

The Second-Generation Polysulfone Gas-Separation Membrane. II. The Relationship between Sol Properties, Gel Macrovoids, and Fiber Selectivity

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Synopsis

All integrally skinned asymmetric membranes contain some defects which are attributable to the incomplete coalescence of the nodule aggregates of which the skin layer is composed. When such defects are small in size and few in number, they can be effectively sealed by coating with a highly permeable polymer. The resulting composite then exhibits the selectivity to gas permeation which is characteristic of the base polymer. Prior to their sealing, therefore, such membranes can be said to exhibit the potential for intrinsic selectivity. However, not all gas separation membranes can be effectively sealed. In the present study the relationship between sol properties, the presence of macrovoids in the substructure of the gel, and the subsequent failure of the fibers to achieve the potential for intrinsic selectivity are considered. Macrovoid-free fibers with the potential for intrinsic selectivity can be prepared by the utilization of high viscosity, high total solids sols with low nonsolvent tolerance whose solvent vehicles consist of appropriate Lewis acid: base complexes.

INTRODUCTION

In an earlier study of reverse osmosis membranes, the deleterious effects of the presence of macrovoids, the 20–100 μm in diameter cavities sometimes found embedded within the typical fine (0.1–2 μm diameter cells) spongelike membrane substructure, upon salt rejection were shown.¹ In that case macrovoids were found to be related to sol composition, polymer concentration, viscosity, and gelation bath temperature. Macrovoids arise as the result of imbalances between the diffusion of solvent out of, and nonsolvent into, the nascent membrane.² They are of two types: spherical, ellipsoidal, or teardrop shaped cavities, and fingerlike intrusions. The former are the result of the accumulation of pockets of solvent vapor within the gel mass prior to hardening.² The latter are the consequence of the rupture of a fragile skin surmounting a still-fluid sol and the subsequent incursion of cylindrical columns of water followed by circumferential gelation.^{2,3} The presence of macrovoids in high pressure applications is detrimental because of the probability that rupture of the skin into an underlying macrovoid may occur, thereby decreasing the selectivity of the skin layer. Because of the higher fluidity of gases relative to liquids, it is assumed

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TABLE I
Selected Sol and Gel Properties for Fibers Spun from 32% Polysulfone in Neat Solvent Vehicles

Solvent	Sol viscosity (cps at 30°C)	Macrovoid ^a status	O ₂ P/l ^b (GPU)	$\alpha_{N_2}^{O_2}$
2-Chloropropionic acid (2 CP)	750,000	—	21	4.4
Triethylphosphate (TEP)	346,000	—	26.1	3.3
Formyl piperidine (FP)	201,750	+	10.2	2.1
N-methyl pyrrolidone (NMP)	44,000	++	4.4	3.0
Dimethyl formamide (DMF)	23,650	++	4.3	2.9
Dimethyl acetamide (DMAC)	17,300	++	9.4	3.5

^a — macrovoid-free; + intermediate to low concentration; ++ high concentration.

^b GPU = cm³/cm² s cm Hg ($\times 10^6$).

that membrane gas separations are even more sensitive to the presence of macrovoids than are liquid separations.⁴

EXPERIMENTAL

The details of sol preparation, fiber spinning, and permeability measurement have been presented elsewhere.^{5,6}

Scanning Electron Microscopy

Pentane-wet membranes were immersed in liquid nitrogen until frozen, removed from liquid nitrogen, and slowly flexed until a clean cross-sectional fracture occurred. The fibers were then sputter-coated with gold *in vacuo*.

Nonsolvent Tolerance

Nonsolvent tolerance, that is, the proximity of a sol to the point of incipient gelation, was estimated from the coagulation value *G*. The latter is defined as the grams of water which when added to 100 g of a sol containing 2 g of polymer at 30°C will effect phase separation.⁷ The lower the *G*, the more rapidly a sol will gel when immersed in water, and the less will be the densification.

Viscosimetry

Sol viscosity was measured with a Brookfield rotary viscometer.

