A Qualitative Skin Layer Formation Mechanism for Membranes Made by Dry/Wet Phase Inversion

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SYNOPSIS

Optimized membranes made by a dry/wet phase inversion process using forced-convective evaporation consist of an ultrathin *and* pore-free skin layer supported by a nodular transition layer and an underlying open-cell, sponge-like substructure. It is suggested that the outermost region of such cast membranes undergo phase separation by spinodal decomposition in the initial stages of the evaporation process. As a result of the small scale of phase separation present in polymer–solvent systems, an appreciable capillary pressure occurs in the interstitial space filled with the polymer-poor phase in contact with air. The resulting force acts normal to the membrane–air interface, which tends to consolidate the polymer-rich phase to form a nonporous surface layer. © 1993 John Wiley & Sons, Inc.

Keywords: integrally-skinned asymmetric membranes • skin layer formation • dry/wet phase inversion process • capillary pressure • surface tension • coalescence

INTRODUCTION

Asymmetric membranes are most commonly prepared by a *wet* phase inversion process.[1] A homogeneous polymer solution is cast as a flat film or spun as a fiber, exposed to air for a specific time and thereafter, immersed in a quench medium which is a nonsolvent for the membrane-forming polymer. Phase inversion occurs by bringing the initially thermodynamically stable polymer solution to an unstable state by solvent/nonsolvent exchange *during* the quench step.

The formation of integrally skinned asymmetric membranes made by the wet phase inversion process has been ascribed to an asymmetric polymer distribution at the onset of liquid–liquid (L–L) phase separation in the immersed film.[2-6] Thus, the ultimate determining factor for the formation of the skin layer is a higher local polymer concentration in the outermost region compared with that in the sublayer of a cast film.[2,3] Two different concepts have been proposed for the cause of the asymmetric polymer distribution at the onset of L–L phase separation:

1. A high local polymer concentration is the result of solvent removal from the outermost region of the cast film by evaporation *prior* to the quench step.[7-9]
2. A high local polymer concentration in the membrane top region is the result of the extremely rapid solvent outflow relative to the nonsolvent inflow occurring *during* the initial stages of the quench step.[2-6]

It has been demonstrated experimentally that integrally skinned asymmetric membranes can be formed without an evaporation step (i.e., by direct immersion of a cast film in a quench medium).[10-12] Other studies showed that the skin layer thickness and its porosity can be controlled by including an evaporation step in the wet phase inversion process.[13-15]

Ideal asymmetric membranes for gas separations, as considered here, must meet the following requirements: (1) the skin layer must be defect free to assure that the gas transport is controlled exclusively by a solution/diffusion mechanism to achieve the maximum selectivity, (2) the skin layer should be

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as thin as possible to maximize the membrane productivity, and (3) the substructure should not contribute any resistance to gas transport, but provide sufficient mechanical strength to support the delicate skin layer during high pressure operation.[16]

The combination of ultrathin and defect-free skin layers are generally not achieved for membranes made by the *wet*-phase inversion process.[17,18] It has even been hypothesized that membranes made by conventional phase inversion processes always contain defects due to incomplete coalescence of the skin layer.[17,19]

Integrally skinned asymmetric membranes can also be formed by a *dry/wet* phase inversion process.[16] In this case, phase separation is induced in the outermost region of the cast membrane during an evaporation step, while L–L phase separation in the bulk film occurs subsequently during a quench step. Recently, it has been demonstrated that essentially defect-free membranes with skin layer thicknesses as thin as 200 Å can be formed from a variety of polymers by the dry/wet phase inversion process using forced-convective evaporation.[20,21] Furthermore, it was shown that the casting solution components and the quench media can be varied to a large extent without jeopardizing the membrane properties.[21]

The goal of this report is to present a physically meaningful mechanism for the formation of ultrathin and defect-free skin layers of membranes made by dry/wet phase inversion. To establish such a mechanism, it seems appropriate to summarize the empirically developed rules for the formation of optimized asymmetric membranes made by the dry/wet phase inversion process:[21]

1. The casting solution must consist of at least three components: the polymer, a solvent, and a nonsolvent. The solvent must have a higher vapor pressure than the nonsolvent component, so that phase separation can be induced during an evaporation step.

2. The composition of the casting solution should be as close as possible to the thermodynamic instability limit: binodal composition.

3. The evaporation should be carried out by forcing a gas stream across the cast membrane to induce phase separation in the outermost region of the cast film (dry-phase inversion).

4. The quench step (wet-phase inversion) should be carried out in a thermodynamically strong nonsolvent for the membrane forming

polymer. The quench medium must be miscible with the solvents and nonsolvents of the casting solution.

