The Four Tiers of Structure in Integrally Skinned Phase Inversion Membranes and Their Relevance to the Various Separation Regimes

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Synopsis

There are four superimposed tiers of structure in integrally skinned phase inversion membranes: *macromolecules* (functionally submacromolecules, that is, displacements between chain segments); *nodules*—approximately 200 Å in diameter spherical macromolecular aggregates, each of which contains several tens of macromolecules (nodule interiors are denser than interstitial regimes, therefore, chain segment displacements within and between nodules differ and hence constitute a bimodal pore size distribution which may account for the dual mode sorption and permeation of gases; transport of water in reverse osmosis occurs primarily through the less dense interstitial domains); *nodule aggregates*—400–1000 Å in diameter spherical clumps of nodules (the skins of reverse osmosis and gas separation membranes consist of a single layer of coalesced nodule aggregates; ultrafiltration pores are the spaces between incompletely coalesced nodule aggregates, and residual ultrafiltration pores are the defect pores found in reverse osmosis membranes); *supernodular aggregates*—aggregates of nodule aggregates which constitute the walls of the 0.1–2 μm in diameter open cells in the membrane substructure (microfiltration pores are the surface extensions of openings between adjacent cell walls).

INTRODUCTION

A fundamental premise of membranology is the existence of relationships between structure and function.[1] Size, shape, and interaction (solubility) parameters of both permeants and membrane pores determine permeability and selectivity. Until about 1960, only two types of membrane were available: thick dense film monolayers, and microporous membranes. The former were limited because of their high resistance to slow concentration-driven processes such as dialysis and gas separation. The latter were—and continue to be—applied to microfiltration, the pressure-driven separation of micrometer and submicrometer-sized particles from solutions or suspensions. It was incorrectly assumed by most membranologists that the structures of dense films were relatively simple and in an equilibrium state. However, the structures of microporous membranes were known to consist of a slightly anisotropic open-celled foam or spongelike matrix and a skin which was a denser extension of the porous substructure. Dense films were generally prepared from sols in neat solvents which were cast and allowed to evaporate to completion. Microporous membranes, on the other hand, were cast from sols containing multicomponent vehicles. Such sols undergo a process now known as phase inversion,[1-5] in which they separate into two interdispersed liquid phases prior to gelation. In 1960, Loeb and Sourirajan[5] added a new dimension to membranology with

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their invention of the first finely porous integrally skinned bilayer membrane consisting of a thin ($\approx$ 0.2 μm) finely porous skin and a thick ($\approx$ 100 μm) more coarsely porous substructure. The thin skin is the functional portion of the membrane. Its high density results in a selectivity which, in the most finely porous regimes (reverse osmosis and gas separation), approaches that of a thick dense film. Its thinness is responsible for its low resistance, and hence its high product rate. The porous substructure, on the other hand, functions solely as a mechanical support for the skin. The increased permeability of integrally skinned bilayer membranes relative to that of dense monolayer films, coupled with a selectivity which is virtually equivalent to that of dense films, was the reason for the emergence of the current worldwide interest in membrane separations.

A broad spectrum of membrane separation regimes and corresponding integrally skinned membranes is available. They differ from one another with respect to pore diameter ranges and the size of particles which they retain. The present work is believed to be the first which encompasses the entire spectrum. Its basic premise is that pores are more or less static two-dimensional or fractal empty spaces which are bounded by various structural elements.[7] The pores together with their rim elements constitute sieves which separate potential penetrants based largely (but not entirely) upon the size and shape of both pores and penetrants. The principal pore regimes and their approximate diameters are: microfiltration MF (200–100,000 Å), ultrafiltration UF (10–200 Å), reverse osmosis RO (3–10 Å), and gas separation GS (2–5 Å).

Kamide and Manabe have recently presented a scenario for the formation of porous membranes by nucleation and growth. In effect, four tiers of structure were identified: macromolecules, primary particles, secondary particles, and pores. One purpose of the present paper is to accommodate their findings into an overall synthesis which is consistent with information from other sources. Another objective is to correlate the different structural levels with the functionality of the various separation regimes. A third is to establish a historically just and consistent terminology.

DISCUSSION

A proper foundation for comprehending the nature of pores in integrally skinned membranes is an understanding of the phase inversion process by which membranes are formed and during which the various pore rim elements are positioned. Maier and Scheuermann (M–S)[9] first proposed the M–S mechanism for the formation of phase inversion membranes, which is widely accepted today. At that time, the only skinned membranes available were in the coarsely porous MF regime. Following the invention of the first finely porous integrally-skinned membrane by Loeb and Sourirajan,[6] the present author extrapolated the M–S theory to the case of membranes with finely porous skins. I subsequently recognized the commonality of the mechanism of membrane formation in dry, wet, and thermal subdivisions of the general phase inversion process.[1,4] This mechanism will now be refined in light of recent findings from high resolution scanning and transmission electron microscopy and a reevaluation of the earlier literature.

Phase inversion involves the preparation of a polymer solution (sol) in such a way that it exhibits the potentiality for immiscibility, which, when realized, leads to liquid–liquid phase separation. Prior to and following phase inversion, nucleation and growth of fine particles into progressively larger particle aggregates takes place and ultimately results in gelation.[8] The gelation of the skin precedes that of the matrix. If skin formation occurs rapidly, particle growth in the skin will be kept to a minimum, and the skin will consist of coalesced fine particles (and therefore, fine pores). If skin formation is delayed, particle growth continues, and particle and pore size increase. Within the nascent membrane matrix, particle growth continues until gelation. As a result, both particles and pores attain their maximum sizes within the matrix. The nature of the various particles within the phase inversion sols (nascent membranes) will now be considered. The finest possible particles within a polymer solution consist of individual macromolecules. It is generally believed that dispersion down to the macromolecular level does occur in dilute solutions when the vehicles consist of strong solvents. However, the finest particles (nucleation sites) in actual phase inversion solutions consist of macromolecular aggregates rather than individual macromolecules.[8] This is so since polymer–polymer interaction is favored in such solutions both because of high polymer concentration and because of the utilization of multicomponent solvent vehicles whose dispersive powers are relatively weak. Such vehicles are deliberately designed to bring the sol close to immiscibility. Prior to phase inversion, the solutions are in the relatively nonturbid metastable Sol 1 state[1]; thereafter they enter the turbid, unstable Sol 2 state, and nucleation and growth accelerate rapidly.

