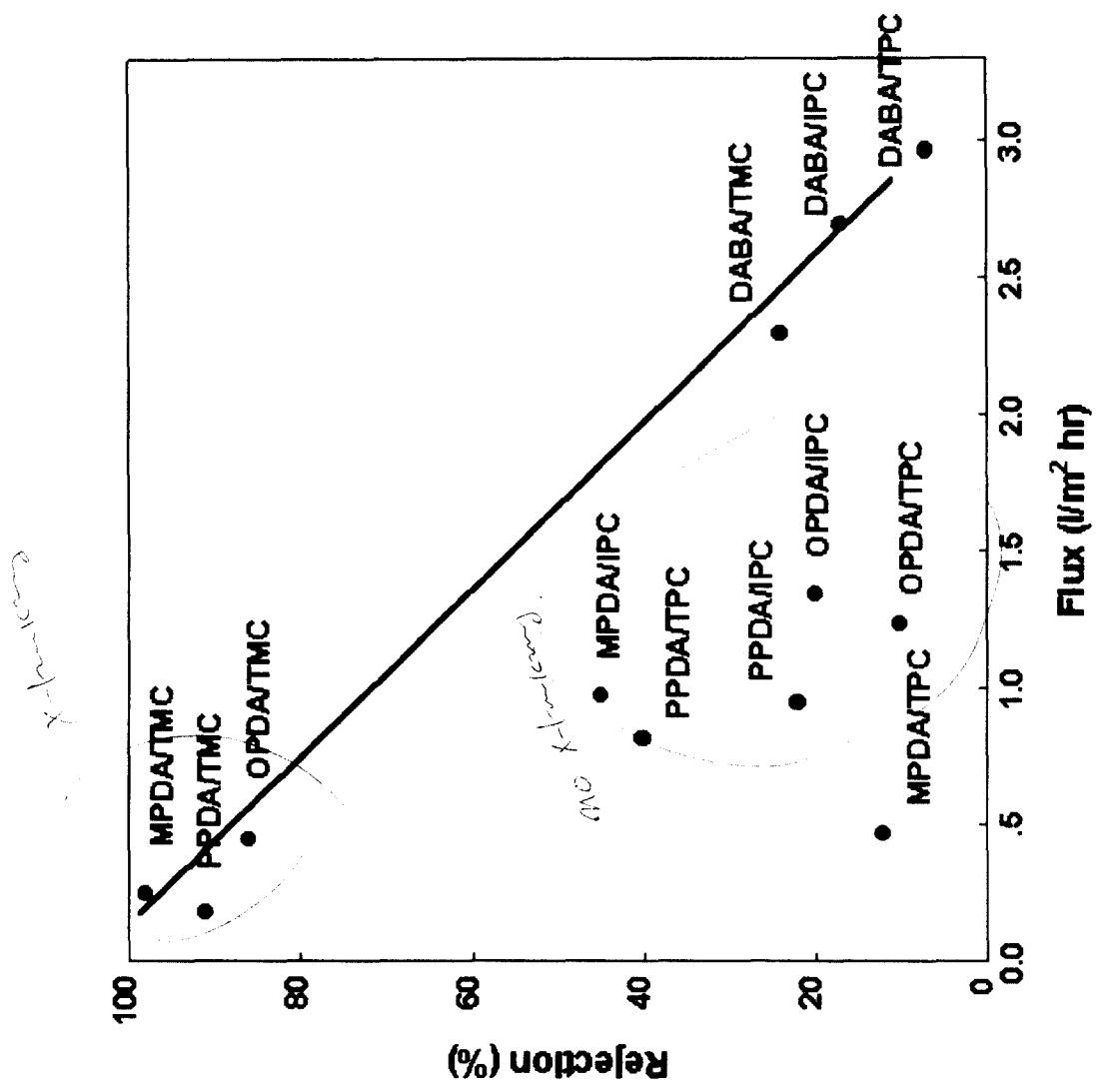
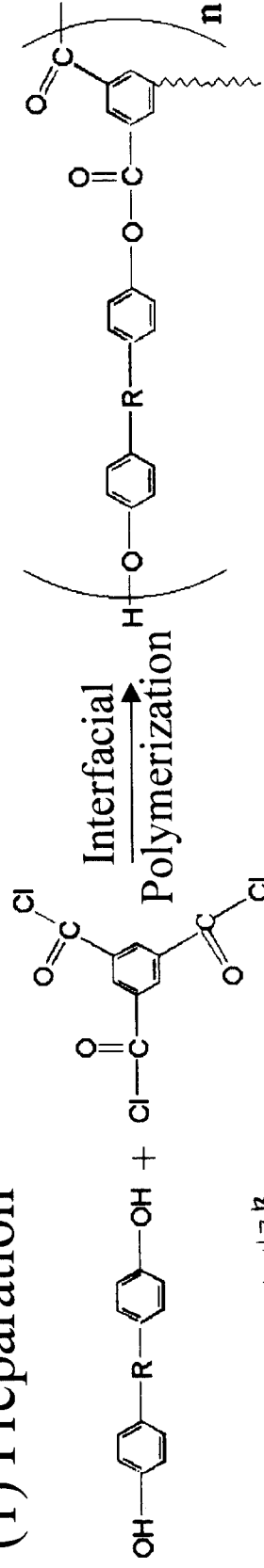


Figure 1 : Trade-off trend of RO Membranes prepared from various aromatic amines and acylhalides.



