

## Polysulfone Hollow Fibers. II. Morphology

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### Synopsis

The morphology of porous polysulfone hollow fibers which were spun by the dry-wet spinning process is discussed. It was demonstrated that a relatively moderate quenching medium should be employed in the bore of the nascent fiber in order to produce an isotropic fiber free of macrovoids and intrusion cells. A rather delicate quantitative balance between the internal precipitant and the spinning solution has to be maintained, especially when low-viscosity polymeric solutions are employed. Scanning electron micrographs of fiber cross sections display highly porous, sponge-structured walls which in some instances exhibit a rather dense interface skin. However, control of the extrusion/coagulation procedure allows the formation of skinned, porous skinned, and non-skinned fibers.

### INTRODUCTION

High-tensile strength and high-modulus porous polysulfone hollow fibers have been developed.<sup>1</sup> The fibers have been reported to withstand hydraulic pressures of more than 1,000 psi while displaying a wide range of hydraulic permeabilities. These polysulfone hollow fibers were spun by the dry-wet spinning technique. Basically, the technique parallels that used for the fabrication of asymmetric cellulose acetate flat-sheet membranes, as first employed by Loeb and Sourirajan.<sup>2</sup> The spinning (or the casting) process is accomplished in two steps: (1) exposure of spun (or cast) solution to a gas phase, followed by (2) its immersion in a liquid phase of coagulating (nonsolvent) liquid. Numerous polymeric membranes in the forms of flat, tubular, and hollow fiber membranes displaying a wide range of separation capabilities have been produced by this technique.<sup>3</sup> Nevertheless, many of the procedures (concerning such parameters as viscosity, solvents, nonsolvents, etc.) were formulated empirically, and the factors governing membrane structure and characteristics are still poorly understood. It has been shown that the morphology of a cast membrane can be dramatically altered by imposing a minor change on one of the many parameters involved in the formation of a nascent membrane. This is a direct result of the fact that the formation of a membrane includes a series of dependent parameters (cascade effect).

In a previous paper,<sup>1</sup> we have discussed the influence of the spinning conditions on some mechanical and transport properties of the spun fibers. In the present paper, we wish to discuss some of the parameters that influence the morphology of the spun hollow fiber.

The dry-wet spinning procedure is often accompanied by the formation of

cavities and intrusion ("finger-like") cells within hollow fibers. Frommer and Matz<sup>4</sup> have reported and investigated these phenomena in cellulose acetate flat-sheet and tubular membranes. King et al.<sup>5</sup> reported cavities in the casting of cellulose acetate blend membranes. Model and Lee<sup>6</sup> reported large concentrations of radial voids in PBI hollow fibers. Other polymers, such as polyamide and polyacrylonitrile, also display the same phenomena when cast as membrane under certain dry-wet process conditions as reported by Strathmann et al.<sup>7</sup>

Macrovoids and finger-like intrusions considerably influence fiber performance under hydraulic pressure. The terms finger-like intrusion or intrusion cells relate to those macrovoids that extend to the fibers external or internal surfaces. Fibers with finger-like intrusions tend to puncture and result in penetrations of pinholes under modest pressure.<sup>4</sup> Another morphological outcome is the associated anisotropic character of the spun fiber. The wet-spinning technique can provide a range of anisotropics depending upon the spinning formulation and conditions.

The spinning formulations described previously<sup>1</sup> were directed toward the production of porous structures which provide high hydraulic permeability and which can be coated with an ultrathin membrane.

The present paper describes the morphology of polysulfone hollow fibers formulated from a ternary-component spinning solution. However, the conclusions from this study can be applied to other spun polymer, and have thus been employed by us in the spinning of acrylic polymers into hollow fibers.<sup>8</sup>

## EXPERIMENTAL

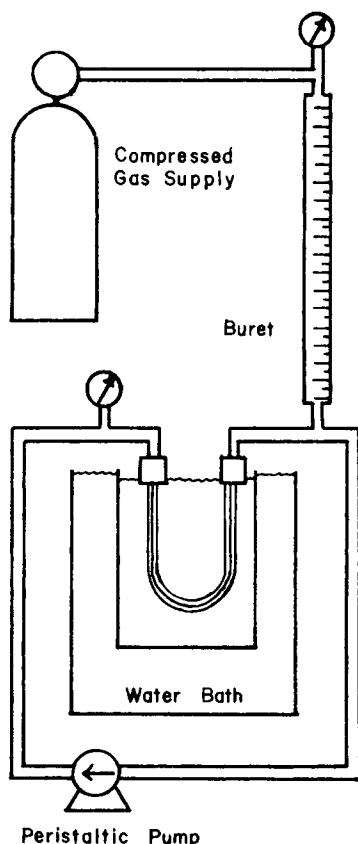
### Spinning Procedure

The spinning procedures are discussed thoroughly in a previous paper.<sup>1</sup> In general, hollow fibers are spun from a solution of polysulfone (PS) and poly(vinylpyrrolidone) (PVP) in dimethylacetamide (DMA). The total concentration of polymer in the solution is specified below. The spinning procedure is performed by a tube-in-jet technique. The preferred outside quench media for the nascent fiber is air, followed by water. The center quench media are injected through the inner annulus, and numerous quench compositions are discussed below.