The first direct evidence for what are now believed to be macromolecular aggregates was found in the skins of wet process cellulose acetate RO membranes by Schultz and Asunmaa[10] (Fig. 1). They called these approximately 200 Å in

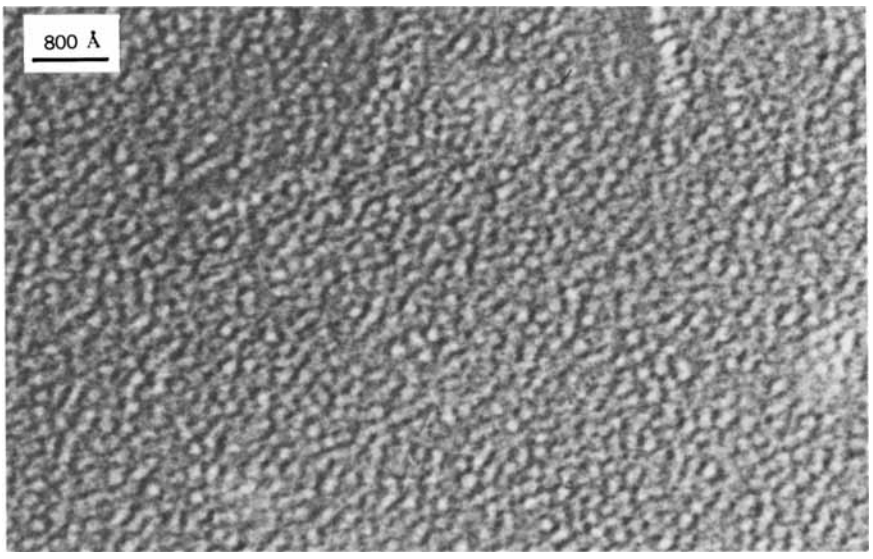

Fig. 1. Electron photomicrograph of Pt–C preshadowed carbon replica of the surface of the active desalination layer of a Loeb–Sourirajan cellulose acetate membrane (from Schultz and Asunmaa[10]).

diameter structures "spheres" and schematically represented them as a closely packed hexagonal array (Fig. 2). Schultz and Asunmaa believed that the interstices between the spheres represented the pores through which water permeates in RO. They suggested that the interstices were empty capillaries whose walls ordered the contained water into a non-ionsolvating form. Kesting[11] subsequently obtained evidence for the existence of similarly-sized ellipsoids in the skins of dry process cellulose acetate RO membranes. Recently, similar spherical structures have been observed in the skins of polysulfone gas separation membranes by Fritzsche et al.[12] (Fig. 3). Although I agree with Schultz and Asunmaa that the interstices between the spheroids (or ellipsoids) are the most likely pathways for the passage of water in RO, I also agree with Kedem[13] that these interstices are not free of matter, but rather are domains of lower polymer density. Similar spheroidal structures were seen earlier in polymer films by Sjöstrand,[14] Schoon and Kretschmar,[15] Yeh and Geil,[16] and Keith.[17] They were entitled "nodules," and were generally credited with the possibility of possessing some paracrystalline order. In view of the universality of these structures and their prior discovery in films, it seems appropriate that the term "nodule" should be retained for their manifestation within membranes as well. There is as yet no conclusive evidence concerning the disposition of polymer molecules within and between these nodules. Indeed, to be frank, there is still some contention that the nodules do not exist at all, but are mere artifacts arising from "micromixing during the staining process."[18] However, a consensus[19] of polymer physicists credits both the existence of nodules and a fair amount of amorphous order in the form of folded chain segments which parallel one another over distances of at least 10 Å.[20] Recently, Menczel and Wunderlich[21] have used heat capacity analyses to demonstrate the simultaneous presence of rigid and mobile amorphous phases in polymers such as bisphenol A polycarbonate, poly(ethylene terephthalate), and poly(butylene terephthalate). They found that the content of the rigid amorphous phase was generally higher than that of the mobile phase. The existence of two amorphous phases is consistent with the assumption of dense nodules and less dense interstitial domains. It also suggests a possible origin for dual mode sorption and permeation in gas separation.[7] The smaller displacements between chain segments within the nodules can now be seen as the Henry's mode sites, whereas the larger

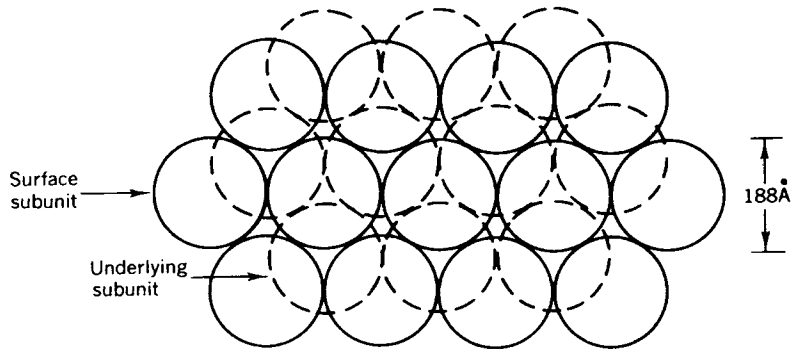

Fig. 2. Active desalination layer of cellulose acetate membrane idealized as an assembly of close-packed 188-Å-diam spheres (from Schultz and Asunmaa[10]).

displacements between chain segments in the interstitial domains are believed to correspond to the Langmuir sorption sites (Fig. 4). In gas separation, permeation can occur both within and between nodules. In RO, on the other hand, permeation only takes place between adjacent nodules.

