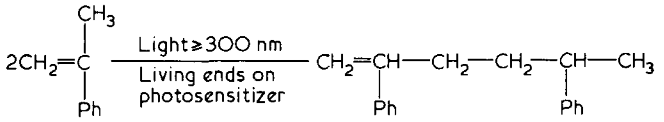
monomer in the ageing of α-methylstyryl anions, we determined the extinction coefficient for DPE monomer. After allowing for overlapping absorbances at 250 nm, (*Figure 2*), it can be shown that a small but significant excess of monomer, 2×10^{-3} mol dm^{-3}, was present during ageing.

Only about 60% of the anions were killed by the addition of water, and the remaining anions subsequently decayed at a lower rate than observed with a fresh solution; the first order rate constant was now 1×10^{-8} s^{-1}. A similar decay rate was observed when sodium tetraphenylborate was added to the dianion solution. The ion-pairs in DPE dimer dianion are probably partially dissociated to free ions in THF, in a similar manner to those of α-methylstyrene living ends[5]. If the free anion is more reactive than the ion-pair in the decay reaction, then suppression of ionic dissociation by sodium ions derived from either sodium hydroxide (produced by termination with water) or sodium tetraphenylborate would lead to a lowering of the decay rate.

Implications for α-methylstyrene living ends

We have shown[1,2] that the transformation of α-methylstyrene living ends is dependent upon the photochemical dimerization of monomer to produce 2,5-diphenylhex-l-ene



$$2CH_2{=}\underset{Ph}{\overset{CH_3}{C}} \xrightarrow[\text{Living ends on photosensitizer}]{\text{Light}\geq 300\text{ nm}} CH_2{=}\underset{Ph}{CH}{-}CH_2{-}CH_2{-}\underset{Ph}{CH}{-}CH_3$$

which subsequently is converted by donation of a proton to a living end to another anion which has an absorption peak at 430 nm.

In the case of DPE, the first of these reactions, involving as it does substitution on to the α-methyl group, will clearly not occur. These observations hence support the reaction scheme which we have proposed for the ageing of α-methylstyrene living ends.

The decay process, which occurs both with the DPE and α-methylstyrene dianions, is usually assumed to involve reaction with solvent[6], and hence would be pseudo-first order. The rate of decay is higher with α-methylstyrene dianions (first order rate constant $=9\times10^{-7}$ s^{-1}). However, we have shown[2] that another type of decay involving cyclization could occur in that case. This cyclization requires the addition of another molecule of monomer which is not possible in the case of DPE.

References

1 Comyn, J. and Glasse, M. D. *J. Polym. Sci., Polym. Lett. Edn.* 1980, **18**, 703
2 Comyn, J. and Glasse, M. D. *J. Polym. Sci., Polym Chem. Edn.*
3 Spach, G., Monteiro, H., Levy, M. and Szwarc, M. *Trans. Faraday Soc.* 1962, **58**, 1809
4 Jagur, J., Levy, M., Feld, M. and Szwarc, M. *Trans. Faraday Soc.* 1962, **58**, 2168
5 Comyn, J., Dainton, F. S. and Ivin, K. J. *Eur. Polym. J.* 1970, **6**, 319
6 Fetters, L. J. *Polym. Lett.* 1964, **2**, 425

Studies on syntheses and permeabilities of special polymer membranes: 41. Finger-like cavities in cellulose nitrate membranes from binary organic solvents

Tadashi Uragami, Yoshiaki Ohsumi and Mizuho Sugihara
Department of Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564, *Japan*
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The formation of finger-like cavities in asymmetric cellulose nitrate membranes was investigated by changing the composition of binary mixed casting solvent and the evaporation period during the membrane formation process. The nature of the casting mixture, during the solvent evaporation process, was of coacervated droplets with absorbed water molecules from the atmosphere. Changes in the concentration of cellulose nitrate and the dissolution state of the cellulose nitrate molecules in the evaporation loss of the casting solvent, were clearly related to the formation of the finger-like cavity in the back sponge layer in asymmetric cellulose nitrate membranes.

