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Nonsolvent-Induced Gelation and Its Effect on Membrane Morphology

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ABSTRACT: The addition of nonsolvent in the casting solution can suppress the formation of macrovoids in polymeric membranes if the added nonsolvent can induce polymer gelation. FTIR microscopy reveals that the formation of PMMA gels would result in a great reduction of the nonsolvent flux from coagulation bath to the casting solution, which can well account for the disappearance of macrovoids. The associated gelation mechanism was also investigated. After the phase separation induced by the added nonsolvent, unvitrified polymer gels were obtained if the polymer-rich phase has a suitable elasticity. Although the unvitrified gels are not thermodynamically stable, they can be sustained long enough to affect the membrane morphology during membrane formation. The gelation boundary can be determined by the falling ball experiment, and the equality of the storage and loss moduli in the polymer solution can be used to describe the required rheological property for the gels.

Introduction

Most commercially available polymeric membranes are fabricated by the wet inversion method.[1] It is widely accepted that liquid−liquid demixing is responsible for the initiation and growth of membrane pores in the wet inversion process.[2−4] It has also been pointed out that physical gelation plays an important role in fixing the porous structure and in the formation of membrane skin.[5,6] The liquid−liquid demixing phenomenon during membrane formation has been studied extensively,[7−9] but the role of gelation in membrane preparation is still not clear and requires more investigation. The aim of the present work is to add to our understanding in this regard.

Gel is usually defined as a three-dimensional network that contains predominantly liquid.[10] During gelation, connecting elements (junctions) occur in the initial liquid to form a three-dimensional network and to provide enough mechanical strength for the gel to be self-supporting. These connections can be formed by covalent binding (chemical gels) or by physical associations (physical or thermoreversible gels). In the wet inversion process, chemical gelation is unlikely to occur, and the physical associations are responsible for the gelation process.[11,12] There are several mechanisms for physical gelation.[10,13,14] The formation of microcrystallites can initiate the gelation process because the microcrystallites can serve as the junctions for the three-dimensional network.[6,16] Special interaction between polymer and solvent is another possible mechanism for physical gelation.[17] It was reported that the complex formation between the polymer and the solvent could enhance the rigidity of polymer chains. The enhanced chain rigidity can account for the formation of fiberlike networks (gel).[17] In addition, gelation can occur due to a combination of liquid−liquid demixing and vitrification. In this mechanism, after liquid−liquid demixing, gelation occurs due to the arrest of phase separation by the vitrification of the polymer-rich phase. This mechanism has been successfully used to describe the gelation behavior of a binary solution of an amorphous polymer and a solvent[11,13] and has then been extended[12] to describe the physical gelation of an amorphous polymer in mixtures of solvent and nonsolvent.[18] The above information suggests the mechanism for physical gelation be system-dependent. For example, crystallization might be a mechanism for the physical gelation of semicrystalline polymers, but it cannot account for the gelation of amorphous polymers. To give another example, the mechanism of liquid−liquid demixing obviously cannot explain the formation of gels in good solvent.[19]

Because the membrane formation by the phase inversion method is generally a fast process and the membrane skin is usually formed in a very short time (several seconds), the associated gelation mechanism during membrane formation should also be fast so that gelation can play an important role in determining the membrane structure. The gelation process induced by crystallization or by solvent−polymer complex formation is rather slow; therefore, these two mechanisms are believed to be of little relevance for membrane formation. It seems the mechanism of the arrest of liquid−liquid demixing by vitrification (glass transition) is more suitable to account for the gelation behavior during membrane formation.[11,12] Such a mechanism has been used to describe the membrane formation processes of thermally induced phase separation[11] and nonsolvent-induced phase separation (wet inversion).[12]

On the basis of the mechanism of the arrest of liquid−liquid demixing by vitrification, the gelation boundary can be determined by knowing the phase transition behavior of polymer solution, such as binodal, vitrification (glass transition), and tie lines. In other words, gelation is thermodynamically definable. The mechanism for the fixation of membrane structure is the vitrification of the polymer-rich phase that can arrest the liquid−liquid phase separation. On the other hand, it has been suggested that the fixation of membrane structure can also be due to the kinetic hindering caused by high viscosity.[20] Therefore, several researchers sug-

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gest that the gelation boundary can be determined by using the rheological data of polymer solution. For example, the sol−gel transition is defined as that the solution viscosity reaches a threshold[21] or the transition is determined by the falling ball (mercury drop) method. This viscosity-related gelation mechanism has been used to describe the formation of polymeric membranes.[5]

During membrane formation, gelation is the mechanism for fixing the membrane structure. Hence, the gel should be a state in which the structure is fixed. It has been found[12] that a concentrated polymer solution, although the viscosity is very high, can still undergo phase separation when it is immersed in a coagulation bath. In other words, high-viscosity polymer solution is not a gel. Obviously, the viscosity-related gelation mechanism cannot distinguish a gel from a highly concentrated polymer solution; hence, it is not an appropriate gelation mechanism for membrane formation. It seems that that the vitrification-related gelation mechanism is more suitable to describe the gelation process during membrane formation.[12] However, it is still controversial if polymer vitrification is required to lock the morphology in during membrane formation. Theoretical analysis[22] and experimental data[23] were reported, indicating that it is not necessary to be at the glass transition (vitrification) to arrest the coarsening process during spinodal demixing.

The major aim of the present work is to demonstrate the role of nonsolvent-induced gelation in suppressing macrovoid formation in phase inversion. It has been reported[24] that the addition of nonsolvent can suppress macrovoid formation. And it is widely accepted[8,9,24] that if macrovoid could occur, it is strongly related to the incursion rate of nonsolvent in the dope. But, it is still not clear how the addition of nonsolvent can dramatically slow the incursion rate of nonsolvent. In the present work, we provide evidence showing that gelation is the mechanism that connects the addition of nonsolvent and the slowdown of nonsolvent incursion rate. Data are also provided that can help to resolve the controversy about whether vitrification is required to lock the morphology in during membrane formation. The results to be presented below indicate that, after phase separation, vitrification of the polymer-rich phase is required to form thermodynamically stable gels, but to form gels that only need to be sustained long enough to fix the membrane structure, the polymer-rich phase needs not to vitrify but only requires to have appropriate elasticity.

