

Modification of Cellulose Acetate Reverse Osmosis Membranes by Radiation Grafting*

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Synopsis

Large excesses of a chain transfer agent, carbon tetrachloride, were introduced to a recipe for the mutual radiation grafting of styrene to cellulose acetate film. The effect of the carbon tetrachloride on the molecular characteristics as well as the reverse osmosis and time dependent mechanical properties of resulting graft copolymers was determined. Extremely short side chains were generated as a consequence of the high concentrations of chain transfer agent and the composite results further suggest that the morphology of the grafted films is best described as "destructured" or internally plasticized consequent to grafting in the presence of CCl_4 . Reverse osmosis fluxes increased with per cent graft; salt rejection was high and unaffected by per cent graft up to 40% graft; and the tensile creep under wet conditions was significantly retarded by the grafting. These effects were shown to accrue from grafting *per se* by control experiments involving α -methylstyrene which will not propagate to form a polymer under these conditions. These results are compared and contrasted with earlier work on grafting in the absence of CCl_4 where long side chains of polystyrene were generated resulting in a structuring of the polymer involving domains of polystyrene-rich material and domains of cellulose acetate rich polymer.

INTRODUCTION

The high pressures used for seawater desalination by reverse osmosis lead to the gradual compaction of the expanded Loeb-type cellulose acetate membrane structures with a consequent decrease of the product flux rate and apparent salt rejection. It seemed of interest, therefore, to study modifications of cellulose acetate which would reduce the rate of compressive creep of the modified membrane and, in turn, stabilize the flux-rejection characteristics of the resulting membranes. The effect of styrene grafting to cellulose acetate was studied as a possible technique for mechanically stabilizing cellulose acetate membranes.^{1,2} Styrene was chosen because of its inherently low creep and insensitivity to water. Graft copolymerization is an attractive means for modifying base polymers because grafting frequently results in the superposition of properties relating

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to backbone and pendent chains. Radiation was chosen as the cleanest and most versatile method of grafting available and because the laboratory has had extensive prior experience in this field. The ideal result from this study would be synthesis of membranes exhibiting the time-dependent mechanical properties of polystyrene and the transport properties of cellulose acetate.

The results published earlier^{1,2} revealed that the tensile creep rate of wet styrene-cellulose acetate grafts decreased monotonically with increasing per cent graft. The water sorption equilibria and steady-state water fluxes decreased consequent to grafting. The data strongly suggested that styrene-rich domains were formed in the graft membranes which were water insensitive and functioned as "secondary valence crosslinks."

A considerable array of system parameters affect the characteristics (e.g., per cent graft, molecular weight of the pendent side chains) of a graft copolymer and in turn the ultimate properties of the bulk graft copolymer.² For a given base polymer and a given monomer, one may conveniently vary the total radiation dose, the dose rate, the swelling agent type and concentration, the type and concentration of chain transfer agent, and the addition of small quantities of difunctional monomer; and, therefore, a systematic study of the effect of grafting on ultimate properties must take into account these experimental parameters.

In an attempt to prepare grafts with much shorter side chains, formulations were prepared with an abnormally high ratio of chain transfer agent (carbon tetrachloride) to monomer. The effect of chain transfer agent and, in turn, the molecular weight of the grafted side chains on flux, rejection, and compaction properties is explored in detail. Cografting of styrene with 2-vinylpyridine was studied as well.

EXPERIMENTAL

Materials

Dense cellulose acetate films, 0.05 mm thick, prepared from Eastman E-398-3 cellulose, were kindly supplied by the Gulf General Atomics Corporation of San Diego, California. Commercial-grade styrene was distilled twice under vacuum, and reagent-grade pyridine and carbon tetrachloride were distilled once. Reagent-grade acetone and dioxane were used without further purification.

