# Microporous Anisotropic Phase Inversion Membranes from Bisphenol A Polycarbonate: Effect of Additives to the Polymer Solution

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**ABSTRACT:** Phase inversion is a very flexible technique to obtain membranes with a large sort of morphologies. Membrane properties can vary greatly depending on the kind of polymer system used. Bisphenol A polycarbonate (PC) could be used as a phase inversion membrane base polymer, and presents very good properties. Nevertheless, very little information on membrane preparation using PC and the phase inversion process can be found in the literature. In this work flat-sheet microporous membranes were obtained by the phase inversion process using the immersion precipitation technique. A new polymer system was studied, consisting of polycarbonate, *N*-methyl-2-pyrrolidone as solvent, water as the nonsolvent, and an additive. The influence of some parameters on membrane morphology, such as polymer solution composition, exposition time before immersion into the precipitation bath, and the kind of additive was investigated. Precipitation was followed using light transmission experiments and membrane morphology was observed through Scanning Electron Microscopy (SEM). The viscosity and cloud points of all polymer solutions were also determined. The results were related to the studied synthesis parameters, using the basic principles of membrane formation by the phase inversion technique, looking forward to establishing criteria to control the morphology of flat-sheet membranes using polycarbonate as the base polymer. The results showed that both additives were able to increase pore interconnectivity and even suppress macrovoid formation. The decrease in the miscibility region of the polymer system and increase in mass transfer resistance are found to be the determining factors during polymer solution precipitation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3085–3096, 2002

**Key words:** membranes; polycarbonates; additives

## INTRODUCTION

Microporous polymer membranes may be prepared using the phase inversion process. This process is rather flexible, and membranes suitable for different processes such as microfiltration or gas separation can be obtained, depending on the polymer system and the preparation conditions.[1–3]

In a previous article,[4] microporous membrane formation using a ternary polycarbonate (PC) system and phase inversion by immersion precipitation technique was studied. Polycarbonate is a polymer with excellent properties and widely used in a great number of applications.[5] However, few studies about membrane formation by the wet phase inversion technique using polycarbonate as a base polymer can be found in the literature.[6–9]

Additives are normally used in polymer solutions to enhance final membrane properties. Nevertheless, the use of additives implies in a more complex system, because a fourth component is present. Therefore, further investigation is needed to control membrane final morphology and properties.[10–13]

The aim of this article is to investigate the effect of additives on the preparation of microporous membranes by the phase inversion and immersion precipitation technique, using polycarbonate as the base polymer. A polymeric and an inorganic additive were tested. The behavior of these systems was studied, as well as the phenomena involved in membrane formation by immersion precipitation. The final objective was to obtain a better comprehension of the influence of the synthesis variables on membrane morphology.

### Phase inversion process

Phase inversion is based on bringing a polymer solution to become unstable. To minimize the free energy of a mixture, the solution may separate into two phases. A polymer solution may become unstable by temperature variation, solvent evaporation, or by mass exchange with a nonsolvent bath. After the initial disturbance, a mass transfer process begins, and
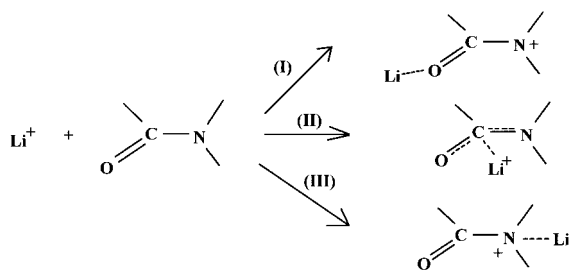
**Figure 1** Interaction possibilities between the Li$^+$ ion and the amide group.[27]

the solution can start demixing into two phases—one rich and the other lean in polymer—in a process called liquid–liquid demixing. After liquid–liquid demixing, the polymer-rich phase may be immobilized by viscous effects promoted by crystallization, gelation, or glass transition, which depend on the kind of polymer system used.