Some of the above rules have recently also been suggested for the formation of asymmetric membranes made by wet phase inversion.[22] However, these previous formation protocols did not lead to membranes showing simultaneously ultrathin *and* defect-free skin layers.

DISCUSSION

The Dry-Phase Inversion Process

The concept of forced convective evaporation-induced phase separation has not previously been identified as a *crucial* element in the formation of defect-free, ultrathin-skinned asymmetric membranes. On the other hand, recent experimental investigations demonstrated clearly that the physical processes which occurred during the *evaporation* step were of utmost importance for the skin layer formation of asymmetric membranes made by dry/wet-phase inversion.[23]

The evaporation process for a typical ternary casting system used for the preparation of membranes made by dry/wet phase inversion is illustrated schematically in Figure 1. The composition of the initially stable polymer solution is given by
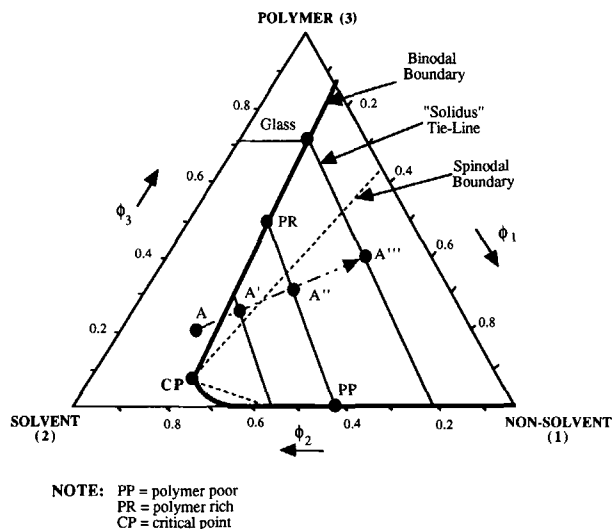

Figure 1. Schematic representation of possible physical events occurring during evaporation of the solvent component from a ternary casting solution.

point A. If the solvent has a substantially higher vapor pressure than the nonsolvent component, it is reasonable as a *first approximation* to assume that only solvent is removed from the outermost region of the cast film during the initial stages of the evaporation process. In this case, the evaporation trajectory is given by a constant ratio of the polymer volume fraction, ϕ_3, to the nonsolvent volume fraction, ϕ_1. As a result of the barely stable casting solution, phase separation will tend to occur instantaneously in the cast film during the forced-convective evaporation process. The resulting physical events which determine the membrane formation process during the dry-phase inversion step will depend strongly on the evaporation kinetics (i.e., the velocity of the gas stream blown across the membrane surface and the evaporation time).

Low gas stream velocities and/or short evaporation times can lead to a compositional change from A to A'. In this case, L–L phase separation will proceed by nucleation and growth, which leads to a dispersion of the polymer-poor phase in the continuous polymer-rich phase.

On the other hand, high gas stream velocities and/or longer evaporation times may lead to an average composition A'' in the outermost membrane region. Since composition A'' resides deep in the unstable region, L–L phase separation will occur by spinodal decomposition. It is evident from Figure 1, that L–L phase separation by spinodal decomposition will lead to a much higher polymer concentration in the polymer-rich phase as compared to that obtained by the corresponding nucleation and growth mechanism. A spinodally decomposed L–L phase separated morphology consists of a highly regular, bicontinuous network of the polymer-rich and the polymer-poor phase.[24]

The top region morphology of a poly(sulfone) membrane formed by dry/wet phase inversion is shown in Figure 2. The photomicrograph identifies clearly that the outermost membrane region consists of (1) a very thin, dense skin layer and (2) a three-dimensionally connected nodular transition layer.

Nodular structures have previously also been observed in membranes formed by dry-[19] and wet-phase inversion.[27-35] Kamide and Manabe suggested that nodule formation results from nucleation and growth of the polymer-rich phase if the initial polymer concentration of the casting solution is lower than that of the critical point of the casting solution.[26] Recently, Kesting hypothesized that nodule formation can occur by nucleation and growth of the polymer-rich phase even if the polymer concentration of the casting system is higher than that of
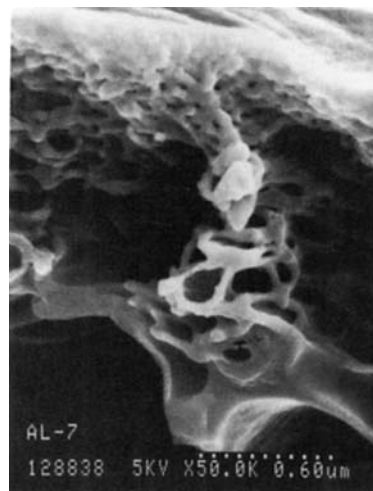

Figure 2. Typical top layer morphology of an asymmetric poly(sulfone) membrane made by dry/wet phase inversion.

the critical point.[19] This concept seems inconsistent with standard nucleation and growth theories[24-26] since nucleation and growth of *polymer-poor* dispersed phase would be expected for cases in which the polymer concentration of the casting system is above that of the critical point.