Graft Copolymerization

Mutual, heterogeneous, radiation-induced, graft copolymerization of styrene to cellulose acetate was carried out in the absence of air. Cellulose acetate film was immersed in the monomer solution, degassed five times, and then sealed under vacuum in a glass ampoule. The ampoule and contents were allowed to equilibrate at room temperature followed by irradiation by ^{60}Co emitted gamma rays from a gamma-cell source at a

dose rate of 0.84 Mrad/hr. Accessible homopolystyrene was extracted from the grafted samples by washing with benzene at room temperature to constant weight, and the per cent graft was calculated from the increase in weight determined after irradiation, extraction, and drying at 45°C under vacuum. The molecular weight of the pendent polystyrene side chains was determined from intrinsic viscosity measurement³ performed in toluene at 30°C on solutions of side chains cleaved from the backbone by acid hydrolysis of the cellulose acetate.⁴

Reverse Osmosis Measurements

The product flux and salt rejection were determined in a test cell first described by McKinney⁵ for reverse osmosis characterization of dense or symmetrical membranes. The test unit is uniquely suited for characterizing transport properties in dense and, therefore, low-flux membranes because of the small downstream dead volume and the simultaneous determination of flux and rejection in a capillary affixed to the downstream receiving volume, instrumented with a microelectrode to monitor downstream salt concentration.

Tensile Creep Measurements

Tensile creep measurements^{1,2} were carried out at 38°C under water at constant temperature ($\pm 0.1^\circ\text{C}$) by monitoring the change in distance as a function of time between two finely ruled lines on a film. The strain expressed as "(length-initial length)/initial length" was measured with a cathetometer accurate to 0.1 mm. Film specimens were initially $\frac{1}{2}$ in. wide, ca. 3 in. long, and $\frac{1}{2}$ mils thick. The films were clamped on the top with brass jaws with rubber inner surfaces. Acrylic jaws with rubber inner surfaces were used at the bottom of the film specimen. Variable loads could be applied to the bottom clamp. Engineering stresses (ca. 10^8 dynes/cm²) were calculated taking into account buoyancy corrections on the clamps and weights.

DISCUSSION OF RESULTS

Styrene Grafting

In an attempt to prepare grafts with much shorter side chains, preparations were made with an abnormally high ratio of the chain transfer agent (carbon tetrachloride) to monomer. The grafting recipes are included in the figurehead of Figure 1. The response of per cent graft to total dose is presented graphically in Figure 1 for the recipes including excess chain transfer agent.

The plateau-type curves found earlier for this grafting system^{1,2} were found slowly to change as the per cent of pyridine (a solvent for cellulose acetate) was increased and became essentially linear above 15% of pyridine in the grafting solution. Presumably the higher concentrations of swelling

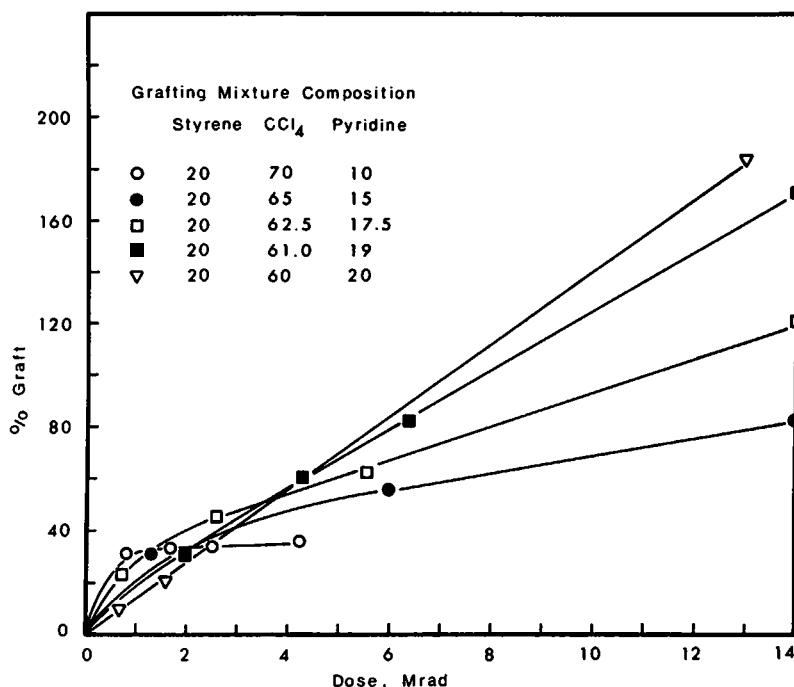


Fig. 1. Grafting yield as a function of dose for styrene grafting to CA in the presence of CCl₄ and pyridine.

agent (pyridine) are sufficient to accommodate an adequate monomer supply to the active growth sites, and diffusion does not limit the grafting kinetics.

