

MODIFICATION OF POLYMERS FOR THE PREPARATION OF SEMIPERMEABLE MEMBRANES

MARIO PEGORARO

*Istituto di Chimica Industriale del Politecnico, Piazza Leonardo da Vinci 32,
20133 Milan, Italy*

ABSTRACT

A short survey is made of the principles to be followed in order to prepare membranes fit for the fractionation of a solute from a solvent. First it is essential to use substances with convenient chemical properties and then to prepare different membrane structures depending on the fractionation to be done.

The reaction of grafting is recognized as a very important means for the preparation of convenient materials. As an example, we report the results obtained in the desalination process using membranes consisting of polyacrylic acid grafted on polypropylene. Membranes may be obtained from solutions or by grafting in the heterogeneous phase on films bi- or mono-oriented through a radical mechanism by peroxidation or γ -irradiation.

Membrane structures observed with the electron microscope are described and the various results obtained in the desalination process are interpreted on the basis of the membrane structure. An interpretation is also given of the several transmission rates of water vapour, detected in the different types of membranes.

As is well known, a membrane is an interface between two fluid regions. By the action of a convenient driving force, chemical substances may pass through the membrane from one region to the other.

The search for artificial membranes through which various chemical species may pass at quite different rates has interested scientists, chemists and physicochemical researchers for more than a century. Research work led on the one hand to a better knowledge of the transfer principles, to the definition of osmotic pressure, to the theory of thermodynamic properties of solutions and to a considerable development of the thermodynamics of irreversible processes^{1, 2}; on the other hand, it led to the study and production of permselective membranes that find very important practical applications: for example desalting of sea and brackish water, artificial kidney, water pollution control, and the separation of isotopes 235 and 238 of uranium^{3, 4}.

The knowledge of the mechanism of selective transfer of substances on the molecular scale is fundamental to producing a membrane convenient for a given fractionation; up to now, however, it is not contained within an adequate theoretical system. Different mechanisms of transfer are often involved and a reliable interpretation can hardly be found: however, some useful qualitative interpretations have been refined.

The simplest possible mechanism for the selective transfer of a substance through a membrane is filtering. For example, using cellophane membranes, and since only the solvent may pass through them, it is possible to measure the osmotic pressure of high polymer solutions. By contrast, using only the simple 'sieve' mechanism, it is impossible to explain the selectivity of membranes hindering the transfer of ions dissolved in aqueous solutions; in fact, their size does not differ markedly from that of water that passes through the membrane (*Table 1*).

Table 1. Sizes of some typical ions²⁸

Ion	H ⁺	OH ⁻	Na ⁺	Cl ⁻	Mg ²⁺
Radius of hydrated ion, Å	2.82	2.46	3.58	3.32	4.28

The permselectivity mechanism can then be associated both with the solubility of the solvent (in the above case, water) in the membrane and with its diffusion (solution diffusion membranes). Although the membrane is macroscopically compact and homogeneous, it is never homogeneous on a molecular scale: actually, it consists of pores and channels whose size fluctuates with time; on the whole they represent the free volume of the polymer. If only the molecules of the solvent—and not those of the solute—can be adsorbed at the pore walls, the solvent fills up the pores and may easily pass from one adsorption centre to a neighbouring one, practically without requiring energy⁵. With cellulose acetate membranes, the adsorption forces of water to the polymer are essentially due to the hydrogen bond⁶.

In solutions in which the size of the solute molecules or ions does not differ much from those of the solvent, the selective transfer of the solvent may be also explained⁷ on the basis of simple considerations of surface tension and use of a membrane model with holes of very small size. It is sufficient that, at the membrane/solution interface, a negative adsorption of the solute takes place: i.e. the solute concentration at the interface is lower than that in the solution. In this way, a layer of pure solvent with thickness t is formed on the membrane. If holes exist with maximum diameter $2t$, there may be a perfect fractionation of the solvent.

By considering the value of $2t$ (a few Å: if the interface is between air and a salt solution, $2t = 8$ Å) this mechanism does not require a physical model of a membrane differing markedly from the previous one.

SOLUTE REJECTION

In order that a membrane may exert a non-transfer action for the solutes, it is useful that the equilibrium partition constant of the solute between the material of the membrane and that of the solution is as low as possible.

However, equilibrium considerations are not enough, as usual, to explain the mechanism of mass transfer and rejection.

A possible explanation that is very convenient for desalination is the one based on the fact that membranes consist of materials having a dielectric constant lower than that of the solvent⁸. It is possible to demonstrate that the energy of an ion contained, for example, in an aqueous hole, is much higher than for an ion in solution: consequently the probability of the ion remaining in solution is high. This mechanism is especially apt for non-polar membranes.

The selective action of repulsion of the salts dissolved in water may be improved by the use of polymers containing ionic active centres (charged membranes). Since electroneutrality must be maintained, the passage of cations will be hindered if the salt anions are blocked by active centres in the membrane and vice versa (Donnan effect⁹).

MEMBRANE CLASSIFICATION

Actually, membranes with sufficiently large pores (porous membranes), several sizes larger than the average free run of passing molecules (100 Å–10 μ), are interesting owing to the possibility of high flowrates, obeying the Poiseuille rule (viscous flow)¹⁰ but less interesting if one has to separate small dissolved ions with dimensions comparable to those of the solvent. Separation of the solvent from the solute is possible only if the concentration of the solute in the liquid pore differs from the concentration in the external solution. This happens only if a membrane effect exists. In general viscous flow (bulk flow) transfer is less selective than that occurring with a solution-diffusion mechanism in compact and non-porous membranes constituting the second limit class of membranes (solution diffusion membranes). Obviously intermediate types of membranes are possible (finely porous membranes), in which transfer occurs partly through a bulk mechanism, although the interactions between membrane and penetrating substance are very important¹¹. Pore diameters in this type have a mean value of 7 to 50 Å.

