POLYMER MEMBRANES

Polymer Membranes -

Materials, Structures and Separation Performance

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(The Smart Chemical Company)

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Organisational Source → BASF AG

Developments in high performance composites are considered with particular attention being paid to carbon fibre reinforced epoxy resins. Activities of BASF in this field are described and information is given on the formation of BASF Structural Materials. The company's calendering facilities for CFRP prepreg manufacture are discussed as is the production of finished articles from such prepregs. Cost comparisons are made with metals, e.g. aluminium, for applications in the aircraft industry. Properties, especially mechanical behaviour, are described and compared with those of steel. ← Abstract

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Contents

1 INTRODUCTION

Membrane processes may be considered to approach ideal separation processes, in that they offer the possibility of selectively permeating one component from a mixture whilst rejecting others, in a continuous steady state. Consequently, membrane processes have gained in importance as economically viable and environmentally friendly methods to solve an increasingly wide range of problems over the last thirty years.

Whilst the principles utilised in membrane processes have often been known for over 150 years, it has not been until the latter part of this century that the technology to exploit these principles efficiently has evolved. As indicated in this review there has been a continuous growth in the number of scientific papers and patents covering all aspects of membrane technology, which shows little sign of diminishing (185, 216, 274, 327). Clearly there is still significant potential for further gains to be made in understanding, as well as improvements in, or development of, new technologies, which will ensure that membrane technology makes a much deeper impact on many aspects of our lives in the future.

Table 1 gives an indication of the very broad range of membrane technologies now available.

Table 1. Membrane Processes

Process	Application
Microfiltration	Separation of suspended particles
Ultrafiltration	Concentration and purification of solvents from macro-molecular solutions
Nanofiltration	Concentration and purification of solvents from medium molecular weight solutes
Membrane Distillation	Desalination and concentration of solutions
Dialysis	Demoval of low MW solutes from macromolecular solutions and suspensions
Electrodialysis	Desalination and de-acidification
Reverse Osmosis	Desalination, concentration of low MW solutes
Gas Permeation	Gas separation
Pervaporation	Separation of azeotropes and liquid mixtures
Liquid Membranes	Separation of ions and solutes from liquids

In general, membranes are thin layers, that can have significantly different structures, but all have the common feature of selective transport to different components in a feed. Membranes may be homogeneous or heterogeneous, symmetrical or asymmetrical, and porous or non-porous. They can be organic or inorganic, liquid or solid. A range of driving forces may be used, e.g. concentration, activity, pressure, electrical properties or temperature. Hence a wide range of processes are encompassed within membrane technology.

For some processes both membrane development and process design are so advanced that groundbreaking innovations cannot be expected for a long time, although existing systems are always open to improvement. Microfiltration, ultrafiltration, reverse osmosis, dialysis and electrodialysis are such processes. There is more potential for improvement, especially in membrane and module design, for nanofiltration, pervaporation, gas separation, controlled release and liquid membrane technology which are already used in some applications. Additionally there is still great potential for completely new developments. Processes based on electrochemical systems, sensors, catalytic membranes and membrane reactors require major developments, although some applications have already been recognised (139, 179, 253).

The overall performance of any particular polymer in a given separation is a function of both the chemical structure of the polymer and the physical form of the membrane. Within this overall structure, the exact way in which the polymer chains arrange themselves will affect the permeation characteristics, i.e. the amount of free volume between the chains and their relative ease of movement as well as the nature of the functional groups along the polymer backbone. Any study of the separation characteristics of polymer membranes needs to take into account these different levels of structure.

Consequently, this review begins with an indication of how separation performance is affected by the membrane structure. Then the processes of reverse osmosis (including nanofiltration), ultrafiltration, gas separation, pervaporation and electrodialysis are discussed, with the aim of providing a brief historical background to each membrane process, a description of the range of polymer membranes presently used, and an indication of some of the influences of polymer structure on performance. Finally recent research and some potential areas for future developments are discussed.