In their exposition of the nucleation and growth mechanism for the formation of porous membranes, Kamide and Manabe[8] present evidence for the existence of $\approx$ 200 Å in diameter "primary particles" which subsequently agglomerate into larger "secondary particles." Furthermore, they estimate that each primary particle consists of several tens of individual macromolecules. Further association of secondary particles leads ultimately to the formation of "pores," that is, open-celled structures. Primary particles correspond to the structures for which I prefer, for reasons already stated, the term "nodules." Therefore, for sake of consistency, I favor the term "nodule aggregate" over its equivalent, secondary particle. This thought process is carried to its logical conclusion by utilization of the term "supernodular aggregate" or "aggregate of nodule aggregates" for the level to which Kamide and Manabe applied the word "pores." Thus, the four tiers of structure in integrally skinned membranes are: macromolecule, nodule (macromolecular aggregate), nodule aggregate, and supernodular aggregate. Occasionally, three of the four elements can be observed simultaneously (Fig. 5); the macromolecular level cannot as yet be seen directly. Such an occurrence requires rapid gelation and desolvation, so that post-gelation plasticization and densification (which tend to conceal these structures) are minimized.

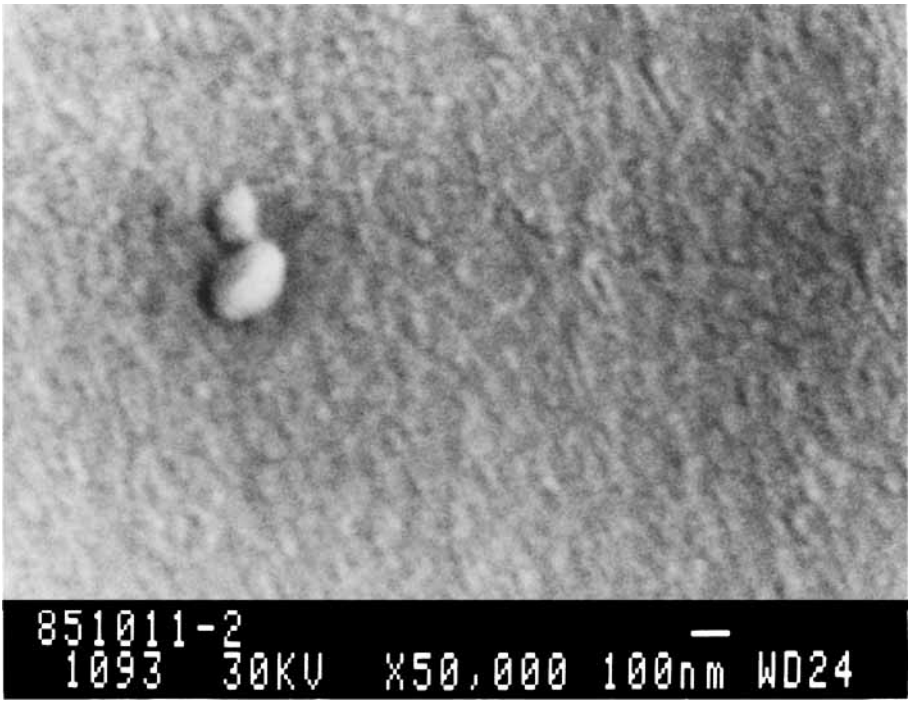

Fig. 3. Scanning electron micrograph of the outer surface of a polysulfone hollow fiber gas separation membrane (from Fritzsche et al.[12]).

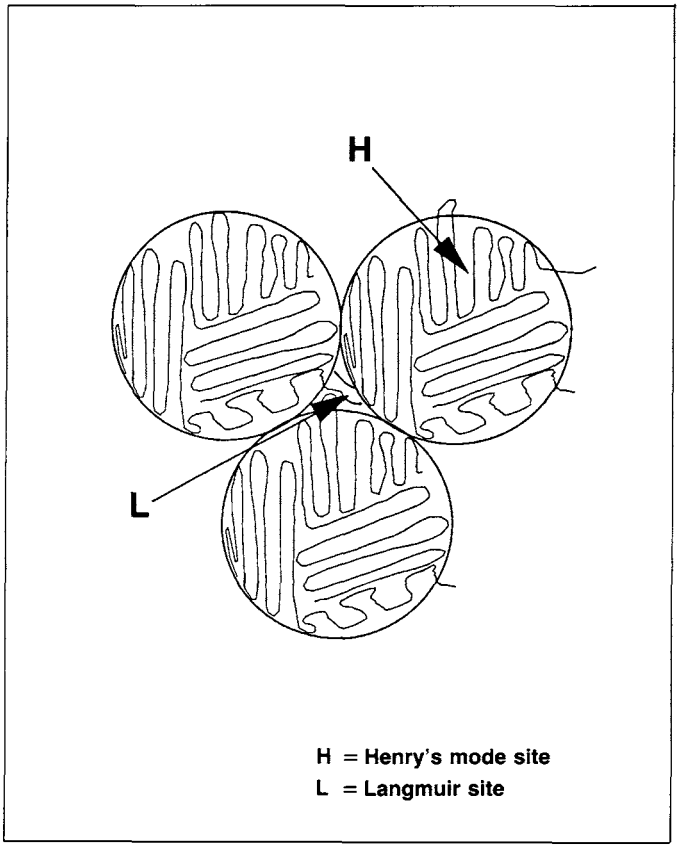

Fig. 4. The intra- and internodular chain displacement/dual mode model.

