

The Formation of Nodular Structures in the Top Layer of Ultrafiltration Membranes

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SYNOPSIS

The formation of nodular structures in the top layer of ultrafiltration membranes is considered. A critical review of mechanisms described in the literature is given. Flat-sheet poly(ether sulfone) membranes and hollow-fiber poly(ether sulfone)/polyvinylpyrrolidone membranes were made by coagulation of a polymer solution in a nonsolvent medium under different circumstances. From these experiments, a number of empirical rules are found to describe the resulting morphology of the top layer. A new mechanism for the formation of a nodular structure is proposed. It is based on the small diffusion coefficient of the polymer molecules compared to the diffusion coefficient of solvent and nonsolvent combined with a high degree of entanglement of the polymer network. For unstable compositions, phase separation will proceed by growth in amplitude of concentration fluctuations. The rapid diffusional exchange of solvent for nonsolvent in the top layer leads to vitrification of the maxima of the concentration fluctuations that form the nodules. Complete disentanglement of the polymer chains between the nodules is not reached, which explains the small pores and the low porosity of ultrafiltration membranes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Asymmetric polymeric ultrafiltration membranes made by the phase-inversion technique usually have a top layer consisting of closely packed spheres or nodules. The pore sizes of these membranes are between 1 and 100 nm and the surface porosities are very low (typically between 2 and 7%).¹ The pore-size distribution of ultrafiltration membranes often has two maxima, as is reported in the literature.²⁻⁵ The presence of nodules is reported by many researchers,^{1,4-18} but an appropriate mechanism for the formation has not yet been found.

In our research on the development of hollow-fiber ultrafiltration membranes from the blend poly(ether sulfone) (PES) and polyvinylpyrrolidone (PVP) as described elsewhere,^{19,20} many membranes have been spun, showing a nodular structure in the top layer. In addition to these results, flat membranes were made from PES. These results are

thought to give a better insight in the formation of nodular structures.

THEORY: A LITERATURE STUDY ON THE MECHANISMS FOR THE FORMATION OF NODULAR STRUCTURES

Panar et al.⁶ were among the first to report on non-crystalline spheres of about 60 nm in the top layer of reverse osmosis membranes. The spheres were called micelles and were thought to be present already in the casting solution. Reverse osmosis cellulose acetate (CA) membranes have been investigated by Kesting.⁷ Nodules of 50–100 nm were believed to be paracrystalline in nature. The nodules are thought to be present in the casting solution and are immobilized in the top layer due to extremely rapid solvent exchange upon immersion into water. In a later stage, aggregation into larger units (300–700 nm) occurs until they have disappeared in the final gel stage. For CA, paracrystallinity is likely to occur; however, nodules are also found in membranes made from amorphous polymers such as PES as is shown in this article.

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The idea that precursors of the entities seen in the membrane structure are initially present in the casting solution is also used by other authors. Inhomogeneity of a polymer solution of CA close to the binodal was shown by Kunst et al.^{8,9} Using activation energies of viscous flow and light-scattering measurements, evidence was found for a supermolecular structure in the polymer solution. The structure was more profound in case of high CA concentrations and for compositions close to the binodal. More structure in the polymer solution resulted in membranes with smaller pores from which Kunst et al. concluded that a network was formed instead of small particles that would aggregate. Other researchers like Boom et al.²¹ concluded from light-scattering measurements of polymer solutions with a composition close to the binodal composition that large concentration fluctuations are present in the solution. Miyano et al.¹⁰ defined a hydrodynamic radius of the polymer in the casting solution. They found a relation between this radius and the average pore size at the membrane surface. However, the hydrodynamic radii were about 30 Å, whereas the pore sizes were 10 times as large. Therefore, these authors assumed the pores to be solvent-filled spaces or spaces generated between aggregates of polymer molecules.

Kamide and Manabe¹¹ described aggregation of primary polymer particles of 20 nm as a step in the membrane-formation process. According to this theory, the primary particles are not present in the casting solution but they are formed by nucleation of a polymer-rich phase. Furthermore, the aggregation process is very slow as it depends on the mobility of primary particles and on the surface free energy. The cellulose membranes studied by Kamide and Manabe were made from a casting solution containing 3–10 wt % cellulose. Phase separation was induced either by evaporation of the solvent when a nonsolvent was present in the casting solution or by immersion in a coagulation bath containing 30% solvent. For these conditions, phase separation takes place at the low polymer concentration side of the critical point. For this system, the mechanism as proposed by these authors (nucleation of the polymer-rich phase) is correct; however, other researchers referred to nucleation of a polymer-rich phase to explain structures formed from more concentrated solutions (definitely beyond the critical point) and under much faster precipitation conditions.

Recently, Kesting⁴ introduced four tiers of structures in membranes: macromolecules, nodules (20 nm), nodular aggregates (40–100 nm), and super-nodular aggregates. With this concept, Kesting ex-

plained membrane formation as an aggregation process stopped at different stages without taking into account the casting conditions and the type of polymer. In this model, the ultrafiltration membranes consist of nodular aggregates and the pores are the spaces between incompletely coalesced nodule aggregates.

Broens et al.¹² found nodules in the top layers of poly(dimethyl phenyleneoxide) (PPO) membranes. PPO is a crystalline polymer. Nodules were described as structural units in the skin layer formed under conditions of fast diffusion processes and originating from gelation or crystallization. According to Ray et al.,¹³ nodules result from perturbations at the interface of polymer solution and coagulation bath. The perturbations are formed due to concentration and temperature fluctuations (Marangoni effect). Normally, they decay but strong interactions between the coagulation medium and the solvent in the polymer solution can lead to stabilization and growth of these perturbations. But if such a surface phenomenon would cause nodule formation, it would not be possible to explain several layers of nodules in the top layer.

In the membrane-formation mechanism as described by Kimmerle and Strathmann,¹⁴ the structure obtained after phase inversion of a polymer solution is dependent on the ratio of the polymer-rich and the polymer-lean phases at the moment of phase separation. In the phase diagram, this ratio is determined by the position of the polymer composition at the tie line. Nodular structures are formed in the top layer of a membrane if strong nonsolvents are used. A strong nonsolvent is a liquid showing a high interaction with the solvent and a low interaction with the polymer. The use of a strong nonsolvent means that upon immersion in a coagulation bath the diffusion processes are very rapid. Kimmerle and Strathmann stated that the composition of the polymer solution deeply enters the immiscibility gap in such a way that the volume of the polymer-rich phase is very small. Phase separation then would result in a discontinuous polymer-rich phase consisting of spheres. However, calculations using mass-transfer models as used by Reuvers et al.²² show that immersion of a polymer solution into a bath of a strong nonsolvent causes an increase of the polymer concentration in the top layer.