Keywords Polymer membrane; cellulose nitrate; asymmetric membrane; binary solvent; water absorption; finger-like cavity; membrane formation process

Introduction

Many workers have found that a finger-like cavity was formed in the back sponge layer of various asymmetric polymer membranes[1-8]. We discussed the mechanism[9] and the conditions[10] of the formation of finger-like cavities in cellulose nitrate membranes from various single pure solvents. In general, many polymer membranes for reverse osmosis and ultrafiltration are prepared from 2 or more mixed casting solvents in order to improve the membrane performance. This method, which uses the mixed casting solvent, can finely control the conformation of the polymer molecules in the casting mixture during the solvent evaporation process. Consequently, it is possible to control the factors that have effect on the permeation characteristics, i.e., pore size pore number in the dense surface layer and thickness of the dense surface layer. For the purpose of investigating the structure of cellulose nitrate membranes from a mixed solvent, in particular this communication deals with the formation of a finger-like cavity in the back sponge layer.

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Experimental

High-purity cellulose nitrate (CN) (Daicel Co.) dried under reduced pressure and having a degree of nitration of 11.5% was employed as membrane substance. Pure ethylene glycol monomethylether (MeCell), *N,N*-dimethyl formamide (DMF), methyl alcohol (MeOH), and n-propyl alcohol (n-PrOH) purified by the usual methods were the solvents for the casting solutions.

Unless otherwise stated the casting solutions consisted of the proportion CN and a binary mixed solvent at 13/87 (wt%) and kept overnight at the casting temperature (6°–7°C). The membranes were made by pouring the casting solutions onto an applicator for thin layer chromatography, drawing the blade across a glass plate, allowing the solvent to evaporate for 7 min at 6°–7°C under a humidity of 90%, and immersing the glass plate together with the membrane into water (6°–7°C). After standing for 24 h in water the membranes were removed from the glass plate.

The apparatus used and the experimental procedure have been described in an earlier paper[11]. Change in the weight of casting mixture per unit area on the glass plate during the membrane formation process is given by the following equation.

$$W=(W_t-W_0)/A$$

where W(g cm^{-2}) is the change in the amount of weight of the casting mixture per unit area after t hours, W_0 (g cm^{-2}) and W_t (g cm^{-2}) are the total weight of the casting mixture and the glass plate at zero time and t hours, respectively, and A (cm^2) is the effective surface area of the glass plate.

The lyophilized membranes were coated with a layer of evaporated gold and then observed by scanning electron microscopy (Japan Electron Optics).

Results and Discussion

The effect of the ratio of n-PrOH/DMF in the casting solution, consisting of CN, n-PrOH, and DMF, on the structure of the cross-sections of membranes is shown in *Figure 1* for a constant concentration of CN of 13 wt% and at a constant evaporation period of 7 min. In all compositions of the casting solution other than the system n-PrOH/DMF = 2/1, the finger-like cavities are found in the back sponge layer of asymmetric membranes, but the system n-PrON/DMF = 2/1 a different type of cavity is observed. DMF used in this system is a very good solvent, but n-PrOH is a poor solvent for CN molecules. Therefore, when the n-PrOH content in the casting solution becomes higher, a mixed solvent is poor for the solubility of CN molecules. Also the boiling points of DMF and n-PrOH are 153.0°C and 97.2°C, respectively. *Figure 2* shows the weights of the casting mixtures for various compositions of casting solution for a 7 min evaporation period. An increase in the weight of the casting mixture in pure DMF is due to an absorption of water molecules into the membrane surface from the atmosphere during the membrane formation process. A decrease in the weight with the increasing content of n-PrOH in the casting solution is dependent on the evaporation loss of n-PrOH during the evaporation process. The water absorption occurs mainly in pure DMF, in n-PrOH/DMF = 1/3–1/1 the evaporation loss of solvent and the water absorption occur simultaneously, and the evaporation loss of solvent occurs mainly in n-PrOH/DMF = 2/1. The amount of evaporation of the casting solvent and the amount of absorption of water into the casting mixture during the evaporation process, are determined by gas chromatography. Therefore, it should be expected that the formation mechanisms of the dense surface layer of asymmetric CN membranes are

