Permeability properties of charged hydrogel-carrying membranes

H. Akin, V. N. Hasirci and N. Hasirci*

Middle East Technical University, Departments of Chemistry and Biological Sciences, Ankara, Turkey

Poly(2-vinylpyridine) is known to be hydrophobic, and a membrane prepared from it would not permeate water-soluble substances in aqueous media. By introducing hydrophilic poly(2-vinyl-N-methylpyridinium iodide) particles into the membrane, it would be possible to control permeation. This type of membrane was prepared and an increase in permeability was observed on increasing the amount of hydrophilic component in the membrane and decreasing the crosslink density of the hydrogel part. The size of the hydrogel particles did not have a significant effect on permeability. Scanning electron microscopy and microscopic examinations showed a homogeneous distribution of hydrogel particles in the membrane matrix.

(Keywords: permeability; hydrogel; membrane)

INTRODUCTION

The transport of substances through membranes under the influence of a chemical potential gradient occurs primarily by the process of diffusion of the permeating species through the membrane. Often but not invariably the membrane is a thin film. The stability of any given membrane for any particular operation is determined by a number of factors. A very important requirement is that the membrane should be chemically stable. Besides this stability, it should have sufficient mechanical strength, low electrical resistance, dimensional stability under different wetting conditions and sufficient flexibility. Both organic and inorganic polymeric materials can be shaped into a wide variety of forms with tailored macromolecular morphology, good physical properties, a wide range of chemical properties and a fair degree of physical and chemical stability; therefore they dominate in membrane production.

Synthetic polymeric membranes have been widely used in commercial products requiring separation of two or more components and preferential permeation of some of the components. Polymer systems that are significantly swollen by the permeating substances are interesting because their permeabilities are higher in the swollen form than in the non-swollen state. If the polymeric network swells in an aqueous medium, it is called a hydrogel. This type of water-swollen hydrophilic structure has been the focus of much research directed towards the development of new materials[1–4].

Hydrogel structures can be obtained in a wide range of physical shapes changing from compact gels to cellular sponges. Also, their permeability properties can be easily altered and controlled by changing their degree of hydration, crosslink density, porosity, etc. Therefore, hydrogels have very high potential in controlled-release systems. Hydrogels are generally formed from water-soluble polymers by crosslinking them either using radiation or chemically or by polymerizing hydrophilic monomers in the presence of crosslinker.

If a hydrogel is used in an aqueous medium, there will be an osmotic driving force for the water to enter the water-free region, the permeant concentration in the membrane increases, permeant–polymer interactions come into effect and polymer chain segments are loosened and become more mobile. Permeant diffusivity becomes a rapidly increasing function of permeant concentration. The factors that favour swelling are high free volume, high chain flexibility, low crosslink density in the gel structure and strong attractions with water. In this study, membranes were prepared from poly(2-vinylpyridine) (PVN) and poly(2-vinyl-N-methylpyridinium iodide) (PVNMeI). The main body of the membranes was PVN and into these structures were embedded hydrogel particles (PVNMeI). The diffusion of a model water-soluble permeant was examined. The effects of the amount, crosslink density and particle size of the hydrogel particles on the diffusion rates were examined.

EXPERIMENTAL

Purification of poly(2-vinylpyridine) (PVN)

2-Vinylpyridine (Fluka AG) was thermally polymerized by itself. The polymer was separated from its monomer as follows. The polymer mixture was dissolved in an excess of ethanol and the alcohol was evaporated to some extent by the use of a rotary evaporator. The polymer was then precipitated by dropwise addition into water. The precipitate was separated, dried and dissolved in ethanol and reprecipitated in water. This process was repeated three times and the final precipitation was carried out in diethyl ether. The precipitate was dried and molecular weight was determined as 433 000 by a viscometric method using the formula[5]:

$$[\eta] = 2.8 \times 10^{-4} M_{\mathrm{W}}^{0.66}$$

Crosslinking of PVN

PVN was dissolved in extra-pure ethanol and 5% solutions were placed into irradiation tubes. Nitrogen gas was flushed through the solutions, the tubes were heat sealed, placed in a ^{60}Co gamma source and irradiated with a dose rate of $0.63 \, kGy \, h^{-1}$.

