MICROSTRUCTURE AND PERMEABILITY OF "DENSE" CELLULOSE ACETATE REVERSE OSMOSIS MEMBRANES

G. ARNERI

University of Zagreb, Zagreb (Yugoslavia)

G.C. RICHARDSON and J.A. SAUER

Rutgers University, New Brunswick, NJ 08903 (U.S.A.)

ABSTRACT

Measurements of water permeability and salt rejection have been made on a series of dense cellulose acetate reverse osmosis membranes prepared from different types of homopolymers and blends, from different solvents, and from different casting solution formulations. Each of the membranes was characterized by means of differential scanning calorimetry measurements. Both the thermal properties and the reverse osmosis performance of the dense films were affected by the composition of the casting solution and by subsequent heat treatment. Development of some degree of microcrystallinity appeared favorable to reverse osmosis performance, possibly because of the restraints it imposed on the amorphous phase. A 50 : 50 blend of cellulose triacetate and CA-398-3 was found to give better reverse osmosis performance than was obtained from films prepared from either homopolymer.

INTRODUCTION

Reverse osmosis (RO) membranes used for the desalination of water, or for the separation of the constituents in a fluid solution, are usually of the asymmetric type, with a dense thin surface layer superimposed on a porous substrate [1—3]. Although much information about the morphology and microstructure of such membranes has been accumulated through the results of many investigators, the precise nature of the surface layer microstructure and its thickness is still a controversial subject [4,5]. This is perhaps not surprising when it is recognized that the microstructure, crystallinity and extent of ordering that exists even in non-asymmetric cellulose acetate cast films is also not yet well established [6—9].

In recent studies by the authors [6,10], an attempt was made to characterize the microstructure of cast cellulose acetate (CA) films by means of differential scanning calorimetry (DSC), along with thermo-optical analysis (TOA), and thermogravimetric analysis (TGA). By use of these combined tools, it was possible to show that varying types of microstructure could exist depending upon conditions. The microstructure was found to vary with the type of secondary cellulose acetate used, with the specific prep-

aration conditions employed in casting the membrane, and with the nature of thermal treatments and past history of the membrane. For a given membrane composition and a given casting procedure, it was observed that a fully amorphous state, even in cellulose triacetate (CTA), could be produced by quenching from elevated temperatures. This quenching operation inhibited formation of microcrystalline domains as there was not sufficient time in the thin films for these domains to nucleate before the temperature fell below the glass-transition temperature, T_g. On the other hand, it was found that microcrystallinity could be induced in most of the films, even those prepared from secondary CA samples, by either cooling slowly from the melt or by annealing for some time at a temperature, such as 215°C, which is above the T_g of dry films. An indication of the extent of micro-ordering that could be produced was obtained from the magnitude of the endothermic peak that was usually found to arise in the vicinity of 225°C. Another indication was the magnitude of the baseline shift that occurred in the vicinity of T_g.

Based on these results, it was conjectured that similar changes in development of microcrystalline order also occurred in asymmetric films, particularly in the active surface layer, when these films were cast and then heat-treated in water at temperatures approaching 80—90°C. This concept is in accord with the results of Baker et al. [11] who showed that X-ray detectable crystallinity could be induced in a cellulose acetate butyrate film by slow cooling from elevated temperatures, by annealing in water at temperatures near to its boiling point, and by exposure to acetone vapor at ambient temperature.

It was also conjectured in our studies [6,10] that the presence of both CTA units and partially substituted CTA units in secondary CA films, might lead to the development of a particular microstructure, obtained either by cooling from the melt or from solvent evaporation, that contained some degree of "amorphous defects". These might be visualized as localized regions of additional free volume, rather like those produced by chain ends or by substituted side branches of different composition that constitute, at least in a dynamic sense, voids or micropores of the type postulated by Sourirajan [2] and others. Casting procedures and subsequent thermal treatments are a means of controlling the size, distribution, and interconnection of these amorphous defects so as to obtain a microstructure leading to the desired RO properties.

The objective of the present study is to explore these ideas by preparing films under a variety of conditions and then determining the RO characteristics of these films as well as characterizing them by means of DSC measurements. It is recognized that DSC is but one useful tool for determining information about the microstructure and extent of ordering in these films and that other tools such as TOA, X-ray, and scanning and transmission electron microscopy would be desirable. However, it was felt that in this initial study of the relationship between film microstructure and transport properties, emphasis would be placed on covering some of the many compositional, solution, and preparation variables that are known to affect the RO performance of cellulose acetate asymmetric membranes. In the current tests, all

measurements are made directly on "dense" membranes, rather than on asymmetric ones, as membrane thickness can then be easily measured rather than inferred and, hopefully, the RO and DSC measurements will be easier to interpret and correlate.

The variables that will be investigated in this combined study of the RO properties and the DSC thermal properties of dense membranes include the following: concentration of CA in the casting solution; changes in solvent composition, including mixed solvents; effects of heat treatment; effects of water and swelling agents in the casting solution; and use of polymer blends as well as homopolymers. All of these variables are known to affect the RO performance of asymmetric membranes [2,3,12,13]. It will thus be of interest to see how they affect the performance of dense membranes and how, and to what extent, the RO performance, as determined by measurements of water permeability and salt rejection, can be correlated with the results of the DSC observation on samples of the same films.

