

DRY-RO Membranes from Cellulose Acetate Carbamates

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Synopsis

Cellulose acetate carbamates (CACs) are the polymers which result when organic isocyanates are reacted with the free hydroxyl groups of cellulose acetate (CA). CACs are more hydrolytically stable and exhibit physical properties which are superior to those of their CA mixed ester analogs. Two synthetic approaches to CACs have been utilized in this study: (1) preformation, i.e., separate synthesis of such polymers prior to their inclusion in solutions for membrane casting; and (2) *in situ* formation, i.e., the inclusion of blocked isocyanates in standard dry process casting solutions of CA followed by thermal activation of the resultant dry membranes leading to regeneration of free isocyanate and subsequent CAC formation. Preformed CAC polymers have been prepared utilizing phenyl-, 3-chloropropyl-, 3-bromopropyl-, and 3-bromopropyl-(isothio)-, isocyanates. Polymers containing omega-halocarbamate moieties were quaternized with dimethylbenzylamine to produce ionogenic (QCAC) polymers containing quaternary ammonium groups. DRY-RO membranes from the QCACs exhibit flux/rejection values varying between 6–8 gfd at 98% rejection and 20 gfd at 90% rejection (0.5% NaCl feed at 400 psi and 25°C). *In situ* formation of CAC membranes has been effected with tolylene- and hexamethylene-diisocyanates, with quaternized isocyanate monomers employed for the preformed CAC polymers, and with specially tailored diisocyanates containing ionogenic groups. Crosslinking rendered all of the membranes acetone insoluble. Inasmuch as *in situ* formation substitutes the easy synthesis of blocked isocyanate monomers for the more difficult separate synthesis of preformed CAC polymers, it is anticipated that the former will replace the latter.

INTRODUCTION

The suitability of CA as a polymer for the preparation of skinned reverse osmosis (RO) membranes was discovered by Loeb and Sourirajan in 1960.¹ Since then, although our understanding of the physical and chemical requirements of RO membrane polymers has increased substantially, CA and its derivatives and blends have maintained a preeminent, if no longer exclusive, position in this field. The evolution of cellulosic RO membrane polymers is depicted chronologically in Figure 1.

The secondary CAs of commerce are prepared by the deacetylation of primary acetate or triacetate (CTA) to a degree of substitution (DS) of approximately 2.45. Since the acetyl is more hydrophobic than the hydroxyl group, hydrophobicity increases with increasing acetyl content. This in turn reduces swelling, thereby increasing permselectivity and decreasing permeability. Further, since structural regularity, and hence crystalline order, also increases with increasing acetyl content, solubility declines in a parallel fashion until, at a DS of approximately 2.7, it drops precipitously.² However, because of the greater permselectivity of higher-DS CAs, many attempts have been made to develop polymers in the trisubstitution range (i.e., $DS \geq 2.75$). The first successful such approach was Cannon's 2.72-DS blend of CA and CTA from a mixed acetone-

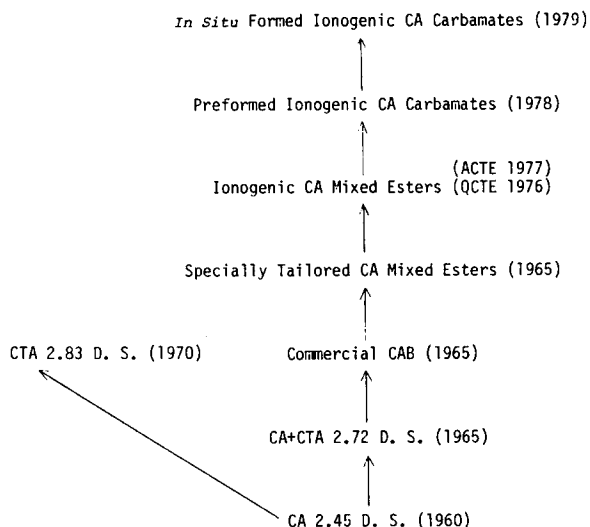


Fig. 1. Evolution of cellulosic RO membrane polymers.