Preparation of poly(2-vinyl-N-methylpyridinium iodide) (PVNMeI)

Methyl iodide (30 g) and PVN (7.6 g) were mixed in nitromethane (120 g) at $-196°C$. The solution was warmed up to room temperature, and then refluxed for 10 h. PVNMeI formed as a yellow precipitate. The excess of solvent and halide were evaporated under vacuum. The reaction is given as:
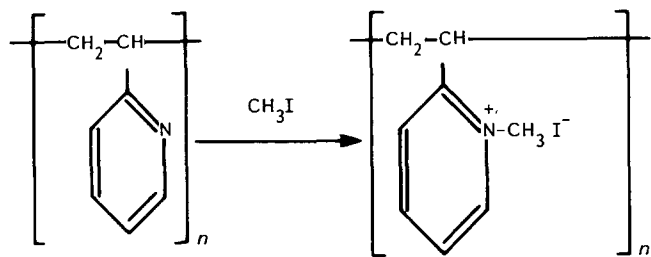
The product was meshed and separated into $0-65 \, \mu m$ and $65-100 \, \mu m$ fractions.

Determination of per cent quaternization

Per cent quaternizations were determined by the Volhard method[6]. Samples of known weight (~0.3 g) were dissolved in water (100 ml) and acidified with HNO_3 (6F, 5 ml). Standard silver nitrate (65 ml) was introduced and iron(III) indicator (5 ml) was added. The excess silver was titrated back with standard thiocyanate solution until the colour of $FeSCN^{2+}$ was permanent.

Per cent quaternization was calculated from:

$$Q(\%) = (EM_w/W) \times 100$$

where $Q(\%) =$ per cent quaternization of methyl salt, $M_w =$ molecular weight of iodine, $W =$ theoretical amount of iodine in methyl salt and $E =$ number of equivalents of iodine $= V_1 N_1 - V_2 N_2$ (V_1 and N_1 are volume and normality of the standard silver nitrate, and V_2 and N_2 are volume and normality of the standard potassium thiocyanate solution).

Preparation of membranes

PVN samples of known weight were dissolved in ethanol and mixed with various amounts of water-swollen PVNMeI particles, vortexed and poured into Petri dishes. Solid films were obtained after keeping them at room temperature for one day. In the resultant films, the hydrogel particles appeared as uniformly distributed yellowish protrusions. The preparation conditions of the membranes are given in *Table 1*.

Measurements of the film thickness

The thickness of a microscope slide was measured with a micrometer. The swollen membrane was then placed on this slide and the thickness was measured again with the micrometer, taking utmost care not to compress the membrane. Film thickness was calculated from the difference. The thicknesses of the dry and swollen membranes were found to be $70-150 \, \mu m$ and $350-500 \, \mu m$, respectively.

Measurement of water contents

The per cent water contents were calculated by using the following formula:

$$H_2O \text{ content } (\% \text{ w/w}) = [(w_s - w_d)/w_s] \times 100$$

where $w_s =$ weight of swollen sample and $w_d =$ weight of dry sample.

Diffusion experiments

A two-chambered horizontal permeation cell was used. The cells were made of Plexiglass and were cylindrical in shape. There was a connection between the cylinders with a membrane holder (inner diameter 1.90 cm). Each chamber had a volume of $435 \, cm^3$. The distilled-water-swollen membrane was placed in its holder with great care in order not to create any folds or cause ruptures. One chamber was filled with a permeant (potassium dichromate) of known concentration and the other with distilled water. From the second chamber, $5 \, cm^3$ aliquots were removed at certain intervals and concentration was determined spectrophotometrically by measuring the absorbance at 373 nm. Distilled water ($5 \, cm^3$) was added to the chamber and the change in concentration was taken into account in the calculations[7].