Contrary to this suggestion, we suggest that nodular structures in dry/wet phase inversion membranes are generated by spinodal decomposition of the initially stable casting solution as a result of instantaneous L–L phase separation induced by evaporation of the solvent during the dry phase inversion step. More or less spherical nodules can arise naturally in some cases by surface tension-induced breakup of the interpenetrating spinodal network. Although the occurrence of a spinodal phase separation mechanism cannot be proven rigorously based only on a morphological analysis,[24] it is supported by the following physical principles:

1. A three-dimensional network is obtained in the initial stages of spinodal decomposition, if the minor phase exceeds about 15 vol %.[24]
2. Nucleation and growth of the polymer-rich phase which could also lead to a nodular structure is believed to occur at rather low polymer concentrations (i.e., phase separation of average compositions below the critical point, CP.[25,26]

However, the casting formulations used for the preparations of dry/wet-phase inversion membranes

contain at least 10 vol% polymer, which is well above the critical point of these solutions. Therefore, the polymer-poor phase is expected to form the dispersed phase in a continuous polymer-rich phase by nucleation and growth, and not vice versa.

Nodular structures have also been observed in recent microscopic studies of paste-like gels of amorphous polymers.[36,37] The outermost region of a cast membrane shows also pasty consistency during the initial stages of the evaporation process, which provides further indirect support for the formation of a nodular structure during the dry-phase inversion process.

Although kinetic aspects are involved in the spinodal phase separation mechanism, they are very rapid and difficult to quantify. In the more completely studied case involving thermally induced spinodal decomposition, it has been estimated that in glass forming systems with diffusion coefficients even as low as 10^{-12} cm^2/s the thermal quenching rate would need to be faster than 1000 °C/s to suppress the spinodal phase separation process.[38] For more mobile systems such as highly fluid polymer solutions with mutual diffusion coefficients as high as 10^{-5} to 10^{-6} cm^2/s, the corresponding quench rates would need to be larger than 10^9 °C/s.[38] Such time scales are for all practical purposes instantaneous. Similarly for the dry phase inversion process, effectively as soon as an air stream is convected over a properly formulated casting solution at the binodal boundary, a fine haze appears on the surface of the nascent membrane in much less than a second. Moreover, consistent with the interpenetrating nature of a spinodally decomposed network, the paste-like phase separated layer is remarkably strong and self-supporting, unlike that expected for a moderately concentrated polymer solution growing distinct nuclei at such short times. While the occurrence of the dry phase inversion step is extremely important for achieving pore-free skin layers, the exact thickness of the dry phase separated structure appears to be of second order importance in the generation of the effective skin layer thickness. This important observation will be explained later in the context of the integrated skin layer formation process.

Some further comments should be addressed to the origin of a nodular structure initiated by spinodal decomposition. In Cahn's pioneering work on spinodal decomposition, it was pointed out that a finely mazed three-dimensional network evolves during the initial stages of spinodal decomposition.[38] However, coarsening of the original network occurs at later stages of the phase separation process, as a result

of the interfacial tension between the two phases.[39] This process leads eventually to a partial breakup of the bicontinuous network and the formation of phase sphericity.[39]

If the spinodal structure in the outermost membrane region vitrifies instantaneously without undergoing further structural changes during the evaporation process, it appears logical that the skin layers of the quenched membranes will be microporous. These pores would result from the interstitial spaces of the polymer-poor phase present in the outermost region of the quenched membrane at the point of vitrification. On the other hand, optimized membranes formed by dry/wet phase inversion show ultrathin and *defect-free* skin layers. Hence, it is suggested that an additional physical process leads to the coalescence of the nodular network into an essentially homogeneous skin layer during the evaporation step. Previous experimental studies showed that coalescence plays an important role in the skin layer formation of membranes formed by *dry* phase inversion (i.e., complete evaporation of solvent and nonsolvent components).[27] However, a detailed description of the physical events which initiate and control such coalescence processes was not provided in these studies.