As clearly shown from the above, in order to obtain a membrane that will allow the selective passage transfer of the solvent and not of the substances dissolved in it, it is necessary: (1) to choose a solid substance insoluble in the solvent, but with a good chemical affinity toward the solvent and not toward the dissolved substances; moreover, it must possess good mechanical properties and good ageing properties; (2) the substance chosen must have an adequate structure, i.e. containing pores with a small equivalent diameter.

Composite structures consisting of a compact thin skin (porous on the molecular scale) and of a thick porous (on a macroscale) layer acting as a skin support, were largely successful¹².

Owing to their easy processability and convenient properties, polymers are widely used for the production of membranes. A number of homopolymers and copolymers¹³ have been studied and some of them are now also used in considerable quantities on a pilot plant or semi-industrial scale. Grafting is certainly one of the most versatile tools for regulating the properties defined at the outset. For example, water-soluble polymers, e.g. polyacrylic acid, may become insoluble by grafting them to an insoluble polymer¹⁴; hence the system may be swollen in water and has good properties of water transfer; polymers that are convenient to desalting (cellulose

acetate but showing irreversible compressibility phenomena become stiffer after polystyrene grafting¹⁵. The reaction of grafting is an additional operator: it does not substantially change the main properties of the backbone polymer (A), but it adds the properties of the grafted polymer (B). Although the two polymers A and B have different cohesive energies, they can become compatible on the visible and macroscopic scale. However, this does not occur on a molecular scale; in fact in the solid state a biphasic structure is formed¹⁶ with finely interdispersed domains of phases. Therefore grafting also markedly influences the structure of the membranes. In particular, grafting may disturb packing of the macromolecules: depending on circumstances, structures may assume a higher or lower free volume (and more or less low densities) than those corresponding to the simple additivity rules and consequently may become more or less permeable.

For example, in the case of polypropylene, grafting of a polyhydrocarbon, such as polystyrene, improves the permeability to water vapour¹⁷.

Moreover, when the membranes are obtained from a solution, the use of a solvent that is good for A and bad for B, makes the molecules of B contract in solution: the structures obtained are completely different from those obtainable with a solvent good for B and bad for A. In this respect, we mention, by way of example, poly-2-vinylpyridine grafted on polystyrene¹⁸.

REACTIONS OF GRAFTING

Materials convenient for membrane production may be prepared by reactions both in the heterogeneous and in the homogeneous phase. In the first case, the starting product is generally a pre-formed film (e.g. nylon, teflon, polypropylene), and grafting is usually done with the chosen monomer in the presence of convenient initiators, often by irradiation¹⁹ or sometimes by using peroxidic functions²⁰ fixed by peroxidation on the film to be grafted or other convenient chemical functions.

These methods are quite handy and relatively simple since they start from a pre-formed matrix. By contrast, when operating in the homogeneous phase, all the reagents must be in solution; moreover, the membrane must be filmed—which is a further difficulty. The latter method, although less easy, is very interesting: by it, in fact, it is possible to obtain different structures depending on the operating conditions.

Among the methods quoted, the technologically simplest one uses radiation grafting starting from a polymeric film. This method is very flexible since it allows grafting of the desired monomers on films of practically any polymer. Since 1957, i.e. since Chen published his research on the preparation of membranes consisting of sulphonated polystyrene grafted on polyethylene by radiation²¹, many articles have been published on this topic¹⁹.

We were the first who in 1968 obtained membranes by chemical grafting in solution of high-melting crystalline polymers followed by high-temperature film-making²⁰.

We report here the main results obtained from the research we carried out concerning the preparation and study of the properties of some membranes from 1967 to the present time.

(a) Preparation of membranes from preformed films

In our laboratory we used polypropylene and Saran films. Grafting was done with different monomers: in the first case the backbone polymer was peroxidized and in the second copper complexes were used²². The structure of the starting film is very important, since phenomena of monomer diffusion and the grafting sites depend on the structure. Looking at the surface and cross section of a bioriented polypropylene film (density 0.90) by scanning microscope, we observed²³ that its structure consists of compact lamellae not easily distinguishable. In order to perform grafting, it is necessary to introduce by oxidation²⁰, after elimination of the stabilizers by carbon tetrachloride extraction, hydroperoxide groups (range 0.1 to 0.6 per cent of active oxygen) which disturb the structure causing reliefs in some regions (*Figure 1a*) and detach the lamellae (*Figure 1b*). After grafting with acrylic acid, the lamellae become much more distinct than before (*Figure 2*), and the shape of superficial irregularities is changed²³.

When starting from a commercially so-called un-oriented film (density 0.89, thickness 20 μ) we observe (*Figure 3*) the section structure prevalingly with one-direction orientation (thick laminae) and several irregularities in the direction perpendicular to it²³. Un-oriented films also show a higher permeability to water vapour than bioriented ones²⁴. After extraction of stabilizers at room temperature by benzene, peroxidation causes some structural modification (laminae detachment²³ and grafting may occur in such a way that the original structure is modified in depth (*Figure 4*): laminae disappear and a microporous structure is generated.

Radiation of moplefan by γ -rays (⁶⁰Co source) causes some changes that appear²³, however, not very important in the scanning microscope especially for bioriented moplefan.