Permeability values are calculated from:

$$\ln(M_t/M_a) = PAt/Vl$$

Table 1 Preparation conditions of the membranes

Membrane	PVNMeI			Amount of PVN (g)	Amount of PVNMeI (g)	PVNMeI/PVN (w/w)
	Radiation time (h)	Mesh size (μm)	Water content (%)			
R1	300	65	95	0.15	0.075	0.50
R2	300	100	95	0.15	0.075	0.50
R3	350	65	–	0.15	0.105	0.70
R4	400	65	94	0.15	0.030	0.20
R5	400	65	94	0.15	0.075	0.50
R6	400	65	94	0.15	0.150	1.00
R7	400	65	94	0.15	0.225	1.50
R8	450	65	–	0.15	0.105	0.70
R9	500	65	91	0.15	0.075	0.50
R10	–	–	–	0.15	–	0.00

where M_t = permeant concentration in the second chamber (receiver) at time t, M_a = permeant concentration in the first chamber (reservoir) at time t, P = permeability $(cm^2 s^{-1})$, A = area of swollen membrane (cm^2), V = volume of one chamber (cm^3), l = thickness of swollen membrane (cm) and t = time (s).

RESULTS

Quaternization of PVN by acids or alkyl halides takes place easily and converts PVN from hydrophobic to hydrophilic by forming a polyelectrolyte. The rate of quaternization is affected by the neighbouring groups or by steric hindrance. When the reaction is carried out between linear PVN (M_w 433 000) and methyl iodide, per cent quaternization is found to be $95.5 \pm 2.0\%$. This yellow product (PVNMeI) is water-soluble. Upon irradiation of its 5% (w/v) solutions in water in order to form a three-dimensional structure, no gel formation could be observed even after very long irradiation times (up to 1000 h). This was thought to be due to the presence of the large iodine ions causing steric hindrance between the neighbouring chains and thus preventing gelation.

Crosslinking of PVNMeI was also tried by using a chemical initiator, ammonium persulphate. Various PVNMeI/ammonium persulphate solutions were prepared (*Table 2*) and heated to 80°C. Although crosslinking under similar conditions was observed previously[8] for poly(2-vinylpyridine *N*-oxide), no gel formation with PVNMeI was observed even after one week. Finally, in order to obtain crosslinked and quaternized PVN, quaternization of crosslinked PVN was attempted by irradiating 5% (w/v) solutions of PVN in extra-pure ethanol. Gel formation was observed after 100 h of irradiation but these gels were not stable and degraded upon swelling. Stable gels could be obtained only after irradiation for 260 h. The extent of quaternization of the samples crosslinked by application of 260 h and 500 h gamma irradiation was found to be 98% and 89%, respectively. It is possible to explain this decrease in per cent quaternization upon increase in degree of crosslinking as due to steric hindrance, which, to some extent, restricts the approach of the iodine to the macromolecule. Both of these per cent quaternization values are in very good agreement with that reported in the literature[9].

In the preparation of the membranes, two different mesh size (0–65 μm and 65–100 μm, in dry form) particles were used. These hydrophilic particles were distributed in the hydrophobic matrix of the membrane which in dry form was 70–150 μm thick. Judging by their sizes in dry form, it can be stated that some of the particles would traverse the membrane while some would be completely embedded. In water, the particles would swell more than the membrane material (see *Tables 1* and *3*), creating an inner pressure. This pressure, however, is not expected to be large enough to cause cracks in the membrane because it is known that, as the water content of the gels

increases, their mechanical strength decreases. Instead, it can be expected that portions of the large particles would be forced to the surface of the membrane as a result of this pressure. This view was supported by the absence of any discontinuities in the swollen membrane surface upon investigation by light microscopy.

All the membranes except R7 were used in the diffusion experiments. R7 did not have sufficient mechanical strength since the PVNMeI/PVN ratio was 1.50. An increase in the relative concentration of hydrophilic component led to a decrease in the stability of the membrane, as expected.

The membranes were compared by determining their potassium dichromate permeability. The amount of permeant diffused was measured at certain time intervals and permeability values were calculated from the slopes of the $\ln(M_t/M_a)$ vs. tA/Vl curves and the results are presented in *Table 3*. In order to test the effect of hydrophilic component, membranes R4, R5, R6 and R10 were used (*Figure 1*). Permeation is quite minimal $(4 \times 10^{-8} cm^2 s^{-1})$ when the membrane does not contain any PVNMeI (membrane R10). Introduction of PVNMeI into the membrane has a positive effect on permeability. For the R6 membrane, which has a PVNMeI/PVN ratio of 1.00, the permeability $(1.48 \times 10^{-6} cm^2 s^{-1})$ is about two orders of magnitude higher than that of R10. These indicate that permeation in these membranes is through the hydrophilic component and has a linear dependence on PVNMeI/PVN ratio (*Figure 2*).

