equal to infinity where L equals $a\alpha/D$ in which a is the radius of the sphere and α is given by the expression

$$3M_\infty/4\pi a^3C_0 = 1/(1 + 1/\alpha) \quad (1)$$

C_0 is the initial concentration in the sphere, *e.g.*

$$C_0 = M_\infty/(4/3)\pi a^3 \quad (2)$$

hence α must equal infinity for these boundary conditions. The ratio M_t/M_∞ is the ratio of hydrogen that has diffused out of the single crystals at time t divided by the initial amount of hydrogen. In Crank's terminology our M_t/M_∞ is equal to his $1 - (M_t/M_\infty)$. Comparison of the data of Figure 2 with the theoretical values are shown in Figure 5. In order to make such a comparison our observed times have been multiplied by a factor such that at M_t/M_∞ equal to 0.5, the observed and theoretical points agreed. At M_t/M_∞ equal to 0.5 there is not much difference between the sphere and the plane sheet data; it is at high values of M_t/M_∞ that the differences between the two assumed shapes become apparent. We conclude that diffusion out of the mats of polyethylene single crystals is more like that from a sphere than from a plane sheet.

Because our estimated activation energy for diffusion from the single crystals is not greatly different from that found for the bulk polyethylene samples,[2,4] the excessively rapid loss of hydrogen from the single crystals on flushing the ambient hydrogen out of the solubility cell as illustrated by the data of Figures 1 and 2 must be the result of a very short diffusion path. We imagine that the hydrogen diffuses for a short distance through the amorphous regions separating the single lamellae. As a single crystal lamella is typically 1–2 μm along one exterior edge of the crystal[8] it is apparent that the diffusion path for hydrogen molecules can be very short.

Acknowledgments. This research was supported by income from the chair in Chemistry at Baylor University endowed by a gift from The Robert A. Welch Foundation. We are indebted to the Phillips Petroleum Co. for the Marlex-6002 polyethylene.

(8) See, for example, B. Wunderlich, "Macromolecular Physics," Academic Press, Inc., New York, N. Y., 1973, p 190.

The Nature of Asymmetry in Reverse Osmosis Membranes

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ABSTRACT: The micellar morphology which may constitute a definition of asymmetry in a common class of reverse osmosis membranes is proposed. The structure, general to a range of polymer classes, is that of a partially fused but nearly pore-free monolayer of deformed spheres (400–800 Å) supported by a substrate composed of the same spheres randomly packed and less deformed so as to leave 75–100 Å interstices. This structure has elements in common with the solution from which the membranes are cast, and the unquenched cast, unprecipitated polymer solution. The morphology of the permeate side of the membrane, in contrast to that of the functioning feed side, can vary with composition and preparation.

This paper proposes a morphology of asymmetric reverse osmosis (RO) membranes of the type prepared by casting from mixed, or salt-containing solutions as first described by Loeb and Sourirajan.[1] The proposed structure is general to a range of polymer classes and, as such, may constitute a practical definition of this most common type of high flux membrane. The membranes are composed of a surface monolayer of polymeric spheres having diameters of several hundred ångstrom units. These spheres are deformed and partly fused so that few permanent pores remain. The surface monolayer is supported by a substrate of similar spheres randomly packed, less perfectly fused and relatively undeformed so that 75- to 100-Å interstices remain. This concept of asymmetry has implications with respect to the permeation mechanism in that it seems most consistent with mechanisms which invoke free volume (dynamic pores) rather than permanent pores. Moreover, the ability to characterize a new membrane class as having the desired morphology, prior to time-consuming optimization, represents an aid to membrane research.

Significant similarities exist between the morphology of the membrane, the structure of the solution from which the membrane is cast and the structure of the cast but unprecipitated protomembrane. Because of this relationship we will refer to the structural units as micelles. They are detected by electron microscopy in the casting solution when it is rapidly frozen to a clear glass and, even more significantly, the surface monolayer can be seen in the protomembrane within seconds after it is cast at room temperature. We suggest that the asymmetric morphology is determined by the liquid phase, and that the procedures used in membrane casting[2,3] perform their function largely by retaining the morphology of the cast solution without permitting total fusion of the micelles. The casting procedure must obviously also control the internal morphology of the micelles and the quantitative degree of fusion of micelles in the surface layer so as to yield the optimum free volume (dynamic pores). These latter topics will not be dealt with in this paper.