It is suggested here that the coalescence process occurs primarily at the membrane-air interface as a result of the *capillary pressure* acting on the spinodally phase separated structure in the outermost membrane region. Furthermore, it is proposed that the basic physical principles involved in the formation of a defect-free skin layer from a spinodally decomposed network are similar to those occurring during the drying of a latex to produce a consolidated nonporous film from an initially discrete array of latex particles. In a nascent membrane the process is promoted by the presence of plasticizing solvent and nonsolvent components in the polymer rich phase. As in the case of the dry-phase inversion step, the formation of latex films from polymer emulsions occurs concurrently with the evaporation of a solvent component. The problem of film formation from discrete latex particles has been analyzed previously by Brown[40] and others.[41-46] It was proposed that the condition for film formation of water-based polymer emulsions must fulfill the following requirement during the drying process:[40]

$$F_C > F_G \qquad (1)$$

where F_C is the force resulting from a capillary pressure and F_G is the resistance of the polymer particle

to deformation. The cast latex film consists of two interpenetrating continuous media (i.e., latex spheres in contact with each other and water pervading the void space). However, only the assemblage of contacting polymer particles is continuous on the *film surface,* which contains isolated concave areas of water.[40] The capillary pressure arises as a result of the curvature of the water in the interstitial capillary system and provides the major driving force for the film formation of latices.[40] With regard to the skin layer formation occurring during the dry phase inversion step, it is suggested that the polymer-poor phase, which fills the interstitial spaces of the polymer-rich phase, will also result in a capillary pressure, in analogy to the latex system.

This capillary pressure is exerted in a direction normal to the water-polymer interface and tends to deform the latex particles in that direction, as schematically shown in Figure 3. The pressure due to the curvature of the air–liquid interface of the capillary of radius r is given by the Young-Laplace equation for perfect wetting (contact angle equal to zero):[40]

$$P_c = \frac{2\gamma}{r} \tag{2}$$

where γ is the surface tension of the interstitial fluid (dynes/cm) and r is the radius of the effective "throat" which exists in the plane passing through the centers of three touching spherical particles. One can relate the capillary pressure acting on the particles to surface tension and the particle radii. For simplicity, considering an array of hexagonal closed-packed latex particles, the capillary pressure (in dynes/cm^2) can be related to the surface tension, γ (in dynes/cm), and the particle size, R (in cm), by:[40]
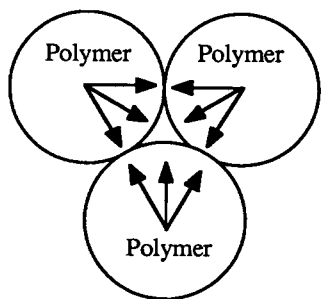
$$P_c = \frac{12.9\gamma}{R} \tag{3}$$

Figure 3. Contracting forces resulting from the capillary pressure in the interstitial spaces of latex films. After Brown.[40]

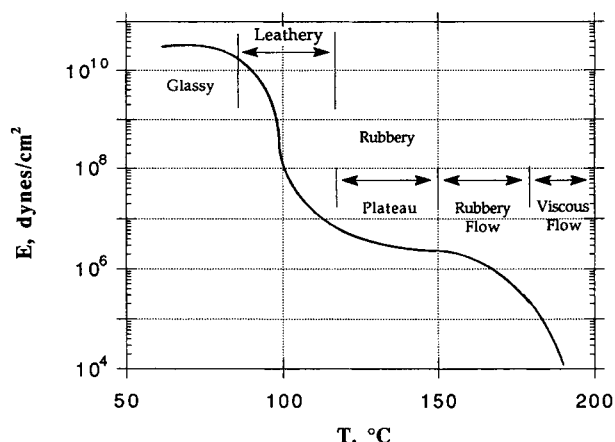**FIVE REGIONS OF VISCOELASTIC BEHAVIOR**

Figure 4. The regions of viscoelastic behavior of amorphous polymers.[47]

Brown estimated that compressive stresses of over 10^8 dynes/cm^2 ($\sim$100 atm) are to be expected during the drying process of typical polymer emulsions.[40] Furthermore, Brown derived the condition for the film formation of hexagonal closed-packed spheres, as given by:

$$G < \frac{35\gamma}{R} \tag{4}$$

where γ is the surface tension (in dynes/cm), G is the polymer shear modulus (in dynes/cm^2) and R is the particle radius (in cm).

Clearly, the morphology of the spinodally formed network in the outermost membrane region is more complex than that for a uniform dispersion of spheres. However, for the qualitative discussion presented here, it appears reasonable to assign an effective spherical radius to the polymer-rich phase of the dry phase separated structure in the outermost membrane region.