The immersion precipitation technique consists in the immersion of a thin polymer solution film, cast onto a suitable surface, into a precipitation bath containing a nonsolvent to the polymer. After the immersion of a polymer solution into the nonsolvent bath, the inflow of nonsolvent into the polymer solution and the outflow of solvent out of the solution will immediately start, what may cause the solution to demix. A ternary system will then be formed, containing polymer, solvent, and nonsolvent. With this technique a number sort of membrane morphologies can be obtained, depending on the choice of the solvent and nonsolvent to the polymer, as well as the precipitation bath composition.

### The influence of an additive to the polymer solution

Additives are frequently used in polymer solutions to enhance final membrane properties. For instance, compounds that are able to form Lewis acid-base com-
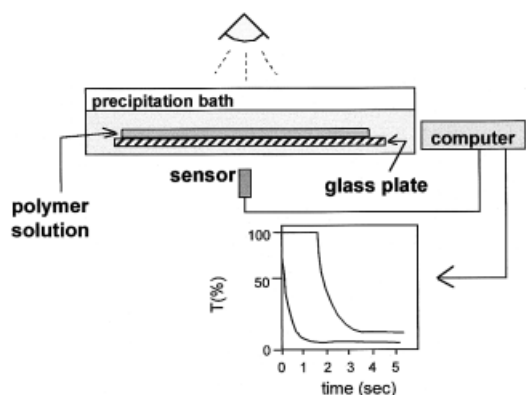


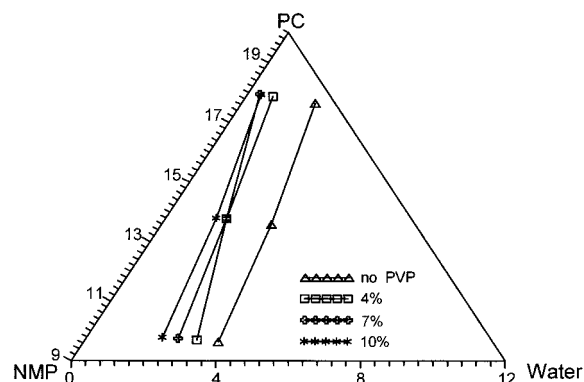**Figure 2** Experimental apparatus for the precipitation kinetics measurements.



**Figure 3** Pseudoternary diagrams for PC/NMP/PVP/water system.

plexes with the solvent of the polymer solution may be employed in the preparation of gas separation membranes.[14–16] Additives are commonly used in ultrafiltration membranes to decrease the tendency of adsorption of some components on the membrane surface, which may reduce membrane performance.[10,17,18] They can also be used when it is necessary to increase solution viscosity without increasing polymer composition. This is very useful when hollow fiber preparation is intended. In hollow fiber spinning, the polymer solution should have a minimum viscosity to make the process feasible.[10,18,19]

The introduction of another component to the polymer solution increases, though, the complexity of the system, changing the phase equilibrium and mass transfer rates. A four-component system, at constant temperature, may be represented by a tetrahedron. In such diagram, each vertex stands for a pure component; each edge represents a mixture of two compo-
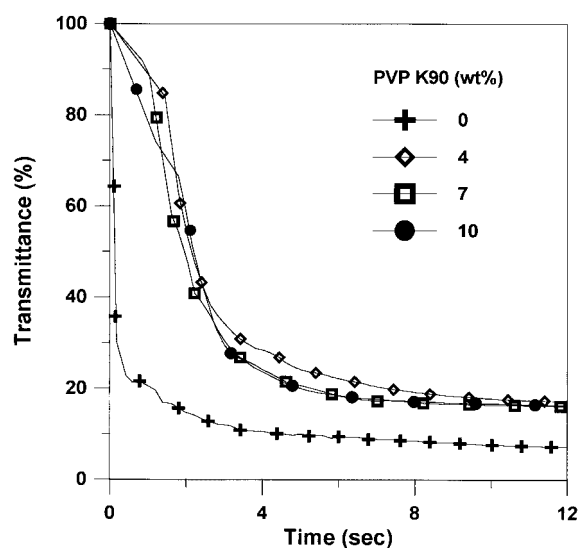