## 2. Aromatic Polyesters

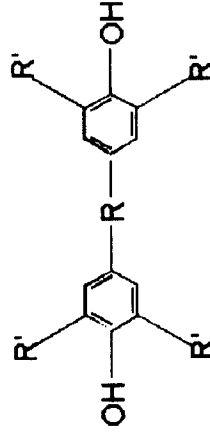
### (1) Preparation



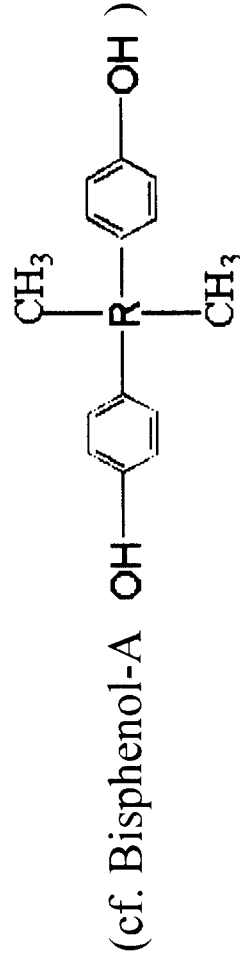
Bisphenol in NaOH  
aqueous solution

Acyl halide in  
organic phase

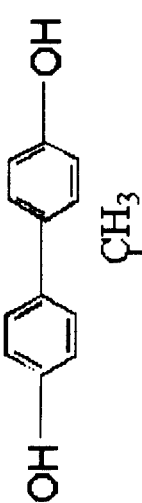
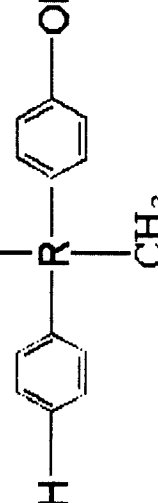
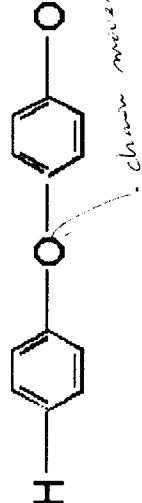
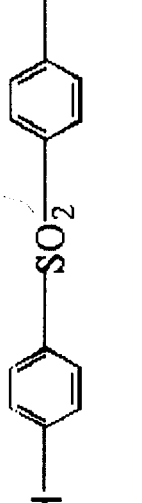
### (2) Structure Changes in Bisphenol



- Connector group (R) changes
- Phenyl ring (R') substitution
- Both (R,R') changes



**Table 4. Performance of RO Membranes Prepared from TMC and Various Bisphenols**

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	<b>BP</b>	60	0.8
	<b>BPA</b>	53	1.3
	<b>DHDPE</b>	50	1.5
	<b>BPS</b>	38	1.9

<sup>a</sup> Test condition : 2,000ppm NaCl, 30 atm, 25° C

(cf. MPDA + TMC (rejection : 98.5%, Flux : 0.25 L/(m<sup>2</sup>/hr))

**Table 5. Performance of RO Membranes Prepared from TMC and Various Bisphenols**

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	<b>BPA</b>	53	2.0
	<b>TCBPA</b>	80	0.22
	<b>TBBPA</b>	85	0.15
	<b>TMPPA</b>	70	0.5