Experimental Section

Material and Solution Preparation. PMMA(18224-9, Aldrich) was dissolved in NMP/water solution at 80 °C to form a clear and homogeneous casting solution. *N*-Methyl-2-pyrrolidone (NMP) from TEDIA was used as the solvent without further purification, and R.O. water was the nonsolvent (coagulant). If the solution would demix at room temperature (25 °C), it was kept at 80 °C. Otherwise, the solution was kept at room temperature.

Membrane Preparation. The polymer solution was usually cast at room temperature on a glass plate to a predetermined thickness of 300 μm. The casting film was then immersed in a water bath. After polymer precipitation, the membranes were peeled off and dried in air. However, if the casting solution would demix at room temperature, casting was carried out at 80 °C instead of room temperature. The casting film was then cooled to the room temperature first, kept at the room temperature for around 10 min, and immersed into the water bath.

Determination of Binodal (Cloud Point Measurement). Cloud point curves were obtained by a simple titration method. PMMA solutions at different concentrations were put in an isothermal bath of 25 °C for 12 h. These homogeneous polymer solutions were titrated with water. The amount of water required to bring the onset of turbidity was measured with a precision of 0.1 mL. At the onset of turbidity, the solution composition was recorded and plotted in the ternary phase diagram. It should be noted that the cloud point curve might not coincide with the binodal for polydisperse polymers. However, for the PMMA used in the present work, it has been reported[25] that the experimental cloud point curve agrees well with the theoretical binodal. Hence, the experimental cloud point curve is interpreted as the binodal in the present work.

Determination of Vitrification Line and Gelation Boundary (Measurement of T_g). The glass transition temperature (T_g) of the polymer solution with a composition on the vitrification line is equal to the system temperature. Differential scanning calorimetry (DSC) measurements were carried out to determine the T_g of the PMMA solution. Samples of PMMA in mixtures of NMP/water were put in pans of stainless steel, and the pans were placed at 110 °C for 2 days to obtain homogeneous polymer solutions. A liquid nitrogen cooled Perkin-Elmer DSC7 apparatus was then used to measure the T_g of the solutions. The vitrification line was obtained by connecting those points of which the T_g is equal to the system temperature (25 °C).

The vitrification-related gelation boundary is a tie line across the intersection of the binodal and the vitrification line (Berghmans point). For a polymer solution with a composition on the gelation boundary, after demixing, the polymer-rich phase locates at the Berghmans point; i.e., the T_g of the polymer-rich phase equals the system temperature. PMMA solutions at various compositions were placed at 25 °C for at least 1 week to allow the phase separation to occur. The polymer-rich phase was then put in the aluminum sample pan to measure its T_g. After the composition was determined at which the T_g of the polymer-rich phase is equal to 25 °C, the gelation boundary can be obtained by drawing a line connecting this point with the Berghmans point. One can refer to the work of Li et al.[12] for more details of how to determine the gelation boundary.

Gelation Composition Determined by the Falling Ball Method. PMMA was dissolved in NMP/water solution in a sealed glass tube to form a homogeneous solution at an appropriate temperature. A steel ball was placed in the solution. The solution was then transferred to a thermal bath with a cooling rate of 1 °C/min. When the bath was cooled to a designated temperature, the glass tube was removed from the bath and turned upside down to see if the steel ball would fall in 20 s. Record the temperature at which the ball would not fall as the gel setting temperature. The gel setting temperature can be interpreted as the gelation temperature. The gelation composition, at which the gelation temperature is 25 °C, can then be determined by measuring the gelation temperatures corresponding to various solution compositions. It should be noted that the time waiting for the ball to fall (20 s) was chosen on the basis of the time needed for the PMMA/NMP solution to form membranes in water bath. In other words, if the ball would not fall in 20 s for a solution at a certain composition, we believe the solution is gelled, and the morphology is locked in during the time period of membrane formation.

Viscoelastic Measurement. The viscometer (RS100, Hakee) with double cone−plate (cone angle 4°, diameter 30 mm) was used to measure the shear modulus of the polymer solution. The shear modulus was measured by an oscillation method, setting the amplitude of shear stress at 5 Pa and the oscillating frequency at 1 Hz.

SEM. The membrane structures were examined by a Hitachi (model S4700) SEM. In SEM studies, membrane samples were fractured in liquid nitrogen and coated with gold.

FTIR Microscopy. An FTIR microscope (Perkin-Elmer LE186-0078) equipped with a liquid cell was used for detecting