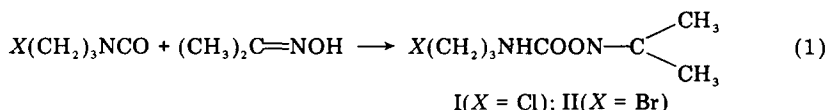
dioxane solvent system.³ This solvent system has also been utilized for the preparation of true CTA membranes with a DS of 2.83.⁴ Because of the generally poor solubility of CTA itself, highly soluble CA-mixed esters have been intensively investigated as candidates for RO membrane polymers. Mixed esters contain a second acyl component (larger than the acetate group), which disrupts order and hence increases accessibility and solubility. Manjikian found, for example, that commercially available CA butyrate (CAB) was capable of being cast into highly permselective membranes.⁵ However, the higher-than-optimum concentration of butyryl groups in commercial CABs brought about internal plasticization and excessive compaction under pressure with the result that they have not found a permanent niche. In 1965 specially tailored CA mixed esters (containing lower concentrations of the second acyl component than are found in commercially available grades) were first utilized in wet RO membranes.⁶ In spite of its early initial promise, this work was abandoned in lieu of the development of the CA + CTA blend membrane. In 1976 the present authors began their development of CA mixed esters containing ionogenic groups—first the quaternized cellulose triesters (QCTEs), which contained quaternary ammonium groups,⁷ and then in 1977 the anionic cellulose triesters (ACTEs), which contained sulfonate groups.⁸ The presence of a low ion-exchange capacity (IEC) of fixed charges within the membrane polymer was found to enhance the permeability of the resultant membranes without any concurrent loss in permselectivity. (It has since become evident that high-performance membranes from noncellulosic polymers are also ionogenic and exhibit IECs comparable to those found to be optimum for the ionogenic CA mixed esters.⁹)

The present paper is concerned with the highly promising new (1978) class of ionogenic CA polymers; viz., the ionogenic CACs. CACs are known to be more hydrolytically stable than the corresponding mixed esters.¹⁰ Furthermore, because no degradation in chain length accompanies their formation, the resultant membranes also exhibit superior physical properties.

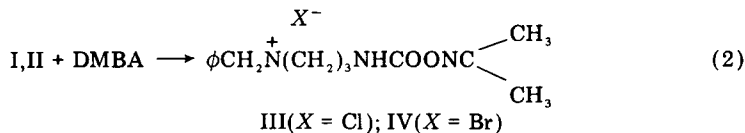
EXPERIMENTAL

Isocyanate Monomers

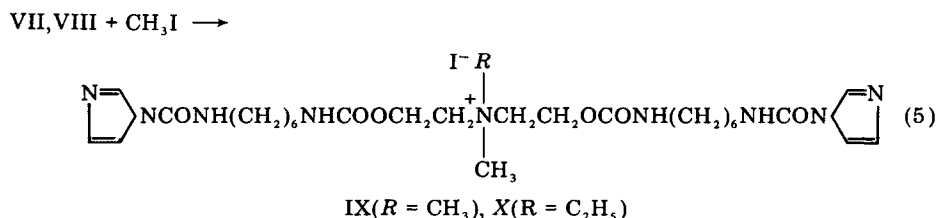
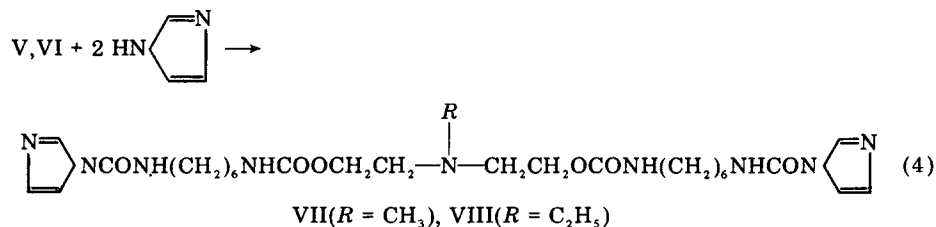
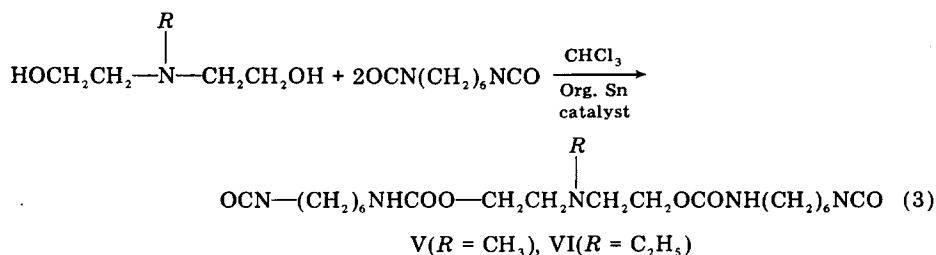
Phenyl isocyanate was purchased and used without further purification. Tolylene (TDI) and hexamethylene- (HDI) diisocyanates were blocked from acetone solutions of acetone oxime. 3-Bromopropyl isothiocyanate was prepared from 3-bromopropyl amine-hydrobromide by the method of Friis.¹¹ 3-Chloropropyl isocyanate was prepared from methoxypropylamine hydrochloride and phosgene according to the method of Petersen.¹² 3-Bromopropyl isocyanate was prepared by phosgenation of 3-bromopropyl amine hydrobromide and by reaction of HBr with hydroxypropyl amine, followed by phosgenation. Quaternized and blocked 3-chloro- and 3-bromo-propylisocyanates were prepared by adding the halopropyl isocyanate dropwise into an acetone solution of oxime:



The blocked isocyanates I and II were then further reacted with dimethylbenzylamine (DMBA) to give the quaternized products, III and IV:

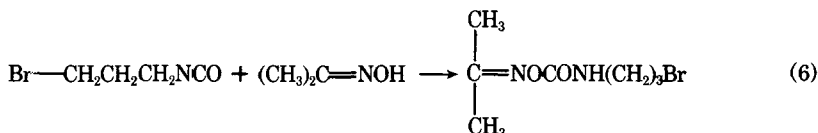


The preparation of monomers each containing a single quaternary ammonium group and two blocked isocyanate groups for subsequent crosslinking is depicted in eqs. (3)–(5):

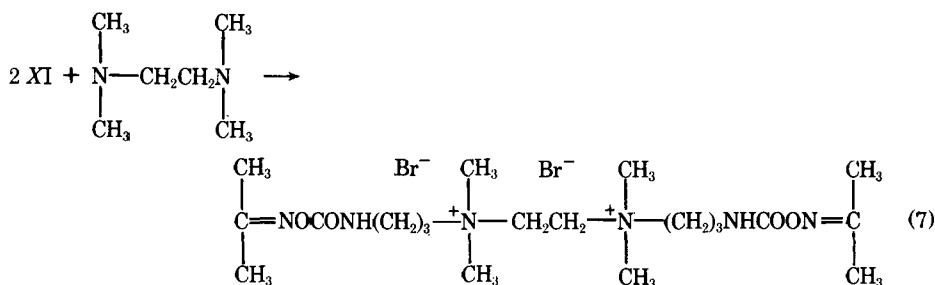


IX and X are acetone-soluble viscous reddish liquids. Dieterich et al. had previously prepared the unblocked counterparts of IX and X for application to quaternized polyurethanes.¹³

A monomer, XII, containing two quaternary ammonium groups and two blocked isocyanate groups was also prepared:



XI



XII

CTC and CACs

Preformed CAC polymers were prepared according to previously described procedures.¹⁴ In the case of the CA carbanilates, 100 g of phenyl isocyanate was added to a dry solution of 250 g CA in 2 l. acetone and 0.5 l. pyridine. Aliquots were taken after 24, 48, and 72 hr at 50°C. Before precipitation into isopropanol, excess methanol was added to combine with any unreacted isocyanate. To form the CACs containing omega-halogen groups, 50 g of the isocyanate was allowed to react for a sufficient period of time to incorporate approximately 0.1 meq/g of the carbamate groups into the CA polymer. The reaction was followed by infrared, a secondary standard previously calibrated against nitrogen analyses by the Kjeldahl method. Quaternization occurred simultaneously with carbamate formation owing to the presence of excess dimethylbenzylamine (DMBA). Cellulose tricarbaniolate (CTC) was prepared according to a previously described method from cellulose which was prepared by the deacetylation of E-394-60 CA in 50/50 isopropanol/conc. NH_4OH .^{10,14} All membranes were prepared according to the following conditions: casting solution temperature, 35°C; casting substrate, nonwoven three-ply polyester fabric (Eaton-Dikeman Type 3381); air temperature, 23°C; air velocity, 500 linear m/min; line speed, 1 m/min; cast solution thickness, 0.25 mm.

In situ formation of CAC polymers was effected by dissolving a given amount of the blocked isocyanates TDI, HDI, III, IV, IX, X, or XII in standard solutions containing CA (400-25) in acetone (or dioxolane)/methanol/isobutanol, followed by filtration, casting, and membrane formation by complete evaporation. The DRY-RO membranes which resulted were skinned microgels of CA which contained encapsulated blocked isocyanates. Heating these membranes at 100°C

for 24 hr resulted in the formation of the CAC *in situ*. All membranes (both preformed and those formed *in situ*) were tested at 25°C on a feed of 0.5% NaCl. The values of flux and rejection cited were those obtained for the formulations cited; other values are obtained from different formulations. The fresh water permeabilities are 20% higher than those shown for 0.5% NaCl feed.

RESULTS AND DISCUSSION

Preformed CTC and CACs

The OH band of the infrared spectrum of CTC is but a residual shoulder on the NH band, which has an absorption maximum at 3.03 μm (Fig. 2). The CH band is a doublet with the 3.3- μm peak believed to represent aromatic contributions and the 3.4- μm peak representing aliphatic contributions. Two aromatic bands are found at 6.23 and 6.63 μm . The maximum of the carbamate C=O stretching band is at 6.50 μm , and the C=O band at 5.75 μm is somewhat broader than that of CA. Membranes and even dense films of CTC proved to be extremely brittle, a property attributable to extreme dilution of the polymer backbone by the high concentration of the comparatively high molecular weight substituent groups. That the aromatic groups also rendered the polymer hydrophobic is evidenced by the impermeability of the resultant membranes (Table I).

Since it was evident that CTC was of no use as a membrane polymer and since earlier studies had indicated that organo-soluble aliphatic cellulose tricarbamates could not be prepared, subsequent work stressed the CACs.

The progressive derivatization of E-400-25 CA with an excess of phenyl isocyanate was followed by infrared (Fig. 3).

As carbanilation proceeded, the OH stretching band with a maximum at 2.88 μm declined and was replaced by the NH stretching band at 3.0 μm . As was the case for CTC, the CH band at 3.4 μm remained, but a shoulder at 3.3 μm appeared

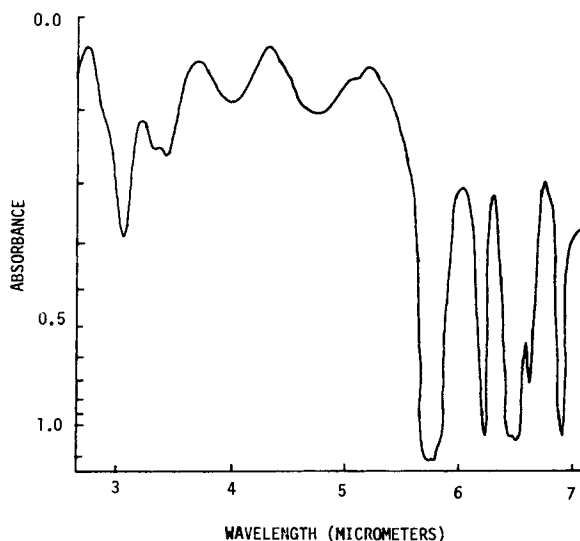


Fig. 2. Infrared spectrum of cellulose tricarbamate.