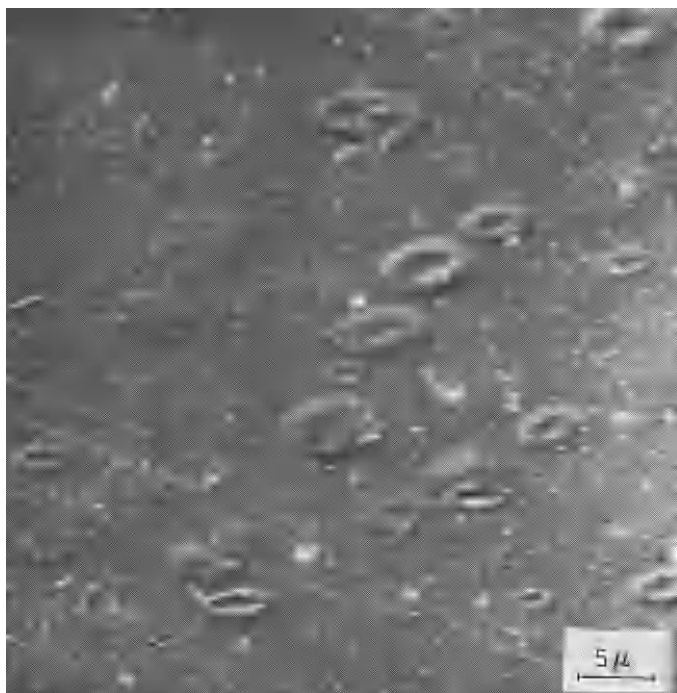
Grafting by irradiation of polyacrylic acid produces modifications of structure with both bioriented and un-oriented (*Figure 5*) moplefan: the original lamellar structure is not maintained.

(b) Preparation of membranes from solutions of grafted polymers

Table 2 shows some of the extraction membrane types obtained after starting with two different backbone polymers, one crystalline and one amorphous; the main monomers used and the conditions adopted for the extraction. Since polypropylene is soluble only at high temperatures, high temperatures must be used for grafted membrane extraction (120° to 140°C). It is convenient to carry out grafting directly at these temperatures, immediately before the extraction. A thorough study of the reaction under such conditions for the grafting of acrylic acid was recently published¹⁴. After completing the reaction, in order to avoid degradation, stabilizers should be added and film-making of the membrane should be carried out quickly.

Film-making may be carried out by various techniques: we found it very convenient to extract a glass cylinder from a hollow cylinder containing the solution operating in a thermostat at a high temperature (120° to 140°C). In this way, depending on the extraction rate and on the composition of the reaction mixture, it is possible to obtain by evaporation membranes of different thicknesses²⁵ between 2 and 30 μ . After forming, membranes are

(a)



(b)

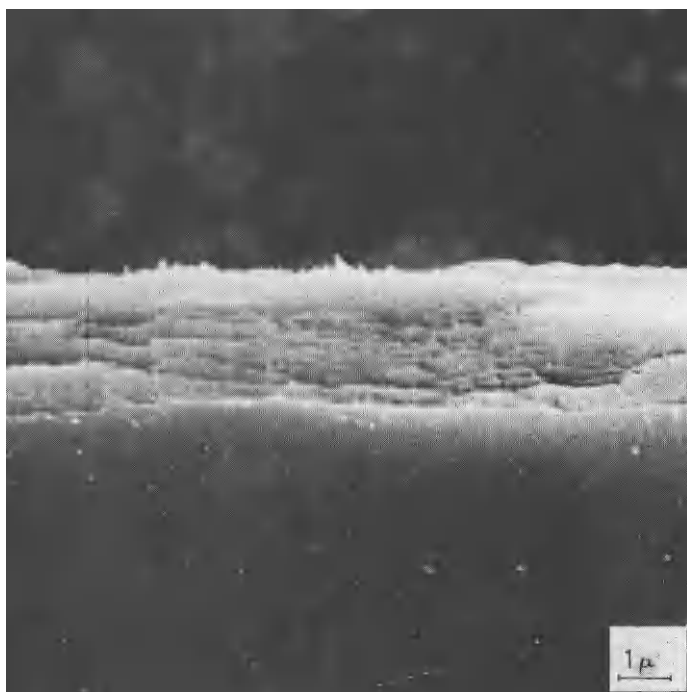


Figure 1. Surface (a) and cross section (b) of bioriented peroxidized moplefan (scanning).

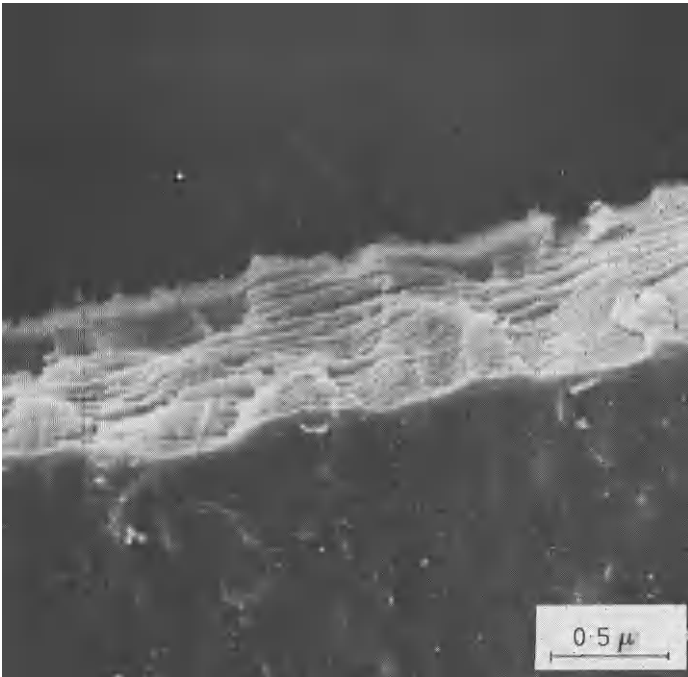


Figure 2. Cross section of bioriented grafted (by oxidation) moplefan (scanning) (PPA content : 55 per cent).