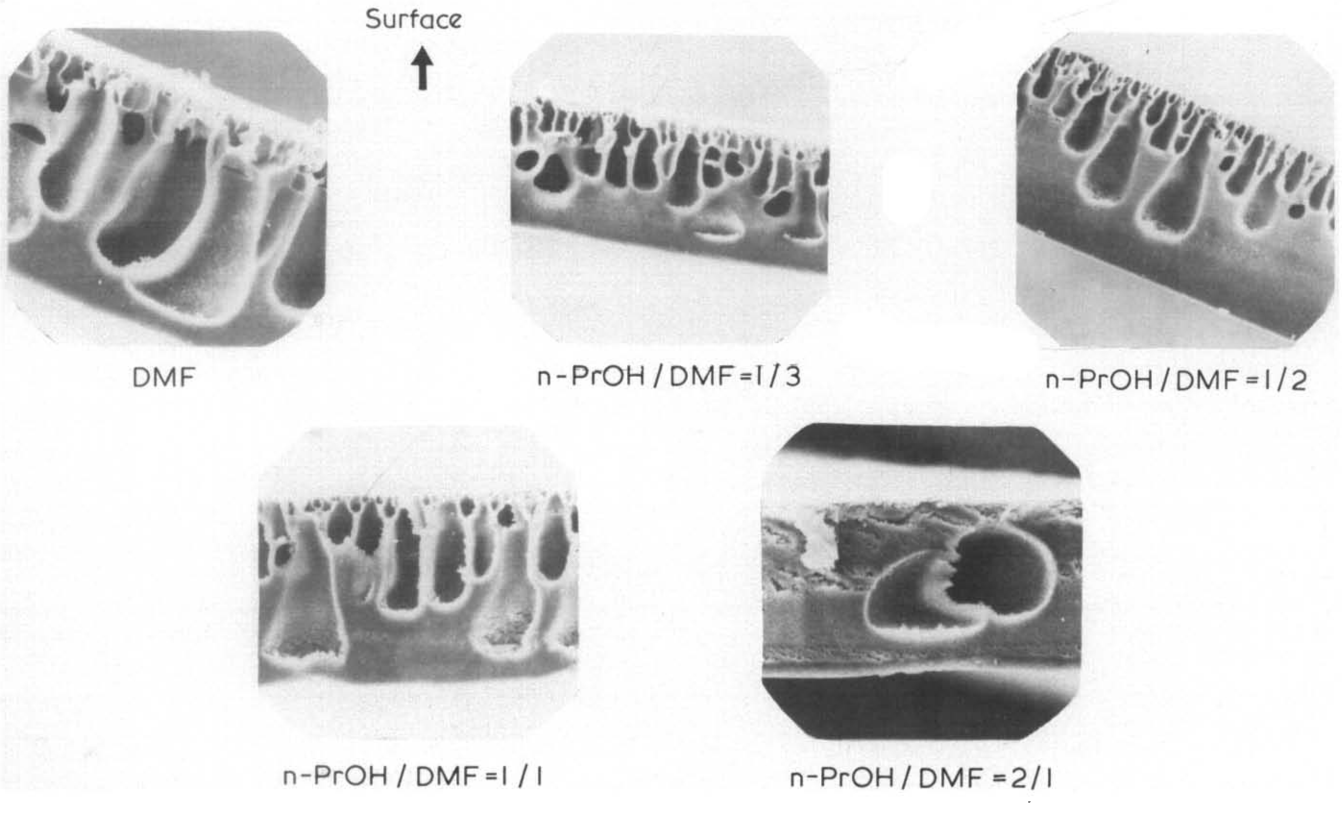


Figure 1 Effect of mixing ratio of n-PrOH/DMF on structure of cross section of CN membranes