The micellar morphology is consistent with the well-established concept that a surface layer of roughly 1000 Å thickness is the functioning part of an asymmetric reverse osmosis membrane.[4] However, most descriptions of the surface layer treat it as being a thin layer which otherwise

(1) S. Loeb and S. Sourirajan, *Advan. Chem. Ser.*, 38, 117 (1963).

(2) S. Sourirajan, "Reverse Osmosis," Academic Press, New York, N. Y., 1970, 153.

(3) U. Rosenthal, J. Nechustan, A. Kedem, D. Lancet, and M. A. Frommer, *Desalination*, 9, 193 (1971).

(4) R. L. Riley, U. Merten, and I. O. Gardner, *Desalination*, 1, 30 (1966); G. J. Gittens, P. A. Hitchcock, D. C. Sammon, and G. E. Wakley, *ibid.*, 8, 369 (1970); R. McKinney, Jr., and J. H. Rhodes, *Macromolecules*, 4, 633 (1971).

is analogous to a normal bulk polymer. A ball-like morphology, recently proposed,[5] is in partial agreement with the implications of this paper.

The proposed morphology derives from an electron microscopic study of asymmetric membranes by the freeze-cleave technique. By this route we were able to obtain clear cross-section micrographs without dehydration of the membrane. Dehydration, which accompanies most methods of microscope sample preparations, leads to complete fusion of the micelles.

Experimental Section

The freeze-cleave technique of sample preparation has been applied widely to biological membranes.[6] In our work the sample, as a stack of wet gel membranes each ⅛ in. × ½ in., was held in a small vise which fitted into a liquid nitrogen cooled cold stage in a vacuum chamber. The membrane held by the vise, was rapidly frozen in liquid nitrogen and mounted in the cooled stage, and the chamber evacuated to 10^{-7} μm. The membrane stack was fractured with a liquid nitrogen cooled knife and the fracture surface replicated at a shadow angle of 40° by evaporation of a Pt/C pellet. The replicas were recovered by the usual procedures and examined in a Zeiss EM 9S electron microscope.

The liquid structure was obtained by fracture of a frozen drop of solution held in a split washer mounted on a microscope cover slip. The frozen organic glass as well as the cover slip was broken by the knife.

The polyamide–hydrazide membranes were of the type described in ref 7a and were prepared in the same manner. The cellulose acetate membrane was prepared following procedures of Manjikian,[7b] using a solution composed of polymer, acetone, and formamide in the proportions 25:45:30. The membrane was cast at 23° and quenched in ice water.

The photographs in this paper are all in the same sense as the original photomicrograph negative. They are best viewed by considering them as a fracture surface illuminated by oblique light. Dense bright areas in certain pictures represent only a steep fracture surface.

Results and Discussion

The surface structure as shown in Figure 1 for a polyamide–hydrazide membrane is formed from a closely packed monolayer of micelles of about 400- to 800-Å diameter. (These structures are not crystalline in X-ray terms. The term "micelle" is used because of this structure's relationship to that of the casting solution, which will be discussed below.) The substrate is composed of similar spherical units randomly oriented with 75- to 100-Å voids between spheres. In the surface layer these structural units are compressed and distorted so that few voids appear. The skin is thus a denser form of the same "micellar" structure which forms the bulk of the membrane.

The diameter of the micelles in each case discussed in this paper is 400–800 Å. The average size in any figure is not only dependent on the solvent composition and the history of the sample but also may be increased by the effects of the heat evolved during replication. Further conclusions concerning size differences between samples cannot be derived from the photographs in this paper and must be deferred to a future communication.