Pinnau and Koros¹⁵ prepared polysulfone gas-separation membranes from a solution containing a volatile solvent and a nonvolatile nonsolvent. After evaporation of the solvent, the polymer solution was quenched in a nonsolvent bath. In these gas-tight membranes, the top layer consisted of nodules. The

nodular structure was said to be formed by spinodal demixing. In a later stage, collapse of the nodules occurred due to capillary forces. Spinodal demixing of the polymer solution resulting in a nodular structure in the top layer of ultrafiltration membranes was also reported by Boom et al.¹⁶ In normal diffusion processes, spinodal demixing is not possible because diffusion coefficients become zero as the composition reaches the spinodal curve. However, it was shown¹⁶ that the composition path is able to cross the spinodal curve due to the relatively small mobility of the polymer molecules compared to that of the solvent and nonsolvent components. Later Boom et al.²³ found strong indications that for membrane systems with a polymeric additive such as PVP spinodal demixing occurs, resulting in a bicontinuous structure. For these membranes, the substructure is bicontinuous with a large pore volume, but in the top layer, a dense nodular structure is found.

Recent developments in microscopic techniques can give better insight into the fine structures of ultrafiltration top layers.^{5,17,18} Commercial polysulfone and PES membranes were studied by Dietz et al.¹ using atomic force microscopy. No information was given on the preparation conditions of the membranes. However, from the pictures shown, it can be concluded that differences in packing modes of nodules of equal size can lead to membranes that differ in pore structure and performance.

EXPERIMENTAL

Poly(ether sulfone) (PES) was purchased from ICI (Victrex 5200P, M_w 44,000 g/mol). Two kinds of polyvinylpyrrolidone (PVP) from Janssen Chimica were used: K90 (M_w 507,000 g/mol) and K30 (M_w 18,000 g/mol). The weight-average molecular weights of the polymers were determined using GPC. The solvent used was 1-methyl-2-pyrrolidone (NMP). The nonsolvents were water and 1-pentanol. NMP and 1-pentanol were purchased from Merck (analysis grade).

Flat membranes were made by casting a polymer solution onto a glass plate followed by immersion in a water bath of 25°C. Hollow fibers were spun using a dry-wet-spinning technique¹⁹ or a wet-spinning technique with a triple orifice spinneret.²⁰

The membrane morphology was studied using a scanning electron microscope (SEM) (JEOL, JSM T220A). The water in the pores was replaced in a sequence of ethanol and hexane; after this, the membranes were dried in air. For the cross sections,

the membranes were broken in liquid nitrogen. For the SEM, a thin (30 nm) gold layer was sputtered on the membranes using a sputter apparatus (Balzers Union SCD 040). Details on the use of microscopy for the characterization of membrane structures are discussed elsewhere.⁵

RESULTS AND DISCUSSION

First, some qualitative relations for the formation of nodular structures are derived. The nodules as they are imaged with the SEM appear to be larger than their realistic size due to the thickness of the gold-coating layer.⁵ Direct estimations of the nodule sizes from SEM photographs are therefore not accurate and can only be used for qualitative mutual comparison. For critical remarks on the use of SEM for structure determination, one is referred to the Appendix.

Flat-sheet PES Membranes

The Polymer Concentration in the Casting Solution

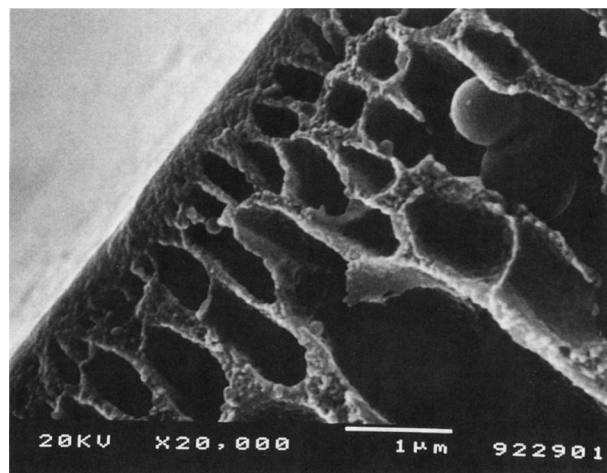
Flat-sheet membranes were cast from solutions containing 10, 20, 30, or 40 wt % PES in NMP and coagulated in water. From the 10 wt % PES solution, only a very thin film could be obtained since most of the polymer was dispersed in the coagulation bath. Photographs of the top layer of these membranes are shown in Figure 1. The more concentrated polymer solution results in a membrane with a thicker top layer. However, the nodule sizes appear to be the same for all three membranes.

Addition of Nonsolvent to the Casting Solution

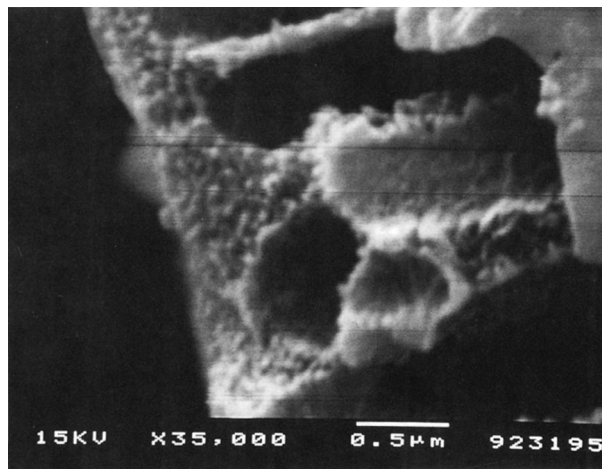
Homogeneous (transparent) solutions could be made containing 20 wt % PES in NMP and 3, 6, or 9 wt % water. Membranes made from these solutions are shown in Figure 2. It can be seen that the nodule sizes are smaller for the membrane cast from the 9 wt % water solution. This indicates that nodules do not arise from aggregates present in the polymer solution because these aggregates would be larger if the composition of the solution lies closer to the binodal.

Change in Viscosity of the Coagulation Bath

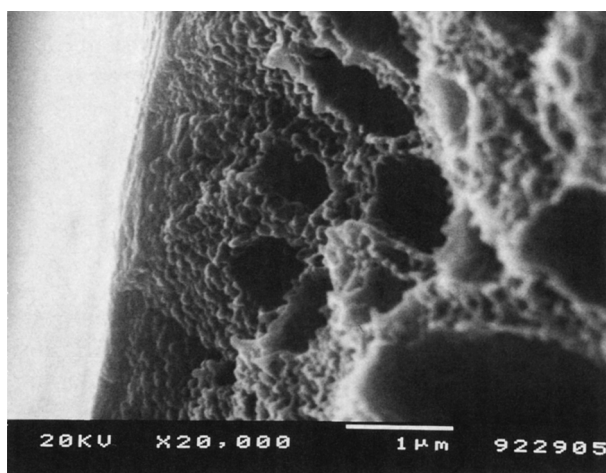
Thin films of a solution containing 25 wt % PES in NMP were coagulated in different water baths. The viscosity of the coagulation baths was increased by