It was shown recently⁶ that when the grafting proceeded at a constant or an accelerating rate, e.g., the butadiene grafted to poly(oxymethylene), the permeabilities of the resulting grafts were higher than the permeability of the base polymer. It would appear that the grafting reaction must proceed isotropically in the film with swelling to obtain good fluxes. Presumably the swelling is sufficient to cause disruption of the crystallites by the grafting and, recrystallization cannot reoccur because of the presence of the grafted side chains.

The pendent chains formed in the presence of swamping excesses of chain transfer agent could be too short to associate and form discrete regions of domains rich in polystyrene; however, the tensile creep data (Fig. 6) suggests that this is not so. Intrinsic viscosity measurements indicate that the molecular weight of the side chains is ca. 4,000, which is a factor of 100 less than the molecular weight of the side chains in the long chain grafts.^{1,2} Presumably, the primary result of the grafting would be the formation of many short chains pendent from the cellulose acetate backbone. Property modifications will accrue from this internal plasticization or destructuring of the cellulose acetate.

The water sorptive capacity of the grafted membrane^{1,2} appeared to be somewhat higher (on the basis of cellulose acetate) than the sorption equilibria for the virgin cellulose acetate. These results are contrary to most reported conventional grafting studies involving hydrophobic monomers and cellulose acetate. This seeming anomaly is a direct consequence of the very short grafted side chains produced in the presence of excess chain transfer agent (CCl₄).

Diffusion coefficients for water in the "short-chain" grafted film are presented in Figure 2. The water diffusivities are distinctly higher in the grafted membrane than in the unmodified cellulose acetate. These data viewed in concert with the grafting kinetics and the sorption equilibria suggest a rather consistent model for the physicochemical effect of "short-

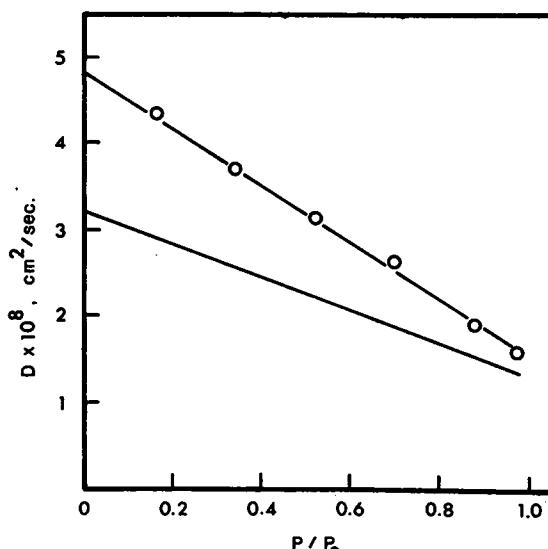


Fig. 2. Concentration dependence of integral diffusion coefficients at 25°C for water vapor in short-chain graft CA: (—) CA; (O) 33.8% styrene-grafted CA prepared in pyridine:styrene:CCl₄ = 20:20:60 mixture (short-chain graft).

chain" grafting. The predominant effect of grafting is destructuring of the cellulose acetate. These effects are distinctly different than the property changes effected by "long-chain" grafting. The long chains form domains which act predominantly as "secondary valence crosslinks" but apparently without effective destructuring.

These long-chain domains are rather water insensitive, resulting in decreased water sorption and a structuring rather than destructuring of the surrounding cellulose acetate. This "structuring" or free-volume filling results in the observed leveling of per cent graft versus total dose. The "structured," low free-volume surface essentially prevents diffusion of monomer to the film core. If the grafted membrane is dissolved and recast, the grafting kinetics are no longer limited by mass transfer in the dense

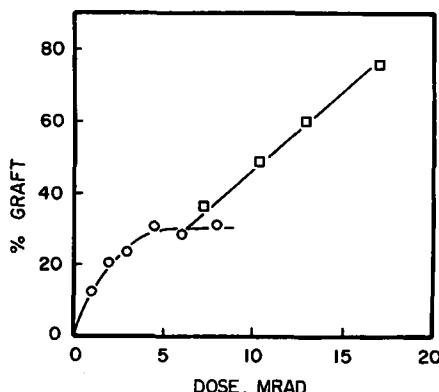


Fig. 3. The effect of recasting on the grafting behavior of styrene-cellulose acetate graft copolymer films; (O) initial grafting behavior; (□) regrafting consequent to solution and recasting.

surface layers, and a linear relationship between per cent graft and dose is observed (see Fig. 3).