EXPERIMENTAL

The cellulose acetate materials used in this study include CA-376, CA-383, CA-398-3, and CTA (CA-435). All were supplied in the form of powders by the Eastman Kodak Corp.

Dense films of these polymers, and of some of their blends, were prepared from thoroughly mixed (48 h) casting solutions by casting onto clean glass plates using a Gardner knife and allowing complete evaporation of the solvent. Casting was carried out under controlled conditions of 24°C and approximately 50% relative humidity. The casting solutions contained a polymer component, either a pure CA or a blend of CA and CTA; a solvent, either acetone, dioxane, or a mixture thereof; and, in some cases, additional components such as water and a swelling agent (magnesium perchlorate).

Some films were prepared from a casting solution (designated 602 type) similar to that used by Kunst et al. [12] in their investigations of RO asymmetric membranes. This solution consisted of CA-398-3 17%, dioxane 10%, acetone 59.2%, water 12.35%, and magnesium perchlorate 1.45%.

The RO tests on the cast dense films were made on a three-cell laboratory unit supplied by the Universal Water Corporation. The feed solution was 4% NaCl, the circulation flow rate 500 cm^3 min^{-1}, and the working pressure 102 atm (1500 psi). The film thickness was determined after completion of the RO tests by means of a precision electric micrometer.

The permeate was measured by direct weighing of collected quantities during known time periods. Appropriate corrections were made when the ambient temperature departed from 25°C so as to have values related to 25°C for all the RO tests. The permeate and the feed solution were analyzed for NaCl using a Beckman expanded scale potentiometer and appropriate calibration curves.

From the RO experiments, the permeability constant for water, p_w (g cm^{-1} sec^{-1} atm^{-1}), and the rejection factor for NaCl, R_f (%), were deter-

mined from the equations

$$F = \frac{p_w(P - \Delta\pi)}{d}$$

and

$$R_f = \left(\frac{C_1 - C_2}{C_1}\right) 100$$

In these equations, F is the flux of water (g cm^{-2} sec^{-1}), P the operating pressure (atm), $\Delta\pi$ the difference in osmotic pressures of the feed and permeate solutions (atm), d the membrane thickness (cm), C_1 the concentration of NaCl in the feed solution, and C_2 the concentration of NaCl in the permeate.

In each RO experiment, three separate membranes were cut from the same dense film and these were tested simultaneously. The values cited in subsequent tables for p_w and R_f are those for the membrane showing the highest salt rejection.

The differential scanning calorimetry determinations for each film were made on a Perkin-Elmer DSC-1B unit at a scan rate of 10°C min^{-1}. In order to avoid oxidative degradation, all runs were made in a positive nitrogen atmosphere. Sample size was maintained at 7.5 mg and samples were tested in an aluminum pan containing a crimped cover.

TEST RESULTS AND DISCUSSION

Effects of polymer concentration in the casting solution

In these studies, three differents sets of films were prepared having, respectively, 10, 17 and 25% polymer. These films were prepared from CA-398-3 using acetone as the solvent. The RO characteristics of these dense membranes are shown in Table 1. It may be noted that the salt rejection was close to 98% for all three types of film and that water permeability increased with increase of polymer concentration.

The DSC scans of samples of each of these three films are shown in Fig. 1. It is evident that changes in polymer concentration produce some significant changes in film morphology. For the film cast from the solution with 25%

TABLE 1

RO characteristics of membranes with various polymer content in membrane casting solution
Dense film, CA-398-3; solvent, acetone.

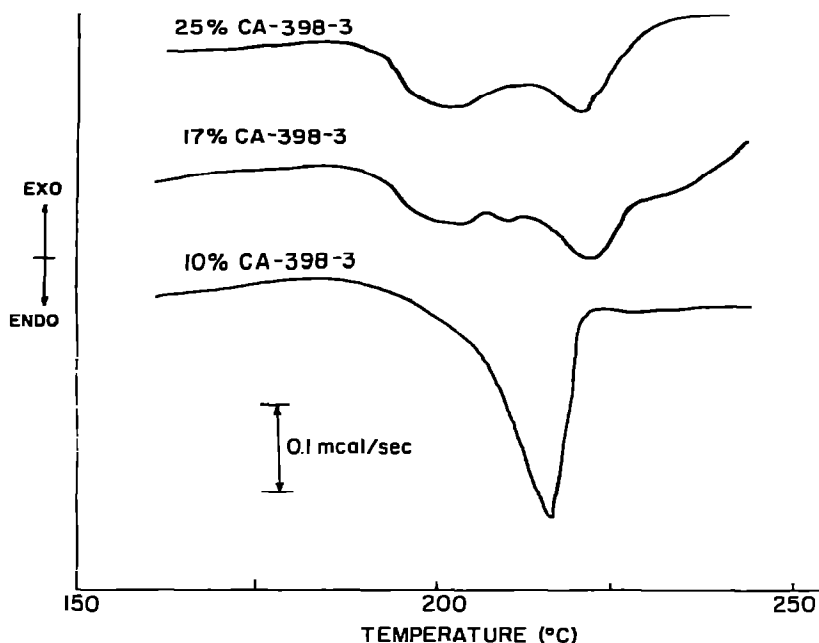| Polymer content in casting solution	$p_w \times 10^{10}$	R_f
10% CA-398-3	1.34	98.17
17% CA-398-3	1.96	97.95
25% CA-398-3	2.37	98.0