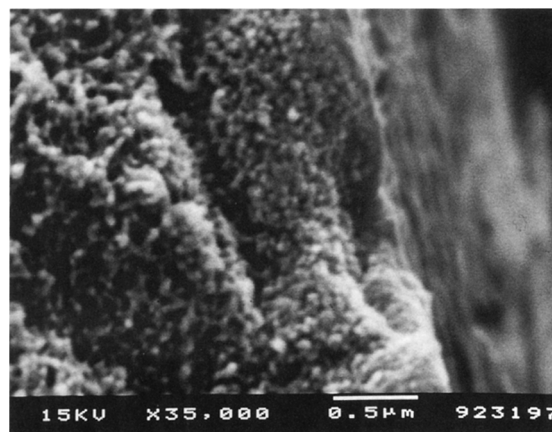
(a)



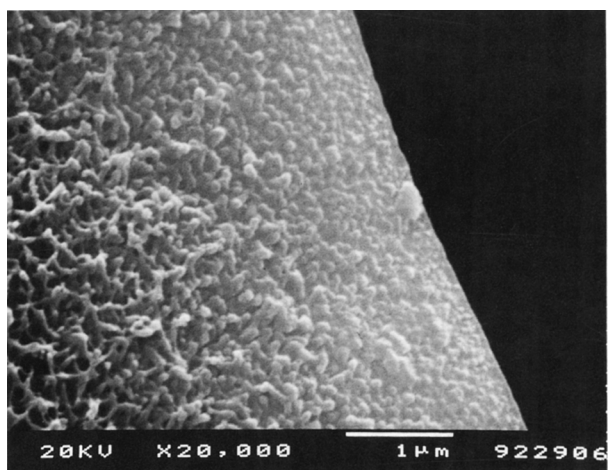
(a)



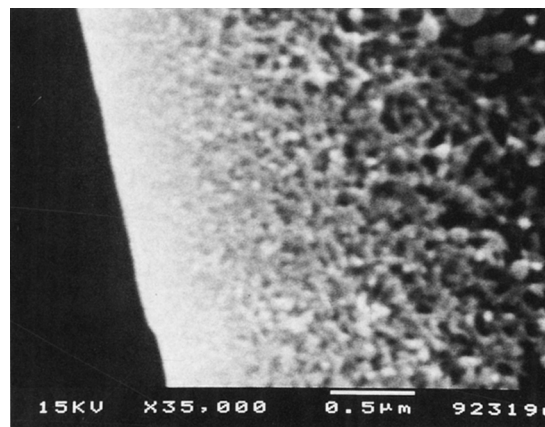
(b)



(b)



(c)



(c)

Figure 1 Cross sections (SEM) of the top layers of PES membranes cast from solutions with different polymer concentrations: (a) 20 wt %; (b) 30 wt %; (c) 40 wt %. Membranes were coagulated in a water bath at room temperature.

Figure 2 Cross sections of the top layers of PES membranes cast from 20 wt % polymer solutions containing different concentrations of water: (a) 3 wt %; (b) 6 wt %; (c) 9 wt %. The membranes were coagulated in a water bath at room temperature.

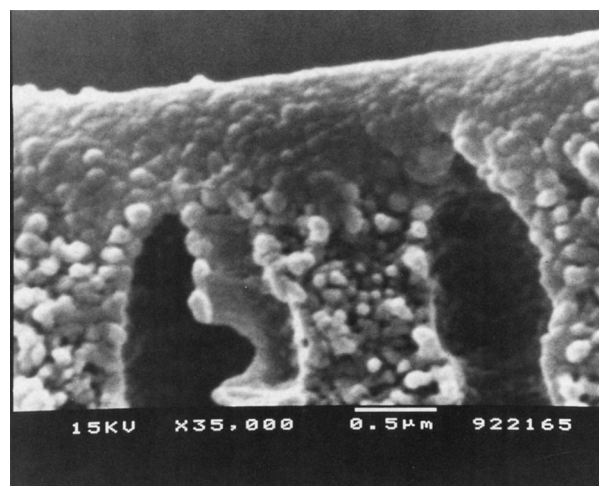
the addition of different amounts of PVP (K90). It was assumed that the only effect of PVP on the phase-separation process is a change in viscosity (i.e., in kinetics), not a change in thermodynamics. The addition of PVP to the coagulation bath slows down the diffusion of both solvent and nonsolvent. Photographs of the top layers of these membranes are given in Figure 3. It is clear that the nodular structure is not present in case the phase-separation process is slow.

Hollow-fiber PES/PVP Membranes

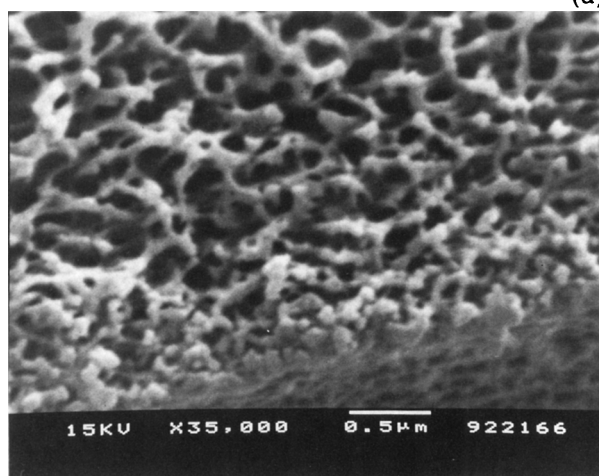
During the dry-wet spinning of a polymer solution containing PES and PVP, the nascent membranes pass an airgap, after which they enter a water bath of 20°C.¹⁹ The humidity in the airgap has been varied by applying a mixture of a dry and a water-saturated nitrogen stream. The surface structure of the membranes obtained can be seen in Figure 4. It is clear from these pictures that pore sizes at the surface are larger if more water vapor has been applied in the airgap. The polymer material surrounding the pores possesses a nodular structure. The sizes of the nodules are larger when the partial pressure of the water vapor in the airgap is higher, but at the highest vapor pressure, the membrane does not show a nodular structure.

