

Dynamically formed hydrous zirconium (IV) oxide-polyelectrolyte membranes. IV: Maleic anhydride copolymers

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Abstract

A series of maleic anhydride copolymers were synthesised. The copolymers were used as polyelectrolytes in dynamically formed hydrous zirconium (IV) oxide-polyelectrolyte membranes. All the copolymers formed dynamic membranes. Two of the copolymer membranes showed salt rejections similar to that of commercially used poly(acrylic acid) dynamic membranes.

Introduction

In a previous paper (Van Reenen and Sanderson, 1989b) the use of acrylic acid and substituted acrylic acid polymers as dynamic membrane polyelectrolytes was described. In this paper the use of maleic anhydride copolymers as dynamic membranes is described.

Background

The premise of a Donnan exclusion rejection mechanism on which this research was based was described in a previous paper and will not be repeated here. The work reported on in this paper was based on the use of maleic anhydride as monomer. After polymerisation and hydrolysis the anhydride functionality changed to a diacid functionality (Fig. 1). By using this dicarboxylic acid monomeric species an attempt was made to create a membrane with a higher charge density than could be achieved with the membrane formed from the commercially used monocarboxylic-based poly(acrylic acid). The following copolymers were to be synthesised:

- Poly(maleic anhydride-co-acrylic acid)
- Poly(maleic anhydride-co-itaconic acid)
- Poly(maleic anhydride-co-vinyl sulfonic acid)
- Poly(maleic anhydride-co-vinyl acetate)
- Poly(maleic anhydride-co-vinyl alcohol).

Experimental

Membrane formation

The equipment for and method of membrane formation and evaluation was described in a previous paper (Van Reenen and Sanderson, 1989b) and will not be repeated here.

Polymerisation

The following polymerisations were done:

Poly(maleic anhydride-co-acrylic acid): according to the method of El Saied *et al.* (1969): code MA/AA.

Poly(maleic anhydride-co-itaconic acid): code MA/VSA.

Poly(maleic anhydride-co-vinyl sulfonic acid): according to the method given in a Japanese patent (1975): code MA/VSA.

Poly(maleic anhydride-co-vinyl acetate): according to the method of Caze and Loucheux (1973): code MA/VA.

Poly(maleic anhydride-co-vinyl alcohol): by alkaline hydrolysis of MA/VA: code MA/VOH.

Characterisation

This was described in a previous paper (Van Reenen and Sanderson, 1989b).

Results and discussion

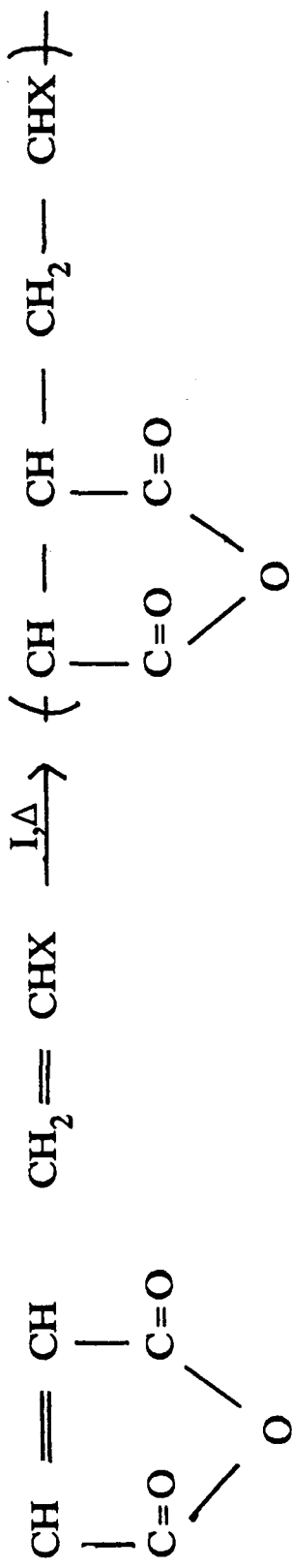
The results are shown in Table 1.