**Figure 4** Effect of PVP concentration on light transmission of solutions (14 wt % PC) directly immersed into the nonsolvent bath.
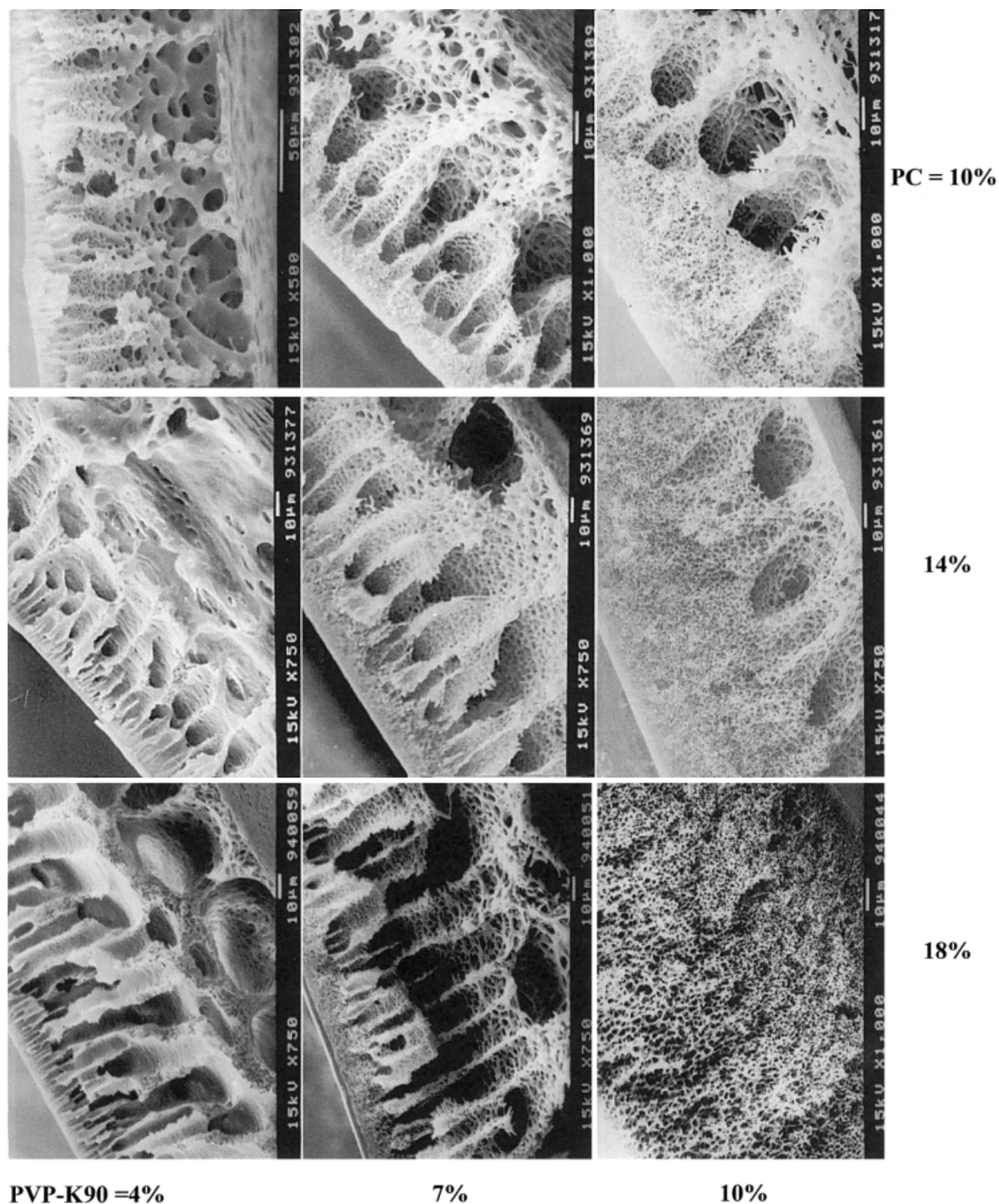
**Figure 5** Effect of PVP K90 and PC concentration on membrane cross-section morphology. Direct immersion into the nonsolvent bath.

nents, while a point in the figure stands for a mixture of the four components. Due to the high complexity, quaternary systems are normally represented by pseudoternary diagrams, where the polymer and additive are represented as a single component.[10] In this work, the cloud-point curves are represented by the intersections between the cloud-point surface and transverse planes to the tetrahedron.