The curve of the modulus versus temperature for amorphous polymers typically has five regions of behavior, as shown in Figure 4 for a sample of polystyrene:[47] (1) the glassy region ($G \sim 10^{10}$ dynes/cm^2), (2) the leathery region (10^{10}–6 $\times$ 10^6 dynes/cm^2), (3) the rubbery plateau ($G \sim 2 - 6 \times 10^6$ dynes/cm^2), (4) the region of rubbery flow (0.3 − 2 $\times$ 10^6 dynes/cm^2), and (5) the viscous flow region ($G < 0.3 \times 10^6$ dynes/cm^2). For different amorphous polymers, the limits of these various "regions" depend upon molecular weight, its distribution and the specific polymer type. Polysulfone and PVC have sub-T_g moduli that are similar to that for polysty-

rene; however, the transition from glassy to rubbery behavior occurs near 180°C for polysulfone and near 85°C for PVC, rather than 100°C as shown for polystyrene. Nevertheless, near the respective T_gs of each material, the same five regions of behavior shown in Figure 4 are to be anticipated.

In the case of membrane formation, the evaporation process is carried out at constant temperature. However, the modulus is expected to vary over the same orders of magnitude as a function of the *composition* of the polymer–solvent system as the effective glass transition is lowered to the range of the casting process. The glassy regions for typical ternary polymer–solvent–nonsolvent casting systems have been estimated to occur at polymer concentrations larger than 70 vol% at a temperature of 25°C.[48,49] In this case at the effective T_g for materials like polystyrene (Fig. 4), polysulfone or PVC, the modulus for polymer concentrations in excess of 70 vol% should be on the order of 10^9–10^{10} dynes/cm². Furthermore, it seems reasonable to assume that for polymer concentrations between ~ 50 and 70 vol% the modulus will range between $2 \times 10^7 - 4 \times 10^8$ dynes/cm² in the leathery or rubbery plateau regions, similar to that reported for highly plasticized poly(vinyl chloride) at room temperature.[50] Using eq. (4) and assuming a reasonable surface tension of 20 dynes/cm for organic solvents employed in the membrane casting formulations,[21] the maximum allowable shear modulus to permit film formation from particles ranging between 100 to 1000 Å is shown in Figure 5. These sizes were selected because (1) the scale of phase separation in polymer-solvent systems has been estimated to be in the range of 150 Å and 6000 Å,[39] and (2) the individual nodules present in the top structure shown in Figure 2 are approximately 200 to 500 Å in diameter. The resulting maximum allowable modulus for complete
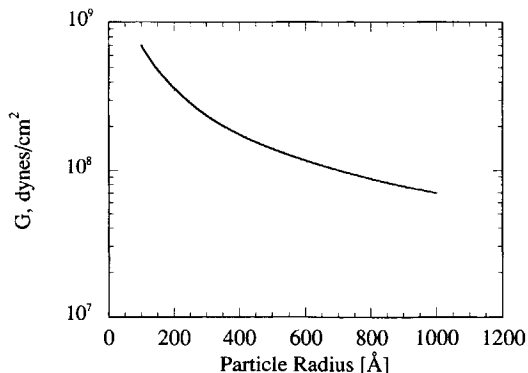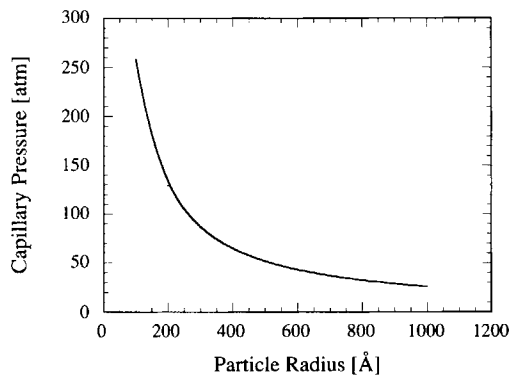

Figure 6. Capillary pressure as a function of the particle radius.

coalescence varies between $7 \times 10^7 - 7 \times 10^8$ dynes/cm². Therefore, the estimated moduli for polymer concentrations between 50% and 70% fall within the range for complete coalescence.