Fig. 1. DSC scans of dense membranes having various concentrations of polymer in the casting solution.

polymer concentration, the DSC scan is similar to that shown in a prior publication [6], where TOA scans were also presented. There is a large baseline shift near 190°C, associated with the onset of the primary amorphous transition, and a small endothermic peak near 225°C indicative of the presence of a microcrystalline or ordered component.

It appears that as the polymer concentration in the casting solution is lowered, the extent of ordering of the resultant dense film is increased. For the film prepared from the 10% solution, the extent of the baseline shift, though difficult to determine precisely because of some overlapping of the T_g transition with onset of melting of the ordered phase, is apparently reduced while the melting endotherm, with peak near 215°C, is markedly increased. In this sample, the increased degree of ordering has led to a slightly higher salt rejection, as the data of Table 1 show, but water permeability is reduced compared with the more amorphous and less ordered film prepared from the solution having 25% polymer concentration. From these results, is appears that while some degree of ordering of the film material is desirable in order to achieve high salt rejection, too high a degree of crystallinity, or of crystalline restraint imposed on the amorphous phase, is not conducive to the best overall RO performance.

Effects of solvent composition in the casting solution

In this phase of our study, dense films of CA-398-3 were prepared from four different solvents, in each of which the polymer concentration was maintained at 17%. The four solutions investigated were pure acetone, pure

dioxane, and mixed acetone—dioxane solvents with proportions of 85 : 15 and 35 : 55. The salt rejection and the water permeability values for these four films, as determined from RO tests, are given in Table 2. Pure dioxane leads to the highest p_w value but salt rejection for the film cast from this solvent is poor. The best overall RO performance was achieved with the film cast from the mixed acetone—dioxane (85 : 15) solution.

The results of the DSC runs on samples of each of the four films are shown in Fig. 2. It appears that increase of dioxane content initially increases the extent of microordering present in the film but at higher concentrations the endothermic peak near 225°C decreases in value. In the film prepared from the 85 : 15 solution, the baseline T_g shift is still large indicating that a large amorphous component is present in the sample, even though the relatively sharp endothermic peak at 225°C implies that a well ordered microcrystalline component is present. Evidently this combination, with the microcrystalline component serving as a kind of active "filler" that influences the microstructure of the amorphous phase, leads both to a high salt rejection (99%) and a comparatively high p_w. The DSC scans for cast film with high dioxane content show that less microcrystallinity has developed in those films and that the T_g baseline shift is larger and more spread out than for the other two samples. This would imply that a greater degree of free volume or of dynamic micropores is present and hence, as Table 2 indicates, salt rejection for these samples is poor.

Effects of heat treatment

The influence of a subsequent heat treatment (80°C for 15 min) on the RO characteristics and on the thermal properties and microstructure, as revealed by DSC measurements, has been investigated for two different types of dense cast films. One set of dense films was prepared with the 602 type of casting solution, containing both water and magnesium perchlorate swelling agent, that has been successfully used for the preparation of asymmetric membranes [12]. The other set of films was prepared with a 10% concentration of CA-398-3 in a mixed acetone—dioxane solvent (35 : 55).

The RO test results for these films, with and without subsequent heat treatment, are given in Table 3. The well known effects of heat treatment on asymmetric CA membranes, viz. to lower water permeability and to increase

TABLE 2

RO characteristics of membranes prepared from various solvents
Dense film, CA-398-3; polymer content in casting solution, 17%.