Many authors have investigated the effect of additives on membrane morphology and properties. Several organic and polymeric additives have already been studied, such as ethyleneglycol,[20] phenantrene, pyrene, and triphenyl phosphate,[13] polyvinylpyrrolidone (PVP),[10,17,18,23] polyethyleneglycol,[12] and polystyrene.[13] Some inorganic additives have also been proposed, such as $CaCl_2$,[11] $CuCl_2$, $CoCl_2$, $FeCl_3$, $ZnCl_2$,[21] and $LiNO_3$.[22]
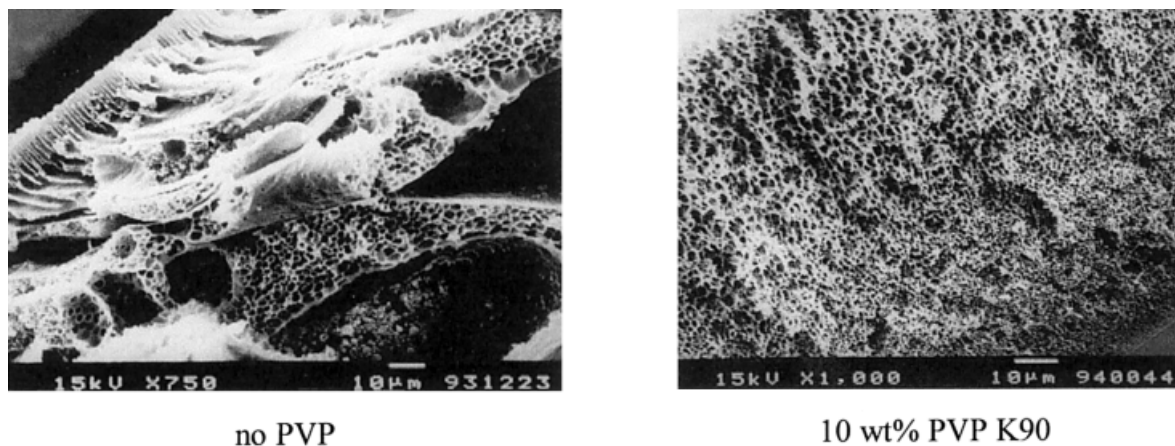
**Figure 6** Comparison between membranes with and without PVP. PC concentration is the same for both membranes (18 wt %).

Polyvinylpyrrolidone (PVP) is remarkably one of the most studied and commercially used additives for microfiltration and ultrafiltration membrane preparation.[10,18,22,24] This is a water-soluble polymer, miscible with many organic solvent and polymers. The main effects of PVP have been found out mostly by morphology and transport properties observation. It is reported that the addition of PVP normally leads to instantaneous demixing, increase on membrane surface porosity and pore interconnectivity.[10,17,18,22] Using a minimal amount of PVP it is also possible to suppress the occurrence of macrovoids in membrane sublayers. Most of the PVP added to the solution is removed during phase inversion process, as well as in the postprecipitation treatment steps,[22] and the remaining of this additive can be found at the membrane surface, what can alter membrane hydrophilicity. A great increase in membrane viscosity is also usual, creating suitable conditions for hollow fiber spinning.

Some authors have proposed mechanisms to explain the effect of PVP on membrane morphology. Roesink[25] suggests that during phase separation, PVP would move from the concentrated base polymer phase to the nuclei containing the diluted phase. By the time of precipitation, a concentration gradient of PVP would be created, leading to high concentration of PVP at the surface of the nuclei, due to the high molecular weight of PVP and its consequent low mobility in the solution. This way, during the drying steps, the thin layer of polymer between two nuclei could break originating pore interconnectivity.