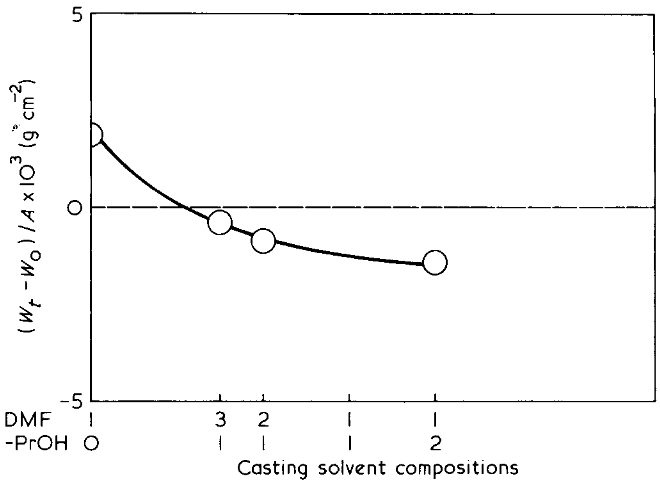


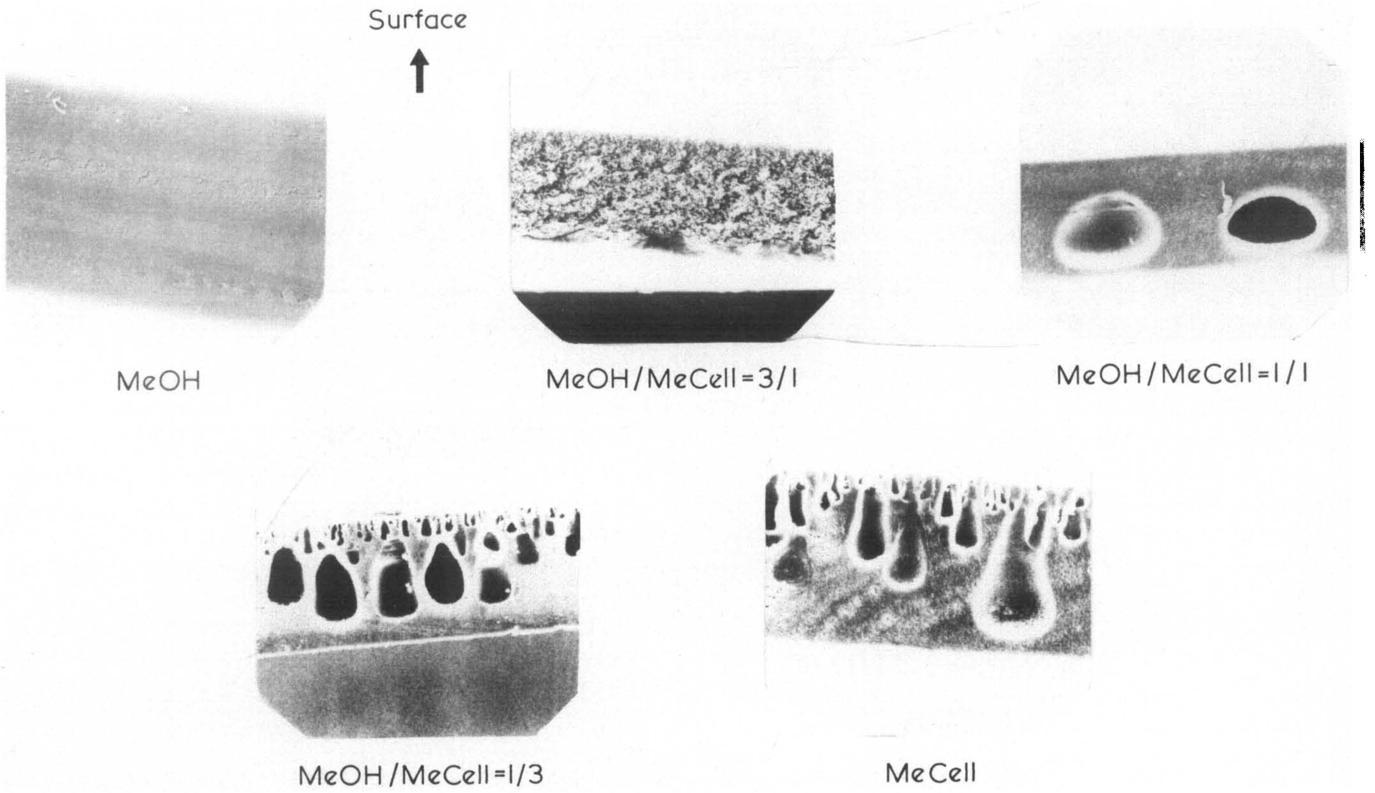
Figure 2 Effect of casting solvent composition(n-PrOH/DMF) on weight change of casting mixture during membrane formation process

different for each system, i.e. for pure DMF, n-PrOH/DMF = 1/3–1/1, and n-PrOH/DMF = 2/1.

In general, the coacervated droplets are formed with the evaporation loss of the good solvent for the particular polymer as the membrane material[12], i.e., the dissolution ability of the solvent for the polymer lowers with the solvent loss. If a nonsolvent for the polymer enters into the casting mixture, the solubility of the polymer decreases significantly, because the water molecules hydrogen bond predominantely to DMF molecules. In the pure DMF system, since the water molecules are a very strong nonsolvent for CN molecules, and as soon as the water molecules are absorbed into the surface of casting mixture, the coacervated droplets which occlude the water molecules are formed and phase separation occurs between these coacervated droplets and the casting matrix solution. In the n-PrOH/DMF = 1/3–1/1 system, the water molecules are absorbed into the concentrated matrix solution layer formed by the evaporation loss of n-PrOH. Therefore, the resulting coacervated droplets in this system are different from the coacervated droplets in pure DMF. The surface layer of the casting mixture in these systems, however, consists of the coacervated droplets whose occurrance is due to water absorption and the casting matrix solution. In these systems the aggregation state of CN molecules in the coacervated droplets is different from that in the matrix solution. Therefore, when the surface layer of the casting mixture is gelled, the permeation rate of the gelation medium (water) through these sites is different. Consequently, the finger-like cavity in the back sponge layer is formed under the larger pores, where the permeation rate of the gelation medium is greater.