RESULTS AND DISCUSSION

A correlation between sol fluidity and the concentration of macrovoids in the gel is apparent from an inspection of the SEM cross sections of fibers spun from six neat solvents (Table I, Fig. 1). Fibers which were spun from fluid sols with a viscosity η somewhat lower than 2×10^5 cps exhibit a high concentration of macrovoids [Fig. 1(a)–(c)]. These sols employed solvents with molar volumes $< \sim 100$ cc/mol.⁵ Sols with $\eta \sim 2 \times 10^5$ cps yield fibers with a more modest concentration of macrovoids [Fig. 1(d)]. The most viscous sols $\eta \geq 3.5$

TABLE II
Effects of Polysulfone Concentrations and A : B Ratio on Sol and Fiber Properties

Fiber	PSU ^a concn (% w/w)	PA : NMP (mol/mol)	Sol properties		Fiber properties		
			Viscosity (cps at 70°C) ($\times 10^{-5}$)	G value (g)	Macrovoid status ^c	O ₂ P/l ^d (GPU)	$\alpha_{N_2}^{O_2}$
1	17	0.42	0.022 ^b	4.4	++	25.3	3.5
2	32	0.42	0.212	4.4	+	29.9	4.5
3	37	0.42	0.650	4.4	+	16.3	4.3
4	32	1.0	0.40	0.6	+	33.9	4
5	37	1.0	1.13	0.6	—	43	5-5.2

^a Udel 3500.

^b At 23°C.

^c — macrovoid-free; + intermediate to low concentration; ++ high concentration.

^d GPU = cm³/cm² s cm Hg ($\times 10^6$).

$\times 10^5$ cps yield macrovoid-free fibers [Fig. 1(e, f)]. [The five macrovoids in Fig. 1(f) are attributable not to sol instability, but rather to the presence of five inlet ports in the spinnerette and the inability of the hyperviscous sol to remerge into a homogeneous mass prior to gelation.] A general relationship exists between sol viscosity, solvent size, and gas permeability (Table I). Larger solvent molecules and surrogate solvent molecules such as Lewis acid: base (A : B) complexes serve as transient templates to increase interchain displacement (free volume) and hence permeability.⁸ Although at first glance the anticipated inverse relationship between selectivity and the presence of macrovoids is lacking; nevertheless, the average O₂/N₂ selectivity for the two macrovoid-free fibers is ~ 3.9 whereas the average for the four macrovoid-ridden fibers is ~ 3.1 .

Macrovoid concentration increases with decreasing polymer concentration, viscosity, and increasing tolerance of the sol for nonsolvents (G value) (Table

TABLE III
Effects of Propionic Acid Concentration in 37% Polysulfone in PA : NMP
upon Sol and Fiber Properties

Membrane	PA : NMP (mol/mol)	Sol properties		Fiber properties		
		Viscosity (cps at 70°C) ($\times 10^{-5}$)	G value (g)	Macrovoid ^a status	O ₂ P/l (GPU) ^b	$\alpha_{N_2}^{O_2}$
1	1.09	1.20	0.15		45.9	4.6
2	1.00	1.13	0.6	—	43	5-5.2
3	0.89	1.07	1.1		33	4.4
4	0.72	—	2.1		25	4.8
5	0.42	0.79	2.9		—	—
6	0.42	—	2.9		16.6	4.3
7 (8)	0.33	0.57	4.5	++	29.6	2.6

^a — macrovoid-free; ++ high concentration of macrovoids.

^b GPU = cm³/cm² s cm Hg ($\times 10^6$).