Boom[10] has studied the influence of this additive in solutions containing Polyethersulfone, *N*-methyl-2-pyrrolidone, and water. He has proposed a thermodynamic model and mechanisms to describe the first moments of the demixing process in such systems based on Reuvers' model[26] to describe ternary systems. The proposed mechanism admits two time
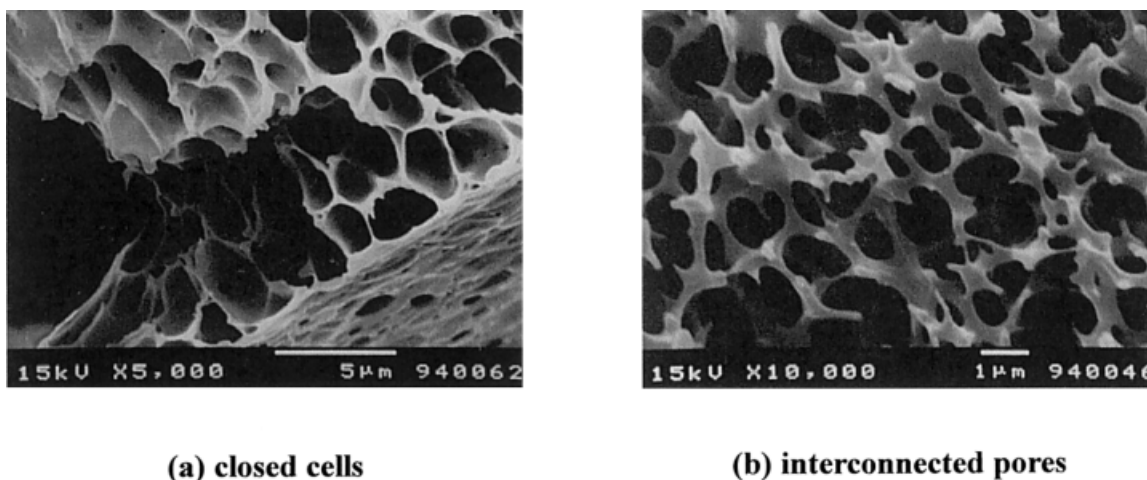


**Figure 7** SEM micrographs of membrane cross-section near inferior surface of membranes obtained from solutions containing 18 wt % PC and (a) 4 wt % PVP K90, and (b) 10 wt % PVP K90.

**TABLE I**
**Effect of PVP Concentration on Precipitation Onset of Polymer Solutions (14 wt %) Precipitated by Long Exposure Time to the Air**

| PVP K90 (wt %) | Precipitation Onset (min) |
| --- | --- |
| 0 | 4.8 |
| 4 | 1.9 |
| 7 | 1.9 |
| 10 | 1.7 |

scales during precipitation. In a short time scale, the base polymer and PVP act like only one component, because the mobility of one polymer in relation to the other is negligible. In a longer time scale, the movement between the two polymers is possible, and the additive moves into the base polymer lean phase. Thus, a "virtual" binodal that is valid for the short time scale may be calculated. This binodal is located nearer the polymer/nonsolvent axis than the actual binodal, increasing the miscibility of the system. Therefore, the system would admit a higher amount of nonsolvent in the short time scale. When the movement between the two polymers is considerable, the actual binodal is valid again, and compositions of some layers along the cross section of the polymer solution film could be located inside the two-phase region, promoting instantaneous demixing or spinodal decomposition. This is characterized by the formation of two new phases, interconnected, without nuclei formation. This kind of mechanism would explain the high interconnectivity observed in membranes obtained from solutions containing PVP.

Among the several additives used in phase inversion process that are reported in literature, some can interact with solvents like N-methyl-2-pyrrolidone, originating complexes, increasing solution viscosity, decreasing miscibility and thus accelerating precipitation. Lithium nitrate ($LiNO_3$) has been used as additive in an earlier investigation.[22] This is a water-soluble salt, also soluble in N-methyl-2-pyrrolidone (NMP). This salt induces the increase in viscosity when added to the polymer solution. This increase can be correlated with the interaction possibilities of the ion $Li^+$ and the amide group present in the solvent NMP, as suggested by the literature,[27] shown in Figure 1. The use of lithium nitrate as additive has an advantage over the use of PVP, because this salt can be easily and almost completely removed from the polymer matrix due to its low molecular weight.