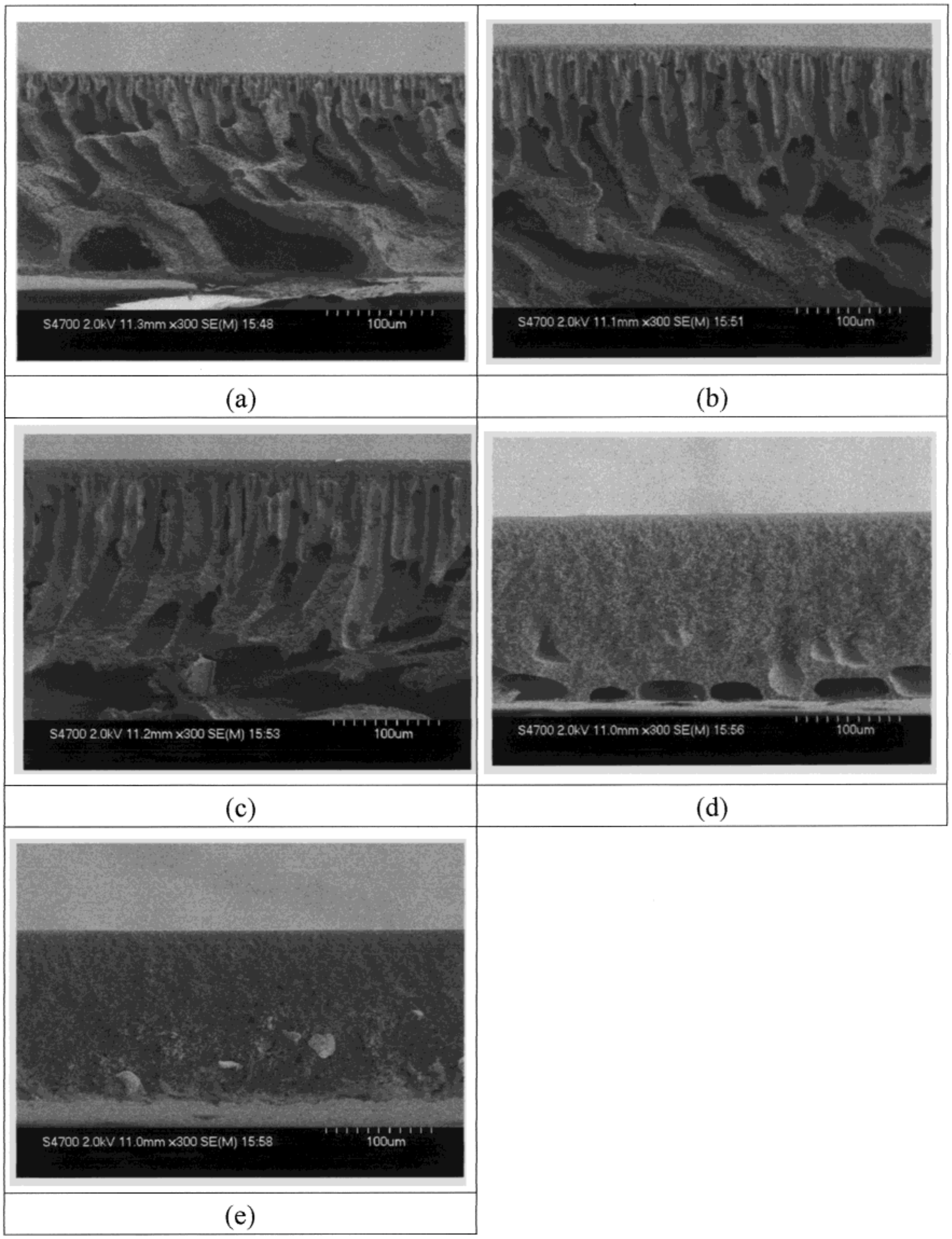


Figure 1. Effect of the addition of water on the structure of PMMA membranes. PMMA concentration: 15 vol %. Water concentration: (a) 0, (b) 5, (c) 8, (d) 11, and (e) 13 vol %.

the increase of water in the casting solution during membrane formation. The polymer solution was placed between two CaF_2 salt plates with a 15 μm spacer in between. Then water was injected into the space between the two salt plates. The microscope was focused on a spot in the casting solution near the interface between water and casting solution. FTIR spectroscopy was used to measure the absorption spectrum at the focused spot. The absorbance at 3535.9 cm^{-1} was used to characterize the water concentration. The time variation of the absorbance at 3535.9 cm^{-1} was measured, and the results can be interpreted as the time dependence of water concentration during membrane formation at the measured spot.

Results and Discussion

Suppression of Macrovoids Due to the Nonsolvent-Induced Gelation. Asymmetric membranes with macrovoids were obtained by immersing the PMMA/NMP solution in a water bath. The addition of water (nonsolvent for PMMA) can suppress the formation of macrovoids, as shown in Figures 1 and 2. When the PMMA concentration is 15 vol %, the addition of 13 vol % of water can completely suppress the formation of macrovoids (Figure 1e), and when the PMMA concentration is 20 vol %, the addition of 11 vol % of water is