In general, the dry-wet<sup>1</sup> (or dry jet-wet) spinning can be divided into three stages: (I) spinning into a gas phase while the center quench medium is either liquid or gas (dry stage); (II) the nascent fiber is ultimately coagulated by a powerful precipitant-water bath (wet stage); (III) the fiber is flushed with water at 60°C.

### Preparation of Polysulfone Hollow Fibers for SEM (Scanning Electron Microscope)

Polysulfone hollow fibers were attached to aluminum disks with a double-surface Scotch tape. Cross sections of polysulfone hollow fibers were prepared for the SEM by breaking the fibers at the temperature of liquid nitrogen. Quick freezing of the fiber to such a temperature does not damage the fiber and leaves an undeformed surface. The mounted specimen was then shadowed (coated) with gold.



#### HOLLOW FIBER ULTRAFILTRATION TEST SET-UP

Fig. 1. Hydraulic permeability ( $L_p$ ) measurement set-up.

#### Viscosity Measurements

All spinning solutions were measured for their viscosity in a Brookfield synchromatic viscometer (Model RVT). All the viscosities quoted in the following were measured at a temperature of 50°C unless a different temperature is quoted.

#### Water Flux Measurements

Ultrafiltration rates were determined by steady-state measurement of the quantity of water permeating a fiber bundle at 4 psi. The fiber bundles were prepared as described in a previous paper.<sup>1</sup> Approximately 100 fibers were potted into either 1/2-in.-diameter polypropylene tubing or 3/8-in. steel tubing. Swagelock fittings were used to connect the experimental bundle to the pressurized water supply (Fig. 1). A 10-ml buret, which was installed between a nitrogen cylinder and the fiber bundle, was used for measuring during the water permeation rate.

The hydraulic permeability  $L_p$  of the polysulfone hollow fiber was calculated from the flux equation:

$$J = AL_p \Delta P \quad (1)$$

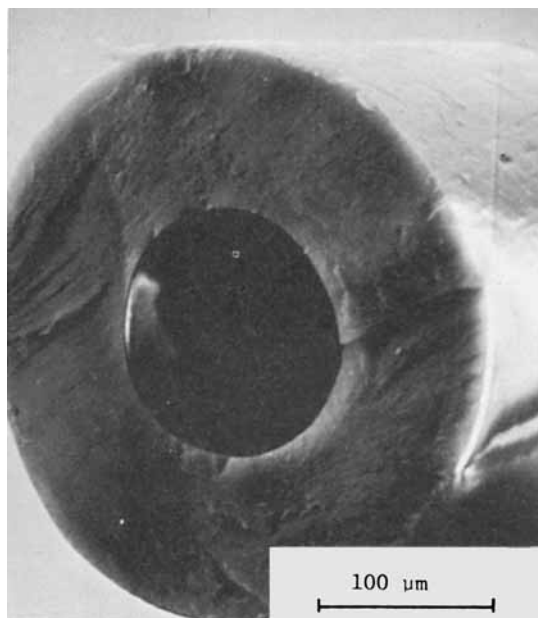


Fig. 2. Polysulfone hollow fiber, Spinning formulation, PS/PVP/DMA = 30/20/50; solution viscosity, 180,000 cP; jet temp., 23°C; bore precipitant, air, 40% relative humidity ( $L_p$  = 49 cm/sec atm).

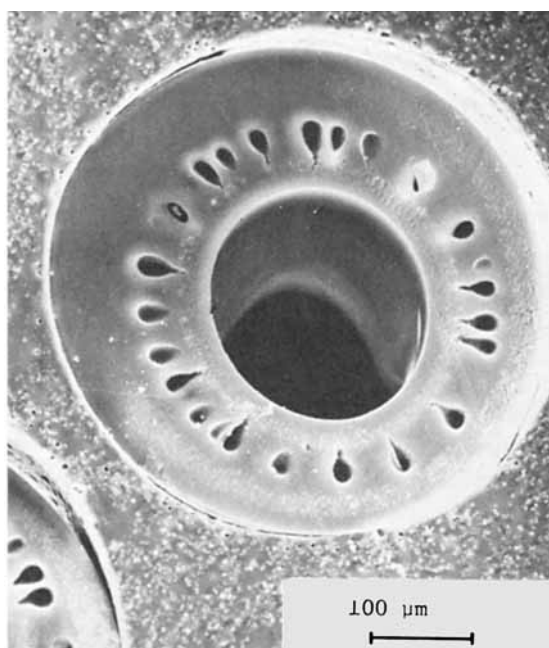


Fig. 3. Polysulfone hollow fiber displaying internal macrovoids. Spinning formulation, PS/PVP/DMA = 24/10/66; viscosity, 10,000 cP; jet temp., 20°C; bore precipitant, DMA/H<sub>2</sub>O = 3/1 ( $L_p$  = 39 cm/sec atm).