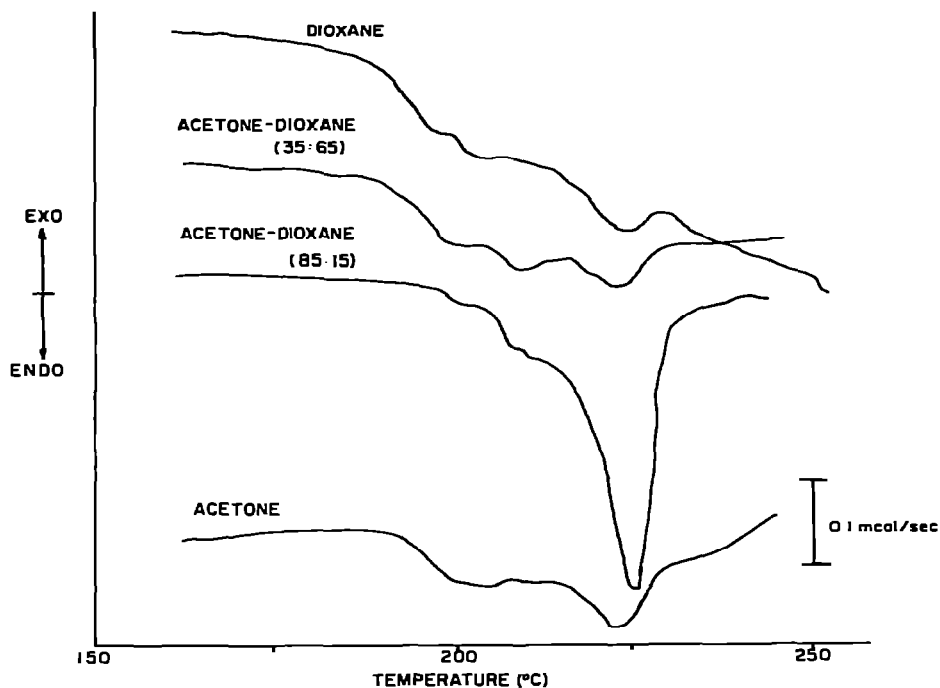| Solvent	$p_w \times 10^{10}$	R_f
Acetone	1.96	97.95
Acetone + dioxane (85:15)	1.95	99.0
Acetone + dioxane (35:55)	1.54	96.96
Dioxane	2.04	86.12

Fig. 2. DSC scans of dense membranes prepared from various solvents.

salt rejection, are also evident upon heat treating both types of dense films. When the RO results are compared for the two types of heat-treated film, prepared from the different solvents, it is seen that the 602 type gives essentially comparable salt rejection to the films cast from acetone—dioxane but with twice the water permeability.

Figure 3 shows the DSC scans of the unheat-treated and the heat-treated films prepared from the 602 type solution and from the mixed acetone—dioxane solution containing 10% of CA-398-3. The differences between the unheat-treated and the heat-treated samples are not very significant though the endothermic peak, indicative of an ordered crystalline phase, does seem to be somewhat enlarged as a result of the heat treatment. This increased degree of crystallinity causes additional restraints on the amorphous phase,

TABLE 3

Effect of heat treatment on RO characteristics of dense membranes

Type of film	$P_{\text{w}} \times 10^{10}$	R_{f}
602 [a], without heat treatment	13.52	79.17
602, heat treated at 80°C	3.42	98.29
10% CA-398-3 in acetone + dioxane (35:55), without heat treatment	3.94	89.58
10% CA-398-3 in acetone + dioxane (35:55), heat treated at 80°C	1.71	98.5

[a] 602 casting solution: 17% CA-398-3; 10% dioxane; 59.2% acetone; 12.35% water; 1.45% magnesium perchlorate.
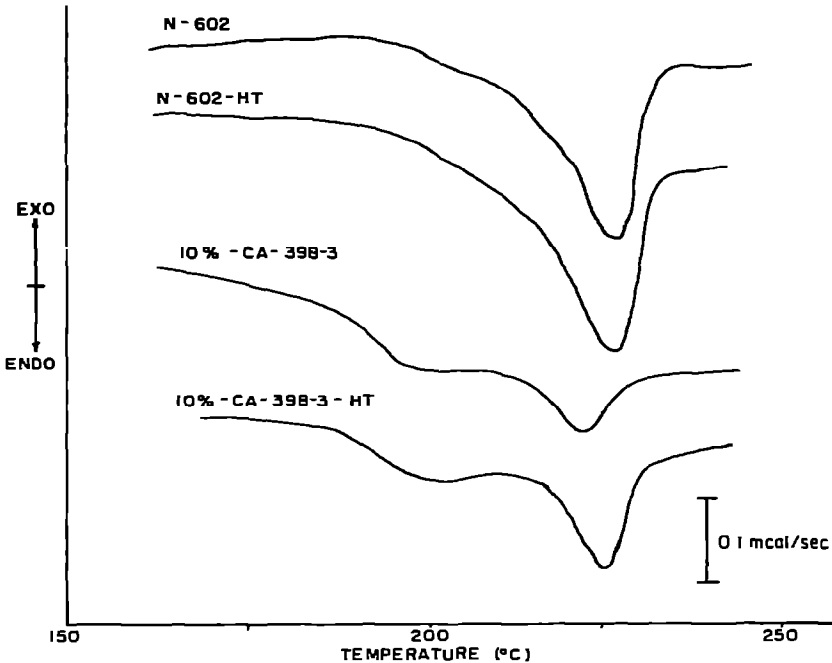
Fig. 3. DSC scans showing the influence of heat treatment on dense membranes prepared from two different casting solutions.

and changes its microstructure, possibly by slightly decreasing the amount of free volume that is present. Thus salt rejection rises and water permeability decreases.

Figure 3 also shows that, for the 602 type films, the glass transition and the melting transition overlap to some extent, while these two processes are clearly separated in the case of the films cast from acetone—dioxane mixtures. This overlapping could arise, in the case of the 602 type films, from the presence of an increased crystalline component as this would lead to a higher T_g as well as to a larger and broader crystalline melting transition near 225°C. There is also some evidence in the DSC scans for the films cast from the mixed acetone—dioxane solution of a slight recrystallization process occurring in the 215°C region. To help resolve these overlapping processes, the T_g transition, recrystallization, and melting of the ordered phase, additional TOA scans would be most helpful [10,14,15].