The crosslink density of the hydrogel component is another parameter that was expected to influence permeability. Although crosslink density was not measured it can be assumed that it is proportional to irradiation period. In order to examine the effect of crosslink density of the PVNMeI on the permeability, R1, R5 and R9 membranes were used (*Figure 3*). In these samples the irradiation periods were different while PVNMeI/PVN ratios and PVNMeI particle sizes were the same. It was observed that permeability increases from $1.5 \times 10^{-7} cm^2 s^{-1}$ to $9.2 \times 10^{-7} cm^2 s^{-1}$ when the irradiation period decreases from 500 h to 300 h. Thus an increase in crosslink density of the hydrogel leads to the expected decrease in permeability (*Figure 4*).

In order to test the effect of particle size on

Table 3 Water content and permeability of membranes

Sample	Water content (% w/w)	$P \times 10^{-6}$ $(cm^2 s^{-1})$
R1	81.4	0.92
R2	82.0	0.95
R4	72.7	0.32
R5	80.9	0.73
R6	81.5	1.48
R9	79.9	0.15
R10	24.0	0.04

Table 2 Composition of the reaction mixture for the crosslinking of PVNMeI

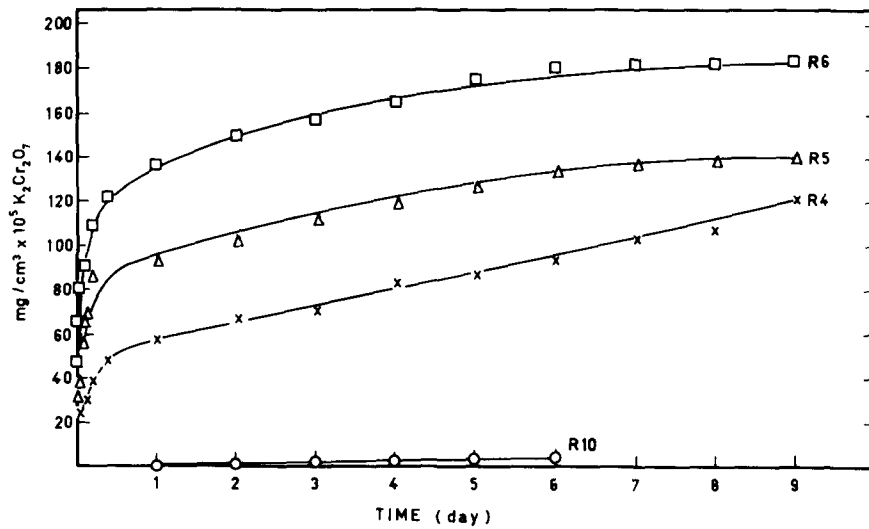| Sample	Total volume (ml)	PVNMeI (mg)	$(NH_4)_2S_2O_8$ (mg)	PVNMeI/$(NH_4)_2S_2O_8$ (mole ratio)
1	2	99.8	92.4	1/1
2	2	99.8	461.9	1/5
3	2	99.8	923.7	1/10

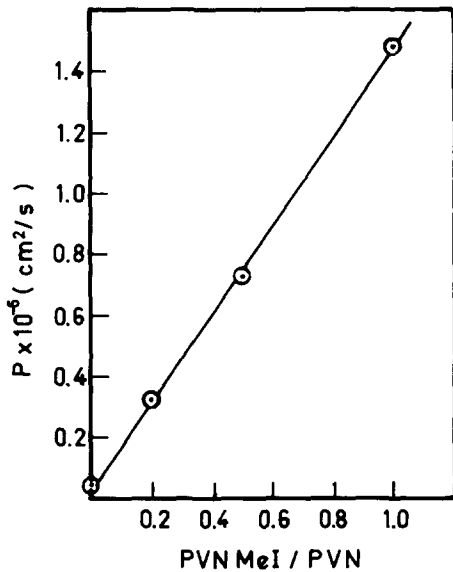**Figure 1** The change of permeation with the hydrophilic part in the membranes

Figure 2 The effect of PVNMeI/PVN ratio on the permeability constant

permeability, R1 and R2 membranes were compared (*Figure 5*). In these membranes crosslink densities and PVNMeI/PVN ratios were the same but the hydrogel particle sizes were different (*Table 1*). It was observed that an increase in particle size from $65\,\mu m$ to $100\,\mu m$ did not lead to a significant change in permeability.