## EXPERIMENTAL

Polycarbonate (Durolon® I-2700, $M_w$ = 40,000, Policarbonatos do Brasil), PC, dried at least for 24 h at 60°C, was dissolved in N-methyl-2-pyrrolidone, NMP (Al-

drich), in a concentration range of 10 to 18 wt %. Polyvinylpyrrolidone, PVP (Sigma) and Lithium nitrate, $LiNO_3$ (Vetec) were also dried for at least 24 h at 60°C. The average molecular weight of PVP used was 360,000 (K90) Dalton, in concentrations ranging from 4 to 10 wt %. $LiNO_3$ concentrations were between 2.0 and 4.5 wt %. The cloud-points were determined at 25°C using a jacketed and sealed flask. Water was added with a syringe, through a septum, to a known amount of the polymer solution, while the solution was constantly stirred. The cloud-point was determined when turbidity of the solution persisted over 24 h. The viscosity of all polymer solutions was measured using a rotating viscometer (Brookfield), at 25°C.

To prepare flat membranes, polymer solutions were cast with a thickness of 0.130 mm onto a glass plate, and were immediately immersed into a water bath. The local relative humidity was in the range of 65–75%. The precipitation of the solution could be followed using the setup presented in Figure 2. Measurements with longer exposure time to the air were carried out placing the glass plate directly above the detector, without the water bath. The precipitation, in this case, occurs due to water absorption from the air. After precipitation, membranes were immersed into a water bath at 60°C for 24 h, and then dried after solvent replacement (ethanol and n-hexane).[28] Membrane samples were broken in liquid nitrogen, metallized, and observed by Scanning Electron Microscopy (SEM, JEOL 5300).

## RESULTS

### Polymeric additive (pvp)

#### Miscibility gap

The cloud-point measurements are represented here as pseudoternary diagrams, where the curves stand for the intersection of the cloud-point surface with the plane of constant PVP concentration.The reduction of the miscibility gap with the increase in PVP concentration can be clearly observed from Figure 3. This behavior could be related to the fact that the mixture of two polymers is not favorable from the entropy point of view. Thus, the addition of the second polymer turns the system more sensitive to disturbances like the addition of nonsolvent.[10]