TABLE I
RO Performance Characteristics of DRY-RO Membranes of the Neutral CA Carbanilates and Cellulose Tricarbanilate

Polymer type	Casting solution composition ^a	Product flux, ^b gfd	Salt rejection, ^b %
CA 400-25, 0.55 DS carbanilate	D70, IBA 60 MeOH, 10	1.7 best result, 1.01 avg.	99 best result, 98.5 avg.
CA 383-40, 0.1 DS carbanilate	D70, IBA 54 MeOH, 10	5.1	95.1
CA 383-40, 0.67 DS carbanilate	D70, IBA 54 MeOH, 10	Too low to measure	—
Cellulose tricarbanilate from deacetylated 394-60 CA	D70, IBA 54	Too low to measure	—
CA 400-25, blank	D70, IBA 54 MeOH, 10	6-8	88-90

^a Polymer concentration, 0.10 g/ml.

^b 0.5 NaCl feed at 400 psi and 25°C.

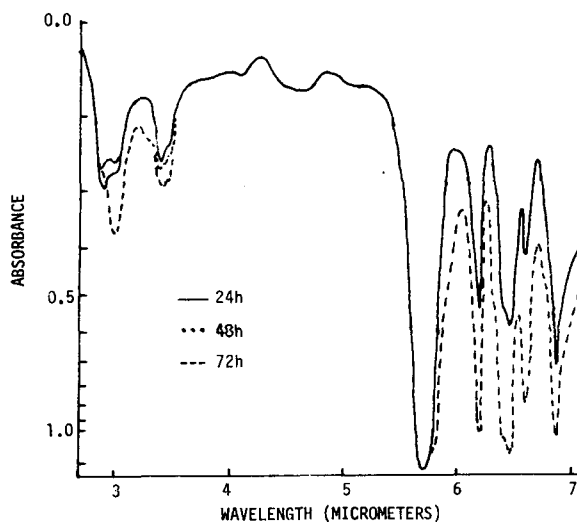


Fig. 3. Infrared spectra of 400-25 CA carbanilates.

(presumably due to aromatic CH—) and grew more intense with increasing time of reaction. Aromatic bands appeared at 6.23 and 6.63 μm . A very strong C=O (from $-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}$) was evident at 6.48 μm . The C=O band at 5.7 μm , which was primarily attributable to the ester carbonyl, was somewhat broadened. As was the case with CTC, the carbanilate group increased the hydrophobicity of the CACs relative to that of CA, with the result that permeability was decreased (Table I).

That a low DS of carbanilate groups may be beneficial to RO performance is suggested by the fact that 0.1 DS of such groups increased the salt rejection from

90 to 95% with only a modest decrease in permeability (Table I). The permeability and physical properties of the CA carbanilates decreased with increasing carbanilate DS. Although high-DS (0.55 DS carbanilate) CA-400-25 maintained some permeability, high-DS (0.67 DS carbanilate) CA-383-40 did not. The latter was also noticeably more brittle than both the CA starting materials and the less highly substituted CA carbanilates.

The benzalkonium salts of CA-3 bromopropyl-carbamate, CA-3-chloropropyl-carbamate, and CA-3-bromopropylthiocarbamate proved to be excellent RO membrane polymers (Table II).

It is evident that ionogenic CACs exhibit much greater permeability at a given permselectivity than does the CA starting material. It is also apparent that thiocarbamate and carbamate bonds are interchangeable (at least insofar as RO performance characteristics are concerned), since the results from CA Q 3-Br propyl thiocarbamate and CA Q 3-Br propyl carbamate of the same IEC are virtually identical. The effect of the nature of the halogen counterion is not felt to be significant. The CA Q 3-Cl propyl carbamate in the table was deliberately formulated to illustrate the higher (relative to CA) permselectivity of ionogenic CA carbamates at a given permeability. The infrared spectrum of the low (~0.1 meq/g) thiocarbamate polymer cited in Table II exhibited a C=S band at 6.50 μm (Fig. 4). A broadening and slight red shift of the OH band at 2.86 μm due

TABLE II
RO Performance Characteristics^a of DRY-RO Membranes of Certain Preformed Quaternized CA Carbamates and Thiocarbamates

Polymer type	Product flux, gfd	Salt rejection, %
CA Q 3-Br propyl thiocarbamate	18.6	90.1
CA Q 3-Br propyl carbamate	18.2	89.9
CA Q 3-Cl propyl carbamate	6-7	97-98
CA	6-8	88-90

^a 0.5% NaCl feed at 400 psi and 25°C.