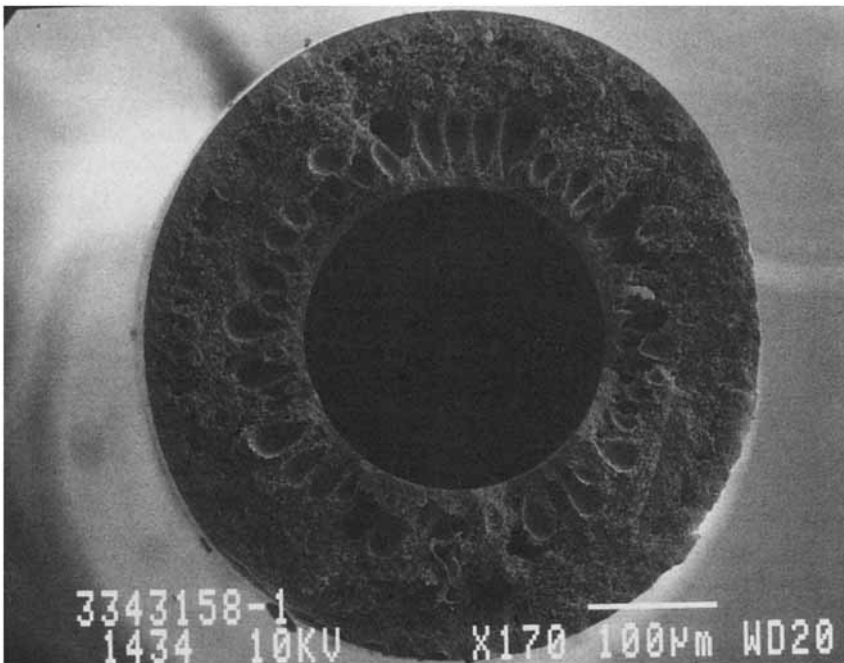
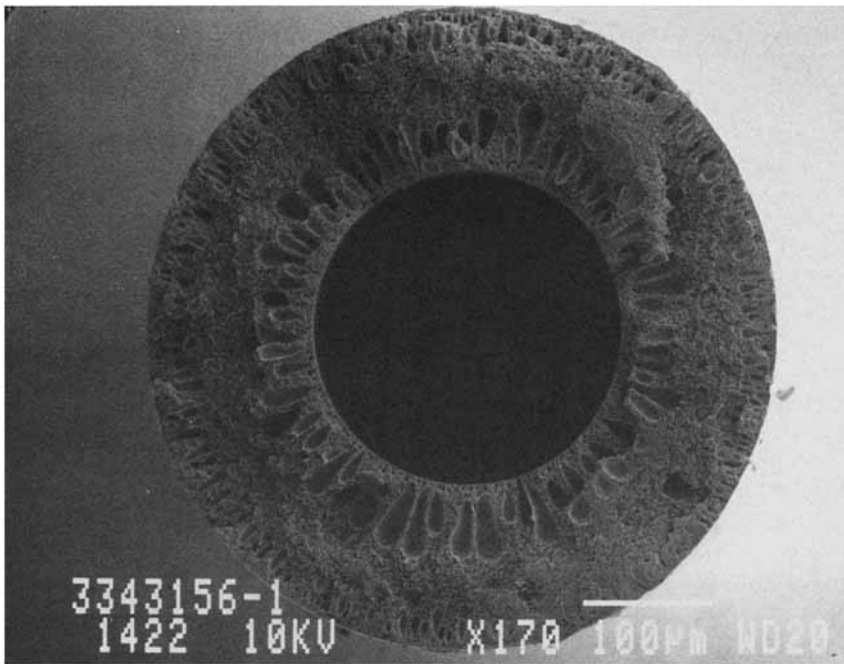


Fig. 1. SEM photomicrographs of cross sections of fibers spun from 32% polysulfone in neat solvent vehicles: (a) DMAC; (b) DMF; (c) NMP; (d) FP; (e) TEP; (f) 2CP.