Spherical nodule aggregates were first observed by Panar et al.[23] They employed the term "*micelle*" which implies an aggregation of some sort, although no suggestion as to its nature was offered in their paper. On the other hand, they appeared to suggest equivalence between their *micelles* and Schultz and Asunmaa's[10] spheres. However, after studying Kamide and Manabe's article[8] and reviewing enlargements of TEM micrographs by Panar et al.,[23] I now feel that *micelles* are nodule aggregates rather than nodules. Hemispherical proturbances, which I believe to be individual nodules, are clearly visible at the surface of the nodule aggregates found in both skin and subdermal regions of a polyamide RO membrane (Fig. 6). Panar et al. demonstrated that the skins of integrally skinned (asymmetric) membranes consisted of a layer, one nodule aggregate thick, of compacted and coalesced nodule aggregates. They also found that occasional gaps in the skin appeared in which the coalescence of nodule aggregates was incomplete. These gaps represent "defect pores" in RO and, together with the functional pores within the nodule interstices, account for the origin of the bimodal pore size distribution in integrally-skinned RO membranes. Although Panar et al. felt that the functional pores in integrally-skinned RO membranes were the interstices between nodule aggregates, I agree with Schultz and Asunmaa that the functional pores are instead the interstices be-

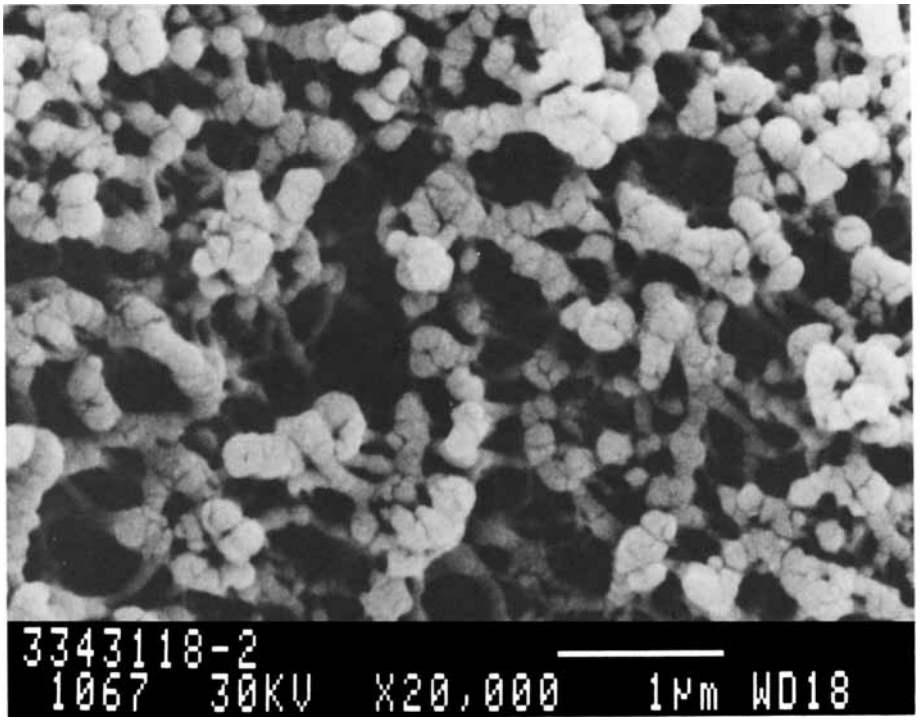

Fig. 5. Scanning electron micrograph of portion of substructure of asymmetric trilayer gas separation membrane (from Kesting et al.[22]).

tween nodules. Views of the top surface of integrally skinned membranes (Figs. 1, 3, and 6) show only nodules—that is, no nodule aggregate boundaries are apparent. The disappearance from top surface views of nodule aggregates can be attributed to flattening of the spherical nodule aggregates as a result both of surface tension and of the restraining effect of contiguous nodule aggregates.

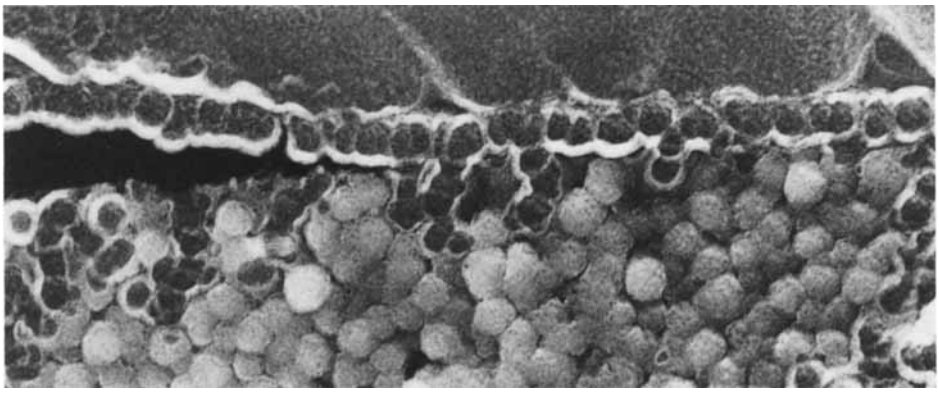

Fig. 6. Skin structure of polyamide skinned membrane (from Panar et al.;[23] reprinted with permission from *Macromolecules,* 1973, American Chemical Society).