2 THE RELATIONSHIP BETWEEN MEMBRANE STRUCTURE AND SEPARATION PROPERTIES

Early work on the development of polymer membranes for desalination quickly showed that the performance requirements would not be met by the use of simple dense films of any polymer (a.1), and the apparent conflict seen in the need for a thin polymer film that was also self-supporting seemed insuperable. However, the development of the integral skinned asymmetric membrane by Loeb and Sourirajan in 1960 led to the breakthrough by the development of a thin (0.2μm) skin of polymer integrally supported on a porous sub-structure. The thin skin is the functional portion of the membrane, with its high density giving a selectivity which approaches that of a thick, dense film. The porous sub-structure functions as a mechanical support for the skin. Derived from this concept of a thin skin supported on a porous sub-structure, a broad range of membrane separation regimes have been developed and are described in this review. They differ from each other with respect to pore diameter of the thin skin and the range of particles that they retain.

Several authors have defined four levels of structure within these membranes through which it is possible to understand the properties of any synthetic membrane, irrespective of the type of polymer used to make the membrane or its application (92, 372, 380, 381, 407). These levels are as follows:

Level 1	Segmental composition of the polymer,
Level 2	Steric relationships in the segmental structure,
Level 3	Morphology of asymmetric membranes,
Level 4	Morphology of thin-film composite membrane.

It is evident that Level 1 affects all of the other levels of structure of the membrane. Levels 1 and 2 are primary properties of the polymer, whilst Levels 3 and 4 are properties of the membrane. Consequently, it follows that the ultimate performance of any membrane is a function of both the polymer type AND its mode of formation.

Whilst the bulk of this review deals with the relationship between polymer structure and membrane performance, the following section highlights the effects that membrane formation can have on performance. It is felt that these aspects are not always appreciated and need to be taken into acount whenever attempts are made to compare the performances of polymers from different manufacturers or scientific papers. In fact, recognition of this importance has led to the development of higher performance membranes then previously thought possible (129, 364, 375, 377, 380, 381).

2.1 Asymmetric Membranes

The details of the theory and practice of the formation of integrally skinned asymmetric membranes by the phase inversion process are discussed elsewhere (For example 92, 102, 129, 280, 283, 364, 381). However, a brief description is useful in order to indicate the many factors involved in the process.

Initially, the membrane may be cast either as a flat film or as a hollow fibre from a solution consisting of polymer, solvent(s) and non-solvent(s). The nascent film is then immersed in a quench medium that is a non-solvent for the polymer. The resulting exchange of solvent from the polymer solution to the quench solution results in a phase separation of the polymer solution into two phases with different compositions. Some non-solvent is incorporated in the initial casting dope in order to speed the precipitation of the polymer film upon the immersion in the quenching medium. The resulting membrane structure is thus determined by the compositions of the phases at the point of solidification of the polymer-rich phase. The actual phase compositions are a complex function of the polymer/solvent/non-solvent system used. Ternary phase diagrams have been used extensively to gain a detailed understanding of these parameters (102, 280, 281). The outer skin layer formation is determined by the higher concentration of polymer in this region which may be achieved by either a 'wet' (solution diffusion governed) or 'dry' (solvent evaporation governed) process in which solvent is removed from this area.