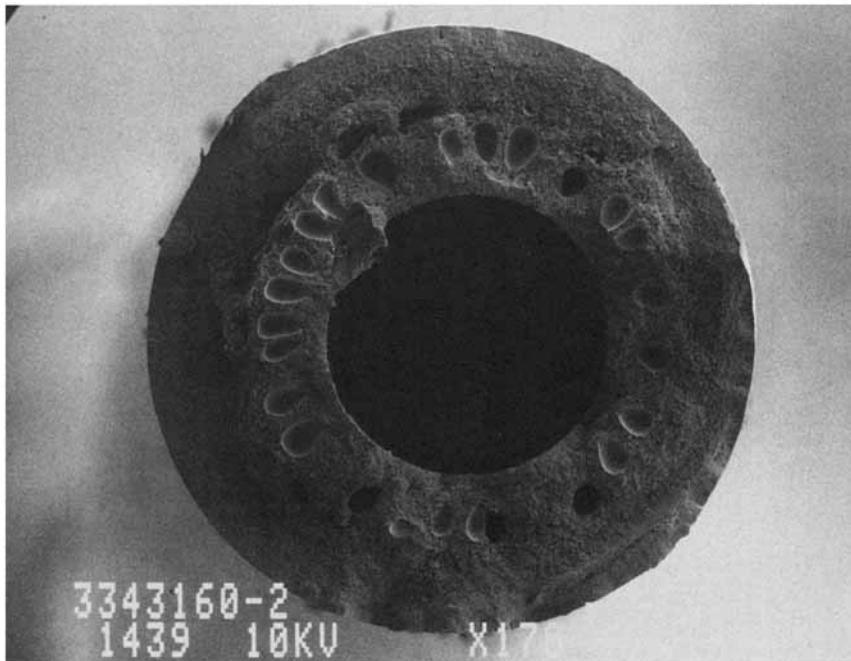
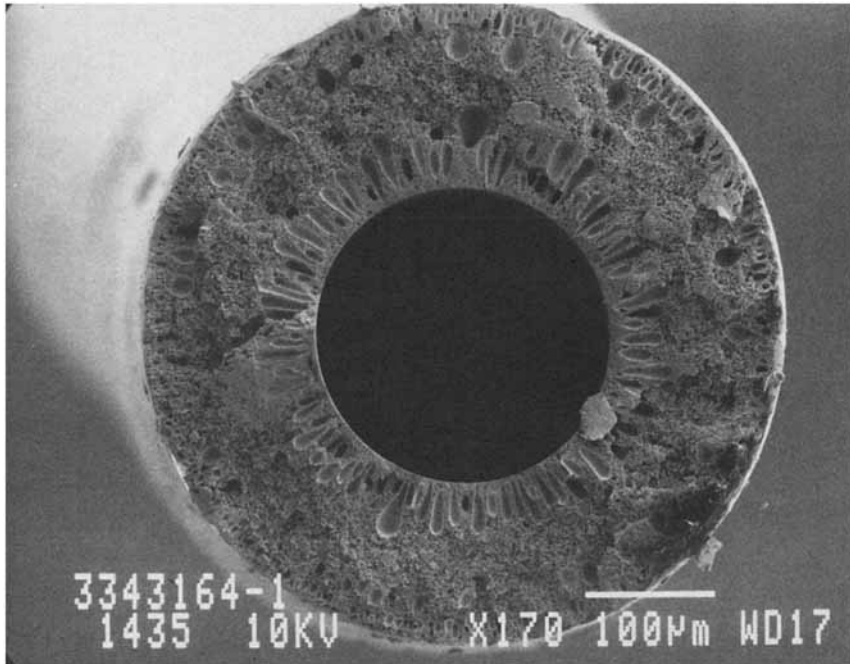


Fig. 1. (Continued from the previous page.)

II). In this instance, the expected inverse relationship between macrovoid concentration and selectivity is observed. The higher nonsolvent tolerance for fibers 1-3 is a result of the lower concentration of nonsolvent (lower A : B ratio) in