Effects of water and swelling agents in the casting solution

To determine the effects produced by the presence of water and of swelling agent in the 602 type of casting solution, four series of dense films were prepared. The first films were cast from the normal solution composition given in the experimental section. The second films were prepared by omitting water from the solution and third films by omitting the magnesium perchlorate. In a fourth set of films, both water and magnesium perchlorate were omitted. RO tests were then made on samples of each of these films and the results are shown in Table 4. When the casting solution contains

TABLE 4

RO characteristics of dense membranes cast from different 602 asymmetric membrane casting solutions

Type of film	$p_w \times 10^{10}$	R_f
602 normal casting solution	13.52	79.17
602 casting solution without water	2.89	62.42
602 casting solution without swelling agent	6.55	78.11
602 casting solution without water and without swelling agent	1.95	99.0

magnesium perchlorate but not water, or when it contains water but not magnesium perchlorate, results are poorer than for the normal casting solution both in water permeability and in salt rejection. For the films cast without water, it was observed that large regions of inhomogeneity were present and these may have contributed to the poor RO performance of these films.

DSC scans on samples of each of the four different films are shown in Fig. 4. All of the samples show evidence of microcrystallinity as all develop an endothermic peak in the 225—230°C region. This peak appears to increase somewhat in magnitude when the magnesium perchlorate is omitted. For the film cast without water or swelling agent, the melting peak is sharper and the T_g and the melting transition are separable. This increase in amount and perfection of the crystalline component and the restraints this imposes on the amorphous component may account for the much higher R_f value and the lower p_w value for this sample.
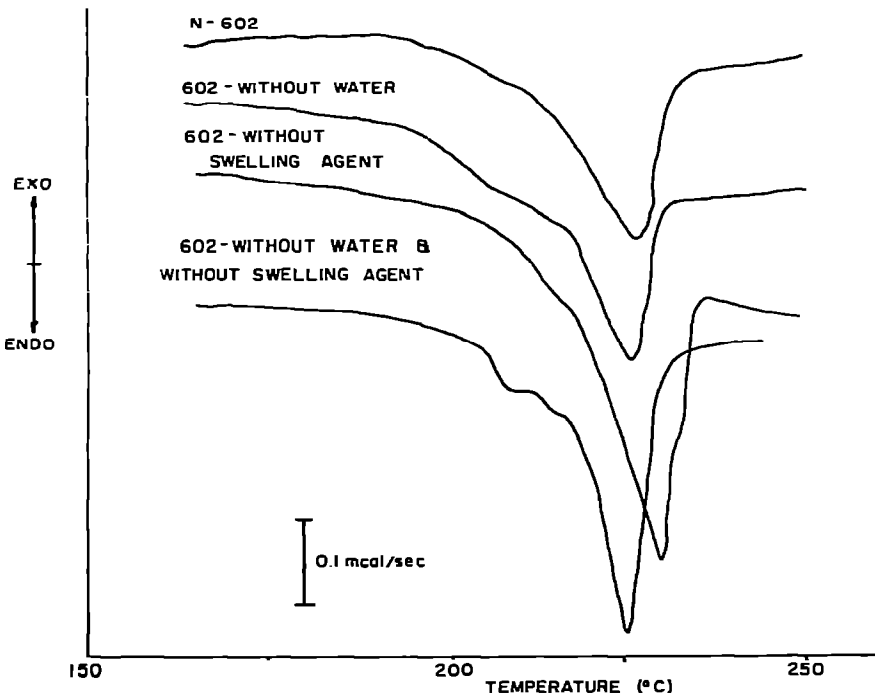

Fig. 4. DSC scans of dense membranes cast from various casting solutions.

Effects of blending CA and CTA compositions

The influence of blending various acetyl grades of CA and CTA has been explored, using in all cases a 10% concentration of polymer and an acetone—dioxane solvent (35 : 55). The RO results obtained on four different homopolymers and on three different blends are shown in Table 5.

Of the films prepared from the homopolymers, the CTA film gives, as expected, the lowest p_w value and the highest salt rejection. This polymer has the fewest OH substitutions on the cellulose triacetate chain and the highest degree of crystalline order, as we shall subsequently see from its DSC scan. Thus, in this film, the density of amorphous defects, or of dynamic micropores, is less than for the other films and they are more isolated from one another.

Of the films prepared from the secondary acetates, the best performance was obtained, for the particular casting conditions used, from the CA-383 material. This film had both a comparatively high salt rejection (97.4%) and a relatively high water permeability (3.72×10^{-10}).

With regard to the blends, the most interesting membrane was that prepared from 5% CTA and 5% CA-398-3. For these films, water permeability was more than doubled compared with results for the CTA films and yet salt rejection remained at the very high value of about 99.7%. The other two blends involved CTA and CA-376 and CTA and CA-398-3. For the first blended pair, the RO results were poorer than for the films prepared directly from the CA-398-3 while for the second blend, the results were mixed, with the water permeability being lower but the salt rejection higher.