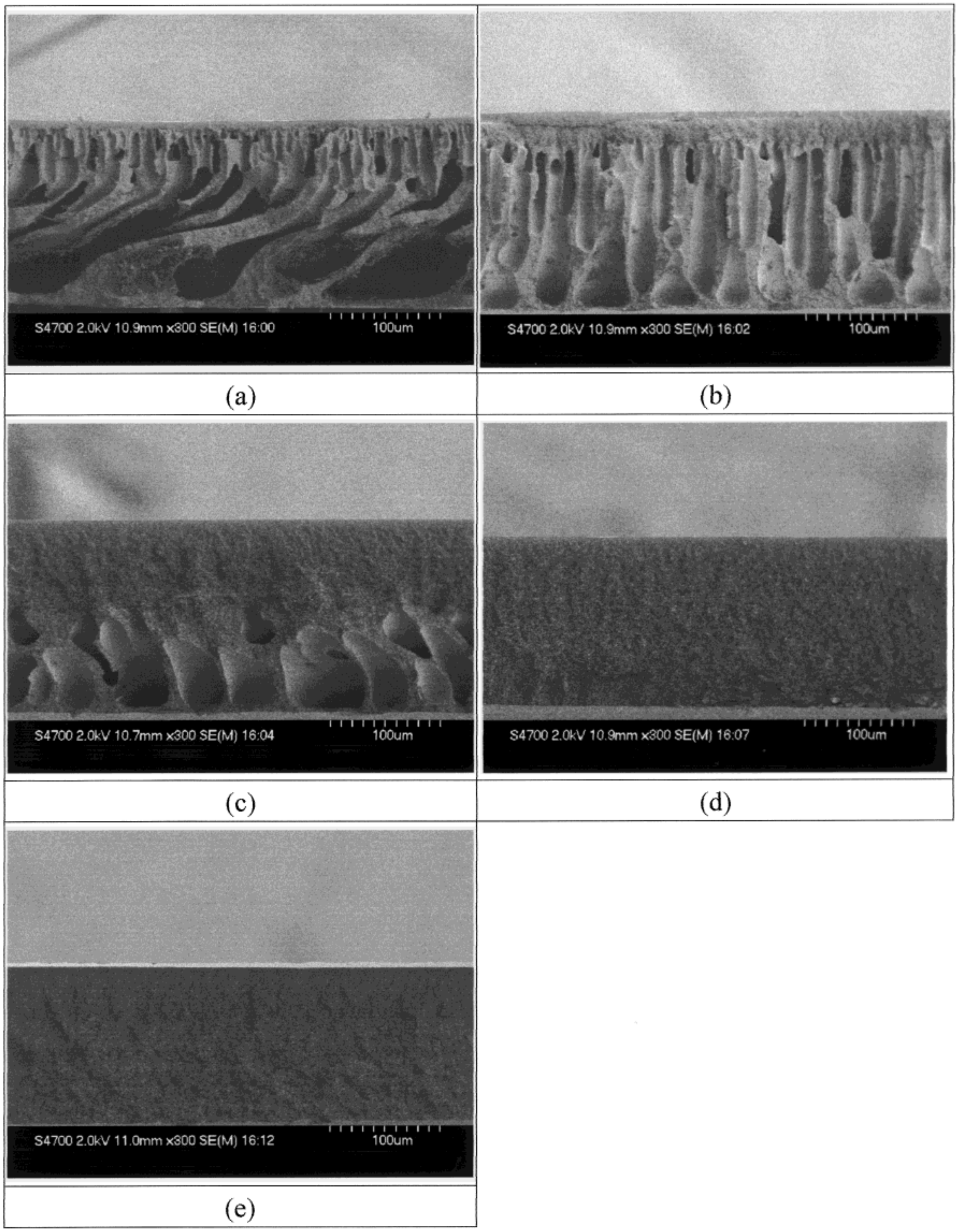


Figure 2. Effect of the addition of water on the structure of PMMA membranes. PMMA concentration: 20 vol %. Water concentration: (a) 0, (b) 5, (c) 8, (d) 11, and (e) 13 vol %.

enough to make the macrovoids disappear (Figure 2d). Usually, the addition of nonsolvent induces the formation of macrovoids because the added nonsolvent makes the dope easier to demix. However, what we observed is in the opposite direction: the growth of macrovoids is inhibited with the addition of nonsolvent. In the following, the associated mechanism of the above observation is discussed.

Evidence was obtained indicating that the effect of water addition on macovoid suppression is strongly related to the gelation of PMMA solution induced by the added water. It was observed that, when enough water was added in the PMMA/NMP solution, the clear homogeneous solution became turbid, indicative of phase separation. Then the solution could either separate to two layers or form a polymer gel (Figure 3). When the solution separated to two layers, the bottom layer was the polymer-rich phase and the top one was the polymer-poor phase. On the other hand, with suitable polymer concentration and enough water, the separation was not observed and the solution became gelled. The amount of water required to induce gelation was found to be almost the same as that required in suppressing macrovoids. For example, when a PMMA/

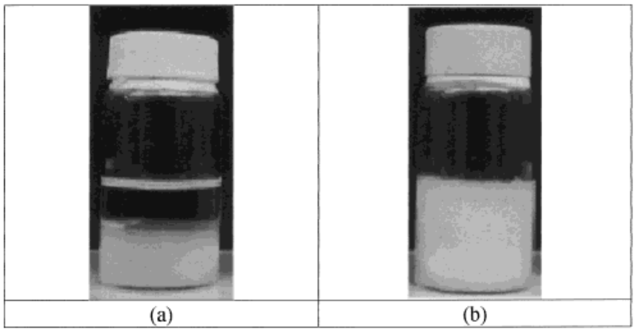


Figure 3. Structure of the demixed solution: (a) separation to two layers; (b) gelation.

NMP/water solution, containing 15 vol % of PMMA and 13 vol % of water, was cooled from 80 to 25 °C, a self-supporting PMMA gel was obtained. When the solution was cast on a glass plate at 80 °C, cooled to 25 °C, and immersed in water to form a membrane, macrovoids did not occur as shown in Figure 1e. On the other hand, when the solution contained 15 vol % of PMMA and 11 vol % of water, although the solution became very viscous, PMMA gels did not form. When the ungelled casting solution was immersed in water, macrovoids were observed in the resulted membrane as indicated in Figure 1d. When the PMMA concentration was raised to 20 vol %, similar results were obtained: the gelled casting solution did not allow the macrovoids to occur (Figure 2d,e), but the immersion of the ungelled solution resulted in membranes with macrovoids (Figure 2a–c). Obviously, there exits a close relationship between the nonsolvent-induced gelation and the macrovoid suppression.

Water Permeation of PMMA Gels. It has been reported[24] that the formation of macrovoids is strongly related to the exchange rate between solvent and nonsolvent during membrane formation. Higher exchange rate indicates a higher tendency for the macrovoids to occur. The exchange rate between solvent and nonsolvent is difficult to measure, and in most research it was estimated by theoretical calculation[24] or by observing the movement of the nonsolvent penetration front.[8] In the present work, FTIR microscopy was used to directly monitor the time dependence of the water concentration in the dope during membrane formation.

The time dependence of water concentration in the dope can be interpreted as the water influx from the coagulation bath to the casting solution. The microscope was focused on a spot in the casting solution near the interface between water and the solution, as shown in Figure 4. FTIR was then used to measure the absorption spectrum at the focused spot. The time dependence of the absorbance at 3536 cm^{-1}, a characteristic wavenumber for water molecules, was measured and is presented in Figure 4. It should be noted that the time scale in Figure 4d,e is seconds but that in Figure 4f is minutes. For the ungelled casting solution (Figure 4d,e), it took about 15 s for water to penetrate from the interface to the measured spot, but it took about 20 min for water to penetrate in the gelled casting solution. It can be seen clearly that the water influx into the gelled casting solution is much lower than that into the ungelled casting solution. The results indicate that, once the casting solution is gelled, the water flux through the gelled layer is greatly reduced. Obviously, the movement of polymer chains in a gel is much more limited than in a viscous solution. Hence, the reduction of water flux could be due to the low mobility of polymer chains in the gelled solution.