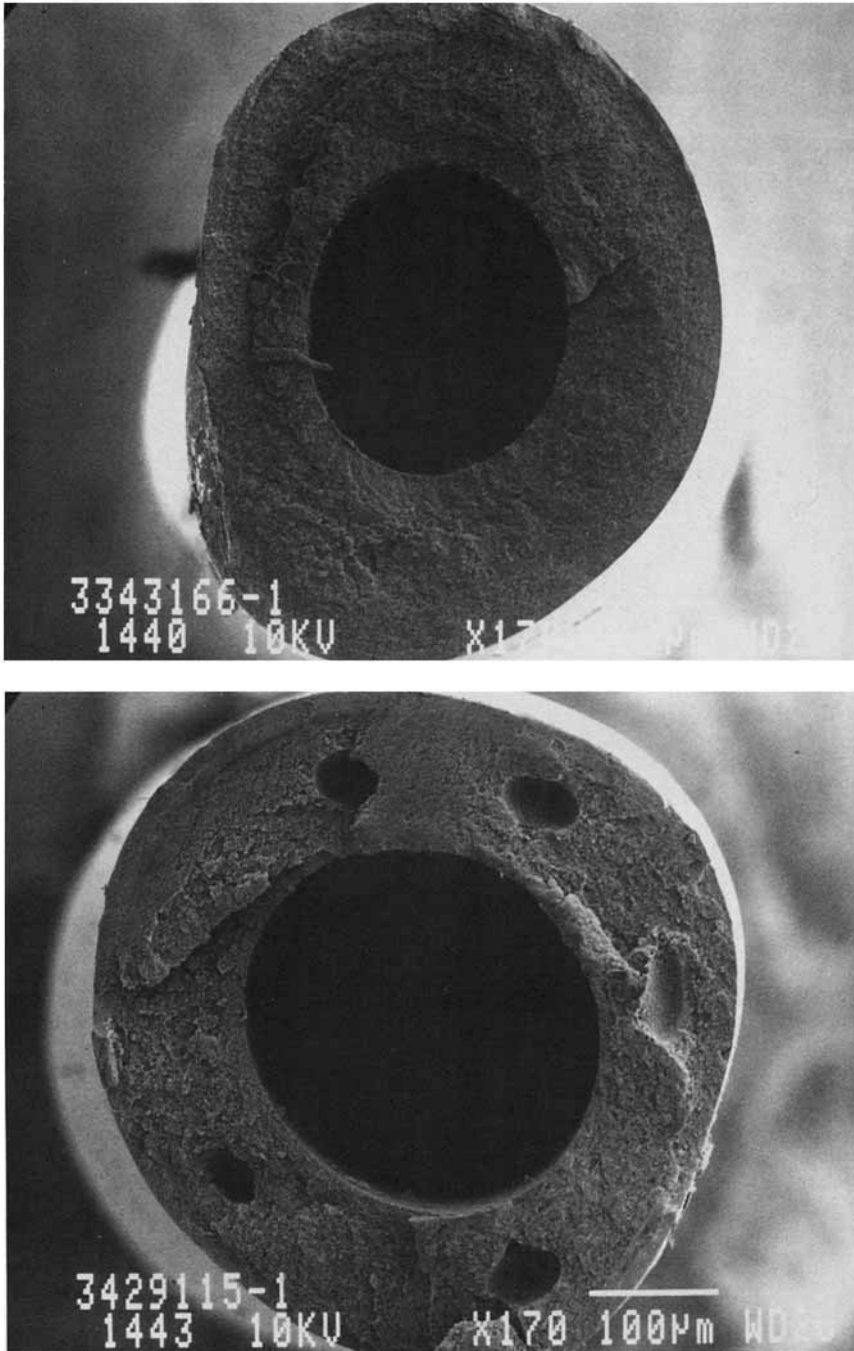


Fig. 1. (Continued from the previous page.)

their sols. As a result, gelation is less rapid and more time is available for the emergence of sol inhomogeneities and their subsequent fixation in the form of macrovoids in the fiber gel. A stark contrast is seen between fibers 1 and 7

(Table II, Fig. 2). The former is a tube consisting of two concentric rings of macrovoids [Fig. 2(a)]. Fibers with this structure do not have the potential for intrinsic selectivity, as is evidenced by the low (3.1) selectivity value for