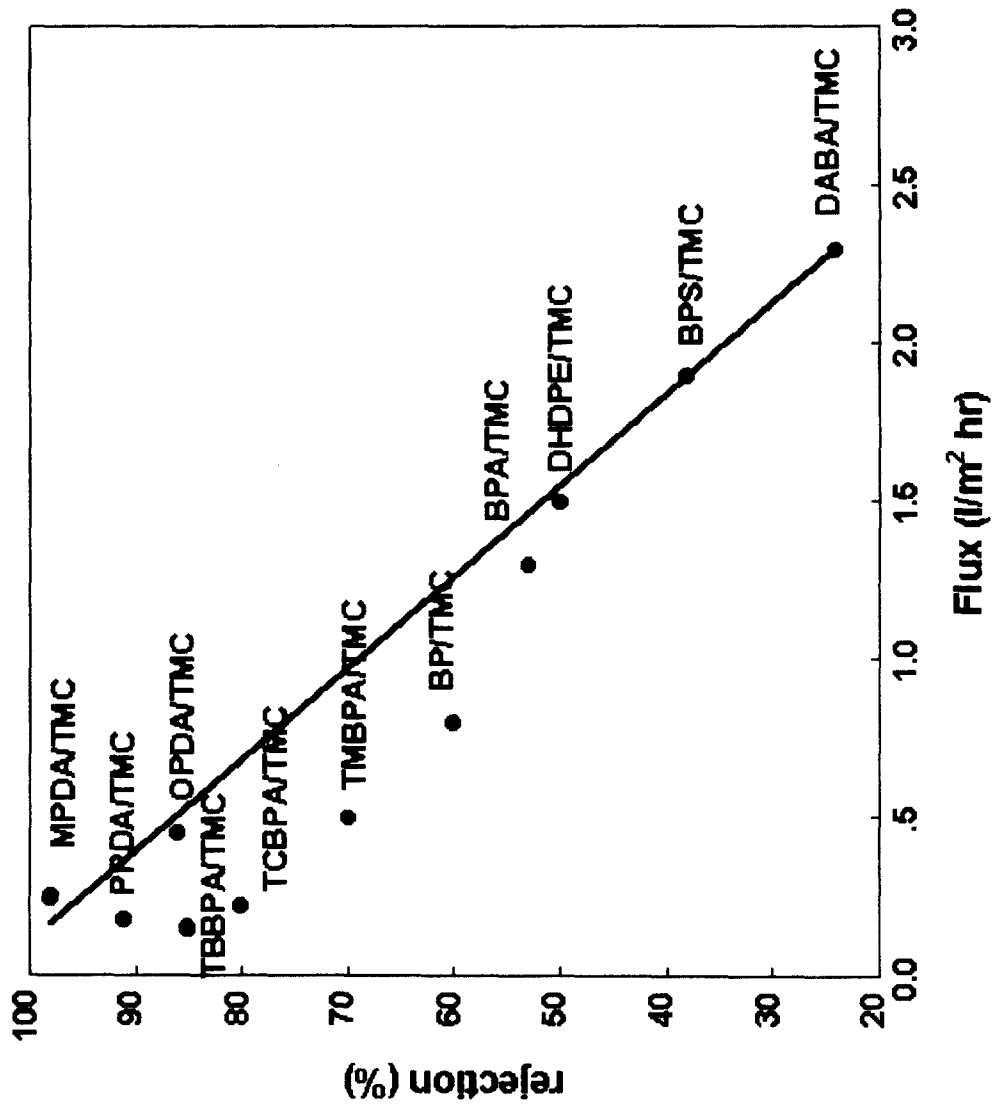
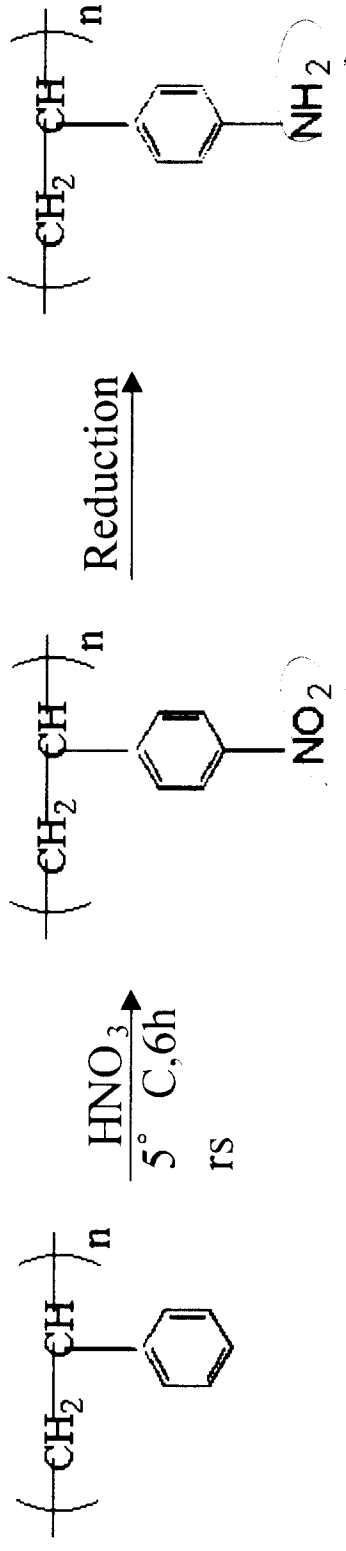


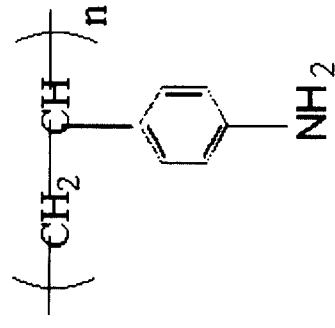
Figure 2 : Trade-off trend of RO membranes prepared from various bisphenols and TMC.