On the basis of the above information, a possible mechanism is proposed to account for how the addition of water can suppress the macrovoids in the PMMA membranes: the addition of water can induce the formation of PMMA gels, in which the water permeability is low because of the low mobility of polymer chains, and the gels would then impede the water penetration rate and thus suppress the formation of macrovoids.

On the Gelation Boundary of PMMA/NMP/Water Solution. As mentioned in the Introduction section, the mechanism of the arrest of liquid–liquid demixing by vitrification can account for the nonsolvent-induced gelation process.[11,12] On the basis of this mechanism, a vitrification-related gelation boundary in the ternary phase diagram can be determined. Following the procedures of Li et al.,[12] we constructed the binodal, vitrification line, and gelation boundary in the ternary phase diagram of the PMMA/NMP/water solution, and the results are depicted in Figure 5. When the polymer concentration was low, the binodal was determined from the cloud point experiments. But when the polymer concentration was high, the solution became very viscous and was difficult to be agitated uniformly. Thus, accurate cloud points could not be obtained. Under this circumstance, theoretical calculation based on the extended Flory–Huggins theory[26] was performed to extend the binodal to the region of high polymer concentration. The vitrification line was obtained by measuring the T_g of the polymer solution. First, the T_g of the PMMA/NMP solution was measured, and the results are shown in Figure 6. It can be seen that, with an increase in the amount of NMP, the T_g of the solution decreases, the so-called T_g depression phenomenon. The vitrification composition was obtained by finding the composition at which the T_g equals to the room temperature (25 °C); that is about 73 vol % of PMMA. Then the T_g of the PMMA/NMP/water solution was measured. The ratio of water to NMP was kept at 5 vol %, and the results are also shown in Figure 6. It can be seen that the vitrification polymer concentration is also around 73 vol %, and the T_g depression of PMMA is not sensitive to the water content in the solution. It should be noted that the polymer vitrification composition is also insensitive to the nonsolvent content in the poly(ether sulfone)/NMP/water solution.[12] By using a line to connect these two measured vitrification compositions, we obtained a vitrification line in the PMMA/NMP/water ternary phase diagram, depicted in Figure 5. The gelation boundary is a tie line that across the intersection of the binodal and the vitrification line. For a polymer solution with a composition on the gelation boundary, after demixing, the polymer-rich phase should locate at the vitrification line, and the T_g of the polymer-rich phase should thus equal to the room temperature (25 °C); that is, the polymer-rich phase vitrifies. We kept the PMMA concentration in the polymer solution at 10 vol % and adjusted the NMP/water ratio to bring about phase separation. The T_g of the polymer-rich phase was measured, and the results are reported in Table 1. It can be seen clearly that, with 18 vol % of water in the solution, the T_g of the polymer-rich phase is the same as the room temperature, suggesting this composition is on the gelation boundary. The vitrification-related

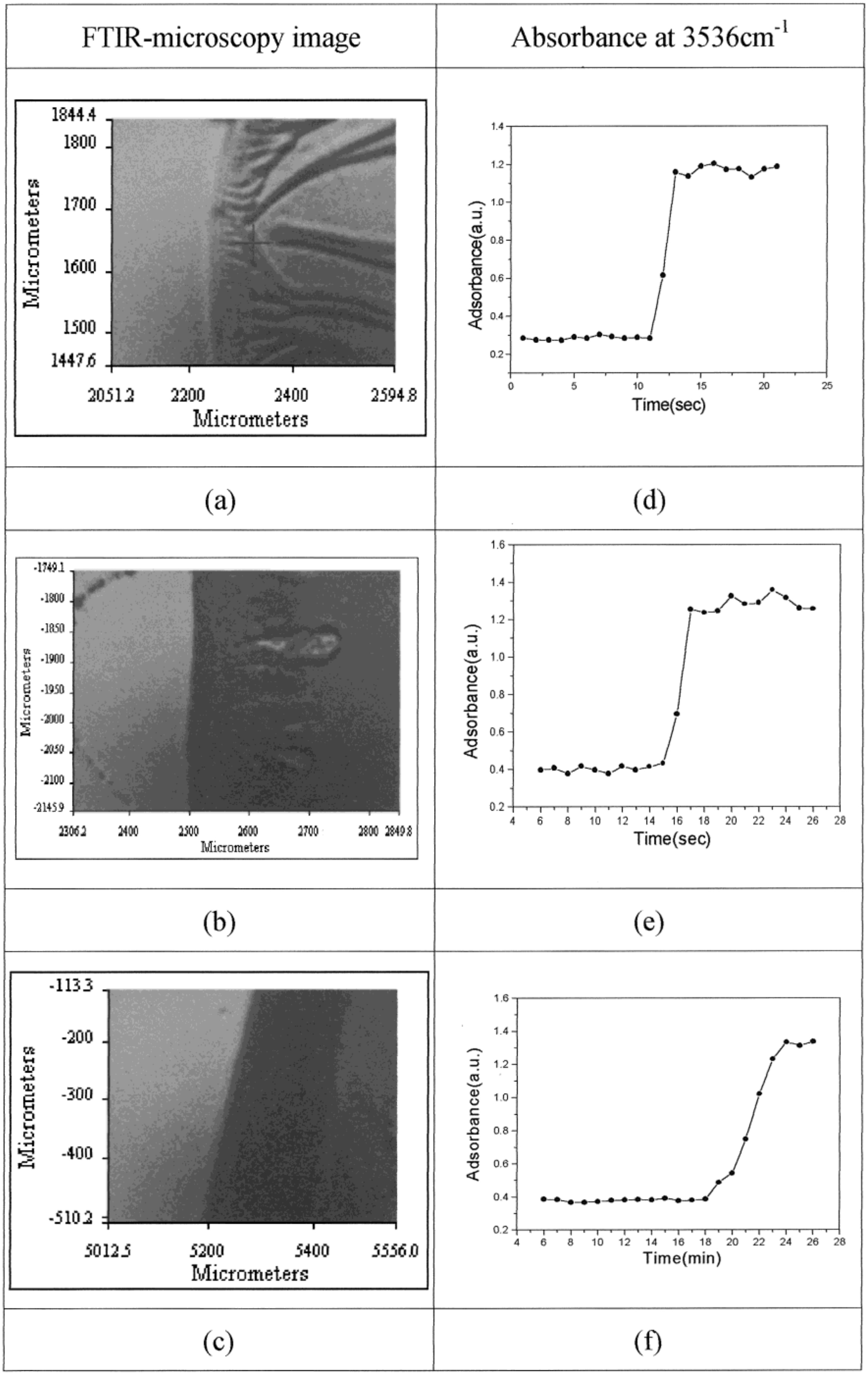
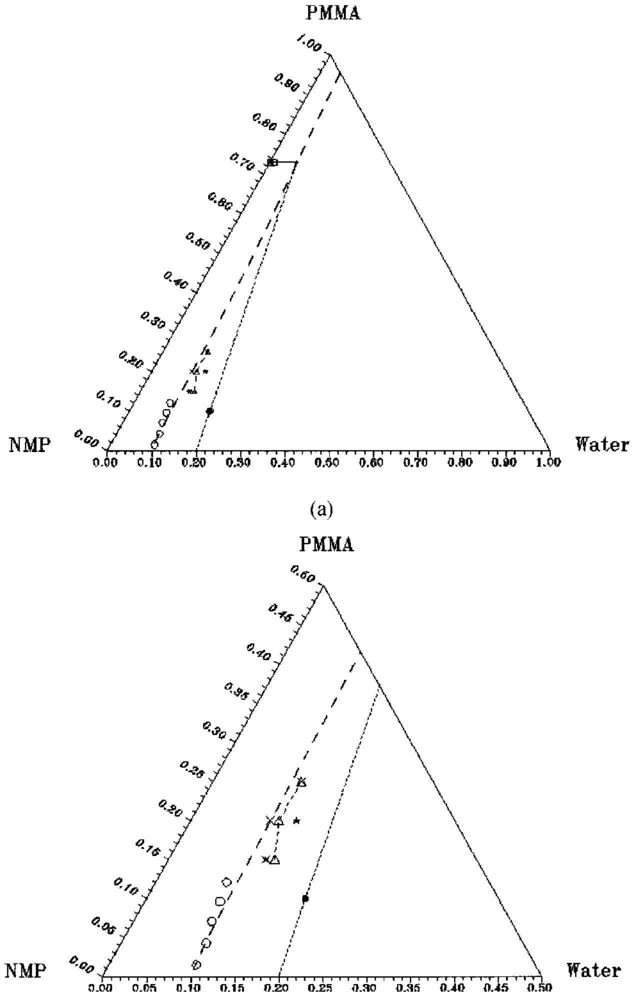