The reverse osmosis properties of unannealed films are presented in Figures 4 and 5. The "short-chain" grafting yielded a markedly more open or destructed membrane, resulting in a monotonic increase in flux with increasing per cent graft and a companion decrease in rejection at

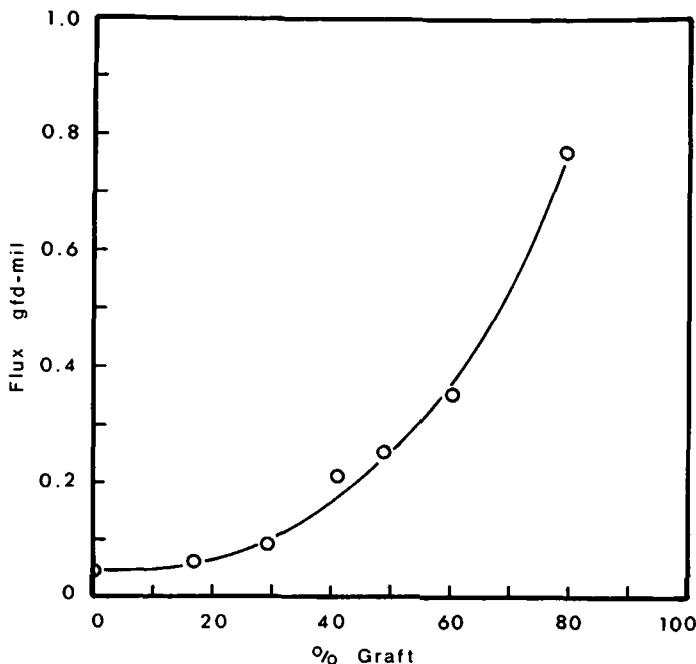


Fig. 4. Product flux as a function of per cent graft for unannealed, dense, short-chain graft membranes.

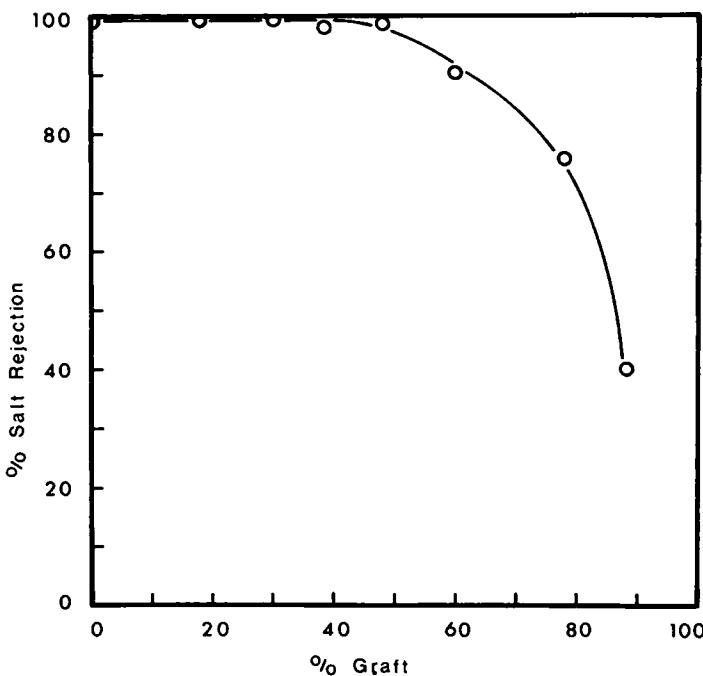


Fig. 5. Salt rejection as a function of per cent graft for unannealed, dense, short-chain graft membranes.

high grafting levels. Annealing at 80°C in water for 1 hr increased the salt rejection and decreased the product flux.

The excellent salt rejection of virgin cellulose acetate was retained past 40% graft, although the product flux increased significantly for membranes in this same range of per cent graft. The tensile creep behavior of these grafts was highly stabilized consequent to grafting, although the fluxes were improved and the excellent salt rejection was unaffected. The ultimate elongation was less than 3% after 500 hr of creep under a constant stress of 10^8 dynes/cm², although the cellulose acetate exhibited accelerated creep leading to failure at 150 hr at an ultimate elongation in excess of 10% (see Fig. 6).