Two more examples of the formation of a nodular structure in PES/PVP membranes will be mentioned here. In these cases, the coagulation media used were not as strong a nonsolvent for PES as in the case of water. The membrane shown in Figure 5 (a) was formed by applying a coagulation medium consisting of 60 wt % solvent (NMP) in water. In this situation, the driving force for the outdiffusion of solvent (which is dependent on the concentration difference) is reduced. The membrane shown in Figure 5 (b) was made using a two-bath system in which 1-pentanol was the first coagulation medium, and water, the second. The membrane formation for this type of spinning technique is discussed elsewhere.²⁰ In the 1-pentanol medium, the indiffusion of the nonsolvent is small so that the outdiffusion of solvent is in excess. Before the nascent membrane reaches the water bath, indiffusion of nonsolvent cannot occur. Still, the presence of PVP causes demixing of the polymer solution already in the 1-pentanol medium.²⁰

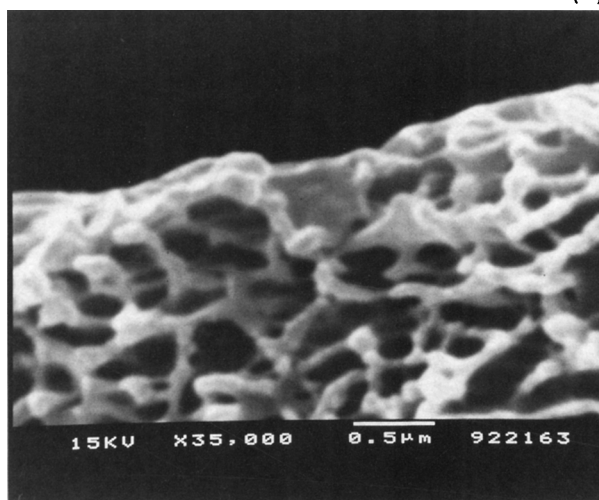
For the two membranes shown in Figure 5, the diffusion processes of solvent and nonsolvent upon immersion of the polymer solution in the coagulation medium were slow when compared to the diffusion



(a)



(b)



(c)

Figure 3 Cross sections of the top layers of PES membranes (25 wt % polymer solution) coagulated in water with different amounts of PVP resulting in different viscosities: (a) low viscosity (0.3 Pa-s); (b) medium viscosity (1.1 Pa-s); (c) high viscosity (5 Pa-s).

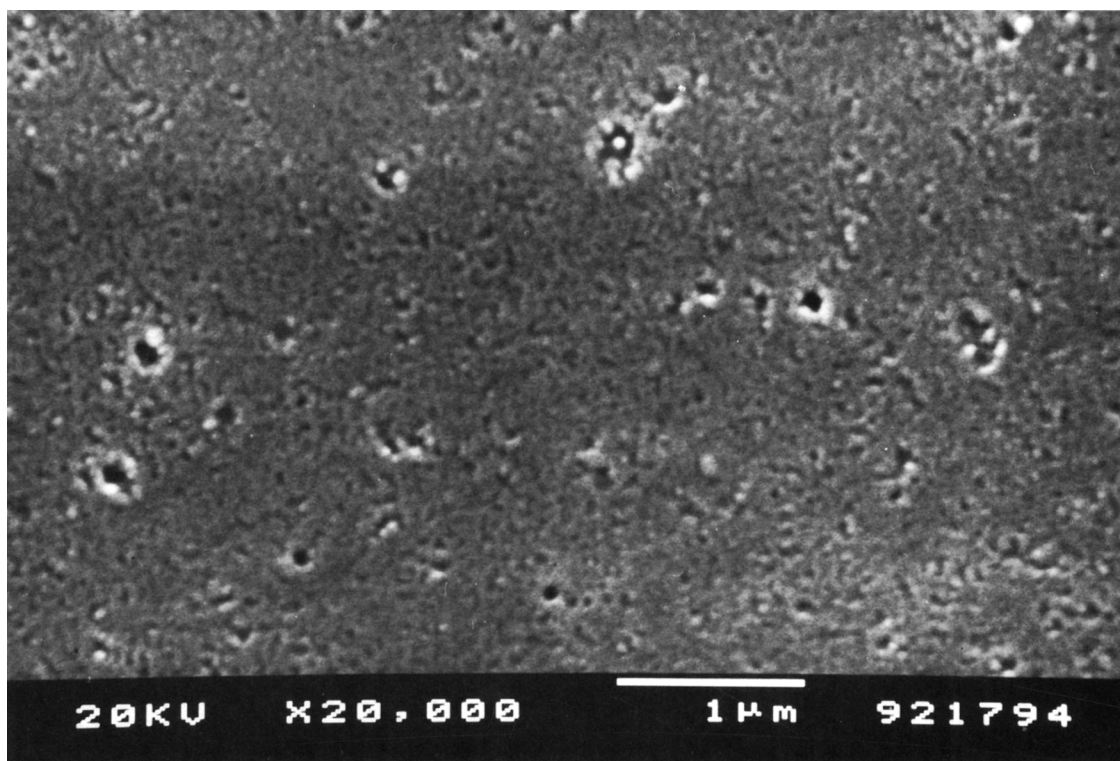
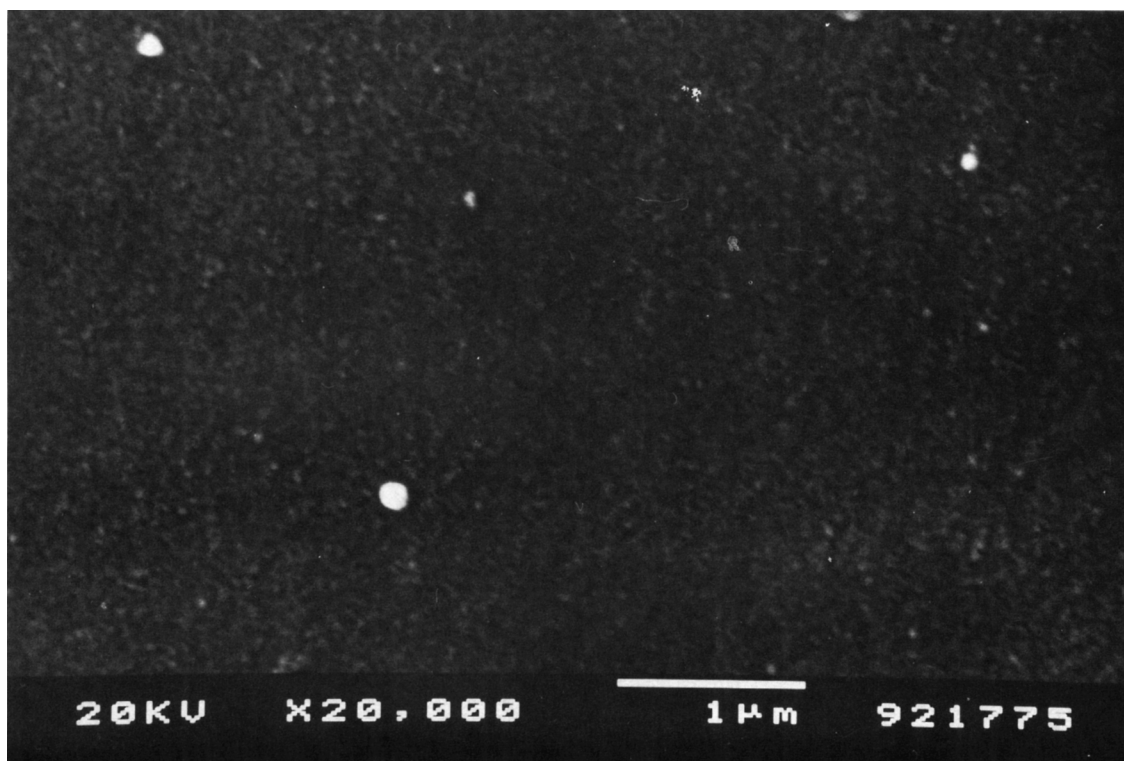


Figure 4 Morphology of the surface of hollow-fiber PES/PVP membranes spun with the dry-wet technique for different humidities of the airgap: (a) 0.036 bar; (b) 0.062 bar; (c) 0.101 bar; (d) 0.114 bar. After a residence time of 2.2 s in the airgap, the fibers entered a water bath of 20°C. The polymer solution used for spinning contained 20 wt % PES, 12.5 wt % PVP (K90), and 5 wt % water in NMP.