As a result it can be stated that the extent of permeation could be controlled effectively by the hydrophilic polymer content and the crosslink density.

The effect of pH (effect of charge) on permeability was tested with R8 type membranes. Test values of 1, 4, 7 and 10 were chosen for the pH. Thymol blue was selected as the permeant because it has both acidic and basic pH ranges, that is, it carries a positive charge in the acidic range and a negative charge in the basic range. The effect of charge on diffusion can be easily observed without changing the shape and size of the permeant. It was observed that, under acidic conditions, membranes did not have sufficient mechanical strength. It was therefore not possible to investigate diffusion under acidic conditions. On the other hand, at alkaline and neutral pH values, no diffusion could be detected. Thymol blue
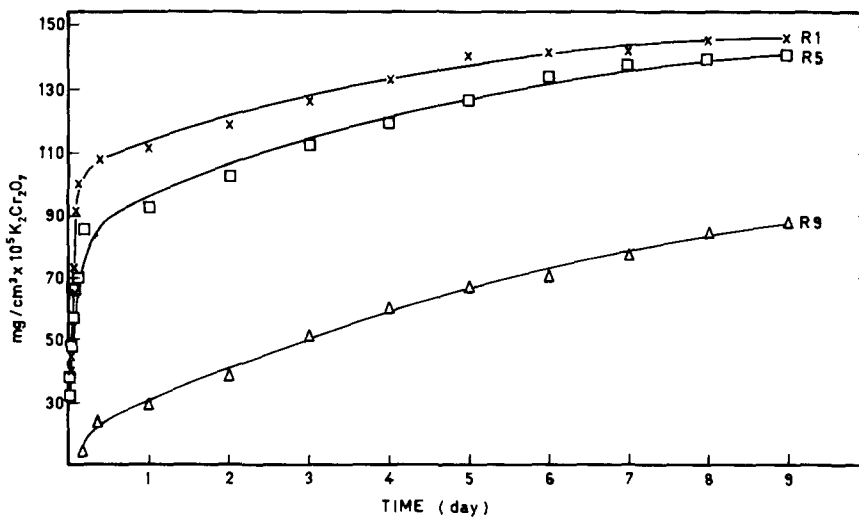

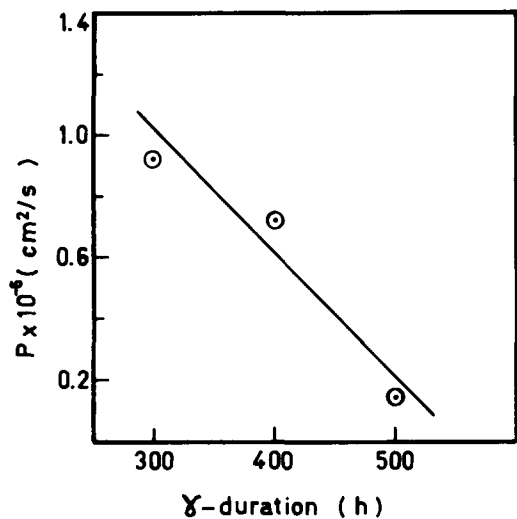**Figure 3** The change of permeation with the crosslink density of the membranes

Figure 4 The effect of applied gamma duration on the permeability constant

was trapped in the hydrogel at those pH values and could not permeate.

The observations showed that this type of membranes could be used as separation membranes as well as in controlled-release devices.

Scanning electron microscopy examinations showed that the hydrophilic PVNMeI particles were distributed homogeneously in the PVN matrix (*Figures 6* and *7*). The gel particles appear dehydrated due to the sample preparation procedure of SEM.

