

## 1,1,1-Tris(hydroxymethyl)propane-Crosslinked Poly(vinyl Alcohol)-Poly(styrene Sodium Sulfonate) Interpolymer Membranes

The crosslinking of poly(vinyl alcohol) has been carried out under many different conditions to yield hydrophilic polymer membranes. Films of these materials are of interest because of their close chemical similarity to cellulose (cellophane) membranes. In contrast to the water-insoluble rigid cellulosic polymer chains, the flexible backbone permits solubility of the PVA in water, and consequently membranes are only stable if a suitable crosslinked network is developed between the chains. Heating to temperatures around 150°C in the presence of an acid catalyst results in both inter- and intramolecular dehydration reactions and the formation of an insoluble film.<sup>1</sup> Esterification with diacids<sup>2,3</sup> and acetal formation with dialdehydes<sup>4-9</sup> have been used to crosslink PVA. In this report we present the results of using a trihydroxy alcohol, 1,1,1-tris(hydroxymethyl)propane, TMP, as a crosslinking agent. In order to increase the porosity of the films and to impart a certain amount of fixed charge capacity, a polyelectrolyte, poly(styrene sodium sulfonate), PSSNa, was incorporated into the films.

The membranes were prepared in the following manner. PVA (Gelvatol 1-90 Monsanto) and PSSNa (Dow Chemical, viscosity-average molecular weight  $5 \times 10^5$ ) were prepared as 10% solutions by weight in water. TMP was used as a 50% aqueous solution. Casting solutions were prepared by combining appropriate amounts of these solutions. The solutions were cast on glass plates, dried in an air oven at 45°, and heated at 150°C for 30 min. Further heating had little effect on the resultant film. The membranes were kept in 0.1N KCl for at least two weeks prior to use. A description of the procedures of membrane characterization is given elsewhere.<sup>10</sup> The ultrafiltration rate was measured at a transmembrane pressure of 6.8 atm under conditions in which the feed solutions were circulated over the surface of the film. The feed solution in these experiments was 0.01N KCl with respect to KCl and 15 ppm with respect to erythrosin. The membrane properties of a selected number of membranes are given in Table I.

The casting solutions, though clear and homogeneous at room temperature, exhibited phase separation in the temperature range of 60–80°C depending on the composition. The amount and molecular weight of the PSSNa was critical. Membrane casting solutions containing 20% of the PSSNa (molecular weight  $5 \times 10^5$ ) were visibly incompatible. Under no circumstances could PSSNa of molecular weight  $7 \times 10^5$  be incorporated into a clear casting solution; conversely, lower molecular weight polyelectrolyte ( $4 \times 10^4$ ) could be incorporated to a higher degree. However, because of its smaller dimensions, low molecular weight PSSNa tended to dissolve out of the membrane more easily when the film was put into water.

In a neutral solution the heat treatment of PVA even in the presence of PSSNa does not lead to the formation of a water-insoluble film. Thus, under these conditions there is little tendency for the secondary hydroxy groups of the PVA to condense forming inter- or intrapolymer ether linkages. Nishimura<sup>1</sup> reported that at pH 2, the heating of PVA gives a change in color and a progressive in-

TABLE I  
Properties of PVA-PSSNa Membranes

	Membrane 1	Membrane 2	Membrane 3
Membrane composition, by weight			
PVA	69.0	44.5	34.5
PSSNa	10.4	11.1	10.4
TMP	21.6	44.4	55.1
Fraction extractable, %	40	52	58
Thickness, microns	36	38	57
Swelling, g H <sub>2</sub> O/g wet membrane	50	54	60
Concentration potential, mV	7.6	8.0	6.9
Hydraulic permeability, cm/sec atm	$0.50 \times 10^{-5}$	$0.65 \times 10^{-5}$	$2.5 \times 10^{-5}$
Erythrosin rejection, %	88	86	81
KCl rejection, %	24	22	28

crease in crosslinking as determined from the swelling in water of the resultant film. However, in the present case with the introduction of a polyfunctional primary alcohol such as TMP (glycerine was also used), a crosslinking reaction proceeds under neutral conditions rapidly at 150°C. The etherification of hydroxy groups is reported under strongly alkaline conditions<sup>11</sup> at 280° and in the presence of strong acid at similar high temperatures.<sup>12</sup> In the absence of the PSSNa there is no reaction. The sodium salt of toluene sulfonic acid proved equally effective in catalyzing the reaction. Membrane properties given in Table I showed little effect of composition in the range given. With weight ratios of of TMP/PVA greater than 0.7 or less than 0.1, the polymer films were highly swollen in water and gelatinous.