These consistent results relating to short-chain grafts are quite encouraging because high fluxes and rejections were coupled with reduced creep.

The results indicating an increase in product flux with grafting suggested that swelling of the membrane *per se* during the grafting procedure may play a significant part in the modification of membrane properties. Control experiments were designed and run, therefore, to separate explicitly swelling and radiation effects from property modifications resulting from grafting *per se*. Cellulose acetate film was immersed in a mixture of 20 parts α -methylstyrene, 20 parts pyridine, and 60 parts CCl_4 to simulate the exact grafting conditions except for the small but significant substitution

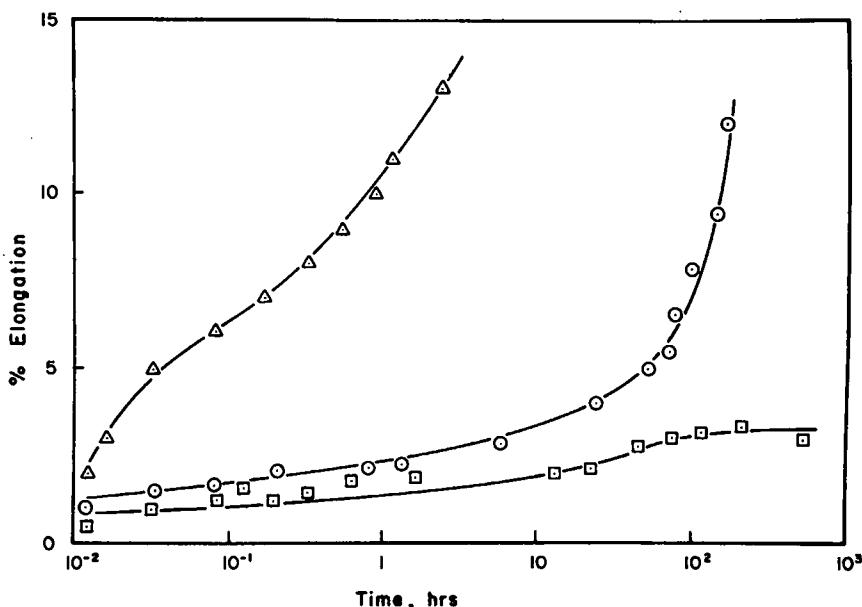


Fig. 6. The effect of graft copolymerization on the tensile creep properties of wet cellulose acetate: (○) cellulose acetate; (□) styrene:pyridine:CCl₄ = 20:20:60, 30.1% graft (3.0 Mrad); (△) α -methylstyrene:pyridine:CCl₄ = 20:20:60 (3.0 Mrad).

of α -methylstyrene for styrene. It was assumed that the hindered α -substituted monomer would not propagate a grafted side chain although it would afford rather similar radiation protection to the cellulose acetate backbone.⁷ Rather similar swelling histories would be expected consequent to immersion in the α -methylstyrene formulation compared with the styrene formulation. Any difference in properties between films similarly irradiated but immersed in the different formulations would be a consequence, therefore, of the grafting *per se* as opposed to irreversible swelling or radiation effects.

Indeed, virtually no graft copolymerization was effected consequent to radiation. This is consistent with the expectation that the chain propagation constant is too low to effect polymerization. The flux-rejection modifications resulting from this treatment are presumably a consequence of all process variables except graft copolymerization. It is intriguing that fluxes decrease as do salt rejection, and there is an anomalous increase in flux at doses in excess of 6 Mrad presumably due to radiation damage at the very high doses.

A comparison between the effects of grafting in the presence of styrene and simple irradiation and swelling in the presence of α -methylstyrene is presented in Figures 6, 7, and 8. The normalized product flux is plotted versus radiation dose in Figure 7 for both styrene and α -methylstyrene. The product flux increases significantly in the case of styrene and is effected only slightly by irradiation in the presence of α -methylstyrene.