### 3. Polyamide Prepared from Poly(p-aminostyrene) and Aryl Halides

- Poly(p-aminostyrene)



- Active Layer



Aqueous phase  
PH = 5

+ Acyl halides

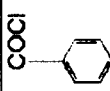
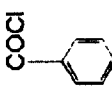
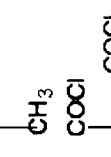
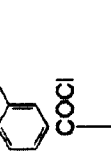
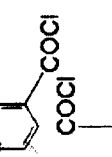
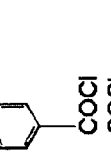
Organic phase

Interfacial  
Polymerization

Polystyreneamide

**Table 6. Performance of RO Membranes Prepared from Poly(p-aminostyrene) and**

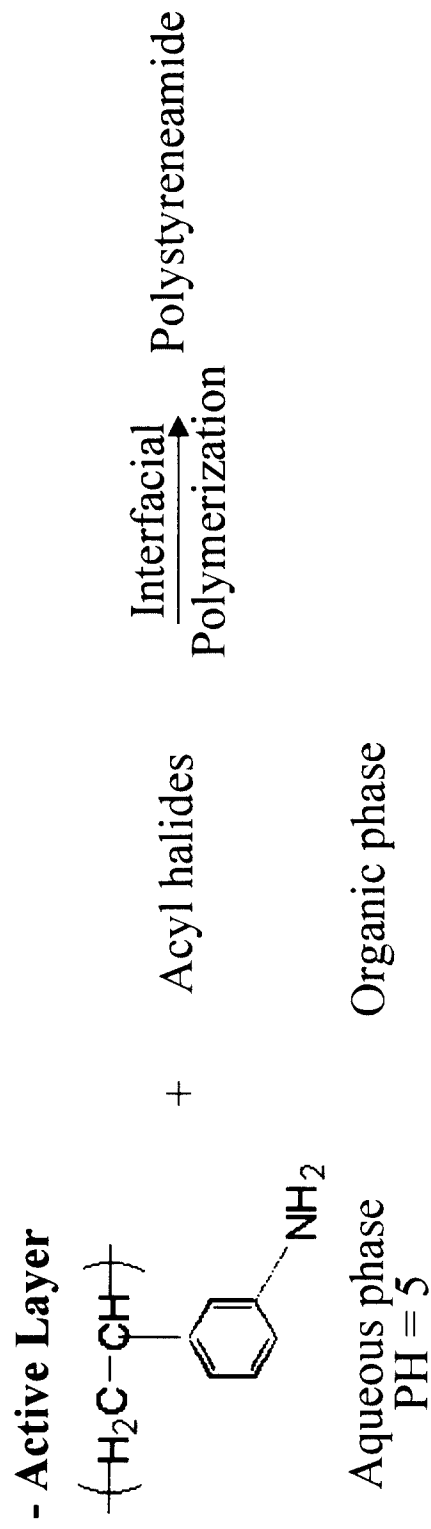
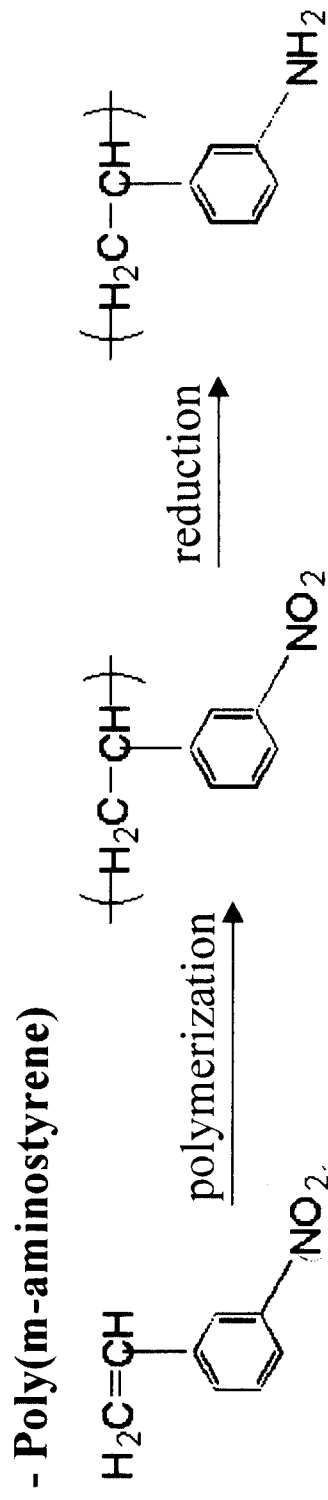
**Various acyl Halides**

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	<b>Benzoyl chloride(BC)</b>	2	3.1
	<b>p-Toluoyl chloride(PTC)</b>	2	2.4
	<b>Phthaloyl chloride(PC)</b>	11	2.2
	<b>Isophthaloyl chloride(IPC)</b>	29	1.0
	<b>Terephthaloyl chloride (TPC)</b>	33	1.6
	<b>Toimesoyl chloride(TMC)</b>	39	1.9