Figure 4. Focused spots and the corresponding time dependence of the absorbance at 3536 cm^{-1}: (a, d) the casting solution containing 20 vol % of PMMA and no water; (b, e) 20 vol % of PMMA and 9 vol % of water; (c, f) 20 vol % of PMMA and 13 vol % of water.



(a)

(b)

Figure 5. (a) Ternary phase diagram of the PMMA/NMP/water solution. (b) Magnification of (a): (— — —) binodal curve (Flory–Huggins theory); (—) vitrification line; (△) elasticity-related gelation boundary; (- - -) vitrification-related gelation boundary; (○) cloud points; (□) vitrification composition (T_g = 25 °C); (△) elation compositions determined by $G' = G''$; (×) compositions to suppress macrovoids; (★) elation compositions determined by falling ball method; (●) composition that the T_g of the polymer-rich phase equals 25 °C.

gelation boundary can then be determined by drawing a line connecting this composition with the intersection of the binodal and the vitrification line (see Figure 5).

We also plot in Figure 5 the compositions at which the macrovoids can be suppressed, the same as the compositions to form self-supporting PMMA gels. These compositions locate in the demixing region but outside the vitrification-related gelation boundary. The results indicate that, after demixing, the polymer-rich phase need not vitrify to bring about polymer gels. The T_g of the polymer gels was measured to further prove that the polymer in gels does not vitrify. The T_g for a gel, with 20 vol % PMMA, 68 vol % NMP, and 12 vol % water, is 0 °C, much lower than the room temperature, indicating that the gel does not vitrify at room temperature. Obviously, a more suitable criterion is needed to determine the gelation boundary other than the vitrification of the polymer-rich phase.

For the nonsolvent-induced gelation process, to from a liquid-containing gel, after demixing, the mobility of the polymer-rich phase should be low enough to hinder the coalescence of the polymer-poor phase. The falling ball method is a simple method to determine whether the movement of polymer-poor phase is hindered. When a steel ball does not fall in a demixing solution, we believe the polymer-poor phase practically does not move at all in that solution. Hence, it is reasonable to use whether or not the ball would fall in a solution to judge if the solution is gelled. The gelation compositions determined by the falling ball method are plotted in Figure 5. It can be seen that the gelation compositions determined by the falling ball method are in good agreement with the compositions at which self-supporting PMMA gels can be obtained, indicating that the falling ball method is an efficient method to determine the gelation boundary.

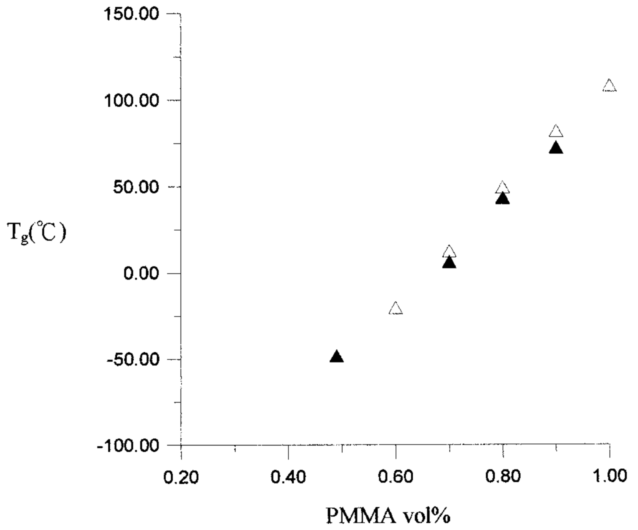


Figure 6. T_g depression for the PMMA/NMP/water solution: △, PMMA/NMP solution; ▲, PMMA/NMP/water solution (ratio of water to NMP: 5 vol %).