The capillary pressure as a function of the polymer particle size is shown in Figure 6; however, it has been noted that the capillary pressure available for the particle coalescence is limited in a practical sense by the tensile strength of the interstitial fluid.[51,52] In the case of water-based emulsions, the maximum achievable capillary pressure is approximately 40 atm.[50,51] Assuming only the availability of this more moderate capillary pressure of 40 atm (4.1 $\times 10^7$ dynes/cm²) as a limiting case, the maximum allowable polymer-rich phase modulus would be on the order of 4×10^7 dynes/cm², corresponding to the *lower* limit of the 50–70% polymer range above. Depending upon which of the maximum capillary pressure estimates applies, film formation from a spinodal network should occur for concentrations below 50–70 vol% polymer in the polymer-rich phase under typical dry phase separation conditions at ambient temperature. If the composition of the outermost polymer-rich membrane region intersects the "solidus" tie-line corresponding to a polymer rich concentration above the critical value to permit satisfying eq. (4) during the evaporation process (point A″ in Fig. 1) and phase separation occurs, the coalescence of the spinodally separated surface layer will fail, and the resulting membrane will show skin layer pores of varying extents. For polymer concentrations that permit satisfying eq. (4), the capillary pressure diminishes upon completion of coalescing the polymer-rich phase in the outermost membrane region, since interfacial tensions are typically much lower in magnitude than air-liquid surface tension. This fortunate effect causes the underlying spinodal structure to maintain its desirable open bicontinuous
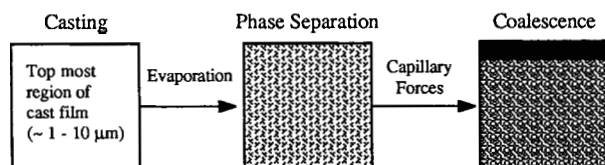

Figure 5. Maximum allowable shear modulus for film formation as a function of the particle radius.

Figure 7. Schematic representation of the hypothetical physical events occurring during the dry phase inversion step in the outermost membrane region.

morphology. Hence, a very thin, essentially *homogeneous surface layer* tends to rest atop a compacted, but interconnected nodular network. During the later stages of the evaporation process, the concentration in the surface layer may continue to evolve somewhat toward higher polymer concentrations and to improve the adhesion between neighboring polymer-rich domains by interdiffusion of polymer chain segments through a reptation mechanism.

The various stages of the proposed structure evolution in the outermost region of a cast film during the dry phase inversion step are schematically illustrated in Figure 7.

The Wet-Phase Inversion Process

Following the events described above, the nascent membrane consists of a *homogeneous surface layer* with a compact, but minimally coalesced transition layer resting atop a layer of solution at a roughly uniform composition similar to the initial composition, A, shown in Figure 1. It is believed that the subsequent wet quench step transforms the highly plasticized, but homogeneous surface layer instantaneously into a largely solvent-free glass containing only the equilibrium amount of the quench medium. As the quench medium permeates across the homogeneous surface layer, solvent and nonsolvent contained in the underlying transition layer are able to move by counter diffusion into the miscible quench bath. It is important to note that the vitrification of the nodular transition layer should occur as rapidly as possible to avoid any loss of the interconnectivity and porosity. The use of a thermodynamically strong nonsolvent such as methanol or water guarantees that the bicontinuous transition layer solidifies almost instantaneously, as recently demonstrated experimentally.[21] Furthermore, the use of a strong quench medium leads to instantaneous L–L phase separation in the bulk of the membrane, for the regions which were not phase inverted during the evaporation process. As commonly observed for membranes made by wet phase inversion,

instantaneous L–L phase separation results in an open-cell, sponge-like substructure.[3]

The Drying Process

After removal of the solvent component in the nascent membranes during a leaching step in the quench medium, the membranes are removed from the quench bath and air-dried.

The structures of asymmetric cellulose acetate membranes made by the original procedure of Loeb and Sourirajan collapse during the removal of the quench medium (i.e., water, as a result of a capillary pressure acting during the drying process).[53] Several methods have been proposed to dry water-wet cellulose acetate membranes.[53,54] It was found that the replacement of water with liquids showing a lower surface tension, such as alcohols or hydrocarbons, prevented the collapse of the membrane structures.

Unlike the drying of integrally skinned asymmetric cellulose acetate membranes, the drying of membranes made by dry/wet phase inversion does not lead to any significant changes in the morphology of the homogeneous skin layer or the bicontinuous transition layer. Even *water-quenched* membranes made by dry/wet phase inversion can be air-dried without the need of any solvent exchange techniques.[20,55]