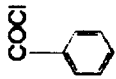
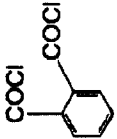
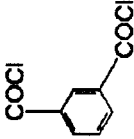
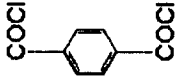
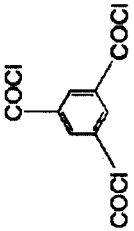
\* Hydroxy

Test condition : 2,000ppm NaCl, 30 atm, 40, 25° C

# 4. Polyamide Prepared from Poly(m-aminostyrene) and Acyl Halides



**Table 7. Performance of RO Membranes Prepared from Poly(m-aminostyrene) and Acyl Halides**

Structure	Abbreviation	Rejection (%)	Water Flux (L/(m <sup>2</sup> /h atm))
	Benzoyl chloride(BC)	—	3.1
	Phthaloyl chloride(PC)	33	1.1
	Isophthaloyl chloride(IPC)	51	0.82
	Terephthaloyl chloride (TPC)	57	1.03
	Toimesoyl chloride(TMC)	71	1.21

Test condition : 2,000ppm NaCl, 440psig, 25° C



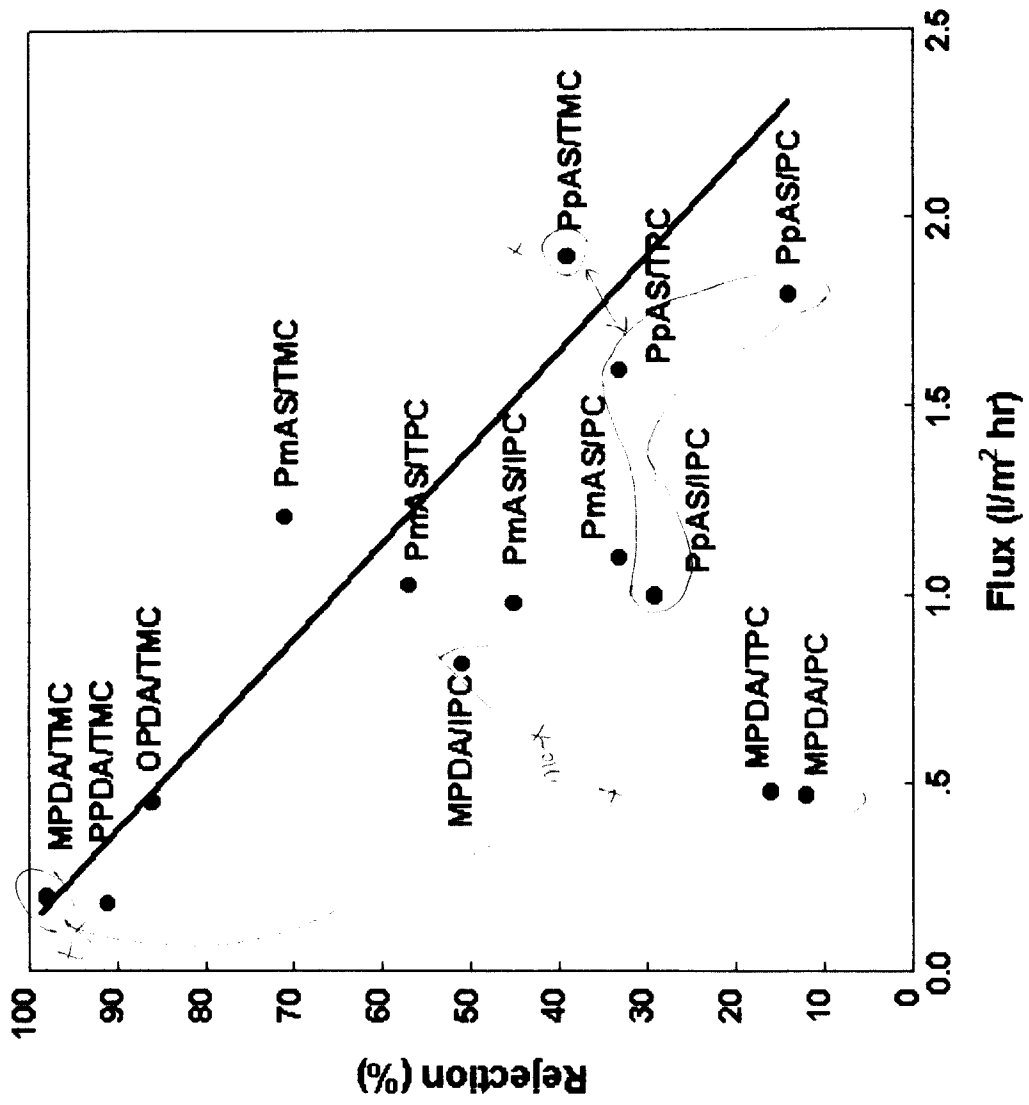


Figure 3 : Trade-off trend of various RO Membranes