It is obvious from Table 1 that all the maleic anhydride copolymers form dynamic membranes. It is further noticeable that the more highly charged copolymers such as MA/IA (two carboxylic acid groups per monomer unit) and MA/AA (one-and-a-half carboxylic acid groups per monomer unit) have rejection far below that of PAA membranes (one acid group per monomer unit). As was shown in a previous paper (Van Reenen and Sanderson, 1989b), increasing the charge density on a dynamically formed polyelectrolyte membrane does not enhance the membrane's salt rejection properties over that of poly(acrylic acid). When a "neutral" comonomer is introduced, such as vinyl acetate, however, the rejection is markedly better, and a performance similar to that of poly(acrylic acid) is achieved. It is therefore clear from these results that the rejections of these membranes are not determined solely by the Donnan exclusion mechanism, but that there is a salt retention due to the hydrophobic (uncharged) sections of the polyelectrolyte membrane. It would appear, as was recently suggested (Keuhl and Sanderson, 1988) that there is a maximum rejection which is attributable to the presence of charge on these membranes, and that increasing the charge density on these membranes will not lead to higher salt retention.

It was these results that led to a change in our research approach, and recent work (Van Reenen, 1988; Van Reenen and Sanderson, 1989a) concentrated on increasing the salt retention due to the presence of hydrophobic groups or areas in the membrane.

It is interesting to note that as the theoretical maximum charge density decreases (MA/IA - MA/AA - PAA) the flux decreases. This could be expected. The higher the charge on the membrane the higher the affinity for water the membrane will have, and the higher the flux should be. The difference in flux between the MA/VOH and MA/VA membranes is due to the different hydro-

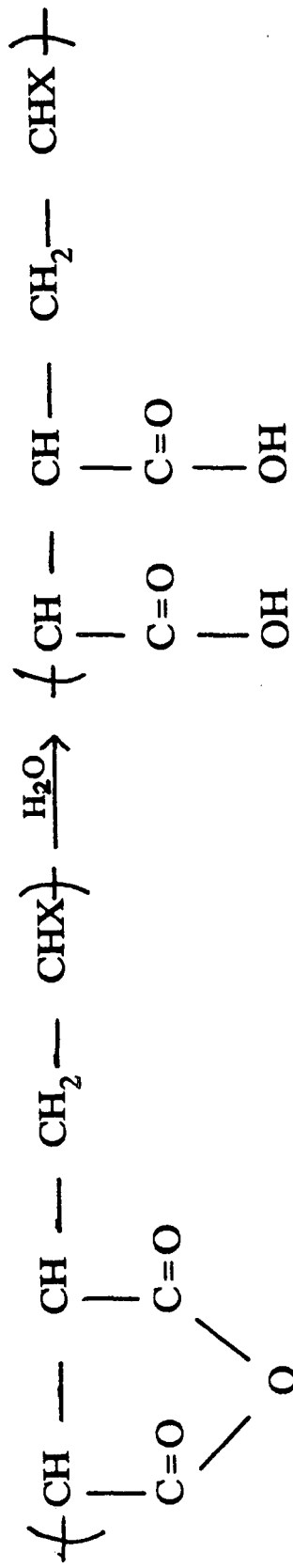
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Maleic anhydride

Comonomer

Polymer repeat unit



Hydrolyzed polymer repeat unit

Figure 1
Schematic representation of the copolymerisation and hydrolysis of maleic anhydride.

TABLE 1
PERFORMANCE OF DYNAMIC ZIRCONIUM OXIDE-MALEIC ANHYDRIDE COPOLYMER MEMBRANES

Polyelectrolyte	Composition (MA:X)	pH 7		pH 8		pH 9	
		R(%)	J(l/md)	R(%)	J(l/md)	R(%)	J(l/md)
PAA*	-	90,0	2 400	92,3	2 200	91,0	2 450
MA/VSA	50:50	58,3	7 420	61,5	7 370	62,3	7 280
MA/IA	50:50	76,7	6 950	79,3	6 890	81,4	6 310
MA/AA	50:50	80,9	5 080	84,2	4 740	81,2	4 980
MA/VOH	50:50	88,2	4 410	90,3	3 930	91,1	2 920
MA/VA	50:50	89,2	2 400	91,0	2 080	90,7	1 950

6 000 kPa, 6m/s, 35°C, 2 000 mg/l NaNO₃, *Poly(acrylic acid)

R : rejection of NaNO₃

J : permeate flux

l/md : l/m².d

phylities of the two comonomers. Vinyl alcohol, having a pendant hydroxyl group, will be far more hydrophilic than the vinyl acetate moiety. Thus the flux of the MA/VOH membranes should be higher than that of the MA/VA, and the results prove this.

Conclusions

All the maleic anhydride copolymers form dynamic membranes. The rejection capabilities of these membranes are not solely governed by the charge density on the membrane, but are due in part to the presence of hydrophobic groups or sections on the membrane-forming polyelectrolyte.

Acknowledgements

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