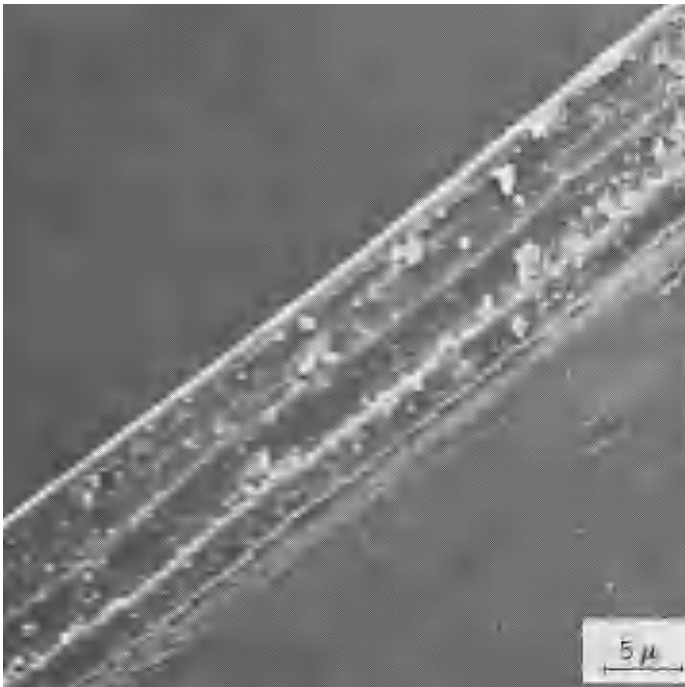


Figure 3. Cross section of un-oriented moplefan. extrusion direction (scanning).

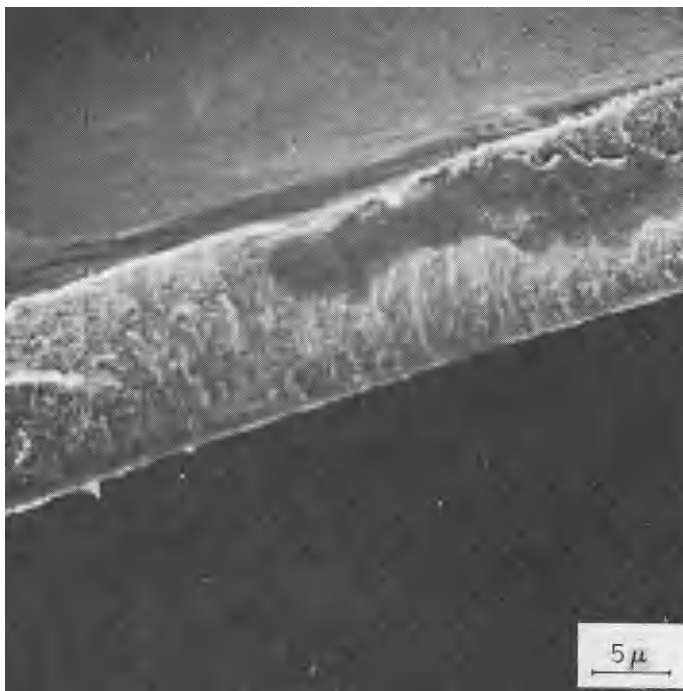


Figure 4. Cross section of grafted (after oxidation) un-oriented moplefan (PAA = 81 per cent) (scanning).

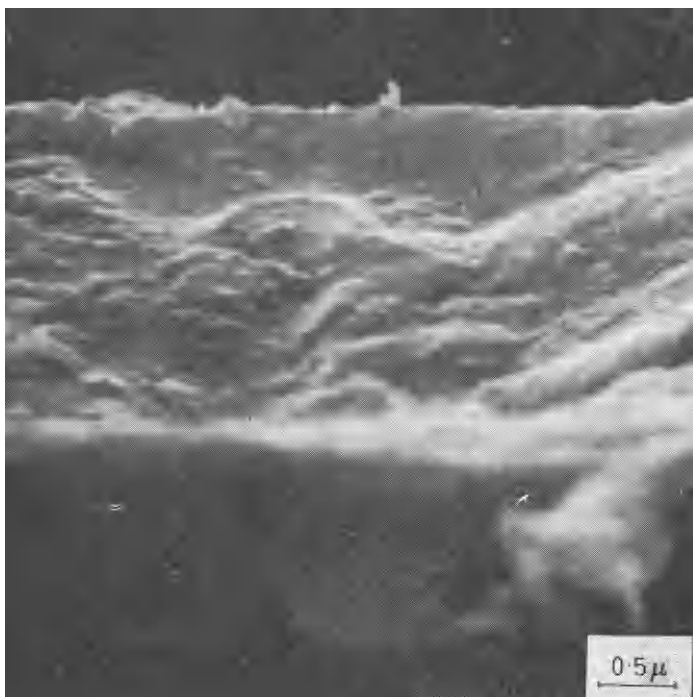


Figure 5. Cross section of radiation grafted un-oriented moplefan (scanning) (PAA = 43 per cent : dose 380000 rad).