DSC scans for the homopolymer films prepared from CTA, CA-398-3, and from 50 : 50 blends of these two are shown in Fig. 5. In the CA-398-3 film, one sees a baseline shift at about 190°C, indicative of the onset of chain motion in the amorphous phase, and a small endothermic peak at 223°C, indicative of the presence of a microcrystalline component. In contrast, the scan for the CTA film shows a baseline shift starting near 180°C that is smaller in magnitude than that associated with the CA film. This is an expected result for a material of a higher degree of crystallinity or order. In addition, the CTA film exhibits an exothermic peak near 215°C, which

TABLE 5

RO characteristics of blended polymer dense membranes
Solvent, acetone + dioxane (35:55).

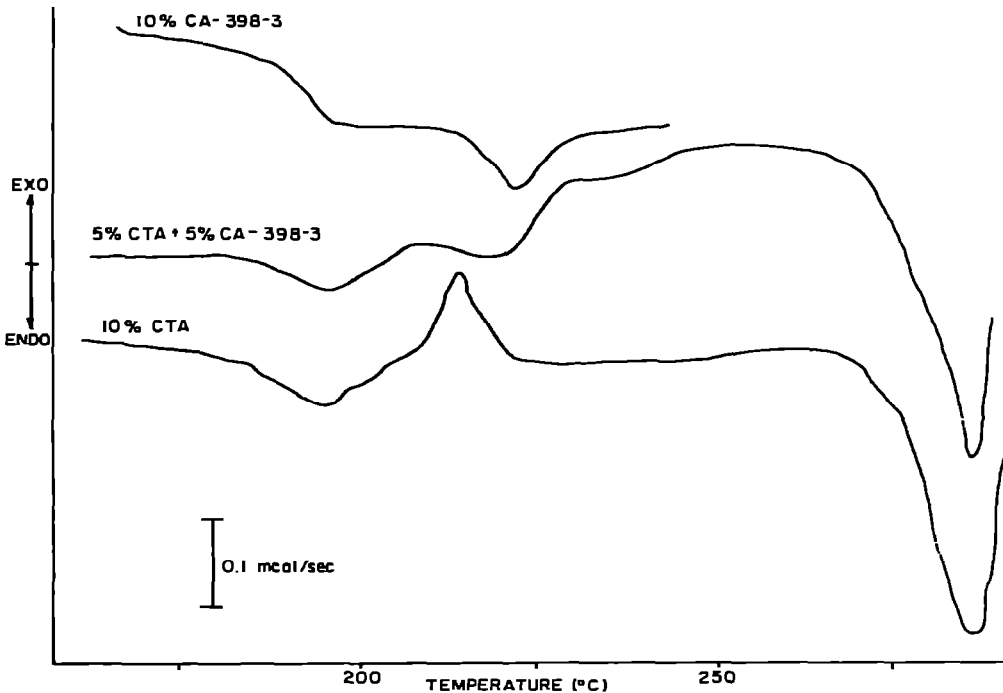| Polymer content in casting solution	$p_w \times 10^{10}$	R_f
10% CTA (CA 435)	1.11	99.72
5% CTA + 5% CA 398-3	2.48	99.66
10% CA 398-3	3.94	89.58
10% CA 376	3.35	90.91
10% CA 383	3.72	97.42
3.73% CTA + 6.27% CA 376	1.71	79.70
3.02% CTA + 6.98% CA 383	1.99	94.88

Fig. 5. DSC scans of dense membranes prepared from CTA, CA-398-3, and a 50 : 50 blend of these two polymers.

indicates that some crystallization is occurring during the DSC run. As a result, the crystallinity of this sample has further increased and there is now a large melting endotherm near 286°C. The CA film shows very little evidence of a recrystallization process and the endothermic rise that is seen near 250°C is probably a result of some degradation process.

The 50 : 50 blend of CTA and CA-398-3 shows mixed behavior. A glass transition is evident in the 180—195°C region, there is some indication of a small exothermic process near 210°C, and there are now two melting endotherms, one located near 220°C, probably arising from a defect crystalline state associated primarily with the secondary CA molecules, and one located near 286°C. This latter is associated with the onset of melting of the more stable and better ordered crystalline phase arising primarily from crystallization of the CTA molecules. Thus it appears from the DSC scan that some phase separation may have occurred during the solidification of this polymer blend during solvent evaporation. The presence of the two crystalline phases and the additional constraints placed on the amorphous phase by their presence appears to have given a microstructure conducive to good RO performance, as the data of Table 5 indicate.

It is also of interest to compare the DSC scan for the CA-398-3 film shown in Fig. 5 with that shown in Fig. 1 for a similar film but prepared from a pure acetone solvent. In the case of the mixed solvent, the T_g transition and the melting process are separated and the melting endotherm is relatively small, while with the film prepared from acetone alone, there is an overlapping of the T_g transition and onset of melting and the melting endo-

therm near 215°C is larger and broader. Also, salt rejection is higher and water permeability lower for this film (Table 1) than for that prepared from the mixed solvent (Table 5). This difference in both DSC behavior and in RO characteristics shows the important role played by the solvent in determining the resulting microstructure and the properties of the membrane.