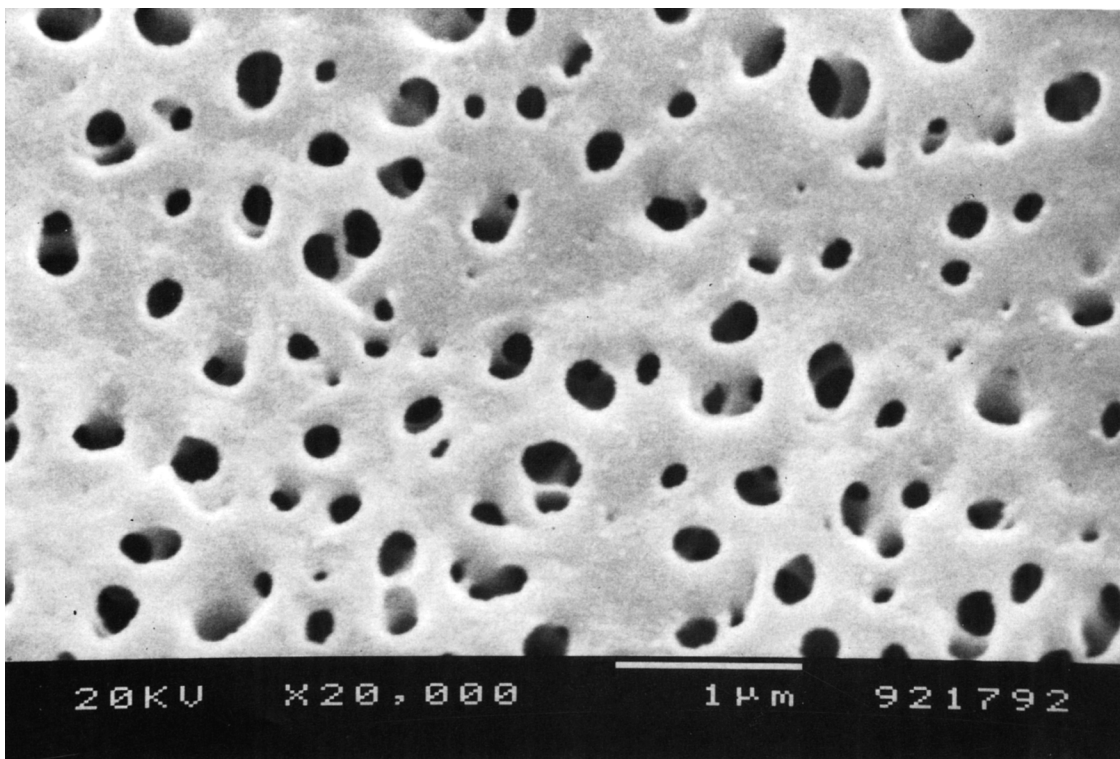
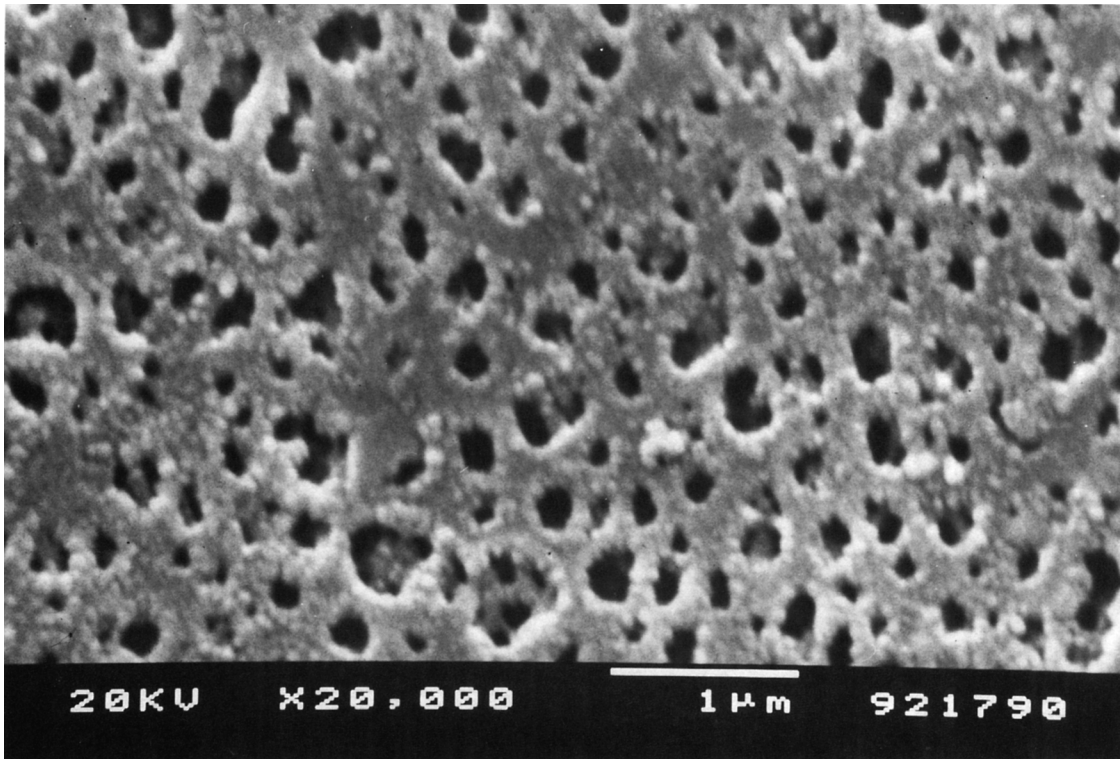


Figure 4 (Continued from the previous page.)