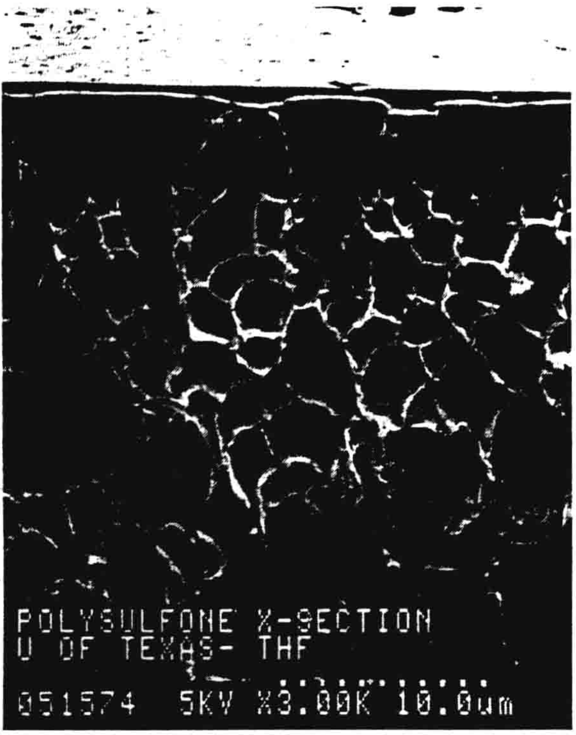

Figure 1

Structure of polysulphone membrane made by wet phase inversion characterised by delayed onset of phase separation. Casting system: 15 wt% polysulphone in tetrahydrofuran
Quench medium: methanol

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Figure 1 shows a typical 'wet' phase inversion membrane structure with a slow demixing step. Generally, these structures are defect-free but gas fluxes are very low due to the formation of thick skin layers (>1µm) and closed cell structures that offer significant resistance to permeate transport in the substrate layer.

A thin skin layer can be formed by the use of a casting solution/quench solution combination that results in an effectively instantaneous phase separation (due to a strong interaction between the casting solution and the quench solvent). The thickness of the skin layer is typically <0.2µm, but usually contains a relatively high proportion of microporous defects (>10^{-4} %). Coating these membranes with a defect-blocking layer of polydimethylsiloxane is necessary to achieve reasonable gas separation performances. **Table 2** indicates the range of performance variability arising from the use of different casting solvents.

It has recently been recognised that there is a relationship between the free volume of the polymer in the skin layer and the size of the solvent molecules in the casting solution (380, 381, 382). This led to the use of Lewis acid/Lewis base solvent systems, enabling the use of large solvent molecules which were readily removed on immersion in the quench solution (due to the break-up of the Lewis acid/Lewis base complex solvent into its component parts).

An additional advantage gained was that this solvent system resulted in the development of an extremely thin skin layer with a transition layer between it and the porous sub-structure, with the overall result of this being an increase in the flux but no loss of selectivity. Comparison between **Tables 2 and 3** indicates the performance improvement achievable by the use of large molar volume solvents.

The solvent system used in Table 3 was N-methylpyrrolidone with propionic acid at a 1:1 molar ratio (the membranes were subsequently coated with a polydimethylsiloxane defect blocking layer).

Table 2. Effect of Different Casting Solvents on the Gas Separation Properties of Asymmetric Polysulphone Hollow Fibre Membranes (381)

Solvent	Pressure normalised flux 10^{-6} cm^3/cm^2.sec.cmHg		Selectivity
	O_2	N_2	O_2/N_2
Triethylphosphate	26.1	7.9	3.3
Formylpiperidine	10.2	4.9	2.1
Dimethylacetamide	9.4	2.7	3.5
N-Methylpyrrolidone	4.4	1.5	3.0
Dimethylformamide	4.3	1.5	2.9

Table 3. Effect of Large Molar Volume Solvents in the Production of Integrally Skinned Asymmetric Membranes (380)

Polymer	Pressure normalised flux 10^{-6} cm^3/cm^2.sec.cmHg		Selectivity
	O_2	N_2	O_2/N_2
Polyetherimide*	0.5	0.063	7.9
Acrylonitrile-styrene copolymer (47% PAN)	10.4	1.73	6.0
Polysulphone*	43.0	8.3	5.2
Polyethersulphone**	13.1	2.6	5.1

* at 30°C; ** at 50°C

Integrally skinned asymmetric membranes are also produced by a dry/wet phase inversion process. In this case, instantaneous phase separation of the skin layer is achieved by solvent evaporation, whilst the bulk of the porous substructure is formed by solvent/non-solvent exchange during a quench step. This technique results in the formation of defect-free ultra-thin skin layers (as thin as 2nm), and is applicable to a wide range of glassy hydrophobic polymers suitable for gas separation (283). **Figure 2** shows a typical cross-section of such a membrane, whilst **Table 4** indicates the range possible (102, 337).