Table 2. Extraction membrane types

Polymers	Monomers	Initiators	Solvents	% of grafting	Temperature of membrane extraction
Polypropylene	Acrylic acid	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	20	120-140
Polypropylene	Acrylic acid	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	27	120-140
Polypropylene	Acrylic acid	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	33	120-140
Polypropylene	Acrylic acid	<i>t</i> -Butyl perbenzoate	<i>o</i> -Dichlorobenzene	41	120-140
Polypropylene	Acrylic acid	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	42	120-140
Polypropylene	Acrylic acid	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	52	120-140
Polypropylene	Acrylic acid	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	57	120-140
Polypropylene	Acrylamide	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	30	120-140
Polypropylene	Acrylamide	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	35	120-140
Polypropylene	2-Hydroxyethylmethacrylate	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	53	120-140
Polypropylene	2-Hydroxyethylmethacrylate	Benzoyl peroxide	<i>o</i> -Dichlorobenzene	78	120-140
Polyvinyl chloride	2-Hydroxyethylmethacrylate	Chelate of bis(—)ephedrine of Cu(II)	Cyclohexanone	35	Room temp.
Polyvinyl chloride	2-Hydroxyethylmethacrylate	Chelate of bis(—)ephedrine of Cu(II)	Cyclohexanone	43	Room temp.
Polyvinyl chloride	Methyl acrylate	Chelate of bis(—)ephedrine of Cu(II)	Cyclohexanone	5	Room temp.



Figure 6. Section of an extracted membrane (PAA = 57 per cent) (transmission).



Figure 7. Section of an extracted membrane (PAA = 12 per cent) (transmission).

PREPARATION OF SEMIPERMEABLE MEMBRANES

stored at room temperature in water which may (at least partially) extract the homopolymer when it is soluble in it (e.g. polyacrylic acid, etc.).

If the backbone polymer (for example PVC, Table 2, and its grafted derivative) is soluble in the reaction solvent at room temperature, film-making of the reaction products is identical, but much easier.

The structures of the membranes obtained may be well shown up in the electron microscope (transmission technique). Figures 6 and 7 show the cross sections of two polypropylene membranes one with 12 and the other with 57 per cent of polyacrylic acid. After treatment with osmium, it is possible to distinguish darker domains (polyacrylic acid) intermingled with lighter regions (polypropylene) arranged in a fairly regular way. The domain area is related to the composition. Also, in the case of moulded products completely free from homopolymer obtained from the same material as that used for membranes the existence of two phases is proved by mechanical dynamic measurements, which show the existence of different relaxation processes characteristic of polypropylene and of polyacrylic acid¹⁶.

PROPERTIES OF THE MEMBRANES

On the basis of the foregoing investigations, both mechanical, dynamic and optical, we conclude that the membranes illustrated above (no matter how obtained) are biphasic after grafting and consist of physically separated regions of polyacrylic acid and of polypropylene. Only the shape and distribution of the two components differ depending on how the membranes were obtained: if made from solution, the components will be distributed in distinct regions: PAA is immersed in the PP matrix; if made from peroxidized bioriented films, the PAA regions are distributed among the PP lamellae in such a way that lamellae persist but become more spaced out; if made from un-oriented peroxidized films the initially stratified structure appears to be severely disturbed. In irradiated films, the distribution of PAA regions in the PP matrix is probably more homogeneous than that in the previous case.

Water vapour transfer through membranes from a saturated vapour

Table 3. Permeability ASTM-E 96-66 cup vapour test: $T = 23^{\circ}\text{C}$. Drying agent: phosphorus pentoxide

Type of material	PAA grafted %	Thickness, μ	mg H ₂ O/h cm ²
Extraction membrane	41	25-40	0.7
	43	3-6	1
	52	10-15	1.4
	57	2-6	1.5
Bioriented irradiated moplefan	30	6 initial	1.2
	23	10 initial	0.2
	45	10 initial	0.8
Not oriented irradiated moplefan	26	20 initial	0.8
Peroxidized bioriented moplefan	81	10 initial	0.3
Peroxidized not oriented moplefan	81	20 initial	1.4

space to a dry one at 23°C was measured by the ASTM E 96-66 cup method. Transfer occurs according to data summarized in *Table 3*. Transfer rates appear to be generally an increasing function of the percentage of PAA.

Transfer rates decrease in the order: extraction membranes, un-oriented irradiated moplefan, bioriented irradiated moplefan, un-oriented peroxidized moplefan, bioriented peroxidized moplefan. This order is connected with the structure, which is more compact for moplefan than for extraction membranes and is more compact for bioriented films than for those not oriented.

With regard to extraction membranes, the rate is independent of thickness: this suggests that the rate of the process is not limited by diffusion inside the membrane, but by evaporation or condensation of water at the interfaces. As to membranes obtained from irradiated films, their rates depend, however, on thickness.

Extraction membranes show higher compressibility than peroxidized or grafted films. *Figure 8*, shows, for example, the effects of compaction on pure water flux through an extraction membrane (PAA = 33 per cent) with particularly high permeability (low thickness) versus time.

The higher compressibility of extraction membranes may act in such a way that the above order of permeability, determined by the cup method, is changed in reverse osmosis plants under high pressures: permeability of membranes may be considerably reduced.

PERMSELECTIVE PROPERTIES OF MEMBRANES

Membranes of PAA grafted on PP may be used for sea or brackish water desalination. Several runs were performed by us in a reverse osmosis plant with water containing sodium chloride (10000 p.p.m.), under pressures of 50 (or 100) atm.

Figure 9 shows the experimental flux/salt rejection curve obtained with all the extraction membranes tested by us, containing 40 to 50 per cent of grafted PAA: rejection increases with decreasing flux. *Figure 10* shows flux at 50 atm versus thickness. The highest rejections obtained (80 per cent) were found by operating with a thickness of 17 μ (flux was 1.1 l./h m² at 50 atm, grafted PAA = 43 per cent).