CONCLUSIONS

Permeability of membranes that contain hydrophilic particles can be controlled via certain parameters. The ratio of the hydrophilic to hydrophobic ingredients and the density of crosslinks in the hydrophilic component are two of these parameters. It would also be possible to control the permeation of charge-carrying substances.
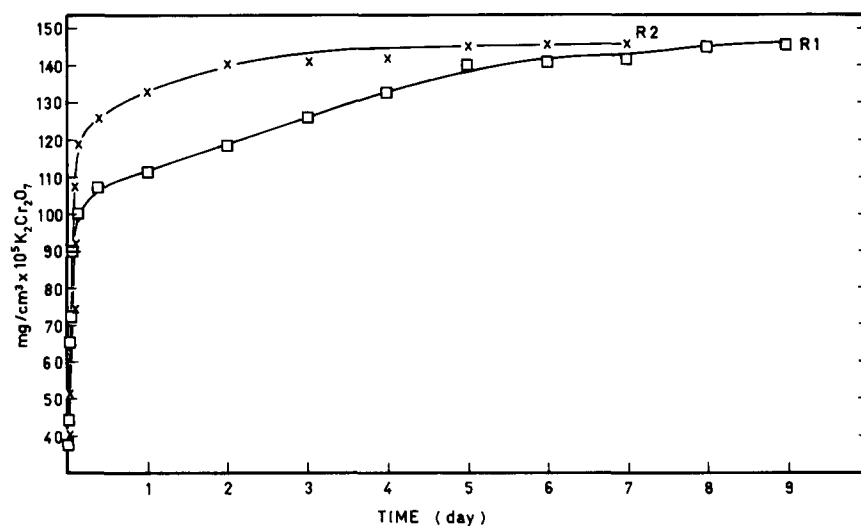

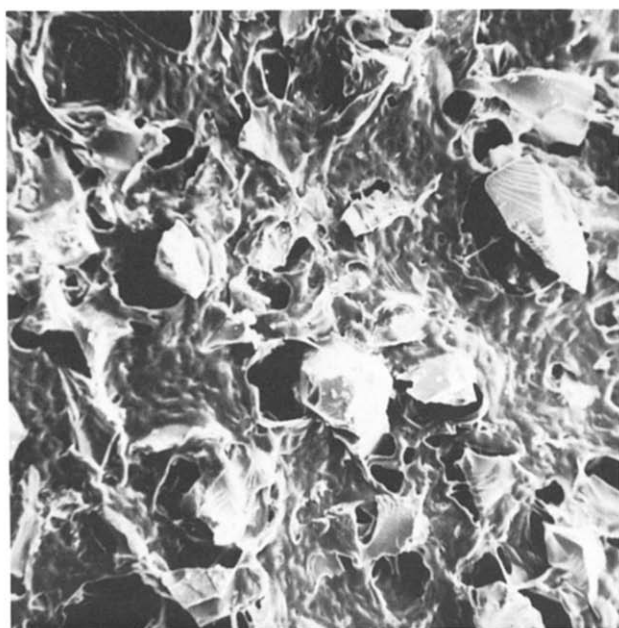**Figure 5** The effect of PVNMeI particle size on the permeation
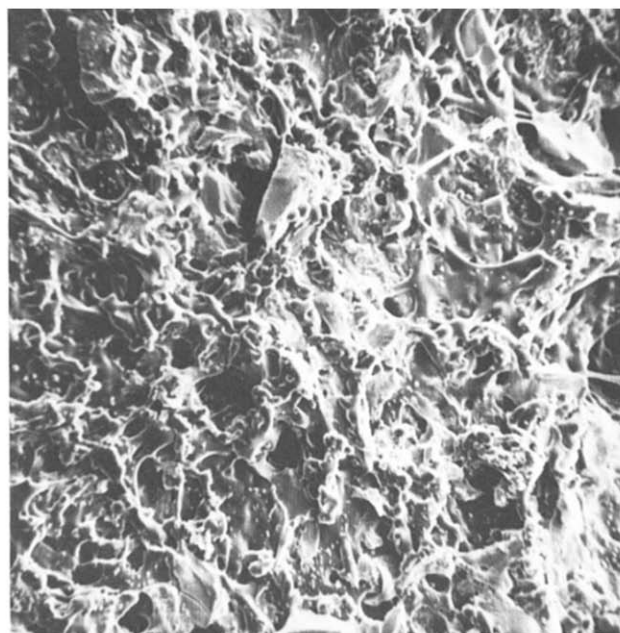

Figure 6 SEM of R1 membrane (× 180)

Figure 7 SEM of R8 membrane (× 180)

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