Production of a defect-free skin layer has been developed very recently by van't Hof et al (a.3).

2.2 Thin Film Composite Membranes

The thin film composite (TFC) membrane was developed as an alternative means of producing a thin separating layer on top of a more porous support layer. The advantage of the TFC is that the roles of the active, separating layer and the support can be separated, and each part made from the optimum polymer, rather than relying upon a single polymer to provide both good separating characteristics and mechanical strength.

They are prepared in two ways, and the first, which is utilised in the production of reverse osmosis membranes, involves the interfacial polymerisation of two components at the surface of a microporous membrane. The thickness of the active layer can vary from 20 to over 500nm depending upon the composition of the active layer (a.4).

The second method entails the application of a dilute polymer solution onto the surface of a microporous support. Whilst this process is essentially very simple, it has proved to be very difficult to form defect-free membranes with active layers much thinner than 1μm (102). This technique has been used for the formation of membranes from rubbery polymers for the removal of vapours from air.

Figure 2

Cross-section of a defect-free integrally skinned asymmetric polysulphone membrane made by dry/wet phase inversion

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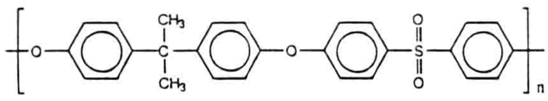
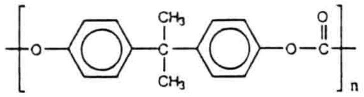
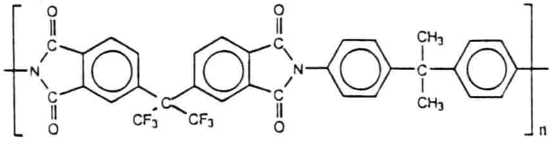
Table 4. Gas Separation Properties of Integrally Skinned Asymmetric Membranes made by Dry/Wet Phase Separation (T=25°C) (a.2)

Polymer	Pressure normalised flux 10^{-6} $cm^3/cm^2.sec.cmHg$		Selectivity		Skin layer thickness[a]
	O_2	H_2	O_2/N_2	H_2/N_2	(Å)
Polysulphone 	28	314	6.0	67	400
Polycarbonate 	52	424	5.1	42	300
Polyimide 	82	663	5.4	43	830

[a] Apparent skin layer thickness based on oxygen permeability coefficient
$P(O_2)$ Polysulphone = 1.1×10^{-10} (cm^3 cm/cm^2.sec.cmHg) (partial pressure)
$P(O_2)$ Polycarbonate = 1.5×10^{-10} (cm^3 cm/cm^2.sec.cmHg)
$P(O_2)$ Polyimide = 6.8×10^{-10} (cm^3 cm/cm^2.sec.cmHg)

Table 5. Gas Separation Properties of Thin Film Composite Membranes (adapted from ref. 102)

Polymer	Pressure normalised flux 10^{-6} cm^3/cm^2.sec.cmHg	Selectivity
	O_2	O_2/N_2
Polytrimethylsilylpropyne	1360	1.4
Polyketoxime organosiloxane	1500	2.2
Polydimethylsiloxane	330	2.1
Polyaminosiloxane	103	2.4
Ethylcellulose	26	3.8
Poly-4-methyl-1-pentene	24	4.3

Some recent studies have shown that it is very difficult to obtain defect-free membranes by this technique due to the non-uniformity of the microporous substrate (102, 277) and references therein). Consequently, it has proved necessary to plug the defects with a thin layer of a material such as polydimethylsiloxane.

Whilst the selective layer is many times less permeable than the microporous support layer, it has been found that when the selective layer is exceptionally thin the resistance to gas transport by the support layer is no longer insignificant. This has the net result that the selectivity of the composite membrane can be lower than that of the selective layer alone, even if it is defect-free (a.5). **Table 5** shows the gas separation properties of a range of thin film composite membranes.