The surface must, however, be considered as a distinct mechanical entity. During the fracture procedure, the skin is frequently separated from the bulk. In Figure 1 it is evident that there are more pronounced cracks between surface and the bulk than between micelles of the surface. In Figure 2 we see a section of surface layer free of its substrate. The grainy surface in this micrograph is the fracture surface of the water surrounding the gel membrane. The skin has been broken off the substrate during fracturing and has adhered to the water "pot." The fact that the surface layer can be separated demonstrates the relatively poor fusion to the micelles directly below the surface. The substrate is itself poorly fused as seen from the frequency of cracks between micelles (Figure 1).

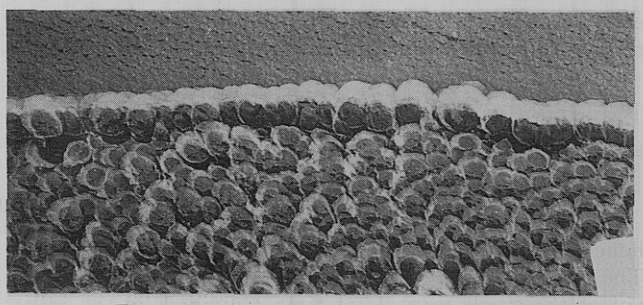

Figure 1. Top edge of cross section of polyamide–hydrazide asymmetric gel membrane.

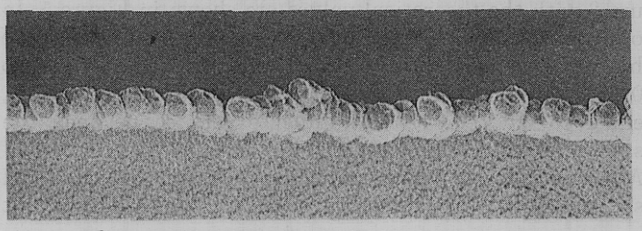

Figure 2. Surface skin of polyamide–hydrazide membrane.

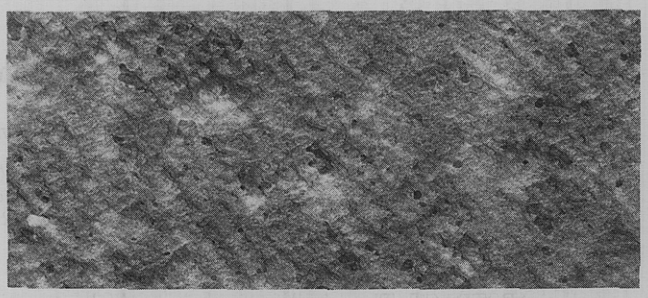

Figure 3. Fracture surface of air-dried polyamide–hydrazide membrane.

The surface layer has evidently been compressed by surface tension forces which have tended to fuse the micelles in the plane of the surface. The micelles directly below and in the bulk have experienced no such forces and remain only poorly fused and relatively spherical.

The picture of the partial fusion of the structural units in an asymmetric gel membrane requires that if the entire structure were exposed to strong surface tension forces, as in the drying of the membrane, the micelles would be expected to fuse, just as a layer of freshly applied latex paint fuses to a solid. Consistently, Figure 3 shows the fracture surface of dried polyamide–hydrazide gel membrane of the type discussed above. The fusion of the micelles to form a typically homogeneous, bulk phase is clearly evident.

The micellar structure of asymmetric membranes having a surface monolayer as the functional portion appears to be general. Polyamides (Figure 4) and cellulose acetate (Figure 5) gel membranes exhibit the same structure, as do freeze-dried polyamide–hydrazides (Figure 6). The

(5) R. D. Schultz and S. K. Asunmaa, *Recent Progr. Surface Sci.*, 3, 291 (1970).

(6) D. Branton, *Proc. Nat. Acad. Sci. U. S.*, 55, 1048 (1966); R. L. Steere, *J. Biophys., Biochem Cytol.*, 7, 167 (1957); H. Moore and K. Muhlethaler, *J. Cell Biol.*, 17, 609 (1963).

(7) (a) P. E. Applegate and C. R. Antonsen in "Reverse Osmosis Membrane Research," H. K. Lansdale and H. E. Podall, Ed., Plenum Press, New York, N. Y., 1972, p 243. (b) Manjikian, S., Loeb, S., and McCutchan, J. W., "Proceeding of the First International Symposium on Water Desalination," U. S. Department of Interior, Office of Saline Water, Washington, D. C., Vol. 2, pp 159–173.