#### Light transmission experiments and membrane morphology

All studied compositions presented instantaneous demixing when immersed into the precipitation bath. Figure 4 shows some plots that illustrate the effect of the addition of PVP K90 to solutions containing 14 wt % PC on the light transmission of the polymer film
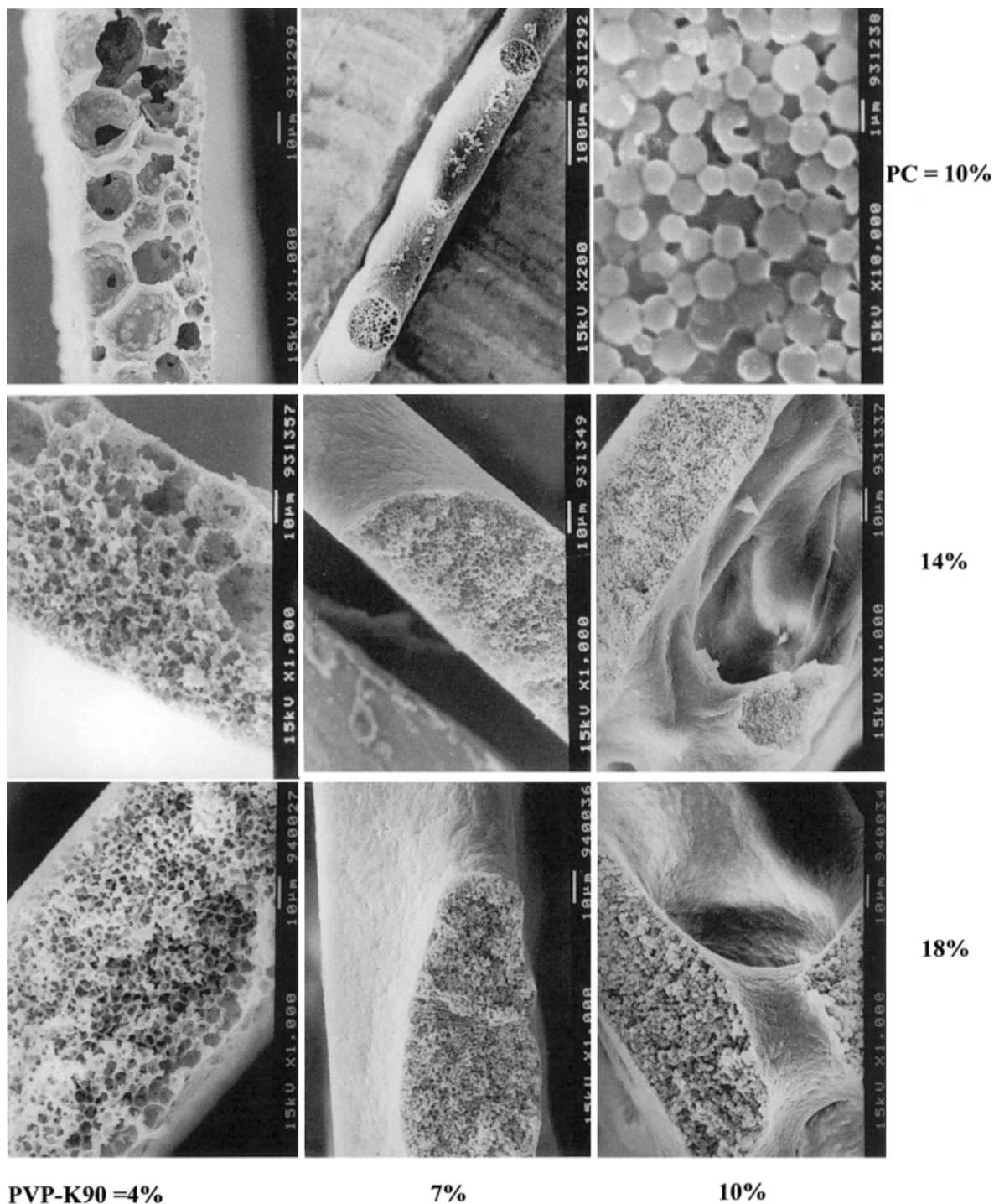
**Figure 8**  Effect of PVP K90 and PC concentration on membrane cross-section morphology. Precipitation by long exposure time to the air.

during precipitation. The results show that the addition of PVP leads to a decrease in the global precipitation rate of the solutions. It can also be noted that no significant difference is observed in the rate when PVP concentration is increased. These behaviors can be attributed to the increase in solution viscosity and the reduction of the miscibility gap, respectively.[10,18,22,29]

Figure 5 shows the influence of PVP K90 and PC concentration on membrane cross-section morphology. The increase of polymer concentration can even suppress macrovoid formation in membrane sublayers. This is related to the fact that a higher polymer concentration decreases the miscibility gap. Consequently, highly unstable compositions are generated
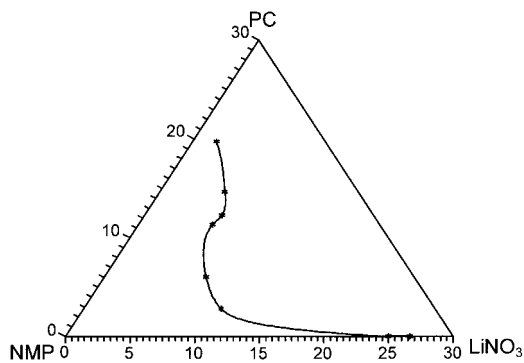
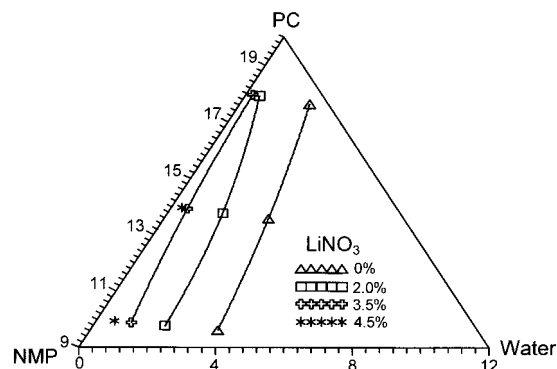**Figure 9** Cloud-point curve for the PC/NMP/LiNO$_3$ system.