2.3 Comparison of Permeation Properties between Asymmetric, Composite and Isotropic Membranes

The fundamental gas transport properties of polymers are often studied on isotropic films having thicknesses that are orders of magnitude larger than those of the skin layer of the final membrane and whose preparation route is radically different.

It is often forgotten that glassy polymers are non-equilibrium materials, and that their permeation properties will therefore depend upon their history and the preparation protocol. This lack of appreciation of the importance of the preparation protocol is evidenced by the small number of studies that have been made on this topic until very recently (232, 255, 260, 302).

Table 6 shows that asymmetric membranes made from a variety of polymers show increased selectivities when compared with isotropic films made from the same polymers.

Table 6.
Selectivity and Membrane Type
(255)

Material	Membrane Type	Selectivity O_2/N_2
Polysulphone	Isotropic Asymmetric	6.4 6.9
Polycarbonate	Isotropic Asymmetric	4.8 5.4
Polyester Carbonate	Isotropic Asymmetric	4.8 5.7

The activation energies for permeation of nitrogen and oxygen were found to be higher in the asymmetric membranes than in the isotropic membranes, suggesting that the free volume of the polymer in the asymmetric skin layer is lower. Most significantly, it was demonstrated that the permeation behaviour of CO_2 was completely different between the two types of membrane. In the isotropic case permeability declined with increasing pressure, whilst for the asymmetric membrane permeability increased with pressure. This clearly indicates that the skin layer morphology of an asymmetric membrane exhibits a smaller/different distribution of free volume than that of isotropic films due to the different preparation route. Similarly, very few studies have been made of the ageing effects of glassy polymer membranes until recently (232). This showed that a very significant time dependence exists for the gas permeation properties as shown in **Table 7**. The results indicate that the dependence may be due to a decrease in the fractional free volume and increased cohesive energy density of the polymers caused by more efficient chain packing.

Table 7. Gas Transport Properties and Selectivities in a 6FDA-IPDA Composite Membrane as a Function of Time (232)

Ageing time (Days)	Gas Flux 10^{-6} cm^3(STP)/cm^2.s.cmHg			Selectivity		
	N_2	O_2	He	O_2/N_2	He/O_2	He/N_2
0	4.1	19.8	115.5	4.9	5.8	28.4
20	0.8	5.2	57.4	6.5	11.1	71.5
Dense Film				5.1	8.8	47.0
Dense film age at test = 5 months						

2.4 Conclusions

The permeation properties of polymer membranes are strongly influenced by both the preparative route used and the final configuration (i.e. isotropic, asymmetric or composite) of the membrane.

The nature of the solvent(s) used can have a major influence on the effective free volume of the active layer as well as the permeability of the support layer due to the thermodynamics and kinetics of the phase separation process.

The non-equilibrium nature of glassy polymers can have a significant effect upon the stability of the performance of a membrane.

In thin film composite membranes, the nature of the substrate can have a marked effect on the final permeation properties.

Insufficient attention has been paid to these factors in much previous work, and if combined with the variable test conditions that are frequently used it is clear that simplistic comparisons of performance between different polymers are likely to be very qualitative at best.

Thus it is apparent that scope still exists for more careful studies to take place of structure/property relationships, taking all the above factors into account.

3 REVERSE OSMOSIS

3.1 Historical Perspective

3.1.1 Asymmetric Membranes

The development of reverse osmosis membranes originated from the investigations of Reid and Breton (a.1) in 1959 on a wide range of dense films. Of these, cellulose acetate (CA) with a degree of acetate substitution of approximately 2.6 gave the best result. This was probably because the material had the correct balance of hydrophilicity with intramolecular hydrogen bonding to give a high water sorption whilst maintaining sufficient structure to give good mobility selectivity.

However, the flux was very low due to the relative thickness of even the thinnest dense films that could be produced. This led to the development by Loeb and Sourirajan of an asymmetric, skinned CA membrane with a flux up to 500 times greater (a.6). A further significant improvement was made by Saltonstall in 1969 with the development of a cellulose triacetate blend membrane with CA (CTA/CA) (a.7) Later, membranes were produced from CTA alone that had superior properties to either the CA or the CTA/CA blend membranes.