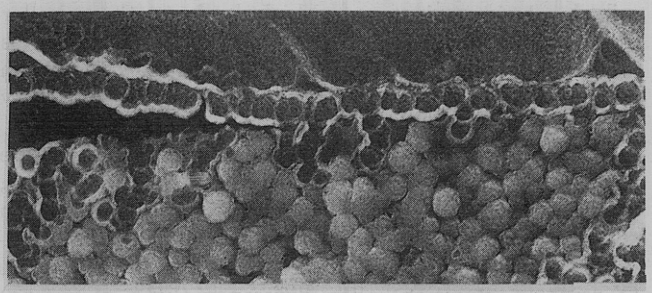

Figure 4. Skin structure of polyamide asymmetric membrane.

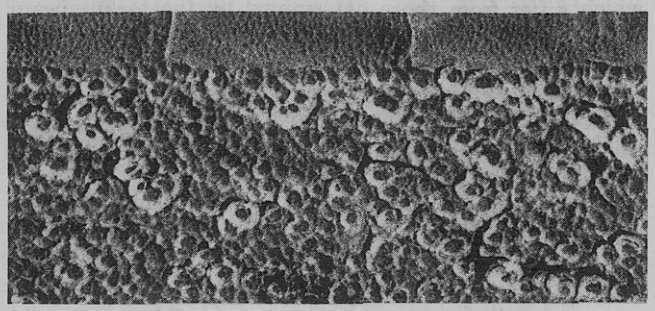

Figure 5. Skin structure of cellulose acetate membrane.

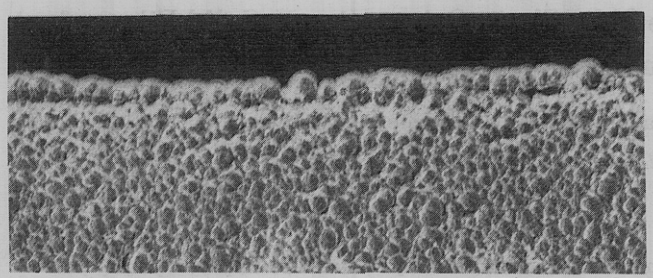

Figure 6. Skin structure of freeze-dried polyamide–hydrazide membrane.

freeze-drying procedure, by obviating surface tension forces, apparently permits the micellar structure to be retained in the dry state.

The closely packed micellar morphology of the surface layer supports mechanistic hypotheses which assume permeation through free volume (dynamic pores) rather than through static pores. It seems reasonable that most permeation takes place through the anomalously high free volume in the zones between micelles where the deformed spheres are imperfectly fused.

Areas in the surface which are imperfectly ordered, such as the gap visible in the right side of Figure 2 and the central region in Figure 5, represent defects because they occur too infrequently to be the significant morphology. These static pores would permit salt passage. The substrate presents comparatively little impedence to flow because water can move through the 100-Å gaps between the spheres.

The structure just described is independent of the observed gross decrease in density toward the rear of the film.[1-4] This decrease in density to what frequently appears to be a spongy structure, can result from either a complete change in morphology to a fibrous structure, or less extreme, to a structure in which the spheres have associated to sheets which form pores in the micrometer range. The morphology of the permeate side is, however, dependent on composition and casting conditions, and no generalized conclusions can be drawn.

The micellar structures of which the membranes are formed appear to derive, at least for polyamide–hydrazides, from the structure of the solution from which the

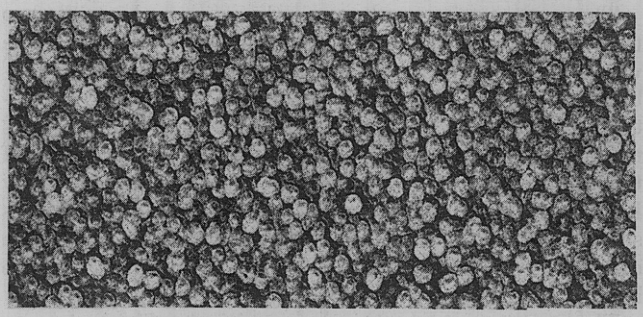

Figure 7. Fracture surface of casting solution of polyamide–hydrazide.