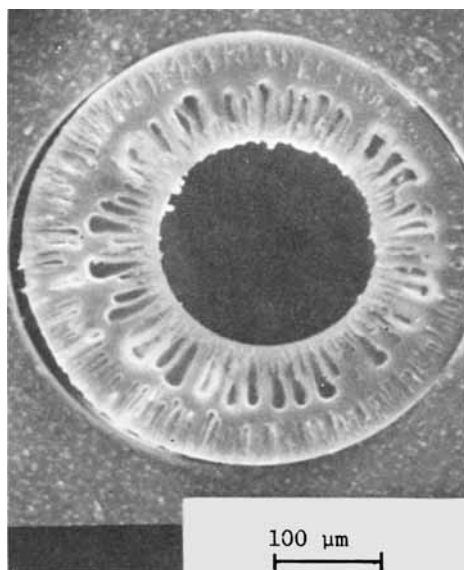


Fig. 4. Polysulfone hollow fiber displaying external and internal intrusion cells. Spinning formulation, PS/PVP/DMA = 15/10/75; viscosity, 3000 cP; bore precipitant, DMA/H<sub>2</sub>O = 1/1.

where  $J$  = permeation rate (cm<sup>3</sup>/sec);  $A$  = area (cm<sup>2</sup>) of the measured polysulfone hollow fiber; and  $\Delta P$  = differential pressure applied, i.e., ( $P_{\text{internal}} - P_{\text{external}}$ ) (atm).

## RESULTS AND DISCUSSION

### Macrostructure

The macrostructures of three different spun polysulfone hollow fibers are shown in Figures 2–4. These cross sections are representative of the dry-wet spinning products of polysulfone hollow fibers. The cross section in Figure 2 appears uniform compared to those shown in Figures 3 and 4, which contain cavities and finger-like intrusion cells.

The formation of cavities and finger-like intrusions is a function of the polymer coagulation rate and of the polymeric chain texture in the spinning solution when the sol-to-gel transition occurs. Frommer and Matz,<sup>4</sup> who thoroughly investigated the formation of macrovoids in cellulose acetate, set up two phenomenological prescriptions to avoid macrovoid formation in dry-wet cast membranes: (1) a lowering of the tendency of the nonsolvent to penetrate into the cast solution; (2) an increase in the viscosity of the cast solution, or the creation of a thick gel layer on top of it. These two are interrelated and, in general, appear to be in accord with our observations in the polysulfone hollow fiber spinning process.

The polysulfone hollow fiber shown in Figure 2 was spun from a high-viscosity spinning solution, 180,000 cP. The fiber was spun with a jet temperature of 20°C and was air quenched from the center. Figure 3 shows a polysulfone hollow fiber spun from a spinning solution of rather low viscosity, 10,000 cP, under the same

conditions of operation but with an internal precipitant of DMA/water (3/1 w/w) (the spinning of low-viscosity solutions dictates the use of a liquid as an internal quench media to maintain a production of nondeformed fiber). In order to study the influence of the internal quench on the morphology, this fiber (Fig. 3) was spun with an internal core slightly off center. It can be clearly deduced from the cross section that the center quench caused the formation of macrovoids, since the circle drawn by the macrovoids is precisely concentric with the internal core circle. That is, distance measured from void center to the core is equal for all the voids.

Further reduction in the viscosity of the spinning solution results in finger-like intrusions as shown in Figure 4.

The fact that the highly viscous spinning solutions (Fig. 2) result in uniform fiber structure accords with the two above-mentioned concepts of Frommer and Matz.<sup>4</sup> However, in order to understand the mechanisms of the fibers structural formation, it has to be emphasized here that the high viscosities are a direct outcome of relatively high polymer concentrations in the spinning solutions, and in spite of interrelation between these two parameters, the second one has a sharper effect on the morphology. Similar observations were previously reported. For example, flat-sheet cellulose acetate (CA) membranes were cast from DMSO solutions and subsequently coagulated in an ice-water bath.<sup>5</sup> The tendency of the CA/DMSO solution to occlude large cavities in the cast membrane decreased when the polymer concentration in the mixture was increased from 20% to 30%. Strathman et al.,<sup>7</sup> in a recent publication, report also the same observation for polyamids and other polymers. In their work, they have also drawn the schematic of the concentrations profiles of the solvent, polymer, and precipitant through a precipitation step of flat-sheet membrane that was cast on a glass plate and subsequently was quenched in a precipitant bath. These profiles are in agreement with our observation. However, for a hollow fiber, they represent only half of the picture, since the fiber is quenched from both internal and external surfaces.

### Formation of Intrusion Cells in the External Periphery

The location of the intrusion cells and cavities depends upon the quenching power of the precipitants facing these surfaces, as shown in Figures 3 and 4. The general observation, which is in agreement with previous work,<sup>4,7</sup> is that low concentration solutions, when combined with a relatively powerful precipitant, favor intrusion cells and cavities structure. Close observation of the cavities in Figure 3 and comparing them with the finger-like intrusion cells in Figure 4 leads to the conclusion that they originated from the same phenomenon. In the first stage of the spinning, both fibers were exposed to DMA/water from the inner surface and to air from the external one. In this stage, the nascent fibers were exposed to the internal precipitant only a few seconds (1–5 sec) before the external surface was subjected to the water. No intrusion cells are found in the external belt of the fiber shown in Figure 3, and those in Figure 4 are much smaller than the internal ones.