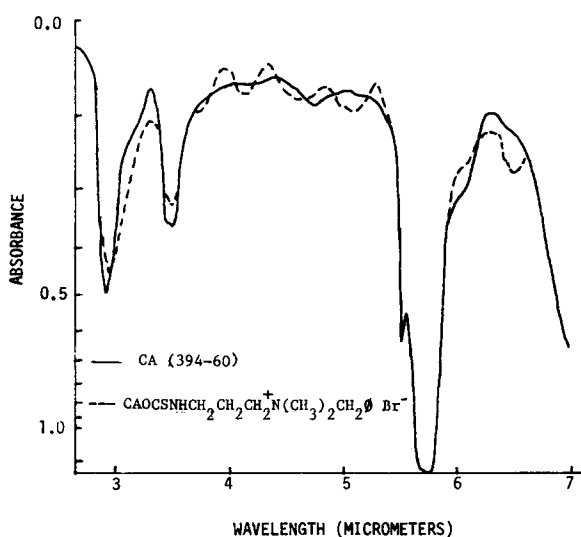
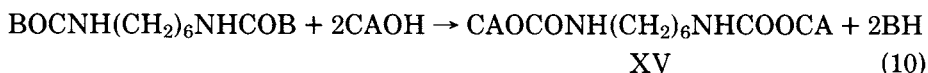


Fig. 4. Infrared spectrum of 394-60 CA Q 3-bromopropylthiocarbamate.

to NH band influence were also apparent. Casting solution viscosity of CAC polymers was higher than that of analogous QCTE polymers, in which the quaternary ammonium moiety was attached to CA via ester rather than carbamate groups (Table III). This is attributable to the fact that carbamate formation does not cause chain degradation, whereas the liberation of hydrogen chloride during the reaction of acylchlorides with CA will result, even in the presence of proton acceptors, in some cleavage of the cellulose backbone. This is probably the principal reason why the physical properties of ionogenic CACs prepared from aliphatic isocyanates are superior to those of their ionogenic CA mixed ester analogs. However, the toughness and abrasion resistance of the chemically related polyurethanes may also be encountered in the aliphatic CACs. If this is so, the high cohesive energy density of the —OCONH— group, due to its strong capacity for hydrogen bonding, may be responsible.¹⁵ One further observation should be made. The skins of *all* of the CAC membranes are easily recognized by virtue of their extremely high reflectivity. Perhaps it is more than coincidental that high gloss is characteristic of polyurethane coatings.

CACs Formed *In Situ*

The basic technique for determining the splitting temperature for isocyanates blocked with various compounds is due to Petersen¹²:



He incorporated HDI blocked by various splitters into solutions of CA which were then cast into dense films. The resultant films were then heated at various temperatures for a half-hour and their acetone solubility determined. The temperature at which complete acetone insolubility occurred was considered the splitting temperature and, of course, corresponded to the temperature of formation of crosslinked CACs (XV).

Because dry skinned microgel membranes are more susceptible to densification during annealing than are already dense films, Petersen's technique was modified to permit annealing at lower temperatures for longer periods of time, i.e., for 24 hr at 100°C rather than a half-hour at 150°C.

After annealing, acetone solubility was qualitatively estimated, and samples of membranes were tested for flux and rejection (Table IV). At the same time, unannealed membranes (figures in parentheses) were tested. No significant difference was found between HDI and TDI. The higher the concentration of diisocyanate, the less permeable the membranes. The fact that permeability

TABLE III
Viscosities of Casting Solutions of CA and the Benzalkonium Salts of CA 6-Br Caproate and CA 3-Br Propylthiocarbamate

Polymer species	Polymer type	Casting solution ^a viscosity, centipoise
CA 394-60	CA	1650
Q CA 6-Br caproate	CA mixed ester	570
Q CA 3-bromopropyl thiocarbamate	CA carbamate	1868

^a Polymer concentration, 0.1 g/ml, D 70, IBA 54, MeOH 10.