SUMMARY AND CONCLUSIONS

Optimized membranes formed by a dry/wet phase inversion process using forced-convective evaporation consist of an ultrathin and pore-free skin layer supported by a nodular transition layer and an underlying open-cell, sponge-like substructure. It is suggested that the outermost membrane region undergoes phase separation by spinodal decomposition in the initial stages of the evaporation process. As a result of the small scale of phase separation present in polymer–solvent systems, an appreciable capillary pressure occurs in the interstitial space filled with the polymer-poor phase in contact with air. The resulting force acts normal to the membrane-air interface, and, therefore, tends to pull the polymer-rich phase together to form a homogeneous surface layer. The force resisting the deformation is determined by the viscoelastic properties of the polymer-rich phase. A semi-quantitative model originally developed for the coalescence of discrete latex particles was applied for the surface layer formation occurring during the dry phase inversion step. Although highly hypothetical, the model predicted that film forma-

tion should occur for polymer concentrations below ~ 70 vol% in the polymer-rich phase. At higher polymer concentrations, the force resisting the deformation was estimated to be higher than that provided by the capillary pressure. Hence, it is suggested that the formation of a homogeneous surface layer will not be possible if the evaporation of the solvent during the dry phase inversion step leads to an average composition located on the solidus tie-line. Additional complexity may arise as the interval between the onset of such a surface tension-driven healing process and the wet-phase inversion step is shortened. Under these conditions, viscoelastic phenomenon may alter the apparent response of the polymer rich phase to stress.

The homogeneous surface layer does not appear to undergo significant further structural changes during the wet phase inversion step. On the other hand, the nodular transition layer might lose its interconnectivity if the structure is not solidified instantaneously to a glass during the quench process. Furthermore, optimized integrally skinned asymmetric membranes made by dry/wet phase inversion are obtained when the quench medium induces instantaneous L-L phase separation in the bulk membrane. The resulting membranes can be dried without any additional solvent exchange techniques.

Although highly hypothetical, the present skin layer formation mechanism provides a reasonable physical framework for an understanding and rationalization of membranes made by dry/wet phase inversion. However, the complexity and the speed of the membrane formation process currently preclude providing definitive proof for the role of the proposed intertwined events. On the other hand, the outlined arguments lead naturally to explanations of morphologies which are actually observed, thereby providing at least indirect support for the proposed skin layer formation mechanism.

REFERENCES AND NOTES

1. R. E. Kesting, Synthetic Polymeric Membranes, McGraw Hill, New York, 1972.
2. C. A. Smolders, in Ultrafiltration and Applications, I. Cooper, Ed., Plenum Press, New York, 1980, p. 161–171.
3. B. Reuvers, Ph.D. dissertation, University of Twente, The Netherlands (1987).
4. Th. van den Boomgard, R. M. Boom, and C. A. Smolders, Makromol. Chem., Macromol. Symp., 39, 271–281 (1990).
5. C. S. Tsay and A. J. McHugh, J. Pol. Sci.: Pol. Phys. Edn., 28, 1327–1365 (1990).
6. L. Yilmaz and A. J. McHugh, J. Membr. Sci., 28, 287–310 (1986).
7. J. E. Anderson and R. Ullman, J. Appl. Phys., 44, 4303–4311 (1974).
8. C. Castellari and S. Ottani, J. Membr. Sci., 9, 29–41 (1981).
9. W. B. Krantz, R. R. Ray, R. L. Sani, and K. J. Gleason, J. Membr. Sci., 29, 11–36 (1986).
10. A. S. Michaels, U.S. Patent 3,615,024 (1971).
11. M. H. V. Mulder, J. Oude Hendrikman, J. G. Wijmans, and C. A. Smolders, J. Appl. Polym. Sci., 30, 2805–2820 (1985).
12. J. G. Wijmans, J. Kant, M. H. V. Mulder, and C. A. Smolders, Polymer, 26, 1539–1545 (1985).
13. R. W. Baker, U.S. Patent 3,567,810 (1971).
14. H. Strathmann, P. Scheible, and R. W. Baker, J. Appl. Polym. Sci., 15, 811–828 (1971).
15. T. C. Shen and I. Cabasso, in Macromolecular Solutions, Solvent-Property Relationships in Polymers, R. B. Seymour and G. A. Stahl, Eds., Pergamon Press, New York, 1982, pp. 108–119.
16. I. Pinnau, J. Wind, and K.-V. Peinemann, Ind. Eng. Chem. Res., 29, 2028–2032 (1990).
17. R. E. Kesting, Synthetic Polymeric Membranes: A Structural Perspective, John Wiley & Sons, New York, 1985, p. 31.
18. R. E. Kesting, A. K. Fritzsche, C. A. Cruse, and M. D. Moore, J. Appl. Polym. Sci., 40, 1575–1582 (1990).
19. R. E. Kesting, J. Appl. Polym. Sci., 41, 2739–2752 (1990).
20. I. Pinnau and W. J. Koros, US Patent 4,902,422 (1990).
21. I. Pinnau, Ph.D. dissertation, The University of Texas at Austin (1991).
22. E. Klein and J. K. Smith, in Reverse Osmosis Membrane Research, H. K. Lonsdale and H. E. Powall, Eds., Plenum Press, New York, 1972, pp. 61–84.
23. I. Pinnau and W. J. Koros, J. Appl. Polym. Sci., 43, 1491–1502 (1991).
24. J. W. Cahn, J. Chem. Phys., 42, 93–99 (1965).
25. D. M. Koehnen, M. H. V. Mulder, and C. A. Smolders, J. Appl. Polym. Sci., 21, 199–215 (1977).
26. K. Kamide and S.-I. Manabe, in Materials Science of Synthetic Membranes, D. R. Lloyd, Ed., ACS Symposium Series 269, American Chemical Society, Washington, D.C., 1985, pp. 197–228.
27. R. E. Kesting, J. Appl. Polym. Sci., 17, 1771 (1973).
28. R. D. Schultz and S. K. Asunmaa, Rec. Progr. Surface Sci., 3, 291 (1970).
29. M. Panar, H. H. Hoehn, and R. Hebert, Macromolecules, 6, 777 (1973).
30. C. W. Alegranti, D. G. Pye, H. H. Hoehn, and M. Panar, J. Appl. Polym. Sci., 19, 1475 (1975).