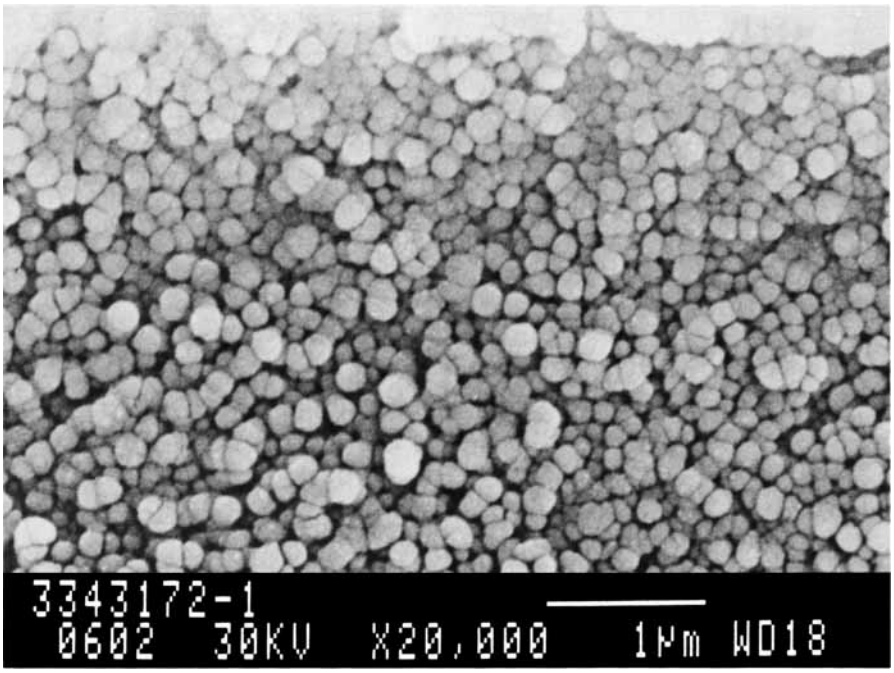

Fig. 7. Scanning electron micrograph of a partial cross section in the neighborhood of the skin of a polyethersulfone hollow fiber (Fritzsche[24]).

Originally spherical nodule aggregates tend towards an almost cubical configuration in the skin (Fig. 7). This shows the considerable distensibility of nodule aggregates. In contrast, individual nodules appear to be more uniform and less easily distended.

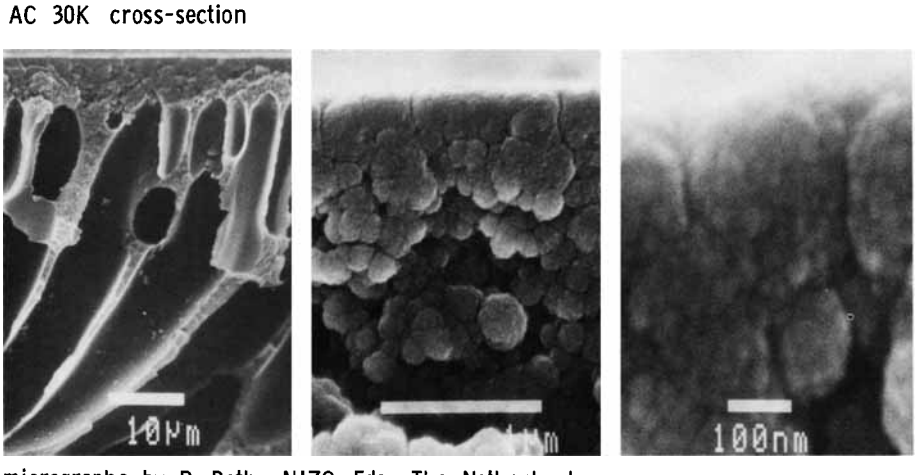

Fig. 8. Scanning electron micrograph of the cross section of an acrylic ultrafiltration membrane with 30,000 dalton cut-off (from Hanemaaijer et al.[25]).

Owing to the increased resolution of modern scanning electron microscopes, the nature of the pores in integrally-skinned UF membranes can now for the first time be unequivocally identified. Ultrafiltration pores are the gaps between incompletely coalesced nodule aggregates (Fig. 8). Top surface views suggest that these pores are roughly circular (Figs. 9 and 10). Thus, the long surmised structural equivalency between RO defects and UF pores has now been established. Prior to annealing, wet process RO membranes do not reject salt ions and are, in effect, UF membranes. Indeed the first UF membranes were nothing more than unannealed RO membranes. Annealing continues the process of coalescence of nodule aggregates in the skin, which was interrupted at the time of gelation. However, even after annealing, some domains of incomplete nodule aggregate coalescence remain. These are the defect pores in RO membranes. Although such defects do not pose a problem for most RO applications, the greater fluidity of gases requires that they be sealed, if the selectivity attainable from a thick dense film is to be achieved by an integrally skinned membrane of the same material. This is usually effected by coating the base membrane with a highly permeable polymer such as silicone.[26]

The origin of the micrometer and submicrometer pores found in microfiltration membranes is best understood by reference to the classical M–S model of phase inversion.[1,9] Following the Sol 1 → Sol 2 transition (phase inversion),