When using membranes obtained from not oriented peroxidized and grafted moplefan (thickness = 20 μ), fluxes are comparable with those of extraction membranes, and rejections are even better (maximum obtained, 97 per cent) (see *Table 4*).

If membranes are obtained from bioriented moplefan, grafted after peroxidation (thickness = 20 μ), fluxes are zero for a long time; with high percentages of grafting, the flux only begins to rise after more than twenty hours (0.04 l./h m²) with fairly high rejections (66 per cent).

Finally, when using radiation membranes higher fluxes are observed and rejections are zero. After operating at 50 kg/cm² and 10000 p.p.m. of sodium chloride and after an induction period of more than ten hours, we found fluxes of 3.5 l./h m², using initially bioriented moplefan (thickness 10 μ , PAA = 38 per cent) and we found fluxes of 8.1 l./h m² using un-oriented moplefan (thickness 20 μ , PAA = 40 per cent). Radiation-grafted moplefans

PREPARATION OF SEMIPERMEABLE MEMBRANES

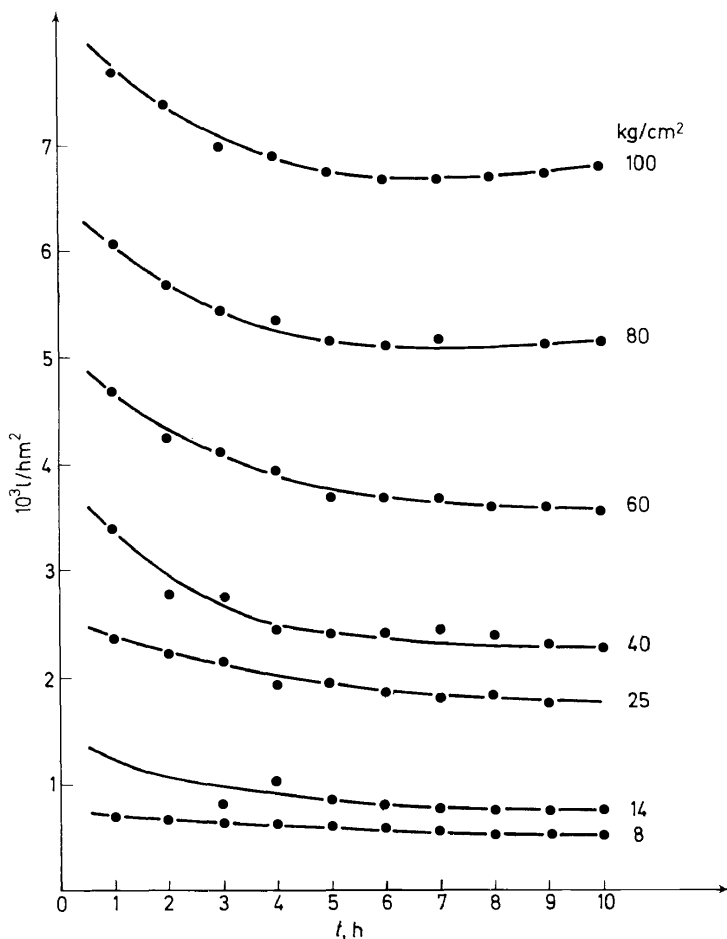


Figure 8. Compaction effects on an extraction membrane 5 μ thick. PAA = 33 per cent. Flux versus time at different constant pressures.

Table 4. Desalination properties of grafted moplefans (10 000 p.p.m. sodium chloride in water, pressure 100 atm)

Type	Type of grafting	Initial thickness μ	PAA grafted %	Flux l./h m ²	Mean rejection %	Notes
Not oriented	Peroxidation	20	81	0.8	92	
Not oriented	Peroxidation	20	69	0.5	87	
Bioriented	Peroxidation	12.5	55	0.04	66	Flux starts after 23 h
Bioriented	Peroxidation	20	32	—	—	No flux for 48 h

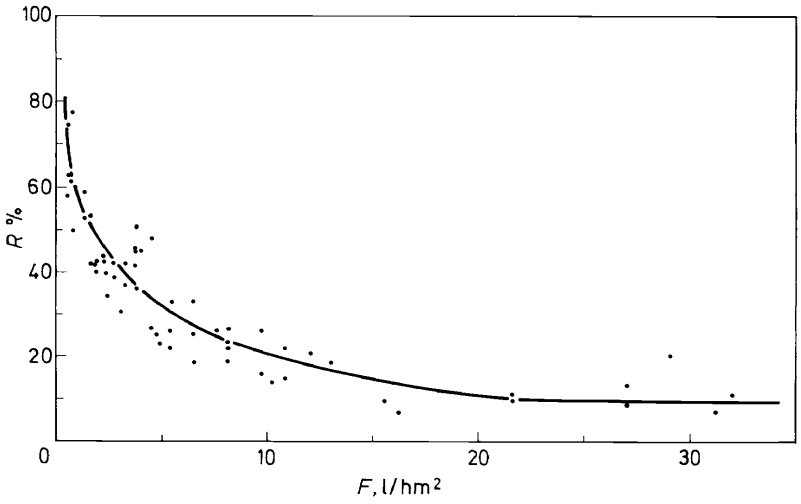


Figure 9. Extraction membranes: flux versus rejection (Sodium chloride 10000 p.p.m.; 50 atm).