DSC scans for the two secondary acetate homopolymer films prepared from CA-383 and CA-376 are shown in Fig. 6 and the results obtained on the CTA film are given for comparison. It is clear that the thermal behavior, which is indicative of the film microstructure, is markedly different for the two secondary acetates than for the CTA. In the secondary acetates, the baseline shift, associated with the T_g transition of the amorphous phase, occurs at a higher temperature (190—195°C) compared with a value of about 175°C for the triacetate film. This upward shift is a result of increased intermolecular forces in the secondary acetates due to their higher OH content. The two secondary acetates also show no indication of a recrystallization process above the T_g region or of any crystalline melting process. Despite the absence of a microcrystalline component, the RO performance of the film prepared from the CA-383 material was quite respectable.

In Fig. 7, DSC scans are presented for the two blends CTA + CA-383, and CTA + CA-376. For comparison purposes, the DSC scan is also given for the film prepared from the homopolymer CA-398-3 having essentially the same average acetyl content as the blends. Despite this, the thermal behavior of the blends is markedly different from that from CA-398-3. The blends, in fact, show some of the features present in the DSC scan of CTA (Fig. 6). For example, they too show evidence of a recrystallization process occurring
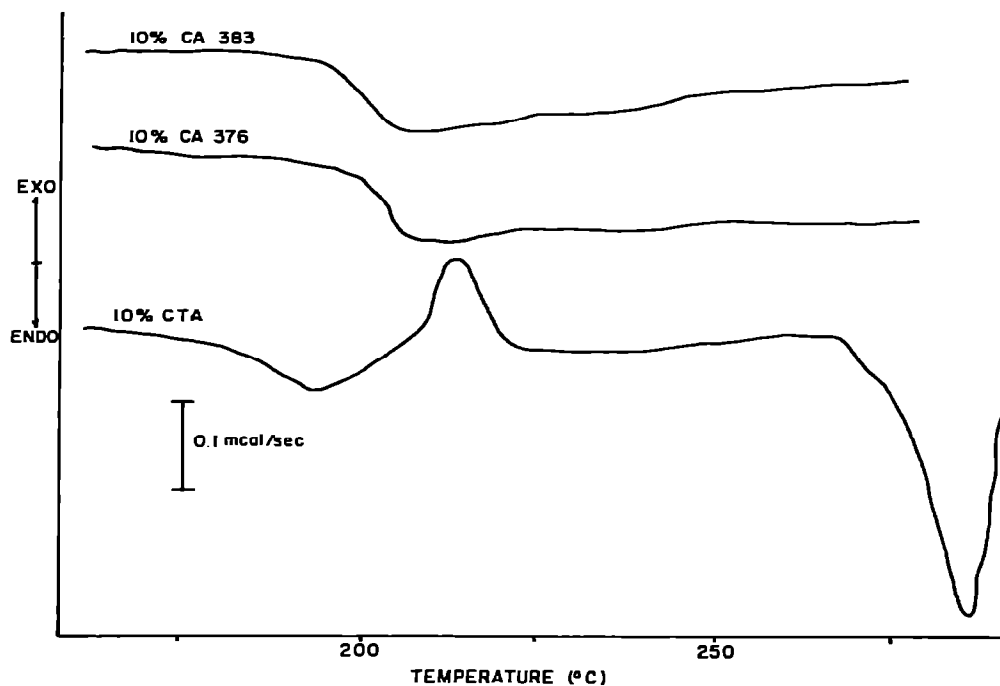

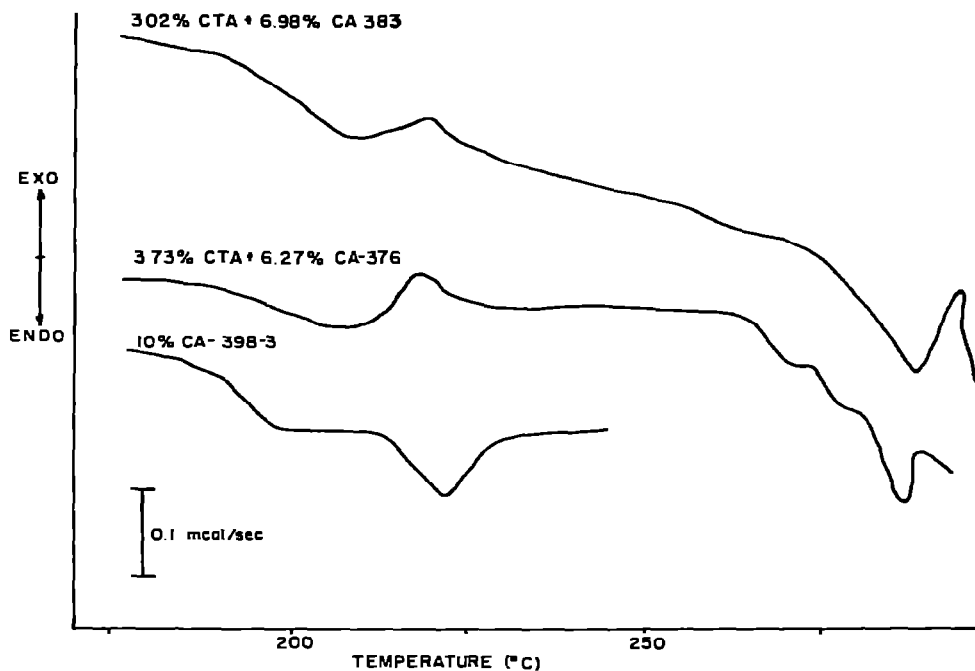Fig. 6. DSC scans of dense membranes prepared from CA-383, CA-376 and CTA.