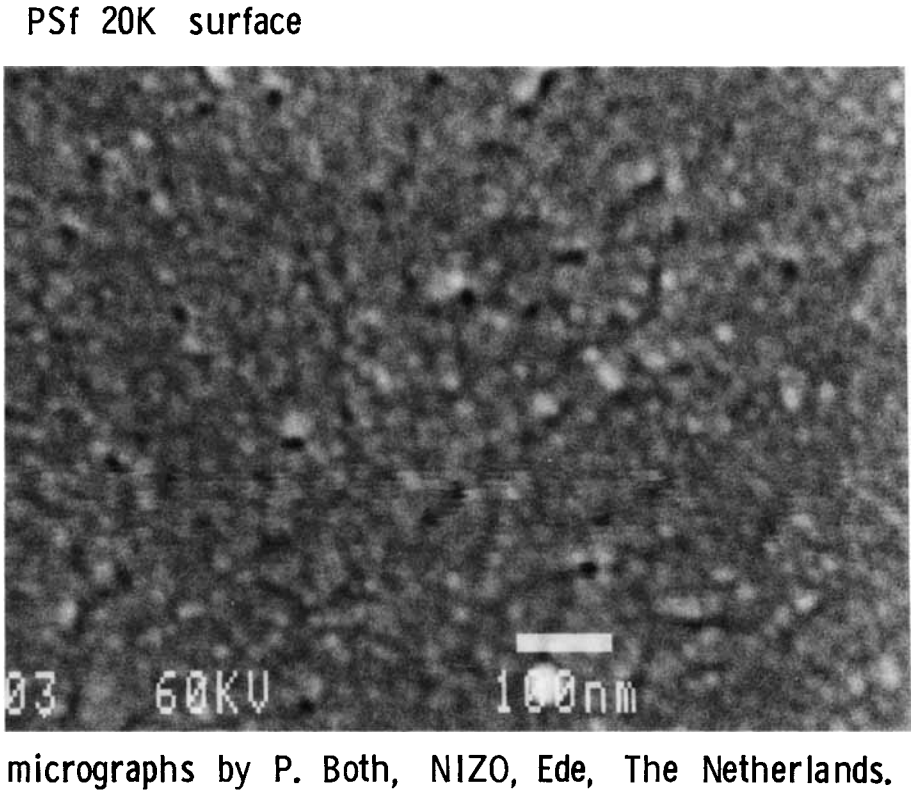

Fig. 9. Scanning electron micrograph of the surface of a polysulfone ultrafiltration membrane with 20,000 dalton cutoff (from Hanemaaijer et al.[25]).

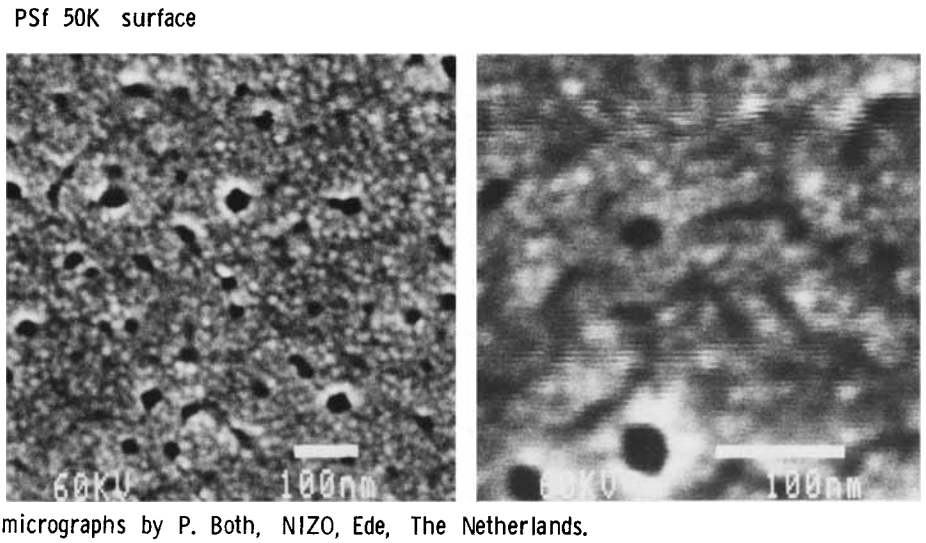

Fig. 10. Scanning electron micrographs of the surface of a polysulfone ultrafiltration membrane with 50,000 dalton cutoff (from Hanemaaijer et al.[25]).

spherical droplets of the dispersed phase appear. Supernodular aggregates form at the surfaces of these droplets. The resulting polymer-coated droplets are mobile nascent cells which after gelation gradually harden into rigid spongelike cells. Contraction of the cell walls as a result of the replacement of the solvent vehicle by nonsolvent and syneresis lead to tearing of the walls between adjacent cells and hence to the open-cell structure which is characteristic of the matrix of microfiltration membranes. Meanwhile the high concentration of nodule aggregates at the membrane surfaces can lead to skinning. If the skin layer is only one nodule aggregate layer thick and not supported by a transition layer, the skin can tear and form pores during contraction of the cell walls in the membrane interior. In such cases the skin will be a slightly denser extension of the structure which is found in the subdermal matrix (Fig. 11). At the present time skinless membranes are favored because of their higher permeability and filtration capacity. Two types are available—isotropic (Fig. 12) and highly anisotropic (Fig. 13). A summary of the pore types in integrally-skinned phase inversion membranes and of the various structural elements which rim their borders is found in Table I.

CONCLUSIONS

1. There are four structural elements in integrally skinned phase inversion membranes: macromolecules, nodules, nodule aggregates, and supernodular aggregates.
2. Nodules are macromolecular aggregates consisting of several tens of individual macromolecules.
3. The skins of integrally skinned membranes consist of a single layer—one nodule aggregate thick—of coalesced and compacted nodule aggregates.