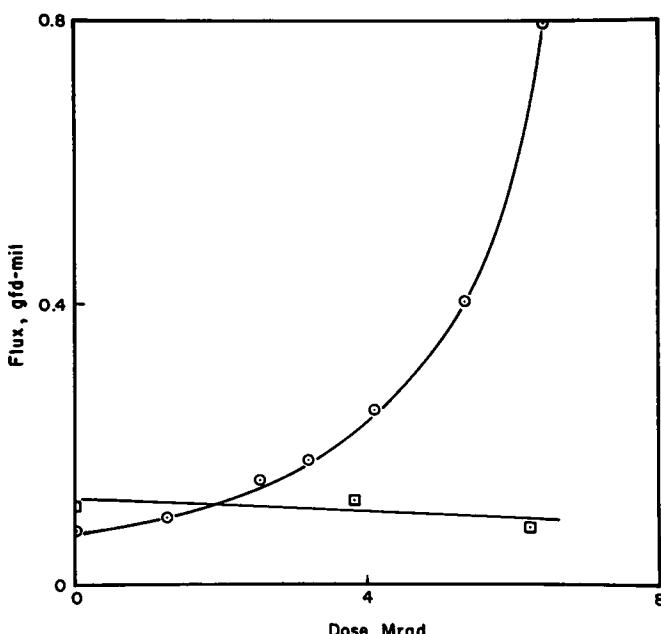


Fig. 7. Product flux as a function of dose for unannealed dense membranes: (O) styrene:pyridine:CCl₄ = 20:20:60; (□) α -methylstyrene:pyridine:CCl₄ = 20:20:60.

At doses in excess of 6 Mrad the apparent flux through the α -methylstyrene-treated membrane was abnormally high accompanied by zero rejection, suggesting that radiation induced failure in the highly irradiated film.

The salt rejection behavior (presented in Fig. 8) for the two systems (styrene versus α -methylstyrene) is virtually identical up to a dose of 4 Mrad, although the observed drop in rejection as a consequence of dose actually reached a value of zero for the α -methylstyrene system.

The results of a further set of tensile creep experiments are presented in Figure 6. Wet tensile creep measurements were performed on virgin cellulose acetate film, cellulose acetate grafted with styrene, and cellulose acetate immersed in an α -methylstyrene formulation and irradiated. A substantial reduction in the wet tensile creep rate was effected by the grafting, although the α -methylstyrene treatment actually accelerated the creep process.

The composite results, including flux rejection and creep behavior, clearly indicate that short-chain grafting of styrene to cellulose acetate improves the flux and stabilizes the viscoelastic creep, and the excellent salt rejection of cellulose acetate is retained. In addition, it appears that these improvements are mainly a direct consequence of grafting *per se*.

In some initial attempts to prepare an asymmetric membrane, a purified graft copolymer prepared in the presence of large excesses of CCl₄ (chain transfer agent) was cast from a 20% solution in pure acetone. The mem-

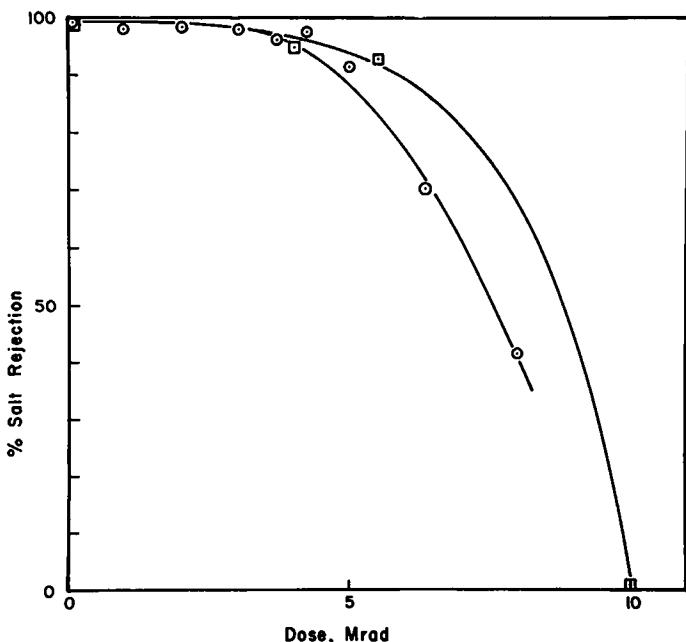


Fig. 8. Salt rejection as a function of dose for unannealed dense membranes: (○) styrene:pyridine:CCl₄ = 20:20:60; (□) α -methylstyrene:pyridine:CCl₄ = 20:20:60.

brane, when allowed to dry at room temperature for 15 sec, submerged in water at 0°C, and subsequently annealed at 80°C for 30 min, provided a flux of 10.4 gfd-mil and a salt reject on of 93%. Similar attempts to cast from acetone/dioxane mixtures were unsuccessful, leading to membranes providing no salt rejection. Some loss of weight was found on dissolving and recasting.