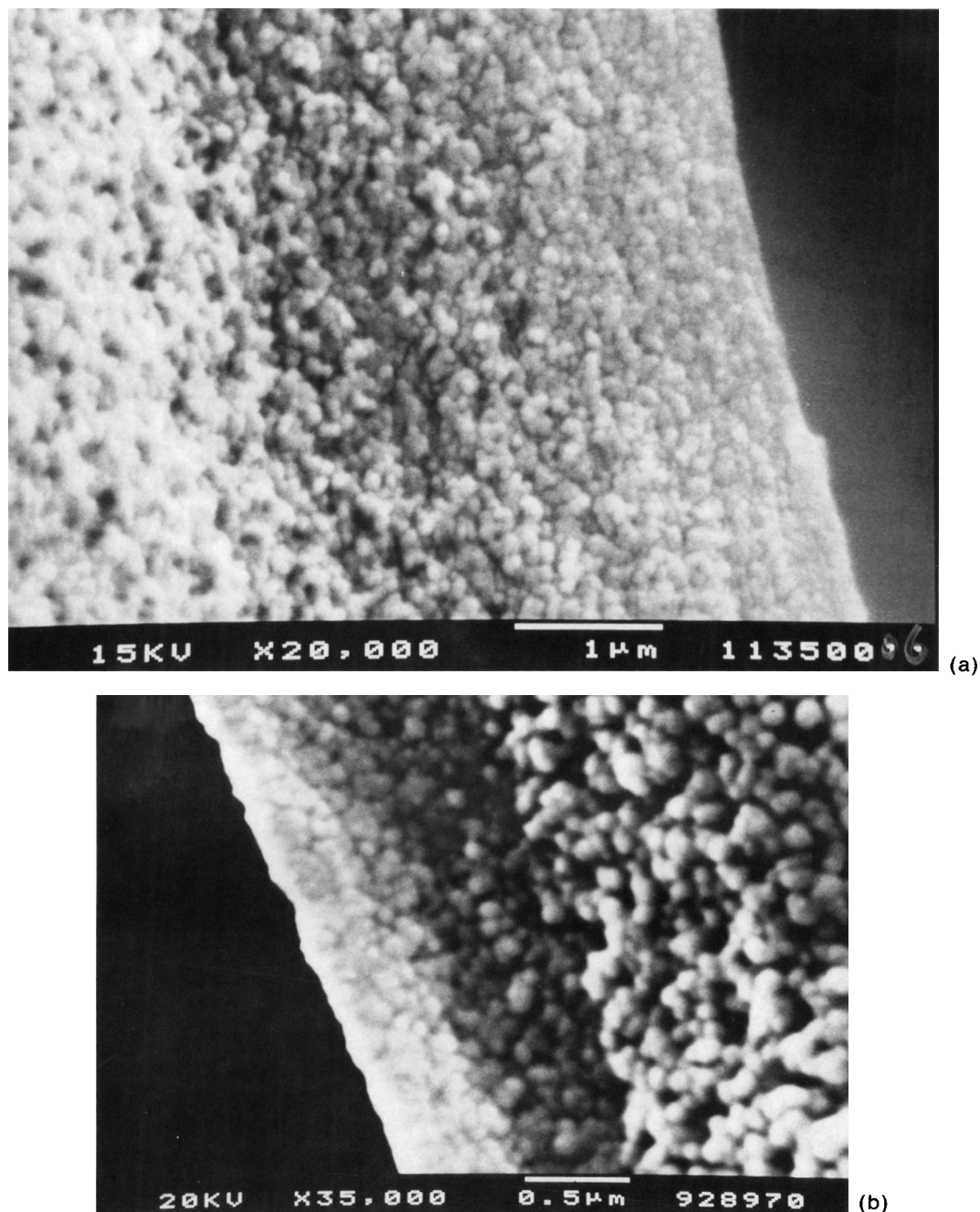


Figure 5 Cross sections of the morphology of the top layer of hollow-fiber PES/PVP membranes. The polymer solution contained 20 wt % PES and 10 wt % PVP. Coagulation media: (a) bore side, internal coagulation medium was 60 wt % NMP in water; (b) outer surface, spun with a triple-layer spinneret, external coagulation medium was 1-pentanol. After 0.5 s contact time with the first medium, the fibers entered a water bath of 20°C.

processes upon coagulation in a water bath. If a polymer solution consists of PES only, the slow diffusion processes do not cause the formation of a nodular structure as was shown in Figure 3(c). However, the presence of PVP leads to a nodular

structure even under conditions of slow diffusion of solvent and nonsolvent. The two photographs in Figure 5 also show that the nodule sizes are the smallest at the surface and increase further into the film.

From the experiments, the following conclusions can be drawn:

- Nodules are polymer spheres, present in the top layers of asymmetric ultrafiltration membranes.
- The diameter of nodules is difficult to estimate but it is in the order of 50 nm.
- Nodules are formed in a phase-separation process under conditions of fast outdiffusion of solvent and fast indiffusion of nonsolvent.
- Since PES is an amorphous polymer, nodule formation is not caused by (partial) crystallization.
- The size of the nodules is the smallest at the surface and increases deeper into the film until it gradually transforms into a porous structure.
- The size of the nodules is smaller if the composition of the original polymer solution is lying closer to the binodal composition.
- The size of the nodules is independent of the polymer concentration of the casting solution.
- There is no indication that nodules are agglomerates of smaller spheres.
- If PVP is present in the polymer solution, the nodules are also formed at less rapid coagulation conditions.
- A nodular structure can also be formed in a second coagulation step during spinning.
- The size of the nodules is not directly linked to a certain pore size (this is also clear from the work of Dietz et al.¹).

A New Mechanism for the Formation of Nodular Structures

Membranes Prepared from a Solution Containing One Polymer

In the first moments upon immersion of a polymer solution in a coagulation bath of a strong nonsolvent, fast diffusion processes of solvent and nonsolvent take place in the top layer. Since in the top layer excess outdiffusion of the solvent occurs, the polymer concentration is increased and the diffusion processes are rapidly followed by vitrification of the polymer matrix. In this section, it is discussed how this can result in a nodular structure.

Due to the large differences in molecular weight, the transport of small components (solvent and nonsolvent) in the system is much faster compared to the mobility of the polymer molecules. Using the nomenclature of de Gennes,²⁴ the *cooperative* dif-

fusion describes the transport of solvent and non-solvent in a polymer matrix. The mobility of a polymer molecule relative to other polymer molecules is called *reptation* (or tracer) diffusion. For a solution of 30 wt % PES in NMP, the cooperative diffusion coefficient is $6.6 \times 10^{-11} \text{ m}^2/\text{s}$ and the tracer diffusion is $7.5 \times 10^{-16} \text{ m}^2/\text{s}$ as measured by Tkacik.²⁵ This means that during a short period of time the mobility of the polymer molecules is restricted to short distances and a large-scale rearrangement of the polymer network is impossible.