# Monomer Blend for RO Membrane

## 1. (Bisphenol with aromatic diamine) / TMC = 5:5

→ Forms random copolymer of aromatic polyester and aromatic polyamide

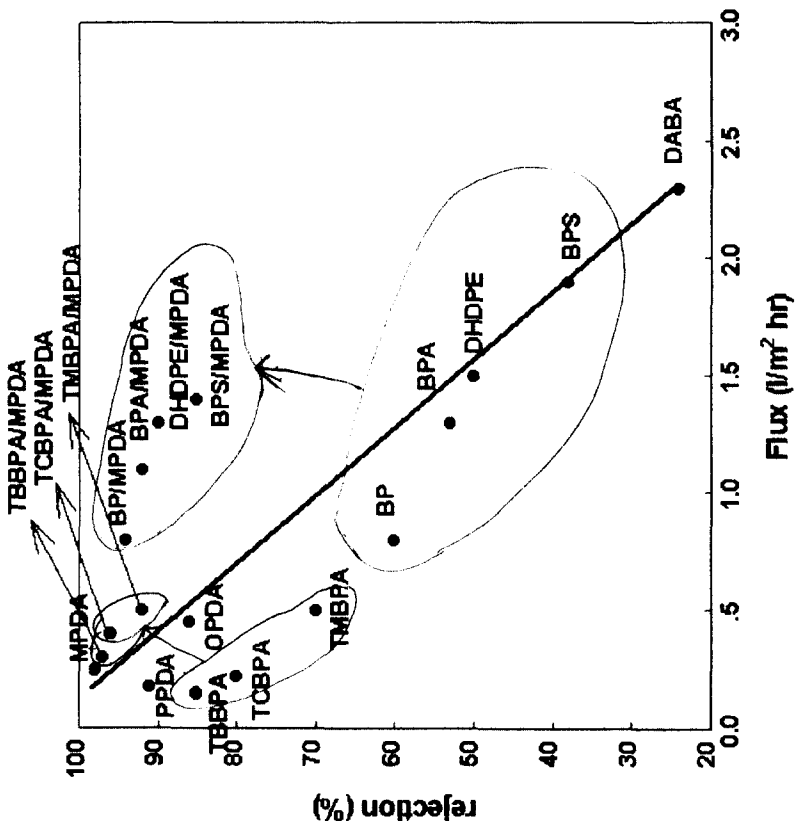


Figure 4 : Trade-off trand of RO membranes. TMC was used as a reactant of organic phase.

## 2. (PpAS with Aromatic diamine) / TMC

Active layer : composed of  $\left\{ \begin{array}{l} \text{Polystyrene amide} \\ \text{Aromatic polyamide} \end{array} \right\}$  blend

i) (PpAS + MPDA) / TMC

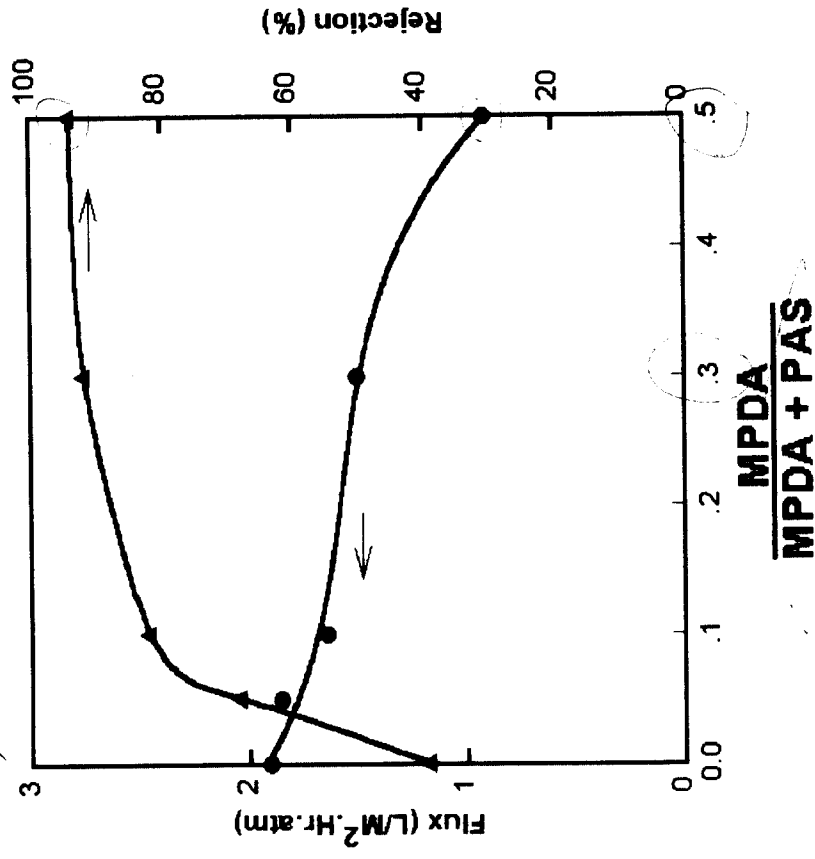
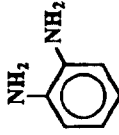
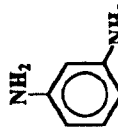
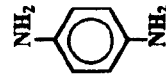
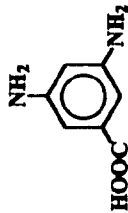


Figure 5 : Effects of MPDA content in the mixed solution of MPDA and PpAS. Mixed solution was reacted with TMC.