Figure 3 shows a typical flat sheet asymmetric membrane structure.

A later development was the production of hollow fibre membranes from CTA by Dow Chemical (a.8). A problem with the CA type membranes is their tendency to hydrolyse slowly with time, with the rate of hydrolysis being dependent upon the feed constituents and the pH (a.9). In addition, they are prone to compaction under the high applied operating pressures used. Many variants on cellulose acetate have been proposed and studied (for example, 183, 344, 371), but in most cases overall performance has not warranted their replacing CA membranes completely (a.10). Use of cellulose acetate butyrate has been evaluated for the separation of organic mixtures (319).

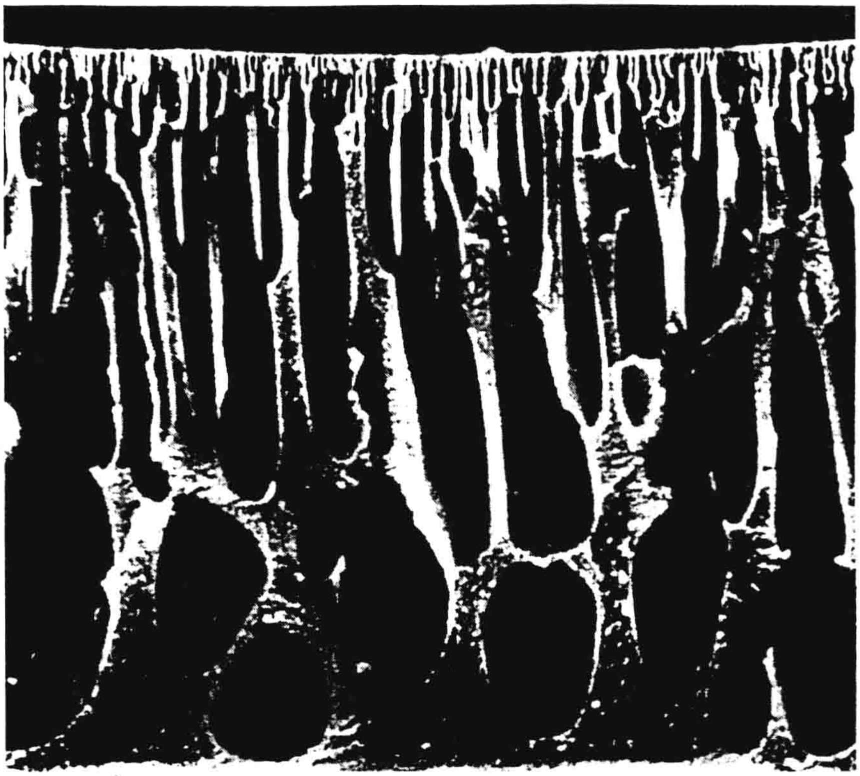


Figure 3

Scanning electron micrograph of the substructure of asymmetric membranes showing dense skin and porous substructure. Flat cellulose acetate membrane (total thickness ~ 100µm)

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Whilst the work of Reid and Breton attempted to relate polymer structure to performance, the revolutionary result of Loeb and Sourirajan in discovering how to produce a high flux, high selectivity membrane led to a concentration on improved methods of asymmetric membrane production, rather than further attempts to identify other polymer structures that would give a combination of high flux with high selectivity. This approach, of modifying the casting dope formulation tended to dominate published reverse osmosis research throughout the sixties and seventies, rather than a detailed partitioning of solubility and mobility factors that has been used in the gas separation area.