Further studies revealed that in order to eliminate intrusion cells on the external belt of the fiber, a rather delicate quantitative balance between the internal precipitant and the spinning solution has to be maintained. This is demon-

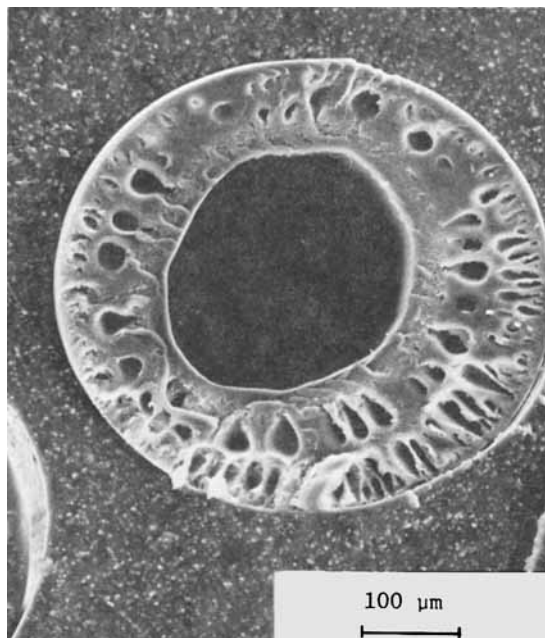


Fig. 5. Polysulfone hollow fiber spun with the same formulation as shown in Fig. 3, but with only 2/3 of its solution delivery rate ( $L_p = 81$  cm/sec atm).

strated in the following examples. The first one represents the case where reduction in the volume of polymer extrusion takes place; i.e., the amount of spinning solution that was pumped (delivered) through the jet was reduced while all the other variables remained unchanged, including the volume of precipitant that was injected through the center core. The significant change in the spinning condition, hence, was a reduced ratio of the quantity of polymer solution to the quantity of internal quench medium. The hollow fibers shown in Figures 3 and 5 were taken such an experiment. The solution delivery rate of the second one (Fig. 5) was only 2/3 of the first one (Fig. 3). The figures indicate that when the internal quench is quantitatively increased (i.e., the ratio of spinning solution to quench medium is decreased), the void dimensions on the internal belt is increased.

However, a more significant result is the presence of intrusion cells on the external belt. This outcome can be explained as follows: Figure 2 shows that when a highly viscous solution enters the water quench bath (stage 2), no intrusion cells are formed. The higher viscous, concentrated solution is near its gelation point which prevents the formation of intrusion cells. Therefore, one must conclude that similar conditions are generated in the external structure shown for the fiber in Figure 3. When this fiber enters the water bath, its outer periphery is already structured to the point that intrusion cells cannot be formed. When comparing this fiber to the fiber shown in Figure 5, where a higher ratio of precipitant resulted in intrusion cells emanating from the outer diameter, one is led to the conclusion that the ratio of precipitant to polymeric solution (Fig. 3) provides sufficient coagulant to the outer periphery to increase viscosity without causing a complete precipitation of the polymer until after the fiber penetrates the water bath.

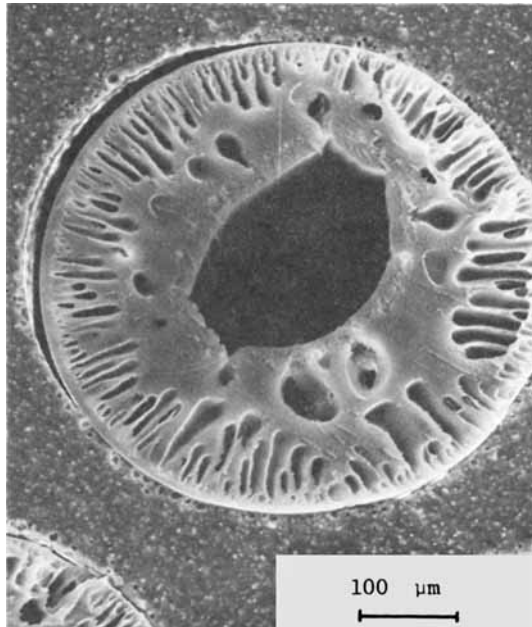


Fig. 6. Polysulfone hollow fiber spun with the same formulation as shown in Fig. 3, but with half the delivery rate of bore precipitant which was composed of DMA/H<sub>2</sub>O = 1/1 ( $L_p = 116$  cm/sec atm).