**Table 8. The performance of membranes prepared by interfacial polymerization of TMC with a mixed solution containing equal amount of PAS and various diaminobenzene**

Diamine monomer blended with p-PAS		Rejection (%)	Water flux (l /m <sup>2</sup> .hr.atm)
Structure	Abbreviation name		
	OPDA	52	1.58
	MPDA	94	0.91
	PPDA	81	0.78
	DABA	10	9.87

\* Test condition: 2,000 ppm NaCl, 30 atm, 25 C

\* Mixing ratio of diamine and polyaminostyrene is equal

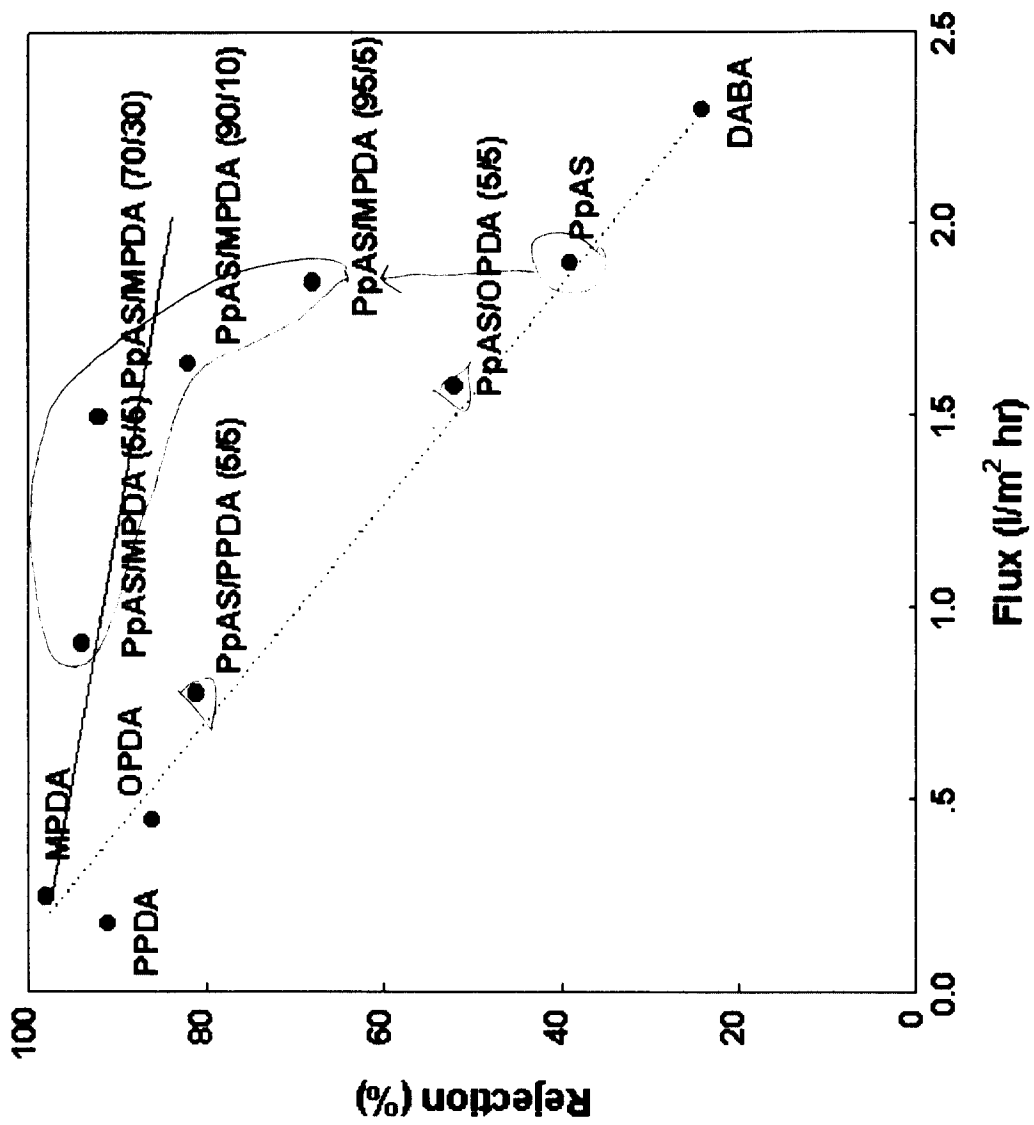


Figure 6 : Rejection vs. flux trade-off among the membranes obtained from the various polyamides. Polyamides were reacted with TMC.