In the case of n-PrOH/DMF = 2/1, the main evaporation loss is n-PrOH, the poor solvent for CN molecules. Therefore, the coacervated droplets already present in the casting solution decrease gradually with the evaporation loss of n-PrOH. The casting mixture passes into the concentrated matrix solution. The permeation of the gelation medium into the casting mixture through the matrix solution is slower and homogeneous. Therefore, the gelation of CN molecules proceeds homogeneously and the finger-like cavity cannot be formed in the back sponge layer. In the n-PrOH/DMF = 2/1 system, however, the spherical-like cavity is observed in the back sponge layer. This phenomena will be the subject of future investigation.

The scanning electron photomicrographs of the cross-section of membranes prepared from CN, MeOH, and MeCell for a constant concentration of CN of 13 wt% and at a constant evaporation period of 7 min are shown in *Figure 3*. The main characteristic in this system is the fact



MeOH

MeOH/MeCell = 3/1

MeOH/MeCell = 1/1

MeOH/MeCell = 1/3

MeCell

Figure 3 Effect of mixing ratio of MeOH/MeCell on structure of cross section of CN membranes

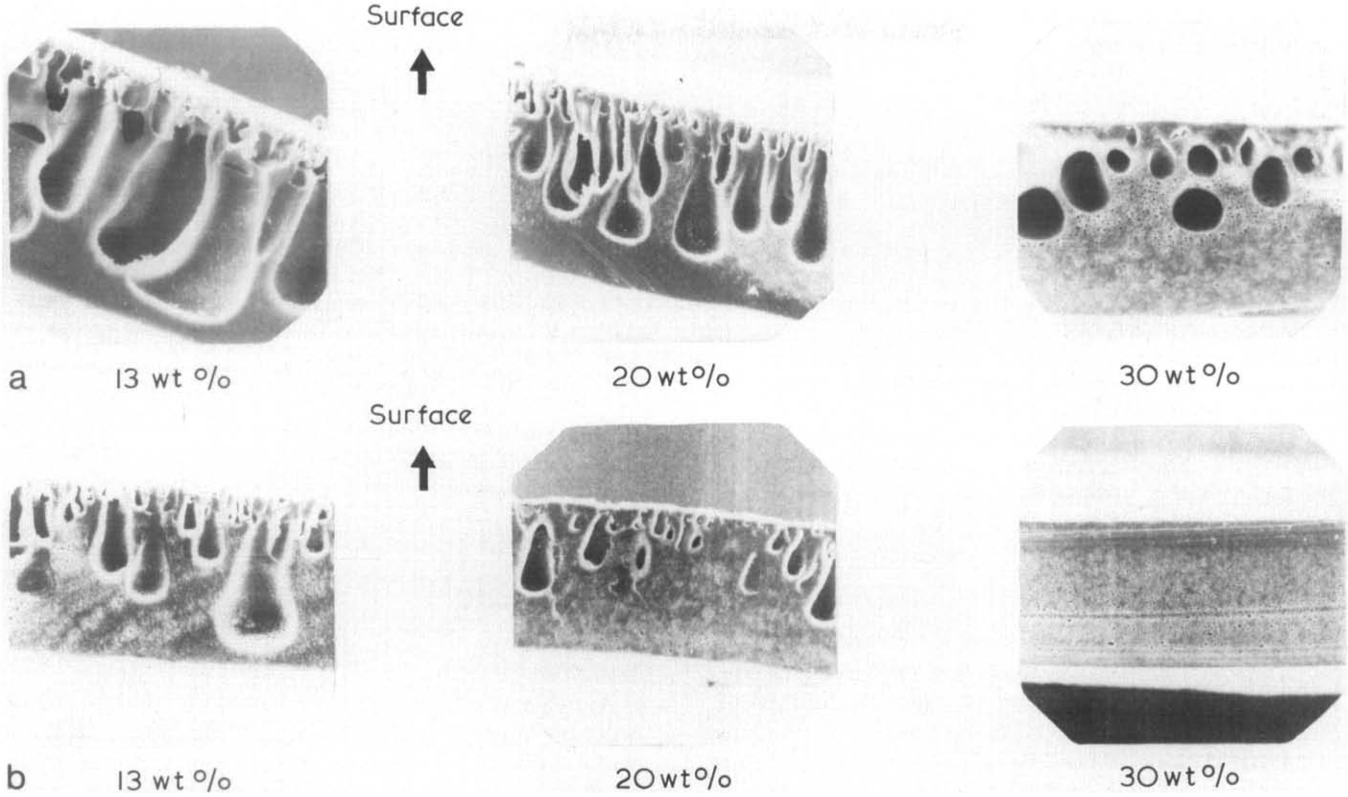


Figure 4 Effect of CN concentration on formation of finger-like cavity. Casting solvent, a: DMF, b: MeCell

that CN molecules are dissolved in pure MeOH and pure MeCell. Namely, the structural change of CN molecules in the casting mixture with the evaporation loss of the casting solvent is relatively small. Also, the effect of the water absorption into the casting mixture from the atmosphere during the evaporation process becomes very small, because the evaporation loss of MeOH is greater. In the system n-PrOH and DMF, the solubility of CN molecules is remarkably different, but the difference in the solubility in this system is small. The finger-like cavity is found in the pure MeCell and MeOH/MeCell = 1/3 systems, but not in the MeOH/MeCell = 3/1 and pure MeOH systems. In the MeOH/MeCell = 1/1 system, a spherical-like cavity is observed. In previous papers[9,10], we reported that the conditions of the formation of finger-like cavities in asymmetric CN membranes prepared from single pure solvent were as follows: the casting solvent was a very good solvent for CN molecules, had high hygroscopicity, and had strong affinity