The use of a larger volume of coagulant (Fig. 5) caused complete precipitation of the polymer as the coagulant penetrated from the bore toward the outer periphery. The complete precipitation act as a barrier to the diffusion of further coagulant, so that the viscosity of the outer diameter remains low or unchanged when it encounters the water bath. This, in turn, leads to the formation of large intrusion cells. This same explanation is supported by the second example shown in Figure 6, where a smaller volume, but of stronger coagulant, was used in the bore. Again, the cross section indicates that the intrusion cells originated from the water bath and that the bore coagulant inhibited compliance of the structure. When the fiber is extruded directly into the quench bath ("wet spinning," the spinning jet was immersed  $\frac{1}{2}$  in. in water) without an intermediate period for bore fluid diffusion, the external morphology is the same as that shown in Figure 6. This indicates that precipitation of the unaltered polymer solution by an excess of strong coagulant (water) will lead to formation of intrusion cells. But when the polymer solution is preconditioned to a high viscosity by the introduction of a limited amount of precipitant (s in Fig. 3), the effect is negated.

### Spinning High-Viscose Solution

Spinning solutions of high viscosities and high polymer concentration solidify very fast even in the presence of a weak participant. In such cases, a fast coagulation rate of the nascent polysulfone hollow fiber can be observed in dry-wet spinning into high relative humidity air. In such a case, coagulation of the fiber begins in the "dry" state of the dry-wet spinning and the nascent fiber becomes opaque before it hits the water bath (the porous polysulfone hollow fibers are white, opaque fibers). Dimethylacetamide (DMA) is a nonvolatile solvent





Fig. 7. Concentric split hollow fiber—"fiber within a fiber." Spinning formulation, PS/PVP/DMA = 31/15/54; viscosity, 76,000 cP; bore precipitant, DMA/water = 3/1; jet temp., 52°C ( $L_p = 6$  cm/sec atm).

(boiling temperature  $>165^\circ\text{C}$ ) and is highly hygroscopic. In an atmosphere of high relative humidity, the DMA picks up enough water from the air to start coagulation if the exposure time is sufficient. The effect of relative humidity has to be related to the specific spinning conditions, i.e., polymer concentration, temperature, etc.

Very interesting phenomena occur when a powerful quenching medium is applied on the internal surface of a solution having an initially high viscosity, as shown in Figure 7. This fiber was spun from a solution of 76,000 cP with an internal quench medium of 3/1 DMA/water (w/w) and a jet temperature of 52°C. Rapid gelation occurs in the internal core, which is associated with some contraction, while the external portion of nascent fiber flows above until it gels ("freezes"). The result, seen in one extreme case, is a "fiber within a fiber." Sometimes, these "two fibers" are physically detached from each other and separated by several microns. The same solution, when spun with an internal low-humidity air quench, results in uniform structure such as that shown in Figure 2.

### Spinning Low-Viscose Solution

In order to avoid macrovoid formation in solutions which have relatively low viscosities (or low solids content), several parameters which control the coagulation and contraction of the fiber have been investigated. Coagulation mode, which "freezes" the polymeric texture instantaneously and uniformly, is very difficult to achieve when spinning such solutions. In fact, any attempt to "freeze" the solution thread that comes out of the spinning jet by conventional coagulation

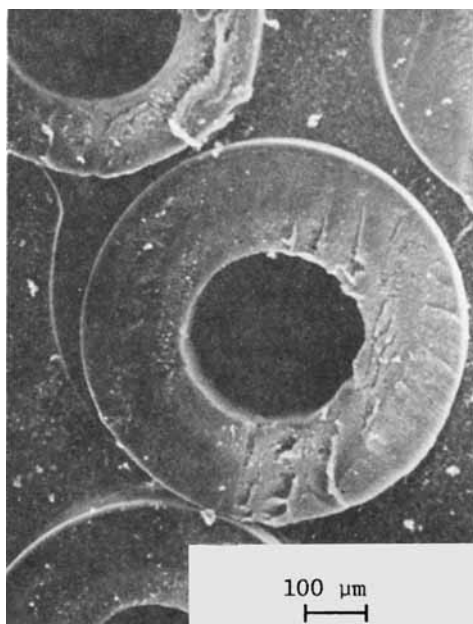


Fig. 8. Isotropic polysulfone hollow fiber spun from a relatively low-viscosity solution. Spinning formulation, PS/PVP/DMA = 26/15/59; viscosity, 19,600 cP; jet temp., 53°C; bore precipitant, DMA/water = 4/1 ( $L_p$  = 32 cm/sec atm).