### 3. PmAS Blend

- i) ( PmAS/Aromatic diamine = 5/5 ) with TMC  
→ ( PmAS / MPDA blend showed best performance )
- ii) ( TMC / di or monofunctional acyl halide = 5/5 ) with PmAS  
→ ( TMC / BC blend showed positive deviation from trade-off trend )
- iii) amine mixture ( PmAS / MPDA ) reacted with acyl halide mixture  
( TMC / BC )  
→ Large positive deviation from trade-off trend

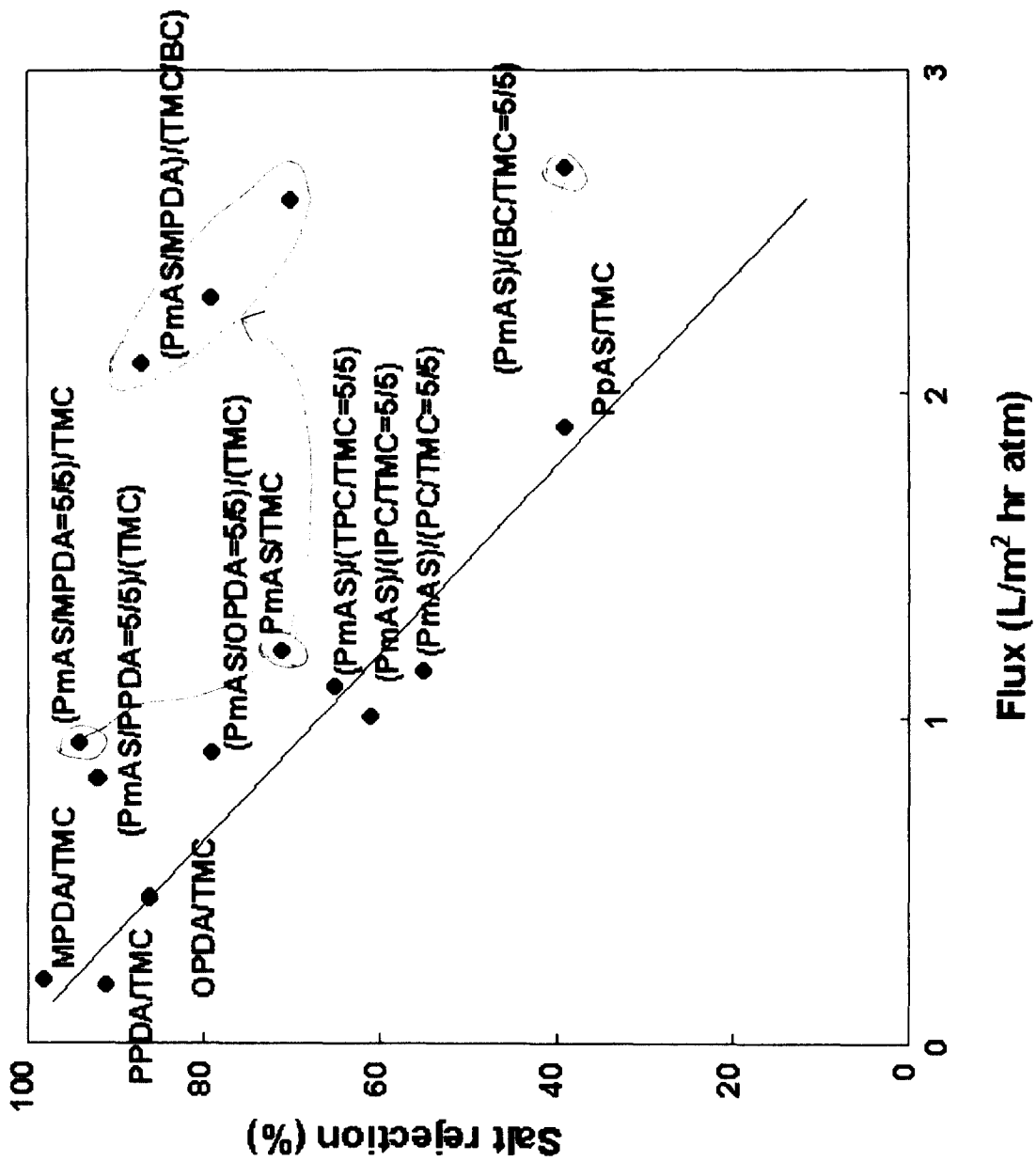


Figure 7 : Rejection vs. flux trade-off among the membranes obtained from the various polyamides.

# Summary

1. Performance of RO membrane depends on chain structure ( packing density )
2. Crosslinking of main chain is essential for the high performance RO membranes
3. Various bisphenols and polyaminostyrene can be promising materials for the fabrication of RO membranes.
4. By using of blend technique of reactant, we can expect broad spectrum of RO membrane and synergetic effects in membrane performance.