Fig. 7. DSC scans of dense membranes cast from a blend of CTA and CA-383, a blend of CTA and CA-376, and from CA-398-3.

near 223°C and some indication of the melting of a CTA type crystalline component with an endothermic peak near 286°C. However, they show no evidence of a crystalline melting peak near 225°C such as occurs in CA-398-3 and which also appears in the 50 : 50 blend of CTA and CA-398-3 (Fig. 5). Thus the restraints imposed on the amorphous phase in these two blends is not as great as for the blend of CA-398-3 and CTA and RO performance is poorer.

CONCLUSIONS

Both the microstructure and the RO performance of the dense CA membranes are affected by the composition of the CA used, by the nature of the solvent, by the polymer concentration in the casting solution, and by subsequent heat treatment.

As noted previously [6], DSC scans of cast dense CA films show a baseline shift in the temperature region near 190°C that is associated with the onset of chain motion in the amorphous phase. Films prepared from CTA show a smaller step-like change occurring at a lower T_g temperature in the neighborhood of 175°C. CTA films also show a higher degree of order and crystallinity than is present in CA films. This is manifest by a large melting endotherm near 286°C, compared with a much smaller melting endotherm in the CA sample near 225°C. One result of this increased degree of order in the CTA dense membranes is that salt rejection is higher and water permeability lower than for any of the CA films.

Good RO performance was obtained with films prepared from 50 : 50 blends of CTA and CA-398-3 and the DSC behavior of these blends indicated that some phase separation had occurred during the casting and solution evaporation process, and that two types of crystallites were present in the cast films.

No direct correlation was found, for the various films cast under different composition and casting conditions, between their RO performance and their specific DSC behavior. In several cases, however, it appeared that better RO performance was obtained when some degree of microcrystallinity was present in the cast films and when the T_g transition and the crystalline melting process were clearly separated. The ordered component acts somewhat like an active "filler" in that it influences the microstructure of the amorphous phase and thus affects both water permeability and salt rejection.

The effectiveness of CA dense membranes is influenced by the nature of the amorphous phase and by restraints imposed by any crystalline phase that is present. Similarly, in terms of the micellar structure postulated for asymmetric films [4,16], it is essential for good RO performance to develop an increased degree of order. This is accomplished by heat treatment or other techniques that fuse the macromolecular aggregates and reduce the size of voids or pores that are present.

REFERENCES

1 S. Loeb and S. Sourirajan, Adv. Chem. Ser., 38 (1963) 117.
2 S. Sourirajan, Reverse Osmosis, Academic Press, New York, 1970.
3 R.E. Kesting, Synthetic Polymeric Membranes, McGraw-Hill, New York, 1971.
4 M. Panar, H.A. Hoehn and R.R. Hebert, Macromolecules. 6 (1973) 777.
5 J. Dickson, in K.D. Pae, D.R. Morrow and Yu Chen (Eds.), Advances in Polymer Science and Engineering, Plenum Press, New York, 1972, p. 307.
6 G. Arneri and J.A. Sauer, Polym. Eng. Sci., 15 (1975) 795.
7 A.S. Buntjakov and V.M. Averyanove, J. Polym. Sci. Part C, 38 (1972) 109.
8 R.D. Sudduth and C.E. Rogers, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 14 (1973) 591.
9 R.E. Boy, Jr., R.M. Schulken, Jr. and J.W. Tamblyn, J. Appl. Polym. Sci., 11 (1967) 2453.
10 G. Arneri and J.A. Sauer, Thermochim. Acta, 15 (1976) 29.
11 W.D. Baker, C.S. Fuller and N.R. Pape, J. Am. Chem. Soc., 64 (1942) 776.
12 E. Kunst, G. Arneri and A. Basnec, Proc. 4th Int. Symp. Fresh Water from the Sea, Heidelberg, Vol. 4, 1973, A. Delyannis and E. Delyannis, Athens-Amaroussion, Greece, p. 217.
13 W.M. King, D.L. Hoernschemeyer and C.W. Saltonstall, Jr., in H.K. Lonsdale and H.E. Podall (Eds.), Reverse Osmosis Membrane Research, Plenum Press, New York, 1972, p. 131.
14 A.J. Kovacs and S.Y. Hubbs, J. Appl. Polym. Sci., 16 (1972) 301.
15 C.E. Wilkes and M.H. Lehr, J. Macromol. Sci. Phys., 7 (1973) 225.
16 R.E. Kesting, J. Appl. Polym. Sci., 17 (1973) 1771.