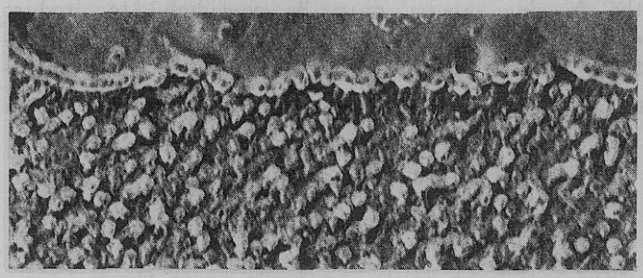

Figure 8. Air–solution interface of polyamide–hydrazide casting solution.

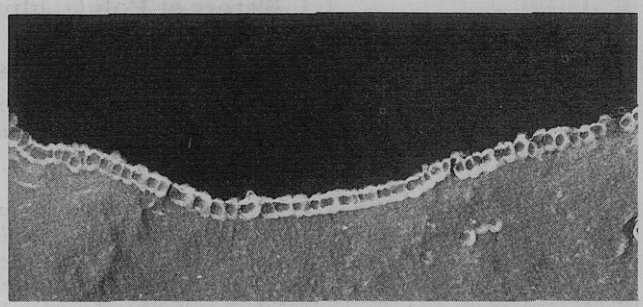

Figure 9. Air–solution "skin" of polyamide–hydrazide casting solution.

membrane is cast. The casting solution not only exhibits the same micellar structure as the bulk (Figure 7) but the micelles form a surface monolayer under the influence of surface tension. Figure 8 is the fracture cross section of an air–liquid interface of the dimethylacetamide solution of the polyamide–hydrazides used to cast the membranes discussed above. The angle of view represented in Figure 8 is at 45° to the fracture cross section so that one sees the fracture surface at one side of the photograph and a section of the air interface at the other. The air interface appears structureless probably because of the effect of surface tension on the solvent. The micelles are only visible where a fracture has emphasized the mechanical differences between micelles and solvent.[8]

The brief period between forming the air interface and freezing the solution to a rigid glass (about 60 sec at 25° in this case) is apparently sufficient to result in a surface layer of some mechanical integrity as can be seen in Figure 9 in which a section of surface layer has, during fracturing, broken free.

The rapid appearance of the surface monolayer after casting is consistent with the demonstrated importance of air exposure prior to precipitation in determining membrane properties.[3]

(8) The micellar structure is not consistently visible on the surface of a dry asymmetric membrane, *e.g.*, a freeze-dried gel membrane of a polyamide–hydrazide. When not visible the micellar nature can be made clear by a brief oxidative etching of the surface.

The asymmetric membrane is thus seen to be related to the structure of the freshly cast polymer solution. The various procedures devised to prepare a high flux membrane appear to have been optimized to retain the solution structure in the solid phase. One may consider this trapped solution morphology as a functional definition of the asymmetric membrane of the type first described by Loeb and Sourirajan. This viewpoint clearly differentiates such membranes which have yielded the highest reverse osmosis fluxes from those fabricated with a thin dense layer of normal solid morphology.

The question of whether the micelles in the casting solution exist at room temperature, or form during the rapid freezing to a glass, requires comment. In the latter case, the freezing process must be considered to produce changes analogous to those occurring during precipitation,[9] and the discussion above would refer to an undescribed solution orientation which leads to the micellar structures on freezing. The prior existence of the micelles is, however, suggested by the constancy of their sizes when a solution is frozen either very slowly or extremely rapidly in the form of a capillary film.

The micelles in the polyamide–hydrazide solution are not apparent in small-angle X-ray scattering experiments, possibly because of insufficient density variation between the swollen polymer and the solvent. It is, of course, conceivable that experiments based on density differences (X-ray) or refractive index difference (light scattering) may measure dimensions of the basic micellar morphology which differ from those determined by the techniques of this paper.