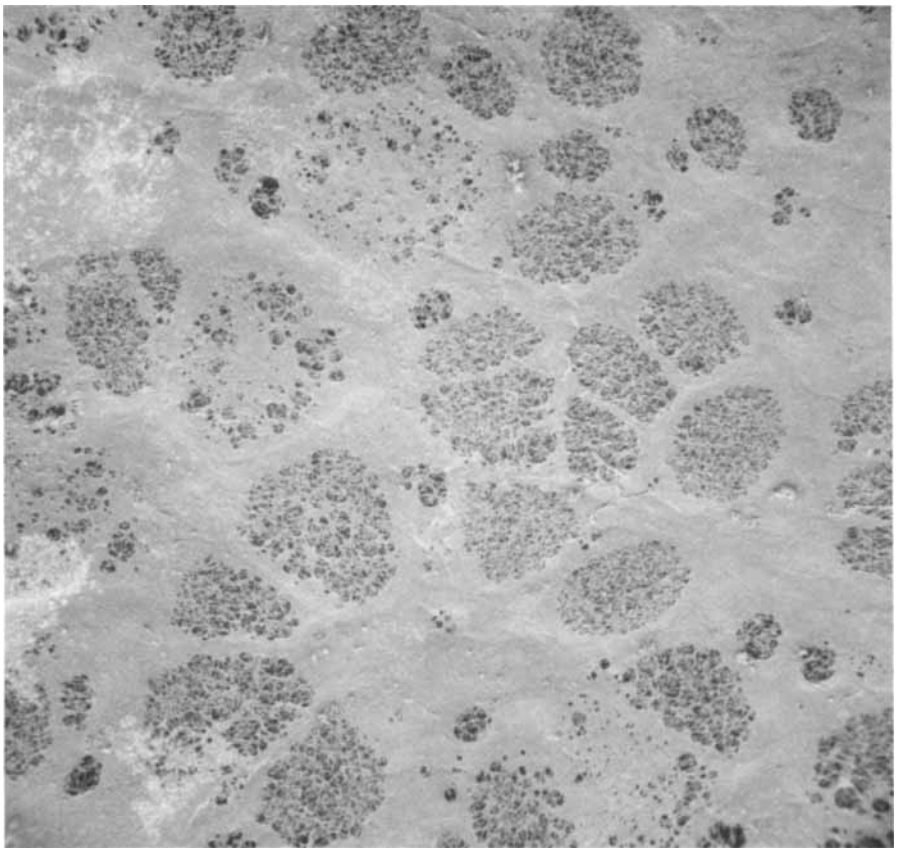

Fig. 11. Scanning electron micrograph of the surface of a skinned cellulose acetate microfiltration membrane (from Kesting[11]).

4. Pores in the various separation regimes: GS, RO, UF, and MF can be seen as more or less static two-dimensional (or fractal) spaces which are bounded by progressively larger structural subelements and elements.
5. Two types of pore are found in the skins of GS membranes and these may account for the origin of dual mode sorption and permeation of gases. The smaller pores, the Henry's mode sites, are the average interchain displacements between parallel chain segments within the nodule. The large pores, the Langmuir sorption sites, are the average interchain displacements in the low density domains where the nodules impinge on one another.
6. Two types of pore are also found in the skins of RO membranes. The finer pores correspond to the Langmuir sorption sites in GS membranes. The coarser pores are defects, that is domains of incomplete nodule aggregate coalescence.
7. Ultrafiltration pores are empty spaces between incompletely coalesced nodule aggregates. They are structurally similar to the defect pores found in RO membranes.

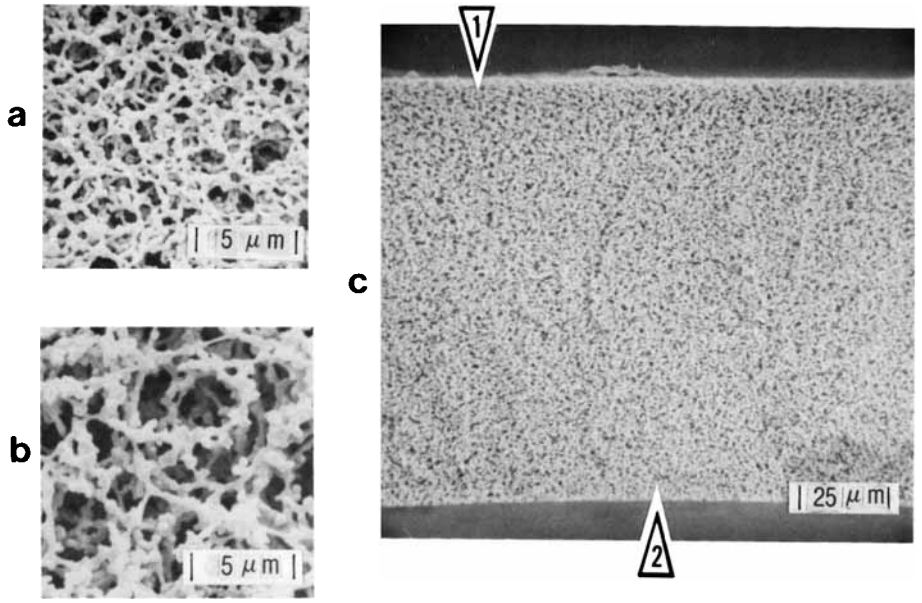

Fig. 12. Scanning electron micrographs of an isotropic 0.45 μm membrane: (a) surface at 1; (b) surface at 2; (c) cross section (from Kesting et al.[27]).