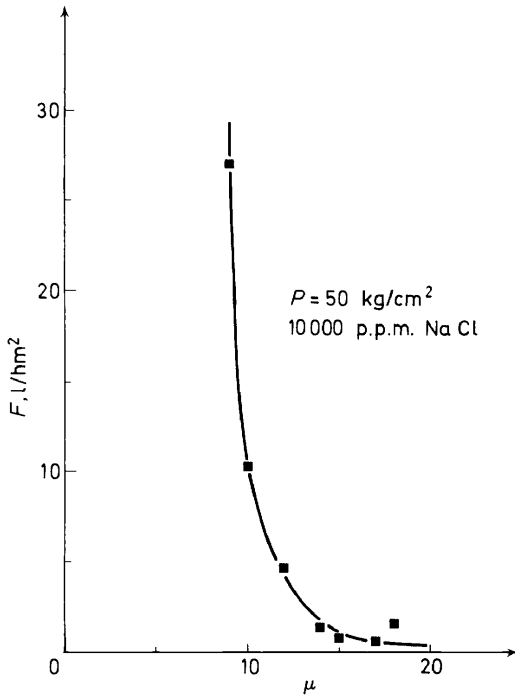
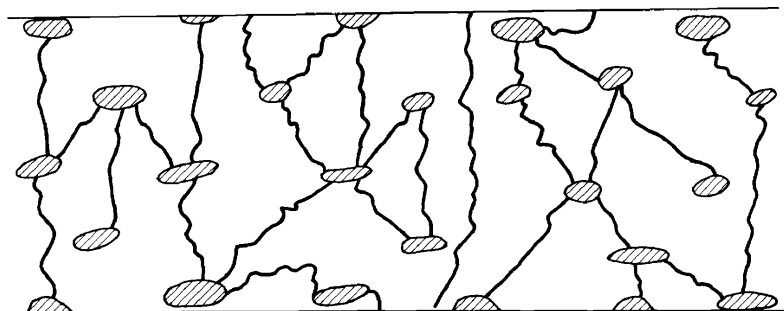


Figure 10. Extraction membranes: flux versus thickness (Sodium chloride 10000 p.p.m.; pressure 50 kg/cm²).

PREPARATION OF SEMIPERMEABLE MEMBRANES

Extraction membrane



Grafted film

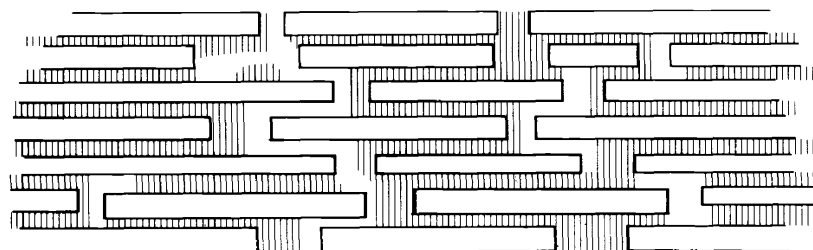


Figure 11. Model of PP-PAA grafted membranes.

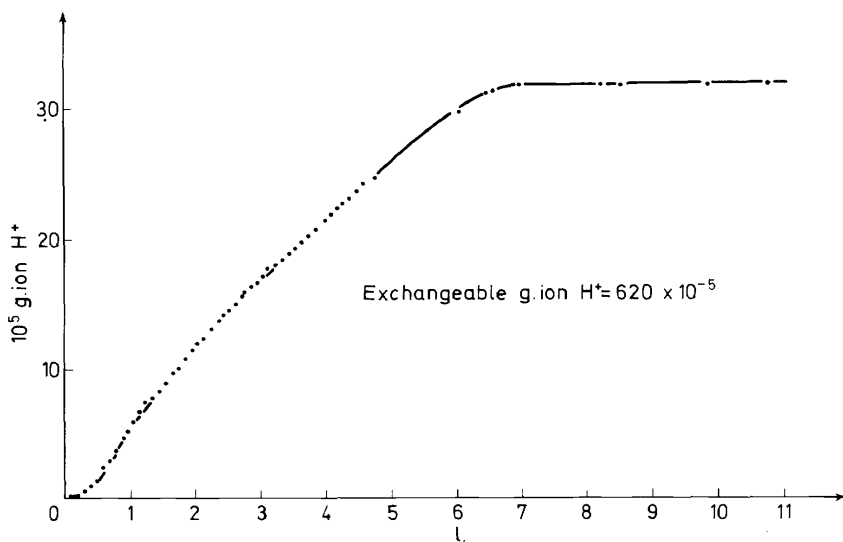


Figure 12. Hydrogen ions exchanged versus volume (litres) of 3.5 per cent sodium chloride solution eluted through grafted powder (PAA = 45 per cent).

using other monomers (say, 2-vinyl pyridine) after iodomethylation appear to give satisfactory salt rejections²⁶.

Desalination may be interpreted by assuming a membrane model of the type shown in *Figure 11* (a) (extraction membrane) or in *Figure 11* (b) (membrane from film). PAA and PP regions must necessarily show low adhesion: furthermore, water swells PAA remarkably, causing internal stresses and possible microfractures, which must necessarily have an extremely small equivalent diameter; in fact, determinations of surface area made by us have shown that extraction membranes are compact. Microfractures may constitute continuous channels: their possibility of passing through the sample is the greater the lower is the extraction membrane thickness. This explains both high fluxes and low rejections of extraction membranes with low thickness: in this case, the liquid flow should be of the bulk type. As to membranes with fairly large thickness, salt water reaches the PAA regions either directly or through microfractures; however, it cannot pass through the membrane by continuous channels. PAA is very hydrophilic and can repel salt owing to the Donnan effect. In fact, it reacts with sodium chloride. *Figure 12* shows the hydrogen ion exchange of a pure grafted powder (PAA grafted on PP equal to 45 per cent, weight 1 g, put in a continuous flux of 3.5 per cent sodium chloride solution). The membrane may then act with a diffusion solution mechanism, which is most effective for desalination. However, too great a thickness reduces the flux, by increasing the number of exchanges and the overall resistance.