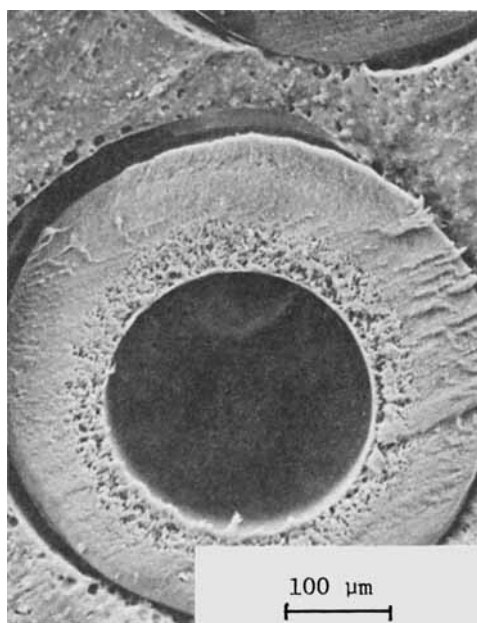


Fig. 9. Polysulfone hollow fiber spun from a low-viscosity solution with relatively high jet temp. Spinning formulation, PS/PVP/DMA = 25/13/62; viscosity, 13,000 cP; jet temp., 65°C; bore precipitant, DMA/water = 3/1 ( $L_p$  = 48 cm/sec atm).

methods results in macrovoids and finger-like intrusions (Fig. 4). To obtain a uniform structure, gradual quenching of the nascent fiber is necessary. The rapid formation of internal stresses must be prevented and viscosity and surface tension gradients caused by the coagulant must be diminished.

This can be achieved by employing a relatively moderate quench medium and by elevating the spinning (jet) temperature (Figs. 8 and 9). When a relatively high ratio of solvent (DMA/nonsolvent water) is employed, the quench medium contains only a small amount of water and will not thoroughly coagulate the fiber. Furthermore, the spinning solution in the sol state can tolerate minor quantities of water at elevated temperatures. However, the elevated temperature accelerates dispersion of the water in the nascent fiber, leading to a substantial increase of the solution viscosity. The gradual cooling that the spun thread encounters in the "dry" stage (from the jet to the water bath) is accompanied by a further increase in its viscosity up to a possible "freeze" gelation even before it hits the water bath. This results in a more uniform coagulation and, hence, a uniform fiber wall structure.

### Quenching Mechanism

Several conclusions can be drawn from the above cases (Figs. 2-9). The more relevant of these is that the mechanism of the coagulation of nascent fiber depends upon the rate at which the precipitant permeates the polymer solution. The rate at which the precipitant front advances into solutions with high polymer content is less than its rate of advance into solutions with lower polymer content. While the microviscosity of concentrated polymer solutions may not inhibit diffusion of the precipitant into the polymer solution, the concentrated polymer solutions are close to the precipitation point of the polymer. The advance of even minute quantities of nonsolvent into the polymer solution causes a rapid viscosity increase, immobilization of the polymer segments, and finally, true solidification. Solidification reduces the further transport rate of precipitant. Nevertheless, for such cases, very little nonsolvent must be introduced to "freeze" the entire structure.

In relatively low-viscose polymer solutions, the rate of nonsolvent penetration is not inhibited until phase separation occurs. This often requires a higher volume fraction of nonsolvent to be present than is required with concentrated polymer solutions. During the period that the solvent/nonsolvent balance is changing by diffusion, the polymer solution can undergo phase separation<sup>7</sup> leading to the formation of some domains rich in polymer and other domains depleted of polymer. Depleted domains eventually become pore voids.

This provides an explanation for the above spinning results: As illustrated by the case shown in Figure 3, a relatively rapid phase separation occurs when precipitant permeates through the internal surface and leads to the formation of macrovoids in the internal belt of the fiber. However, further permeation of the precipitant is slowed and its power is diluted when it reaches the external belt. If it is further assumed that the nascent fiber shrinks (toward its center) during coagulation, the absence of intrusion cells on the external belt can be explained by increases in surface viscosity and polymer concentration before the fiber hits the water bath. Figures 5 and 6 present cases where insufficient quantity of the precipitant reaches the external belt of nascent fiber. This can

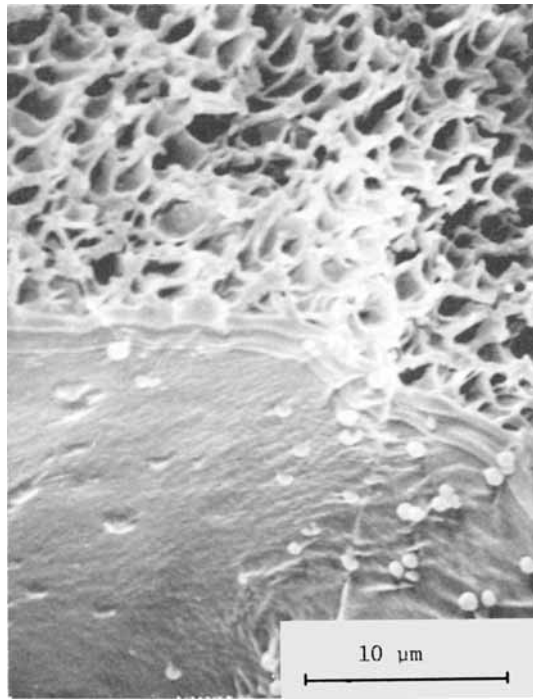


Fig. 10. Internal skin covering a sponge-structured wall of polysulfone hollow fiber. The fiber was spun without any polymeric additive, Spinning formulation, PS/DMA = 35/65; bore precipitant, isopropanol ( $L_p = 2.2$  cm/sec atm).