In Table I the data indicate that significant amounts of the initial components of the casting solutions dissolve from the film rapidly when the membrane is initially placed in water. We conclude that about one half of the PSSNa and the TMP are not firmly attached to the gel. By titration, a capacity of 0.4 to 0.5 meq/g dry membrane was found after a period of two weeks. This value remained constant for over a year of continual use. Considering the swelling of the polymer film, this capacity corresponds to a membrane fixed charge concentration of about 0.3 molal. The concentration potential determined between 0.1N and 0.2N KCl solutions is consistent with this titrated capacity. It is concluded that the PSSNa is permanently trapped within the PVA-TMP matrix since chemical links of the PSSNa to the PVA via  $-\text{SO}_2-\text{O}-$  bridges would be highly unstable in an aqueous environment.

The reported ultrafiltration rate is in the same range as a cellophane film of the same thickness.<sup>13</sup> However, the rejection of ionic solutes is governed by the Donnan exclusion of ionic solutes. The higher rejection of erythrosin reflects its larger molecular size. The rejection pattern is similar to that reported for interpolymer films prepared from poly(vinylidene fluoride), PVdF, and PSSA.<sup>11</sup> However, at a similar fixed charge concentration the PVA films have a lower hydraulic permeability and a lower solute rejection than comparable films prepared with a hydrophobic PVdF matrix. The PVA-TMP membrane provides a barrier that is a quasi-homogeneous gel structure, whereas the PVdF-PSSA system is microporous containing extensive impermeable domains of the PVdF. The gel structure of the PVA exhibits greater resistance to the flow of solvent and at the same time reduces the effect of the polyelectrolyte in screening out the ionic solutes. The mechanical properties of the TMP-PVA films were determined in a standard tensile mode. The ultimate tensile strength was found to be about  $2 \times 10^8$  dynes/cm<sup>2</sup> at an ultimate elongation of about 500%.

### References

1. M. Nishimura, M. Yabu, and M. Sugihara, *Kogyo Kagaku Zashi*, **70** (3), 393 (1967).
2. C. E. Reid and H. G. Spencer, *J. Appl. Polym. Sci.*, **IV** (12), 354 (1960).
3. S. Peter and D. Mittelstadt, *Kolloid-Z. Z. Polym.*, **251**, 225 (1973).
4. M. Nishimura, A. Aoyama, and M. Sigojara, *Kagaku To Kogyo*, **39**, 689 (1965).
5. M. Nishimura, M. Yabu, and M. Sugihara, *Kagaku To Kogyo*, **39**, 736 (1965).
6. Y. Nozawa and F. Higashide, *J. Polym. Sci. B*, **13**, 433 (1975).
7. C. T. Chen, Y. J. Chang, C. M. Chen, and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **17**, 789 (1973).
8. O. M. Ebra-Lima and D. R. Paul, *J. Appl. Polym. Sci.*, **19**, 1381 (1975).
9. D. Braun and E. Walter, *Colloid Polym. Sci.*, **254**, 396 (1976).
10. C. C. Gryte and H. P. Gregor, *J. Polym. Sci., Phys. Ed.*, **14**, 1839 (1976); *ibid.*, **14**, 1855 (1976).
11. R. A. Brett, *J. Oil Color Chem. Assoc.*, **41**, 429 (1958).
12. H. Holschmidt, U.S. Pat. 3,188,353 (1965); *Chem. Abstr.*, **63**, 1170h (1965).
13. D. M. Green, G. Antwiler, J. Moncrief, J. Decherd, and P. R. Popovich, *Trans. Am. Soc. Artif. Intern. Organs*, in press.

CARL C. GRYTE

Department of Chemical Engineering and Applied Chemistry,  
Columbia University,  
New York, New York 10027

Received August 6, 1976  
Revised April 2, 1977