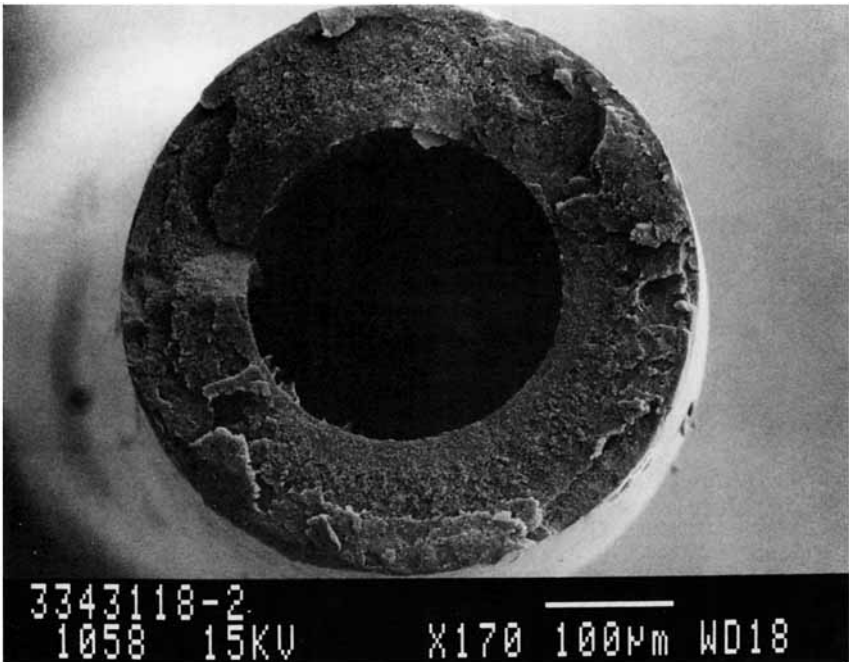
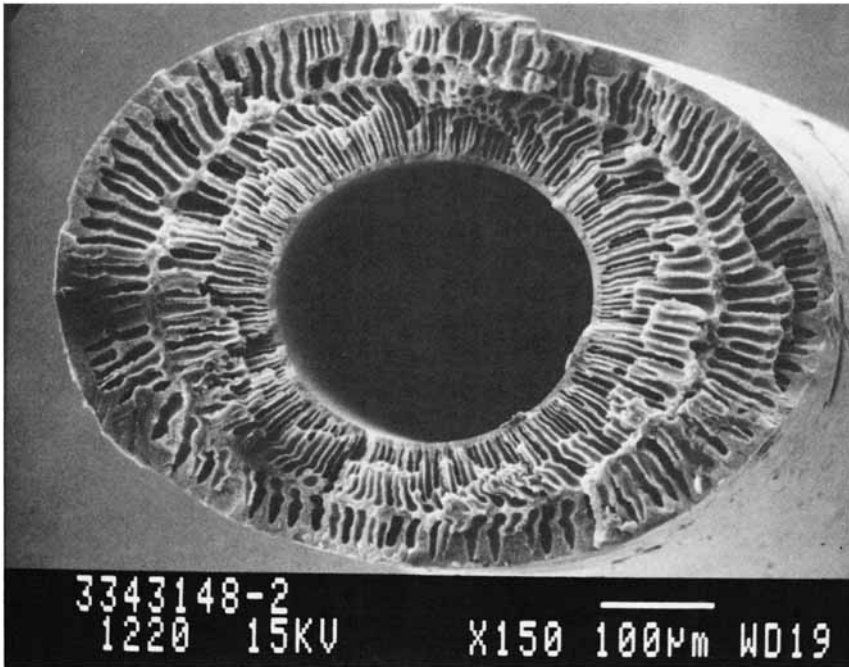


Fig. 2. SEM cross sections of polysulfone fibers: (a) UF; (b) gas sep.

the silicone-coated fiber. Fiber 1 can only be utilized for low pressure applications such as ultrafiltration UF. Fiber 7 [Fig. 2(b)], on the other hand, is the prototype of the second generation PSU fiber and is eminently suited for gas separations. Its O_2/N_2 selectivity of 5–5.2 (13.6 atm air at 50°C) can be attributed to a low porosity skin coupled with a macrovoid-free substructure.

The relationship between sol viscosities and G values and fiber gas permeability and selectivities for fibers for which the polymer concentration was held constant at 37% is shown in Table III. Viscosity increases and nonsolvent tolerance decreases with increasing ratio of the nonsolvent acid A to solvent base B in the Lewis A : B complex. At the same time, permeability increases with increasing A : B ratio. Increasing permeability can be attributed both to a diminution of skin thickness and to an increase in skin free volume. The maintenance of selectivity with increasing free volume is a consequence of a density gradient in the skin such that the densest part of the skin layer maintains the potential for intrinsic rejection. Unfortunately, not every fiber of this series was subjected to SEM analyses. However the two that were (1 and 7) show the expected inverse relationship between selectivity and macrovoid concentration.

CONCLUSIONS

1. The presence of macrovoids in gas separation fibers is detrimental to the attainment of the potential for intrinsic selectivity.
2. Macrovoid concentration decreases with increasing solids and viscosity, and decreasing nonsolvent tolerance.

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