Table 1. Glass Transition Temperatures of the PMMA/NMP/Water Solutions

PMMA (vol %)	NMP (vol %)	water (vol %)	T_g (°C)
10	76.5	13.5	6.3
10	72	18	25
10	67.5	22.5	37.5

By using the falling ball method, although we can determine the gelation compositions at which the movement of the polymer-poor phase is hindered, the mechanism of hindering is still not clear. A possible mechanism is the effect of viscous hindering: the hindering is caused by the high viscosity of the polymer-rich phase. In other words, once the viscosity of the polymer-rich phase reaches a threshold, the movement of the polymer-poor phase is hindered and polymer gels can thus form. However, it has been pointed out[12] that, during membrane formation, high viscosity cannot arrest phase separation and lock the morphology in. In our experience, the polymer solution can be highly viscous but still cannot form self-supporting gels. Hence, we do not think the viscous hindering is suitable to describe the gelation behavior observed in the present work. Because the gels we obtained are self-supporting and elastic, the elasticity of the polymer solution must have played an important role in the gelation process. According to the research works related to chemical gelation,[27,28] the elasticity of the solution increases dramatically during the sol–gel transition, and a suitable definition of a chemical gel is that its storage modulus begins to exceed

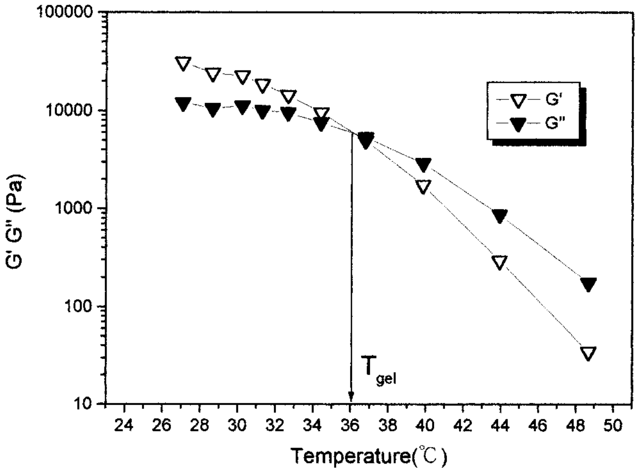


Figure 7. Crossover of the storage and loss moduli and the determination of gelation temperature.

Table 2. Gelation Temperatures ($G' = G''$), in °C, for Various PMMA/NMP/Water Solutions

	water concn (vol %)				
PMMA concn (vol %)	9	10	11	12	13
15		17	22	28	34.5
20		24	31	35	37
25	23	25	33.5	42	

the loss modulus. Hence, a suitable criterion to determine the gelation condition is the crossover of the storage modulus (G') and the loss modulus (G''). In the following we will examine whether $G' = G''$ can also be used to describe the nonsolvent-induced gelation and to see whether the increase in elasticity is the mechanism of hindering.

The procedures used to determine the compositions at which $G' = G''$ are discussed below. In a cooling process, the storage and loss moduli of a polymer solution both increase with decreasing temperature and have a crossover point ($G' = G''$), as shown in Figure 7. The temperature corresponding to the crossover point is defined as the gelation temperature for that polymer solution. To check whether the gelation temperature determined by the above procedure depends on the cooling rate, we measured the gelation temperature at cooling rates of 2 and 10 °C/min. The results indicate that the obtained gelation temperature is insensitive to the cooling rate. When the PMMA solution contains different amounts of water, the gelation temperature changes accordingly, as shown in Table 2. Obviously, the gelation temperature increases with increasing water concentration in the polymer solution, indicating that the PMMA solution containing more water is easier to gel. The composition of the polymer solution of which the gelation temperature is 25 °C is defined as the gelation composition at 25 °C.

In the present work, the measurement of G' and G'' was performed by setting the amplitude of shear stress at 5 Pa and the oscillating frequency at 1 Hz. It is reasonable to suspect that the measurement of gelation temperature and composition might be sensitive to the oscillating frequency and the amplitude of shear stress. We changed the amplitude to 0.5 Pa and remeasured the gelation temperature. The results indicate that, for the two amplitudes, the difference in the gelation temperature is at most 1 °C, and there is almost no difference in the gelation composition. We also adjusted the oscillating frequency to 0.4 and 10 Hz and remeasured the gelation temperature and composition. It was found that, with different oscillating frequency, although the difference in gelation temperature can be up to 10 °C, the difference in gelation composition is only about 1 vol %. Therefore, it can be concluded that the measured gelation composition is not sensitive to the oscillating frequency in the range 0.4−10 Hz and or to the stress amplitude in the range 0.5−5 Pa.

According to Table 2, for a polymer solution with 15 vol % of PMMA, gelation occurs at 25 °C when the water concentration is between 11 and 12 vol %; for 20 vol % of PMMA, gelation occurs with a water concentration between 10 and 11 vol %; and for 25 vol % of PMMA, gelation occurs with a water concentration around 10 vol %. We plot these gelation compositions in the PMMA/NMP/water ternary phase diagram (Figure 5). It can be seen clearly that the gelation compositions, determined via the criterion that $G' = G''$, overlap with the compositions that can suppress the macrovoids, that is, the compositions required to form the self-supporting PMMA gels. The above results support that the criterion of $G' = G''$ can accurately describe the transition from the liquid state to the gel state in the PMMA/NMP/water solution.