TABLE IV
RO Performance Characteristics^a of DRY-RO Membranes Crosslinked Utilizing Diisocyanates
Blocked with Acetone Oxime

Diisocyanate	Concentration ^b	Annealing temp., ^c °C	Product flux, gfd	Salt rejection	Acetone solubility ^d
HDI	5	100 air	(10.2)	(81.8)	+
			2.2	88.7	-
	10	100 air	(13.5)	(74.0)	+
			2.1	34.4	-
	10	100 vacuum	4.1	92.2	-
	20	100 air	(18.81)	(66.4)	+
TDI	5	100 air	4.4	86.0	-
			(12.0)	(72.9)	+
	10	100 air	4.5	90.3	-
			(12.5)	(68.0)	+
	20	100 air	4.9	87.9	-
			(17.5)	(59.4)	+
			1.8	93.5	-

^a 0.5% NaCl feed at 400 psi and 25°C. Values in parentheses for unannealed membranes.

^b Percent by weight relative to CA.

^c Annealing period, 24 hr.

^d + denotes solubility; -, insolubility in acetone.

was severely diminished by crosslinking indicated that the length of the crosslinkers was too short and/or that the crosslinkers were too hydrophobic. Since annealing of noncrosslinked CA blank membranes was without effect, permeability decline was not related to thermal annealing per se. In unannealed membranes, the inclusion of crosslinkers generally lowered rejection and increased permeability. Annealing *in vacuo* appeared to be preferable to annealing in air. Very likely more efficient removal of the blocking agent was responsible for this.

Varying amounts (between 2.5 and 10.0% of the weight of CA) of the quaternized and capped compounds III and IV (see Experimental) were dissolved in CA 400-25 casting solutions, which were then machine cast and cured at 100°C for 24 hr. Nitrogen analyses were run on water-leached unannealed and on water-leached annealed samples of membrane. Although essentially no nitrogen was found on the unannealed samples, the annealed samples contained much of the nitrogen which had been contained in the added compound IV (Table V).

The results clearly support the feasibility of *in situ* formation. CA blank membranes yielded 8 gfd at 88% rejection, whereas a benzalkonium salt of CA-3-chloropropyl carbamate formed *in situ* yielded 16 gfd at the same rejection. Unannealed membranes from which compound IV had been leached prior to testing exhibited higher fluxes, but lower rejections than the CA blanks. This is obviously owing to an increase in the porosity of the skin layer due to leaching of soluble material from an insoluble skin. In every case, annealing—which effected the covalent attachment of the quaternary ammonium groups—did so without any loss of permeability but with a (usually) significant increase in salt rejection. It also appears that the results for the membranes formed *in situ* from CA 3-chloropropyl carbamate (compound III) were superior to those from the 3-bromopropyl analog (compound IV). Differences in compatibility between compounds III and IV and CA may be a factor here.

TABLE V
RO Performance Characteristics^a of DRY-RO Membranes of the Quaternized CA Carbamates Prepared *In Situ*^b

Blocked isocyanate	Concentration ^c	Product flux, ^d gfd	Salt rejection, %
—	0	8	88
III	5	(14.8)	(66.3)
III	5	16.0	88.0
III	10	(24.6)	(52.8)
III	10	24.2	78.7
IV ^e	2.5	(12.8)	(70.8)
IV	2.5	15.3	79.8
IV	5.0	(17.8)	(58.8)
IV	5.0	19.4	72.7
IV	7.5	(20.6)	(52.6)
IV	7.5	25.9	61.1
IV	10.0	(25.0)	(48.6)
IV	10.0	32.8	49.7

^a 0.5% NaCl feed at 400 psi and 25°C.

^b Casting solutions contained E-383-40 CA + indicated percentage (relative to the weight of polymer) of quaternized and blocked ω -halo propylisocyanate. Cast membranes heated for 24 hr at 100°C to prepare CA carbamate polymer *in situ*.