Cografting of Styrene and 2-Vinylpyridine to Cellulose Acetate

Very recently, it was shown that the loss of weight on recasting and at least part of the improved flux were due to tenaciously held, occluded pyridine hydrochloride, presumably formed from the hydrochloric acid produced by the radiolysis of the carbon tetrachloride. This led to some experiments with grafting comonomer mixtures of styrene and 2-vinylpyridine in an attempt to exploit these findings.

The mutual grafting of 2-vinylpyridine to dense cellulose acetate produced, after quaternizing, grafted films with extremely high normalized fluxes, significant but lower salt rejection, and essentially unaltered compaction properties. For example, a 34% 2-vinylpyridine-grafted cellulose acetate membrane showed a flux of 2.4 gfd-mil, salt rejection of 80%, and a compaction resistance of -0.03 at 35,000 ppm NaCl and 1500 psi. The results of the independent styrene grafting and 2-vinylpyridine grafting studies plus the apparently beneficial effect of occluded pyridine hydrochloride

suggested that the cografting of these dissimilar monomers might result in synergistic effects.

The effect of 2-vinylpyridine concentration in the monomer mixture of styrene and 2-vinylpyridine on the grafting and reverse osmosis properties of cografted membranes was studied. The 2-vinylpyridine retards the overall rate of grafting; however, the transport kinetics of the resulting grafted and quaternized membranes indicate that high 2-vinylpyridine concentrations in the monomer solution markedly increase the flux of the cografted membranes. The flux and salt rejection of cografted and quaternized membranes are plotted versus the calculated values of the 2-vinylpyridine content in the membranes in Figure 9. The flux increased mono-

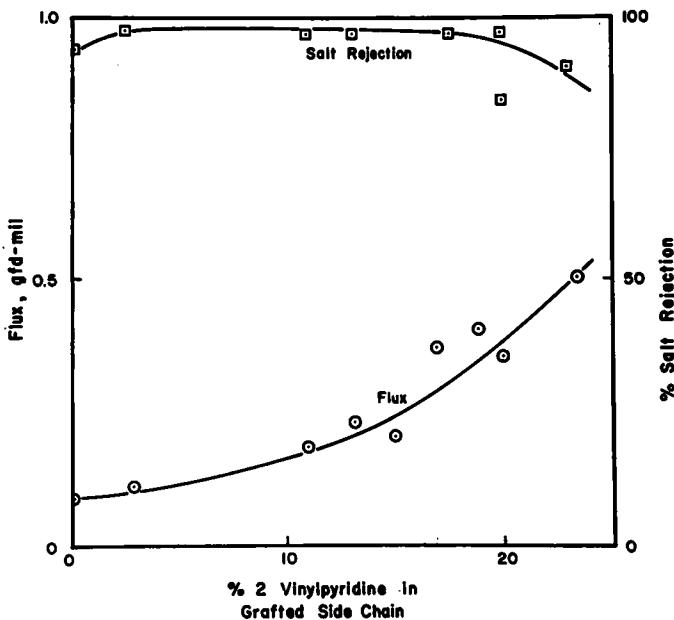


Fig. 9. Reverse osmosis properties of styrene-2-vinylpyridine 40% grafted cellulose acetate membrane as a function of 2-vinylpyridine content. 2-Vinylpyridine content calculated according to the calculational procedure of Burlant et al.⁸

tonically with the quaternized 2-vinylpyridine content; the salt rejection, however, was greater than 98% with up to 20% 2-vinylpyridine in the membrane. Quaternization, although increasing the flux by more than an order of magnitude, did not significantly reduce the salt rejection. It is apparent, therefore, that the rather novel technique of cografting of hydrophobic monomers and hydrophilic amine-type monomers coupled with quaternization affords the possibility of producing a membrane composition with the excellent salt rejection of cellulose acetate but with fluxes improved by an order of magnitude.

Similar studies, still in progress, were made with copolymer grafts of methyl methacrylate and 2-vinylpyridine. The results were found to be

very similar to the styrene graft although in general the methyl methacrylate series gave superior fluxes and salt rejection compared with styrene.

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