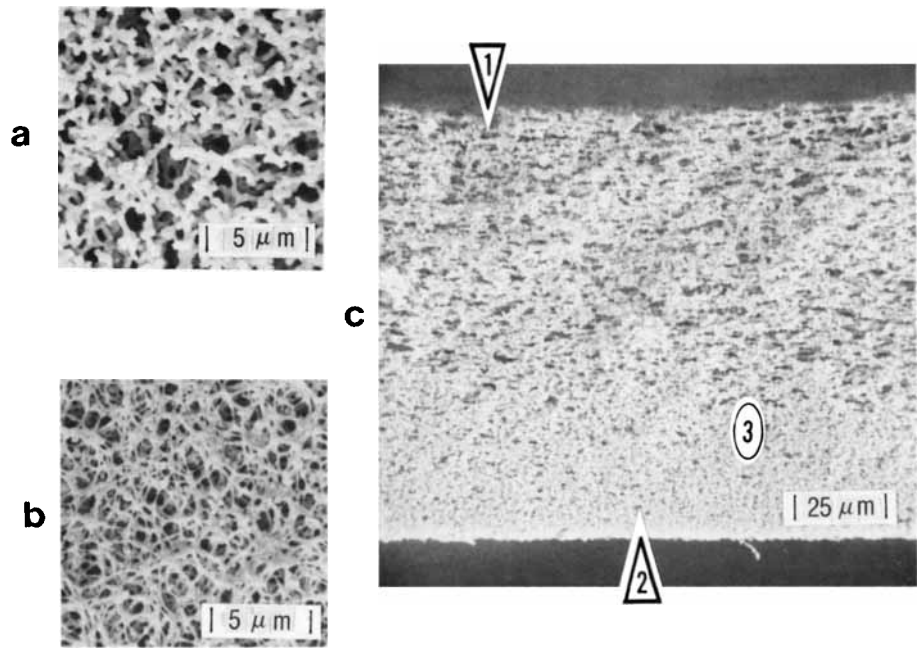

Fig. 13. Scanning electron micrographs of a 0.45 μm highly anisotropic membrane: (a) surface at 1; (b) surface at 2; (c) cross section with the boundary between coarse and fine structures apparent at 3 (from Kesting et al.[27]).

TABLE I
Pore Regimes and the Structural Elements which Rim Their Borders

Pore regime	Porosity range[a] (%)	Relative pore[b] diameter	Nature of pore(s)	Dominant pore rim element(s)	Synonyms for pores and/or pore rim elements
MF	75–90	5000	Surface manifestation of μm-sized apertures between open cells	Aggregates of nodule aggregates	Pores, cells, sponge-, or foamlike structures
UF	65–75	10–20	10–200 Å interstices between incompletely coalesced nodule aggregates	Nodule aggregates	Micelles,[23] secondary particles[8]
RO	55–65	2–3	Two types:		
			(a) 3–10 Å holes in low density spaces between nodules	(a) Nodules, i.e. chain segment displacements in low density domains between,	(a) Paracrystalline nodules,[11] spheres,[10] ellipsoids[11], primary particles[8]
			(b) 20–100 A UF pores (defects)	(b) Nodule aggregates	(b) See UF
GS	50–55	1	Two types:		
			(a) 2–5 Å interchain displacements	(a) Intramolecular chain segment displacements in nodule interior	(a) Mean interchain displacement,[2] free volume V_f
			(b) 3–10 Å holes in low density regions between nodules	(b) Nodules, i.e. chain segment displacements in low density domains between.	(b) See RO

[a] Typical values for macrovoid-free structures. There is, of course, a considerable degree of porosity overlap between adjacent regimes.
[b] Median pore diameter of regime normalized with respect to that of GS.

8. Microfiltration pores are surface extensions of the openings between the cells in the matrix. Their rim elements are supernodular aggregates.

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References

1. R. Kesting, *Synthetic Polymeric Membranes: A Structural Perspective, Second Ed.,* Wiley-Interscience, New York, 1985.

2. R. Kesting, *Synthetic Polymeric Membranes,* McGraw-Hill, New York, 1971.

3. S. Sourirajan and T. Matsuura, *Reverse Osmosis and Ultrafiltration: Science and Principles,* Natl. Res. Council Canada, Publ. 24188, 1985.

4. D. Lloyd, Ed., *Materials Science of Synthetic Membranes,* ACS Symp. Series **269,** Am. Chem. Soc., Washington, DC, 1985.

5. H. Strathmann, *Trennung von molekularen Mischungen mit Hilfe synthetischer Membranen,* Steinkopff, 1979.

6. S. Loeb and S. Sourirajan, U.S. Pat. 3,133,132 (1964).

7. R. Kesting, paper presented at the Industrial and Engineering Chemistry Section Symp. on Recent Advances in RO and UF, Third North American Chemical Congress, Toronto, June 1988.

8. K. Kamide and S. Manabe, in Ref. 4.

9. K. Maier and E. Scheuermann, *Kolloid Z.,* **171,** 122 (1960).

10. R. Schultz and S. Asunmaa, *Rec. Prog. Surface Sci.,* **3,** 291 (1970).

11. R. Kesting, *J. Appl. Polym. Sci.,* **17,** 1771 (1973).

12. A. Fritzsche, B. Armbruster, and P. Fraundorf, to appear.

13. O. Kedem, private communication.

14. F. Sjöstrand, cited in *Structure and Function in Biological Membranes,* Holden Day, 1965, p. 633.

15. T. Schoon and R. Kretzschmar, *Kolloid Z. Z. Polym.,* **211,** 53 (1965).

16. G. Yeh and P. Geil, *J. Macromol. Sci.* B1, **235,** 251 (1967).

17. H. Keith, *Kolloid Z. Z. Polym.,* **231,** 430 (1969).

18. G. Kanig, *Colloid Polym. Sci.,* **265,** 855 (1987).

19. R. Boyer, in *Order in the Amorphous "State" of Polymers,* S. Keinath, R. Miller, and J. Rieke, Eds., Plenum, New York, 1987.

20. R. Pace and A. Datyner, *Polym. Eng. Sci.,* **20**(1), 51 (1980).

21. J. Menczel and B. Wunderlich, *Polym. Prepr.,* **1,** 255 (1986).

22. R. Kesting, A. Fritzsche, M. Murphy, C. Cruse, A. Handermann, and R. Malon, *Asymmetric Gas Separation Membrane Having Graded Density Skins,* U.S. and foreign patents applied for.

23. M. Panar, H. Hoehn, and R. Hebert, *Macromolecules,* **6,** 777 (1973).

24. A. K. Fritzsche, personal communication.

25. J. Hanemaaijer, T. Robbertsen, T. v. d. Bomgaard, C. Olieman, P. Both, and D. Schmidt, *Desalination,* **68,** 93 (1988).

26. J. Henis and M. Tripodi, U.S. Pat. 4,230,463.

27. R. Kesting, A. Murray, K. Jackson, and J. Newman, *Pharm. Technol.,* **5**(5), 52 (1981).

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