Acknowledgment. The authors acknowledge the excellent technical assistance of Mr. Arthur Strickland and to thank Dr. N. L. Cox and Dr. P. Manos for some of the membranes studied.

(9) R. E. Kesting, "Synthetic Polymeric Membranes," McGraw-Hill, New York, N. Y., 1971.

Infrared Studies of the Side-Chain Orientation in Solid Films of Esters of Poly(L-glutamic acid)

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ABSTRACT: Five polymers of substituted benzyl L-glutamates have been studied by infrared spectrophotometry: poly(L-glutamates) of *o*-, *m*-, and *p*-nitrobenzyl, poly(L-glutamate) of *p*-methylbenzyl, and poly(L-glutamate) of 2,4,6-trimethylbenzyl. Two polymers exhibit a significant linear dichroism in the absorption bands of the side-chain chromophores. These are the poly(L-glutamate) of *p*-nitrobenzyl and the poly(L-glutamate) of 2,4,6-trimethylbenzyl. For both of these polymers, the axial rise per residue is slightly different from that of an α helix. But these interactions between side chains do not give a stabilization of the helical structure. Indeed, only the *p*-nitrobenzyl poly(L-glutamates) exhibit a linear dichroism in the absorption bands of the side-chain chromophores, yet the more stable helical structure is obtained with the ortho derivative. Therefore, the interactions of side groups with one another do not play the main role in the stability of the helical form.

In two previous papers[1,2] from this laboratory, several esters of poly(L-glutamic acid) have been studied by circular dichroism (CD) and optical rotatory dispersion (ORD), in order to determine the influence of the side chains on the secondary structure of polypeptides. Five polymers have been synthetized and studied by these methods: the *o*-, *m*-, and *p*-nitrobenzyl poly(L-glutamates),[1] and the *p*-methylbenzyl and 2,4,6-trimethylbenzyl poly(L-glutamates).[2]

It is further known that there is a frequency-conformation correlation for polypeptides in different secondary structures.[3] In addition, dichroic effects in oriented films of polypeptides give an indication of secondary structure and of orientation of side chains.[4]

In the present paper, we report an investigation by infrared spectrophotometry of these polymers. The poly(benzyl L-glutamate) has been studied also as a reference[3] standard for a right-handed α helix.

(1) P. Le Barny and M. H. Loucheux, *10th Prague IUPAC Microsym.*, in press, 1972.
(2) M. Delporte-Leroy and M. H. Loucheux, *Bull. Soc. Chim. Fr.*, 1529 (1972).
(3) E. J. Ambrose and A. Elliott, *Proc. Roy. Soc., Ser. A*, **205**, 47 (1951).
(4) E. M. Bradbury, B. G. Carpenter, and R. M. Stephens, *Macromolecules*, **5**, 8 (1972).

Experimental Section

Materials. The polymers were prepared by polymerization of *N*-carboxyanhydrides of the corresponding L-glutamates.[5] The molecular weights were determined by viscosimetry by using the relation known for poly(benzyl L-glutamate).[6] We have verified this relation for one polymer by using the light-scattering technique. The molecular weights obtained are as follows.

Poly(L-glutamate) of	Mol Wt
o-Nitrobenzyl	180,000
m-Nitrobenzyl	77,000
p-Nitrobenzyl	30,000
p-Methylbenzyl	75,000
2,4,6-Trimethylbenzyl	45,000
Benzyl	220,000

Infrared Spectroscopy. The infrared spectra were recorded on a Perkin-Elmer 257 double-beam spectrometer and on a Perkin-Elmer 225 double-beam spectrometer when polarized radiation was used.

The films of macromolecules were obtained by evaporation of the viscous solutions until dry. The solvents used were chloroform

(5) R. Ledger and F. H. C. Stewart, *Aust. J. Chem.*, **18**, 1477 (1965); *ibid.*, **19**, 1729 (1966). M. H. Loucheux and J. Parrod, *C. R. Acad. Sci.*, **267**, 614 (1968).
(6) P. Doty, J. H. Bradbury, and A. M. Holtzer, *J. Amer. Chem. Soc.*, **78**, 947 (1956).