Membrane research on hollow fibre polyamide membranes in the early 1960s by DuPont (originally for gas separations) led to the introduction of an aromatic polyamide hollow fibre membrane for desalination of brackish water in 1969 (a.11). The materials used resulted from a careful balancing of the polymer composition and the steric relationships in the segmental structure, (structure levels 1 and 2 - see Section 2) by the use of mixed isomeric diamine monomers of phenylediamines with isophthalic and terephthalic diacid chlorides. See **Figure 4**. This approach allowed the use of relatively inexpensive monomers with excellent chain stiffening abilities whilst avoiding crystallisation in the dope or in the skin as would happen with the pure terephthalic or isophthalic aramids.

3.1.2 Thin Film Composite Membranes

The thin film composite (TFC) membrane was developed as an alternative means of producing a thin separating layer on top of a more porous support layer. The advantage of the TFC was that the roles of the active, separating layer and the support could be separated and each part made from the optimum

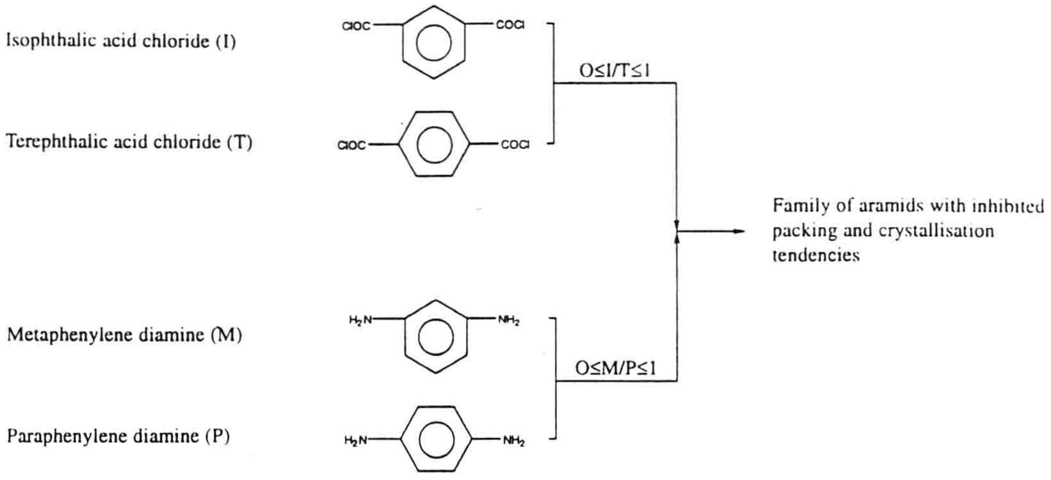

Figure 4

Illustration of tailoring of 'structure level' by copolymerisation

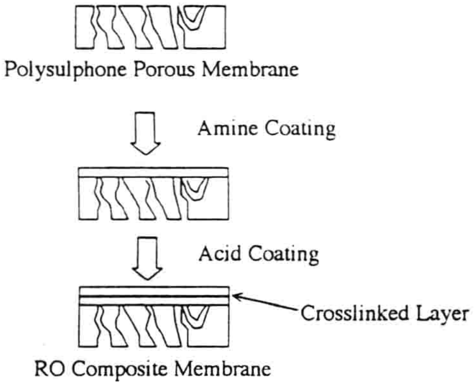

Figure 5

Typical TFC membrane structure made by an in-situ interfacial polycondensation method

polymer, rather than rely on a single polymer to combine both roles of having good separating characteristics as well as having the required mechanical strength for the support layer.

A typical TFC membrane consists of an ultra thin salt barrier layer that covers the surface of a porous polysulphone substrate. The salt barrier is formed by an in-situ interfacial polymerisation reaction or an in-situ crosslinking at the surface of a water soluble polymer layer. See **Figure 5** (a.12, a.13).

The first examples, made in 1964, consisted of cellulose acetate cast onto a porous support, but these never reached commercialisation. However, work by Cadotte in 1972 led to the first true TFC membrane to be commercialised. A detailed description of the history of the development of the TFC membrane has been given elsewhere (a.14).

TFC membranes have reached a major position among reverse osmosis membranes today due to their outstanding performance and durability (347).

3.2 Range of Applications

The main applications for reverse osmosis include production of high purity water, desalination of sea