31. C. Jiayan, B. Shuchun, Z. Xingda, and Z. Lingying, *Desalination*, **34**, 97 (1980).

32. K. A. Lundy and I. Cabasso, *Ind. Eng. Chem. Res.*, **28**, 742 (1989).

33. A. K. Fritzsche, M. K. Murphy, C. A. Cruse, R. F. Malon, and R. E. Kesting, *Gas Sep. Purif.*, **3**, 106 (1989).

34. K. J. Kim, A. G. Fane, C. J. D. Fell, T. Suzuki, and M. R. Dickson, *J. Membr. Sci.*, **54**, 89 (1990).

35. S. Kazama, T. Kaneta, and M. Sakashita, in *Gas Separation Technology*, E. F. Vansant and R. Dewolfs, Eds., Elsevier Science Publishers, B. V., Amsterdam, The Netherlands, 1990, pp. 429–436.

36. S. Callister, A. Keller, and R. M. Hikmet, *Makromol. Chem. Macromol. Symp.*, **39**, 19–54 (1990).

37. P. Vandeweerdt, H. Berghmans, and Y. Tervoort, *Macromolecules*, **24**, 3547 (1991).

38. J. W. Cahn and R. J. Charles, *Phys. Chem. Glasses*, **6**, 181–191 (1965).

39. L. P. McMaster, *Adv. Chem. Ser.*, **142**, 43–65 (1975).

40. G. L. Brown, *J. Polym. Sci.*, **22**, 423–434 (1956).

41. G. Mason, *Br. Polym. J.*, **5**, 101–108 (1973).

42. J. G. Brodnyan and T. Konen, *J. Appl. Polym. Sci.*, **8**, 687–697 (1964).

43. T. Imoto, *Progr. Organ. Coatings*, **2**, 193–205 (1973/74).

44. J. Lamprecht, *Colloid & Polym. Sci.*, **258**, 960–967 (1980).

45. H. Kast, *Makromol. Chem., Suppl.*, **10/11**, 447–461 (1985).

46. S. T. Eckersley and A. Rudin, *J. Coatings Techn.*, **62**, 89–100 (1990).

47. J. J. Aklonis and W. J. MacKnight, *Introduction to Polymer Viscoelasticity*, 2nd ed., Wiley-Interscience Publishers, John Wiley & Sons, New York, 1983, pp. 40–53.

48. W. R. Burghardt, L. Yilmaz, and A. J. McHugh, *Polymer*, **28**, 2085–2092 (1987).

49. G. E. Gaides and A. J. McHugh, *Polymer*, **30**, 2118–2123 (1989).

50. J. A. Sauer and K. D. Pae, in *Introduction to Polymer Science and Technology: An SPE Textbook*, H. S. Kaufman and J. J. Falcetta, Eds., John Wiley & Sons, New York, 1977, p. 401.

51. D. P. Sheetz, *J. Appl. Polym. Sci.*, **9**, 3759–3773 (1965).

52. S. L. Bertha and R. M. Ikeda, *J. Appl. Polym. Sci.*, **15**, 105–109 (1971).

53. K. Vasarhelyi, J. A. Ronner, M. H. V. Mulder, and C. A. Smolders, *Desalination*, **61**, 211–235 (1987).

54. P. Manos, US Patent 4,080,743 (1978).

55. S. C. Pesek and W. J. Koros, paper presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec. 17–22 (1989).