happen either because of an instantaneous precipitation of polymer in the internal belt or because a rather small quantity of precipitant was initially employed (instantaneous precipitation forms a dense solid barrier which causes a manifold decrease in precipitant permeation rate). The fiber shown in Figure

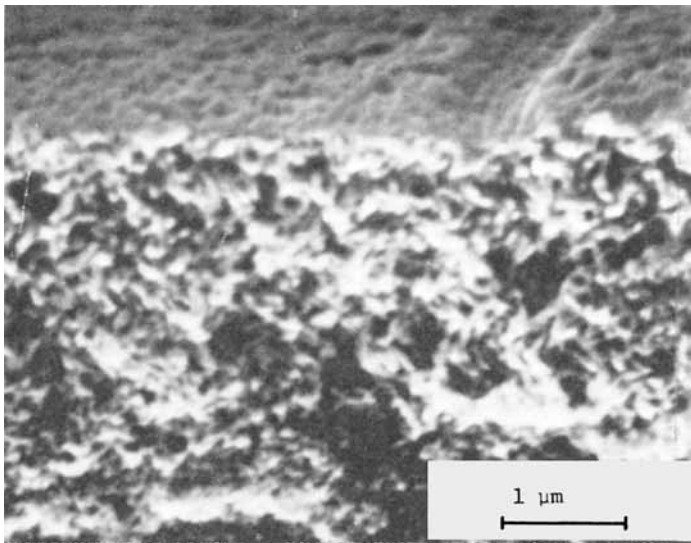


Fig. 11. Wall structure of the fiber shown in Fig. 2.

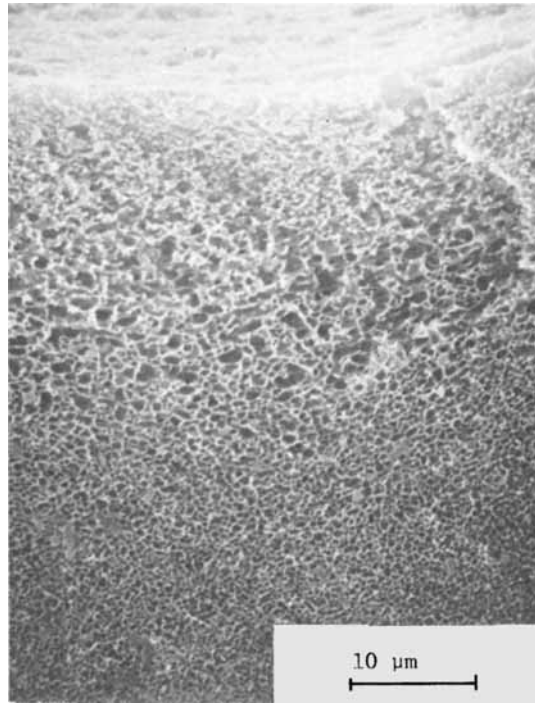


Fig. 12. Internal surface and morphology of nonskinned polysulfone hollow fiber ( $L_p = 80$  cm/sec atm).

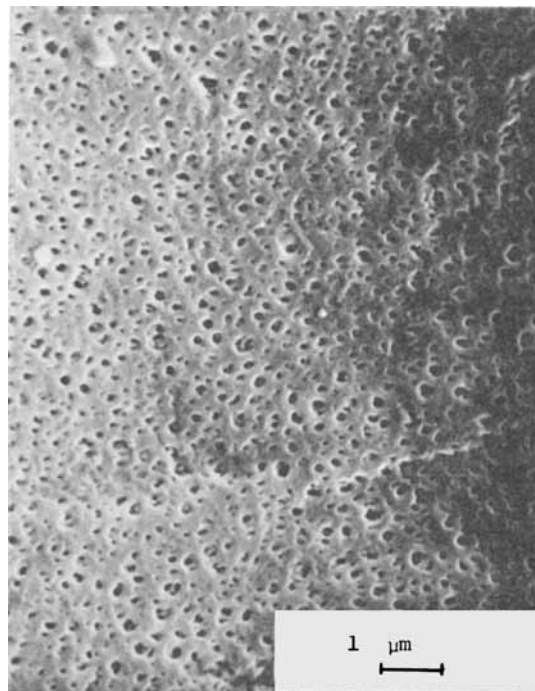


Fig. 13. External surface of the fiber shown in Fig. 2.

5 represents the first case, while the fiber in Figure 6 can represent either situation.

### Microstructure

The mode of coagulation of the polymer involved in the dry-wet spinning process provides a highly porous structure within the fiber walls, as shown in Figures 10 and 11. The differentiation, by definition, between a porous structure and a dense one is that the latter's pore dimensions are in the range of molecular sizes.

Generally, it was found<sup>9</sup> that as the polysulfone content in the solution increases, the average pore size in the fiber wall decreases. This trend is also shown in Figures 11, 12, and 13.