As was suggested in a previous article,¹⁶ the difference in mobility of the low molecular weight components compared to the high molecular weight polymer can lead to a large supersaturation of the polymer solution. Therefore, the composition of the solution can become unstable (spinodal composition) before phase separation by nucleation has taken place in the metastable (binodal) region. Using the spinodal demixing theory as described by Cahn,²⁶ Van Aartsen and Smolders,²⁷ and Smolders et al.,²⁸ it was shown that the dimensions of the nodules found in the ultimate membrane coincide with the fastest-growing wavelength of the concentration fluctuations. With this mechanism of growth of concentration fluctuations, it can be explained that the nodule sizes are smaller in cases where the original composition is closer to the binodal and that they are smaller at the surface than deeper in the top layer. Both loci with a composition initially close to the binodal as well as loci at the surface will deeply enter the immiscibility gap upon immersion. In these cases, the composition will become highly unstable before demixing starts and the wavelength of the concentration fluctuations is smaller.

Due to the difference between diffusion of solvent and nonsolvent, on the one hand, and the relaxation behavior of the polymer, on the other, spinodal demixing is possible. However, it is not yet clear how spinodal decomposition results in a nodular structure since mostly a cocontinuous structure is formed. The formation of a nodular structure will be visualized on a molecular level.

The rapid outdiffusion of the solvent combined with the indiffusion of the nonsolvent confronts the polymer molecules with a noncompatible environment. The reaction of the polymer molecules on this sudden change of state is an attempt to surround themselves with other polymer segments. In solutions of very low polymer concentration, it is a well-known phenomenon that a polymer coil collapses if the solubility strength of the environment is reduced, for instance, by a temperature quench.²⁹ In the systems discussed here, the situation is more compli-

cated. Due to the high polymer concentration, the polymer molecules are not extended chains but highly entangled coils. The collapse of one polymer molecule in a polymer network is a tracer diffusion process and therefore it is rather slow. However, the polymer molecules can diminish their interactions with the nonsolvent by clustering of polymer segments into groups. The polymer clusters may consist of polymer segments of different molecules, and adjacent clusters are connected by entanglements or by sharing polymer molecules.

The clustering of polymer segments is an uphill diffusion process just as is spinodal demixing. The polymer maxima of the concentration fluctuations present in the polymer solution will form the centers of the clusters. In the beginning of this process, the clusters are highly connected because some polymer molecules are entangled in two adjacent clusters. In a later stage, disentanglement of polymer segments between the spheres can lead to the formation of pores. However, excess outdiffusion of the solvent will increase the polymer concentration of the top layer and will very soon result in vitrification of the polymer matrix. In the centers of the cluster, the polymer concentration will be highest and these loci are the first to reach the concentration at which vitrification occurs. Because of the short time between demixing and vitrification, the disentanglement process will not be completed.

When the thermodynamic conditions of demixing are the same as described above but the kinetics of the process are retarded as was the case for the membrane shown in Figure 3(c), no nodular structure is found. The retardation of the diffusion of solvent and nonsolvent makes the time scale of these processes comparable to the diffusion of the polymer molecules. Large supersaturation of the polymer solution will not occur and demixing takes place by nucleation and nucleus growth of a polymer lean phase.

Membranes Prepared from a Solution Containing Two Polymers

For polymer solutions that contain the hydrophilic macromolecular additive PVP, nodules are also formed under circumstances where the diffusion processes of solvent and nonsolvent are not particularly fast. This is due to the influence of PVP on the phase-separation process,^{19,20} based on the theory of Boom et al.^{21,23,30} If PVP is present in the polymer solution, the demixing process starts as soon as the polymer solution contacts the coagulation medium even for conditions where, without

PVP, a significant delay time for demixing might be found. The rate-determining process for the demixing of such a solution is the diffusion of PVP relative to the other polymer: PES.²¹ Thus, although the demixing process starts immediately, the ability of the polymer solution to respond to the changes in composition depends on the diffusion of the two polymers with respect to each other and this is even more restricted than for a polymer solution without an additive.

Boom et al.^{21,23} showed that under these circumstances the co-continuous substructure of the membrane (below the top layer) is formed by spinodal demixing. In the top layer of a membrane, the diffusion processes (solvent/nonsolvent exchange) are faster than in the sublayer and the compositions of loci in the top layer are deeper into the demixing region. Thus, if the sublayer is formed by spinodal decomposition in the top layer, spinodal demixing must also have occurred. This is another strong indication that nodular structures are formed by a spinodal demixing mechanism. The fact that spinodal demixing results in a nodular structure in the top layer and a co-continuous structure in the sublayer has two causes:

- In the top layer, the polymer concentration is higher due to loss of solvent (diffusion of solvent into the coagulation bath).
- In the top layer, the time available for demixing is short as demixing is rapidly followed by solidification of the polymer matrix.

The formation of a membrane matrix consisting of nodules in the top layer surrounding pores with sizes in the microfiltration range can also be explained by the spinodal demixing mechanism. These kinds of membrane structures are shown in Figure 4 and they were obtained by dry-wet spinning of a polymer solution containing PES and PVP. In the airgap, water vapor diffuses into the polymer solution, whereas outdiffusion of the nonvolatile solvent is hardly possible. If the water concentration in the polymer solution has reached a certain value, phase separation occurs. As said before, the determining process for phase separation is the diffusion and phase separation of PVP and PES and spinodal demixing occurs according to the theory of Boom et al.^{21,23,30} Two phases arise: a PES-rich and a PES-lean phase. Both solvent and PVP diffuse from the PES-rich phase toward the PES-lean phase. This PVP phase forms the large pores in the ultimate membrane. Since the diffusion of solvent is faster

than is the diffusion of PVP, the polymer concentration of the PES-rich phase is enhanced.

At the moment that the nascent membrane enters the water bath, it still consists of two liquid phases since no solvent was able to leave the polymer solution by diffusion into the coagulation medium. The PES-rich phase (still containing a reasonable amount of PVP) can now be regarded as a small-scale polymer solution coagulated in a water bath. Once immersed in the water bath, the solvent can diffuse from the PES phase to the water bath. At the same time, the diffusion of nonsolvent that was only slow from the vapor phase is increased. For the PES-rich phase, this causes a new impulse for demixing between PES and PVP. Again, a nodular structure is formed by spinodal decomposition rapidly followed by vitrification due to an excess out-diffusion of solvent.

When going from membranes (a) to (d) (see Fig. 4), the water-vapor concentration is increased while the residence time of the nascent membrane in the airgap is constant and more water vapor diffuses into the polymer solution. For the low vapor concentration (membrane a), the composition of the polymer solution as it enters the water bath is almost equal to the initial composition. Demixing of this solution does not start before it has entered the water bath. In the water bath, spinodal demixing results in a nodular structure. For the higher vapor concentrations (membranes c and d), the demixing starts shortly after the polymer solution enters the airgap. By the time this nascent membrane enters the coagulation bath, the phase separation has already proceeded so far that the polymer concentration in the PES phase has substantially increased and, indeed, in case 4d, has almost reached the vitrification point. In case d, the transition from airgap to water bath has no additional effect on the morphology. Medium vapor concentrations in the airgap result in the formation of a microporous membrane with a nodular structure as described above.