with the gelation medium. MeOH is a very hygroscopic solvent and solvates strongly with water, but is not a sufficiently good solvent for CN molecules compared with MeCell. In the system with a greater content of MeOH, during the evaporation process the evaporation loss of MeOH is predominant and the water absorption into the casting mixture is very low. In the MeOH/MeCell = 3/1 system, the solvent in the casting mixture with the evaporation loss of MeOH is convertible into a good solvent for CN molecules. However, the concentration of CN in the casting mixture becomes higher with the evaporation loss of MeOH. *Figures 4a* and *4b* show the effect of CN concentration in the casting solution on the formation of the finger-like cavity. In spite of the fact that the water absorption into the casting mixture occurs in both the pure DMF and pure MeCell systems, the finger-like cavity disappears with increasing concentration of CN in the casting solution. These results are attributable to a relaxation of the heterogeneous aggregation of CN molecules during the gelation process. That is, the formation of the finger-like cavity is related to a higher gelation velocity of the casting mixture as reported by Frommer *et al.*[13]

References

1 Strathmann, H., Scheible, P. and Baker, R. W. *J. Appl. Polym. Sci.* 1971, **15**, 811
2 Strathmann, H., Kock, K. Amar, P. and Baker, R. W. *Desalination* 1975, **16**, 179
3 Strathmann, H. and Kock, K. *Desalination* 1977, **21**, 241
4 Matz, R. *Desalination* 1972, **10**, 1
5 Trirrell, D. and Vogel, O. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 1889
6 Cabasso, I., Klein, E. and Smith, J. K. *J. Polym. Sci.* 1977, **21**, 165
7 Koenhen, D. M., Mulder, M. H. and Smolders, C. A. *J. Appl. Polym. Sci.* 1977, **21**, 199
8 Hirose, S. and Shimizu, A. *J. Appl. Polym. Sci.* 1979, **23**, 3193
9 Uragami, T., Ohsumi, A. and Sugihara, M. *Polymer* in press
10 Uragami, T., Ohsumi, A. and Sugihara, M. *Desalination* 1981, **37**, in press
11 Uragami, T., Fujino, K. and Sugihara, M. *Angew. Makromol. Chem.* 1976, **55**, 29
12 Kesting, R. E. in 'Synthetic Polymeric Membranes', McGraw-Hill, New York, 1971, p. 84
13 Frommer, M. A. and Lancet, D. in 'Reverse Osmosis Membrane', Reseached by H. K. Lonsdale and H. E. Podall), Plenum Press, New York–London, 1972, Ch. **II**, p. 85–110