The final structure of the fiber is mainly dictated by the quenching and spinning solution composition. The introduction of such additives as PVP and dimethyl cellulose and others assist in bringing the spinning solution to the required viscosity. However, additives also contribute to pores formation, since they are leached from the nascent fiber during the later stages of quenching and flushing.<sup>1</sup> The mechanism of pore formation involves microphase separation during penetration of the quenching liquid. The precipitant is miscible with the additives and with spinning solvent, but is nonmiscible with the fiber-forming polymer. While microphase separation (or macro when voids and intrusion cells are present) occurs within the fiber walls, the fiber interface represents a special case. The fiber shown in Figure 10 was spun from a solution consisting of polysulfone and DMA only. A nonisotropic fiber which consists of a dense layer on a porous sponge structure was formed. This is a typical formation of a so-called asymmetric membrane and follows the same formation mechanism. Furthermore, this case demonstrates that the formation of porous structures does not require the presence of additives in the polymeric solution.

However, the reticulation in the wall does not necessarily extend to the surface of the fiber wall. To form open pores at the interfaces (for this specific formulation), additives are necessary. Thermodynamic considerations<sup>10</sup> predict that under certain spinning conditions, the extension of a porous microstructure to the fiber interface can be accomplished often without any additions at all. However, the use of additives to form a ternary solution (e.g., PS/PVP/DMA) facilitates this and allows it to take place without resorting to extreme spinning conditions. The fiber shown in Figure 10 formed a dense skin at the interface as it was extruded. During the quenching process, the surface skin allows diffusion of both solvent and precipitant in and out of the fiber wall. However, the final fiber shows a drastically reduced hydraulic permeability when compared to fibers prepared with additives (Figs. 11 and 12). This can be attributed to the formation of a relatively dense skin, which increases the resistance to permeation and to the tortuosity of the pores in the walls.<sup>9</sup>

When PVP is the additive, phase separation between PVP and polysulfone also occurs at the fiber/quench fluid interface (Figs. 11-13). The initially homogenous solution<sup>1</sup> of PS/PVP separates into microdomains, and the PVP is eventually dissolved out of the matrix.

The size of the domains are probably governed by the thermodynamic phase relationships and by the kinetics of the phase separation. When dimethyl cel-

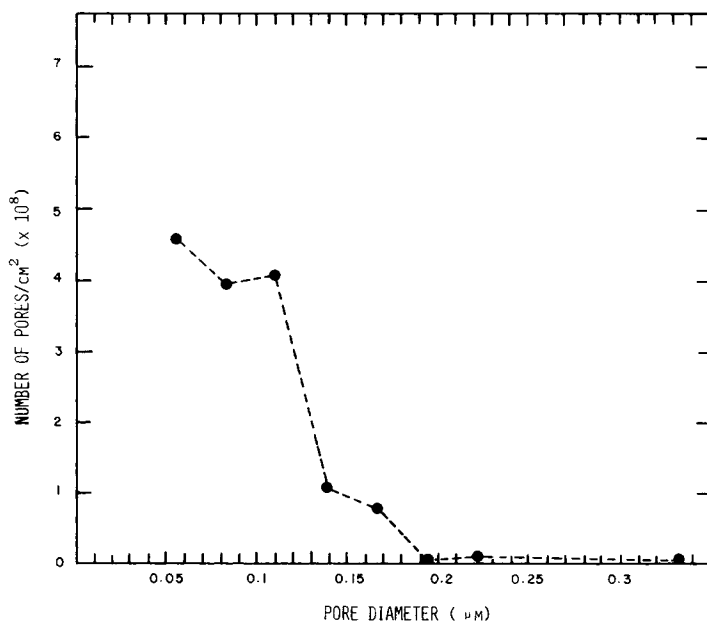


Fig. 14. Surface pore distribution of polysulfone hollow fiber that was spun with PS/PVP = 30/20 composition.

lulosolve was used as an additive, the surface pore sizes were 200 Å on average. When a polymeric additive was used (PVP), pores up to the order of 1 micron could be produced. The size distribution of the pores for a PS/PVP/DMA solution spinning is shown in Figure 14. However, this distribution is not unique to the composition, as would be the case for phase distributions at equilibrium. Alterations in extrusion speed, viscosity, etc., shift the pore size distributions.

### CONCLUSIONS

The dry-wet fiber extrusion process resembles in many aspects the wet coagulation method for the formation of asymmetric membranes. The fibers illustrated in Figures 10 and 14 demonstrate that the formation of a "skin" over a porous substrate does not require an intermediate evaporation step. Control of the extrusion/coagulation procedure allows the formation of skinned, porous skinned, and even nonskinned fibers. The texture of the resulting fiber is apparently controlled by two forces: the stresses resulting from liquid solid phase separation and the rate of solidification. The results presented here do not yield to quantitative analyses. However, three major recommendations can be made for the preparation of macrovoid-free, porous hollow fibers: (1) Relatively moderate quenching conditions should be employed in the bore fluid (first spinning stage). (2) High viscosities of spinning solution and/or initial quench conditions that yield high viscosity (but not necessarily solidification) during the first stage of quenching should be used. (3) Pore sizes at the fiber surfaces can be controlled by the use of selected additives which alter the phase relationships of the polymer and solvent.

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