Table 5. Ultrafiltration properties of extraction membranes²⁷.

Type	% of grafting	Thickness μ	Operating pressure kg/cm^2	% Rejection operating with		
				Flux l/h m^2	5% saccharose solution	0.5% protein solution
Polyacrylamide grafted on polypropylene	30	10	100	5.4	50	—
Poly-2-hydroxyethyl methacrylate grafted on polypropylene	53	5	50	5.4	50	—
Polyacrylic acid grafted on polypropylene	33	5	5	8.3	—	41
		2	20	—	—	60
Poly-2-hydroxyethyl methacrylate grafted on polypropylene	78	7	4	0.9	—	60
		2	3.5	4	—	80

In addition to desalination, the membranes prepared by us may also be useful for many other applications. *Table 5* shows rejections of saccharose and of proteins (α and β lactoalbumins and β lactoglobulins: MW 70 to 250000) from aqueous solutions²⁷.

CONCLUSIONS

Grafting is a very important means for obtaining materials fit for the production of permselective membranes. It is not only important to use polymers with adequate chemical properties, but also to prepare a membrane

structure suitable for fractionation. When using entirely incompatible polymers, such as polyacrylic acid (hydrophilic) and polypropylene (hydrophobic) it is possible to obtain low-thickness very permeable membranes, which may be used for filtering, although they are not selective for low-molecular weight substances, probably owing to the very frequent microfractures generated by grafting.

On the other hand, when using thicker membranes, the transfer process changes and becomes of the solution-diffusion type; hence it allows high rejections, but not very high fluxes.

ACKNOWLEDGEMENT

The financial support of the Italian Institute for Research on Water (IRSA) of the National Council of Research (CNR) is gratefully acknowledged. I thank Dr A. Penati and Dr G. Alessandrini for their valuable cooperation.

REFERENCES

- ¹ S. B. Tuwiner, *Diffusion and Membrane Technology*, Reinhold: New York (1962).
- ² A. Katchalsky and P. F. Curran, *Non-equilibrium Thermodynamics in Biophysics*, Harvard University Press: Cambridge, Mass. (1967).
- ³ S. Sourirajan, *Reverse Osmosis*. Logos Press: London (1970).
- ⁴ *New Scientist*, London, p 225 (29 October 1970).
- ⁵ C. E. Reid in *Desalination by Reverse Osmosis*, p 11 Edited by V. Merten. MIT Press: Cambridge, Mass. (1966).
- ⁶ C. E. Reid and E. J. Breton, *J. Appl. Polym. Sci.* **1**, 133 (1959).
- ⁷ S. Sourirajan, *Industr. Engng Chem. Fundamentals*, **2**, 51 (1963).
- ⁸ E. Glueckauf, Proceedings of the First International Desalination Symposium. Paper SWD/1. Washington, D.C. (3-9 October 1965).
- ⁹ F. G. Donnan, *Chem. Rev.* **7**, 373 (1937).
- ¹⁰ V. Merten, *Desalination by Reverse Osmosis*, p. 22. MIT Press: Cambridge, Mass. (1966).
- ¹¹ H. F. Mark and N. G. Gaylord, *Encyclopedia of Polymer Science and Technology*. Vol. VIII, p 620. Interscience-Wiley: New York (1968).
- ¹² S. Loeb and S. Sourirajan, *Advanc. Chem. Ser.* **38**, 117 (1962).
- ¹³ See for example H. F. Mark and N. G. Gaylord, *Encyclopedia of Polymer Science and Technology*, Vol. VIII, p 628. Interscience-Wiley: New York (1968).
- ¹⁴ M. Pegoraro and A. Penati, *Chim. e Industr.* **53**, 235 (1971).
- ¹⁵ H. B. Hopfenberg, V. Stannett, F. Kimura and P. T. Rigney, *Membranes from Cellulose and Cellulose Derivatives*, p 139. Interscience: New York (1970).
- ¹⁶ M. Pegoraro, L. Szilagyi, A. Penati and G. Alessandrini, *Europ. Polym. J.*, **7**, 1709 (1971).
- ¹⁷ G. Albanesi, E. V. Zaitseva and E. Beati, *Chim. e Industr.* **49**, 1300 (1967).
- ¹⁸ V. Stannett, *J. Macromol. Sci. Chem. A*, **4** (5), 1177 (1970).
- ¹⁹ See for example S. Munari, Fourth International Congress of Radiation Research, Evian (28 June-4 July 1970).
- ²⁰ Quaderni de *La Ricerca Scientifica* No. 58, 91 CNR: Roma (1969).
- ²¹ W. K. Chen and co-workers, *J. Polym. Sci.* **23**, 903 (1957).
- ²² *Italian Pat Appl. No. 20217 A/71*.
- ²³ G. Alessandrini, M. Pegoraro, A. Penati and G. Mossa, *Chim. e Industr.*, **54**, 105 (1972).
- ²⁴ Montecatini Edison Bulletin *Moplefan* (1966).
- ²⁵ M. Pegoraro and A. Penati, unpublished work.
- ²⁶ S. Munari, private communication
- ²⁷ C. Peri and C. Cantarelli, private communication.
- ²⁸ Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, p 28. Wiley: New York (1969).