Pores in a Nodular Structure

The SEM images of nodular structures show a packing of spheres that are more or less interconnected. Because this structure is formed by spinodal demixing as proposed in the previous section, a continuous pore phase is expected to be present. The porous phase is not visible on SEM pictures, but the nodular structures form the top layers of ultrafiltration membranes and, as such, are permeable to a fair amount of water. This implies that a continuous network of pores has to be present among the

spheres. The active pore-size distribution of ultrafiltration membranes often shows two maxima,²⁻⁴ which were also found for the PES/PVP membranes using the liquid displacement method.⁵ One maximum is at a pore size of about 50 nm, and the second, at a pore size smaller than 10 nm. According to the mechanism proposed here, the large pores are found at loci where the disentanglement of polymer chains between the nodules was completed before vitrification occurred. At certain loci in the top layer, as soon as the disentanglement of polymer chains is completed and vitrification has not occurred yet, the polymer-lean phase can grow more easily to form larger pores of about 50 nm. At other places, the nodules are still connected to each other by entangled polymer chains. The polymer concentration between the nodules is much lower than is the concentration in the nodule itself. Spaces in the low concentration regions are the pores smaller than 10 nm. The time for demixing is only very short since the outdiffusion of solvent rapidly leads to vitrification. Thus, the disentanglement process is stopped in an early stage. The polymer concentration in the top layer is also high, which explains the low porosity of ultrafiltration membranes.

CONCLUSIONS

A new mechanism for the formation of nodular structures has been presented. The nodules are polymer spheres of about 50 nm present in the top layers of ultrafiltration membranes. A nodular structure is formed by spinodal demixing of the polymer solution, rapidly followed by vitrification of the polymer matrix. Spinodal conditions are obtained when phase separation of a polymer solution is induced by fast diffusion of the solvent and nonsolvent. A low diffusion coefficient of the polymer molecules combined with a high degree of entanglement in the polymer network make the growth of concentration fluctuations a plausible mechanism for demixing. Due to excess outdiffusion of the solvent, the polymer concentration increases and the vitrification point is reached shortly after the beginning of demixing. The disentanglement process that separates the nodules from each other is not completed during the demixing time. This is the reason for the small pores and the low porosity that are characteristic of ultrafiltration membranes. It was shown that if a hydrophilic polymeric additive is used the nodular structure is also formed in cases of slower diffusion of the solvent and nonsolvent. This result can be explained on the basis of theo-

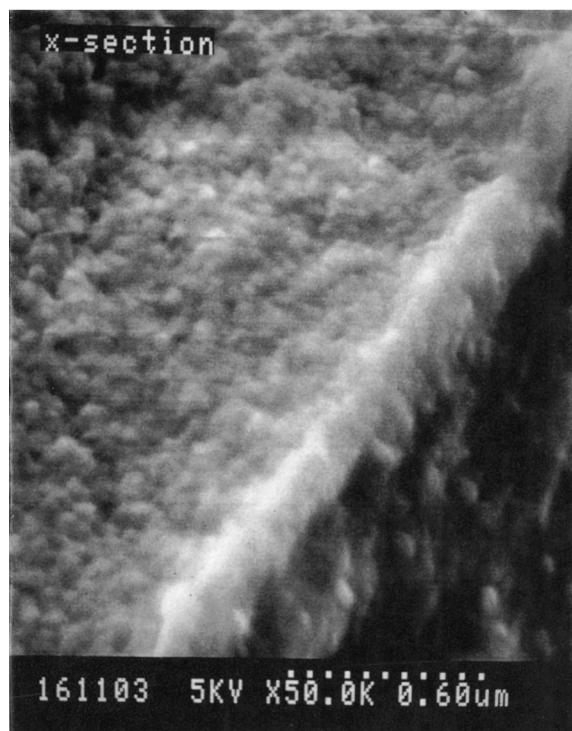
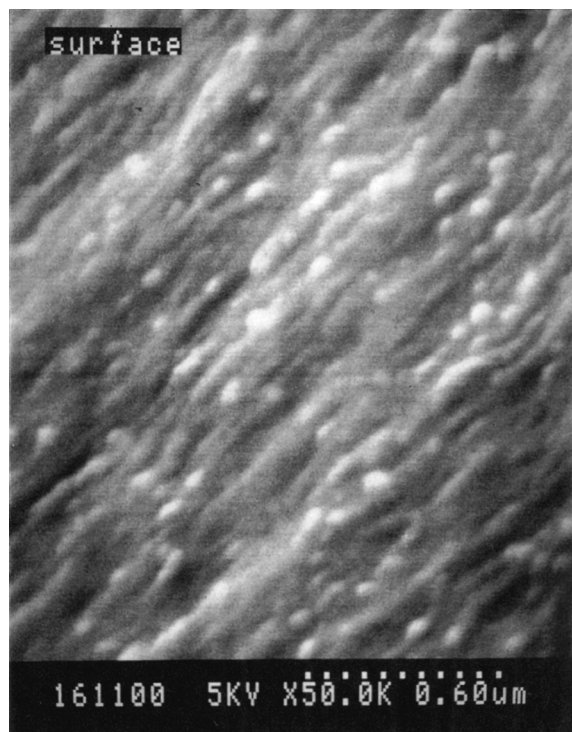


Figure 6 Top view and cross section of the top layer of a PES/PVP ultrafiltration membrane. Images from a field emission electron microscope (Hitachi). The microscope was operated at 5 kV; the membrane was coated with a 40–50 Å-thick carbon layer.

retical views on phase separation in polymeric blends.

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APPENDIX: CRITICAL REMARKS ON THE USE OF SEM FOR STRUCTURE DETERMINATION³¹

The nodular structure in the top layer of the ultrafiltration membranes can be visualized with SEM if magnifications of $\times 35,000$ and higher are used. For a common SEM, clear images at these high magnifications can only be realized with an acceleration voltage of 15–20 kV. The specimens are prevented from beam damage by coating them with a gold layer. The presence of the gold layer with a certain thickness (t) will enlarge the diameter of the polymer spheres from d to $d + 2t$.

Using a field emission microscope, a much thinner carbon layer is sufficient to protect the polymeric materials from beam damage. Photographs of a PES/PVP membrane obtained with this technique can be seen in Figure 6. Unfortunately, it was not possible to study all membranes with this technique.

Atomic force microscopy³² was also used to study the nodular structure. For this technique, a special treatment of the membrane sample is not necessary. However, difficulties arise if the features to be investigated are of the same dimensions as the tip size (10–20 nm). In this case, the line scan gives a profile of the shape of the tip instead of the shape of the sample irregularity. This effect largely diminishes the suitability of this technique for the interpretation of nodular structures. Another disadvantage of the AFM is that the surface roughness should not be too high (not larger than 2 μm). This makes the study of cross sections impossible since the brittle crack usually has a very rough surface.

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