^c Percent by weight relative to CA.

^d Values in parentheses for leached membranes prior to heating.

^e Nitrogen contents: *in situ* polymers form compound IV: A, extracted unannealed membrane 0.001%N; B, 5% annealed 0.26%N; C, 10% annealed 0.42%N.

The crosslinked ionogenic CA carbamates formed *in situ* were prepared by adding compound IX to standard CA casting solutions in varying amounts (Table VI).

The permeability of unannealed membranes increased and rejection decreased with increasing concentration of crosslinker. This is a result of leaching of the water-soluble crosslinker from the membrane. The flux of annealed membranes remained virtually constant, however, whereas the rejection increased with increasing crosslinker concentration and appeared to pass through a maximum at the point where its weight is about 15% that of CA.

Membranes prepared with compound X behaved in the same manner as in the preceding case (Table VII). The permeability of the unannealed membranes increased and the permselectivity decreased with increasing crosslinker con-

TABLE VI
RO Performance Characteristics^a of DRY-RO Membranes Prepared *In Situ* with Quaternized *N*-Methyl Diethanolamine · 2HDI (Compound IX)

Concentration of crosslinker, g/10 g CA	Product flux, gfd		Rejection, %	
	Unannealed membrane	24 hr at 100°C	Unannealed membrane	24 hr at 100°C
0.21	6.2	6.4	86.4	87.6
0.42	7.4	5.3	85.4	90.2
0.83	9.4	7.3	81.2	91.4
1.66	10.8	5.7	76.7	94.8
2.49	14.7	5.7	67.8	93.8
3.32	12.8	6.1	72.7	92.9

^a 0.5% NaCl feed at 400 psi and 25°C.

TABLE VII
RO Performance Characteristics^a of DRY-RO Membranes Prepared *In Situ* with Quaternized *N*-Ethyl Diethanolamine · 2HDI (Compound X)

Concentration of crosslinker, g/10 g CA	Product flux, gfd		Rejection, %	
	Unannealed membranes	24 hr at 100°C	Unannealed membranes	24 hr at 100°C
0.22	7.3	7.2	84.25	85.0
0.43	8.3	7.8	80.7	83.4
0.85	8.5	7.8	77.0	88.8
1.69	13.3	6.8	67.2	92.9

^a 0.5% NaCl feed at 400 psi and 25°C.

TABLE VIII
RO Performance Characteristics^a of DRY-RO Membranes Prepared *In Situ* with Quaternized 3-Bromopropyl Isocyanate Tetramethylethylenediamine

Concentration of crosslinker, g/10 g CA	Product flux, gfd		Rejection, %	
	Unannealed membranes	24 hr at 100°C	Unannealed membranes	24 hr at 100°C
0.7	12.8	14.1	70.0	69.3
1.3	20.6	21.3	55.2	56.3
2.0	23.1	30.1	48.3	51.1
2.6	21.1	33.8	45.3	45.3

^a 0.5% NaCl feed at 400 psi and 25°C.

centration. The permeability of the annealed membranes remained constant, whereas the rejection increased—this time without going through a maximum.

The final example proved that not every blocked isocyanate was suitable for the technique of *in situ* formation. Compound XII was a crystalline solid which was compatible with CA and with dioxolane solutions of CA. Nevertheless, in contrast to experience with compounds IX and X, its incorporation into CA membranes was highly deleterious (Table VIII). There was little, if any, difference between the rejections of annealed and unannealed membranes. The permeabilities of the annealed membranes were actually higher than those of the unannealed membranes, which, in such a case, could only have been due to the hydrophilicity of the two quaternary ammonium groups, whose hydrophilicity and/or swelling actually forced imbibition of more water into the membrane than could have been accommodated by the empty space left when it was leached from an unannealed membrane. This example also suggested the undesirability of too high an overall capacity and/or charge density on a single crosslinker molecule.

Prognosis

The future of ionogenic CACs, particularly those prepared by the technique of *in situ* formation, appears bright indeed! Future work will concentrate on the development of new blocked isocyanate monomers and on the search for blocking groups which split at lower temperatures.

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