On the Gelation Mechanism. The data presented in Figure 5 indicate that the polymer-rich phase does not have to be at the glass transition (vitrification) to lock the morphology in and to form gels. Similar phenomena have been reported in the work of Graham et al.[22] In their work, kinetics of the growth of liquid droplet during nonsolvent-induced phase separation was investigated experimentally by small-angle light scattering[23] and theoretically by spinodal decomposition theory.[22] Their results indicate that the growth of liquid droplets can be practically arrested in the demixing solution once the mobility of the polymer-rich phase is low enough, not necessary to be at the glass transition. On the basis of the work of Graham et al. and the data presented above, it can be deduced that the unvitrified polymer-rich phase can still trap the polymer-poor phase inside, lock the morphology in, and form a liquid-containing polymer gel, once the mobility of the polymer-rich phase is low enough to hinder the movement of the polymer-poor phase. The low mobility of the polymer-rich phase in a gel can be evidenced by the low water permeability shown in Figure 4, and the hinder effect can be indirectly proved by noticing that the steel ball does not fall in a gel.

If vitrification is required to arrest phase separation, the polymer-rich phase must be at the glass transition to form gels.[11,12] However, as discussed in the preceding paragraph, to bring about polymer gels, vitrification is not necessary, and it only requires low mobility of the polymer-rich phase. Then, is there any criterion that can be used to evaluate whether the mobility of the polymer-rich phase is low enough to arrest the phase separation? The present work suggests that the rheological property of the solution is a good choice, and a suitable criterion would be the equality of the storage modulus (G') and the loss modulus (G''). After phase separation, higher polymer concentration in the polymer-rich phase would cause a higher degree of polymer entanglement, indicating higher elasticity and lower mobility in that phase. When the degree of entanglement is high enough to raise the storage modulus to

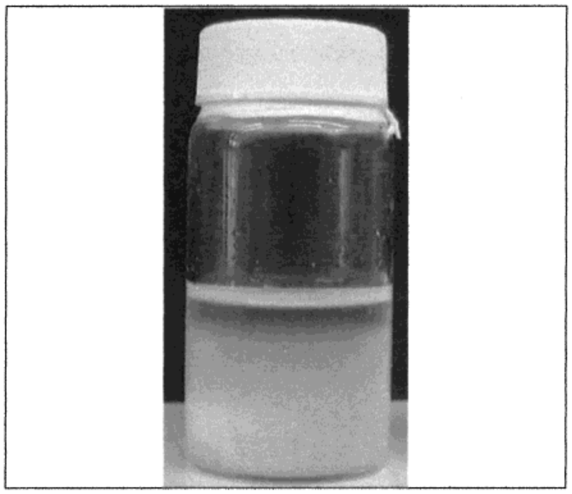


Figure 8. Separation of the unvitrified gels to two layers after the storage of 1 week.

meet $G' = G''$, the mobility of the polymer-rich phase should be low enough to lock the morphology in and to form a polymer gel.

When the polymer-rich phase in a gel does not vitrify but only possesses very low mobility, it is highly possible that the gel structure is not long-term stable because the polymer chain can still move. In fact, the experimental results indicate that the gels we obtained are indeed not stable. As an example, a PMMA/NMP/water solution, containing 20 vol % of PMMA and 12 vol % of water, could form a PMMA gel as illustrated in Figure 3b, but the gel was not stable and would separate to two layers after 1 week as shown in Figure 8. Similar results can also be obtained for the gel from a PMMA solution containing 20 vol % of PMMA and 13 vol %, but it took 2 weeks for the separation to two layers to occur. Obviously, when the composition is closer to the gelation boundary defined by the vitrification of the polymer-rich phase, the gel becomes more stable and takes longer time to separate. Theoretically, if enough water is added to bring the composition into the vitrification-related gelation boundary, a stable gel without separating to two layers should be obtained.

According to the above discussion, it can be concluded that, although polymer gels can form when the polymer-rich phase possesses enough elasticity ($G' = G''$), the unvitrified gels are not stable. To form thermodynamically stable gels, the vitrification of the polymer-rich phase is needed. However, during membrane formation, the gel structure does not need to sustain a couple of weeks to affect the membrane morphology; it only takes seconds or minutes for the membrane structure to be fixed in the wet-inversion process. Hence, to consider the effect of gelation on membrane morphology, the gels need not be thermodynamically stable; a gel that can sustain enough time to affect the penetration of nonsolvent into the casting solution is enough to influence the membrane structure. Considering this, in membrane formation, the vitrification-related gelation boundary is too rigorous. Thus, as indicated in Figure 5, the composition required to generate a gel to suppress macrovoids is outside the vitrification-related gelation boundary. A more suitable gelation boundary can be obtained by using the equality of the storage and loss moduli in the polymer solution.

Conclusion

The addition of nonsolvent in the casting solution can suppress the macrovoids in polymeric membranes if the added nonsolvent can induce polymer gelation. In the model system studied water was added to a PMMA/NMP solution. FTIR microscopy indicated that the formation of PMMA gels results in a great reduction of the water flux from the coagulation bath to the casting solution, which can well account for the disappearance of macrovoids in the PMMA membranes. The associated gelation mechanism was also investigated. A possible mechanism for the nonsolvent-induced gelation, proposed in the literature, is the vitrification of the polymer-rich phase, which can arrest the phase separation and results in liquid (polymer-poor phase) containing gels. However, it was observed that the polymer-rich phase needs not to vitrify to form gels; once it has enough elasticity, self-supporting gels can be obtained. Although the unvitrified gels are not thermodynamically stable, they can be sustained long enough to affect the membrane morphology during membrane formation. The results indicate that the gelation boundary defined by the vitrification mechanism might be suitable to describe the gelation compositions for obtaining thermodynamically stable gels, but to consider the effect of gelation on membrane morphology, it is too rigorous. A new gelation boundary, defined by the equality of the storage and loss moduli in the polymer solution, is more adequate to correlate the effect of gelation on membrane morphology. The gelation compositions on the new gelation boundary are in good agreement with those obtained from the falling ball method.

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