**Figure 10** Pseudoternary diagram for the system PC/NMP/LiNO$_3$/water.

along the cross section, hindering the growth of macrovoids, which need stable compositions around for their growth. It can be clearly noted that a minimum amount of PVP is needed to promote complete suppression of macrovoids.

When membranes obtained from ternary solutions are compared to those using PVP in the polymer solution and the same concentration of PC (Fig. 6), it may be noted that PVP leads to changes in morphology, increasing pore interconnectivity. In a ternary system, poorly interconnected pores are predominant. Those are originated from phase separation by nucleation and growth of the polymer lean phase, in which nuclei expansion was limited. As mentioned before, the interconnectivity obtained when PVP is used in the polymer solution could be result of a spinodal demixing mechanism.

Even with the addition of PVP, "closed-cell" morphology could also be observed in the cross-section of some membranes. Nevertheless, the increase in concentration of PVP causes the complete elimination of

this kind of structures, replaced by interconnected pores. Figure 7 shows the two structures, obtained from direct immersion of solutions containing 18 wt % PC with 4 and 10 wt % PVP K90. It can be observed that in the membrane obtained from solution containing 4 wt % PVP closed cells are still present in its cross section.

Table I shows the effect of PVP concentration on the precipitation onset of solutions containing 14 wt % PC for precipitation by longer exposure time to the air. For higher PVP concentration there is a decrease in precipitation onset. This result is in agreement with the miscibility gap results.

Figure 8 shows the effect of PVP and PC concentration on membrane cross-section morphology, obtained by precipitation by long exposure time to the air. All solution compositions formed membranes, except the one containing 10 wt % PC and 10 wt % PVP, which originated a polymer latex formed by polymer beads. In this case, nucleation and growth
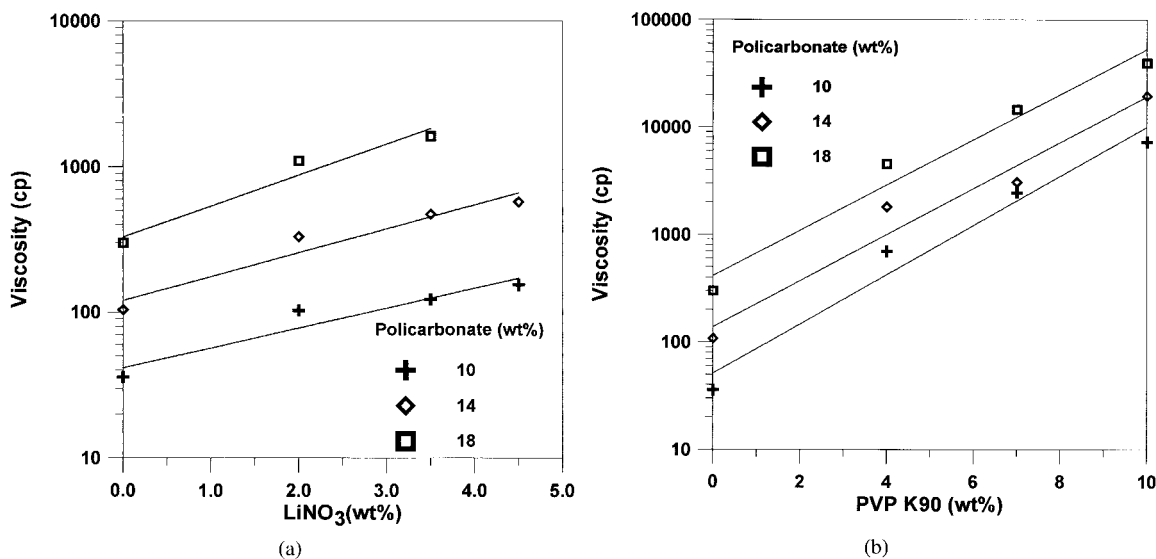


(a)



(b)

**Figure 11** Effect of PC and (a) LiNO$_3$ and (b) PVP on the polymer solution viscosity.
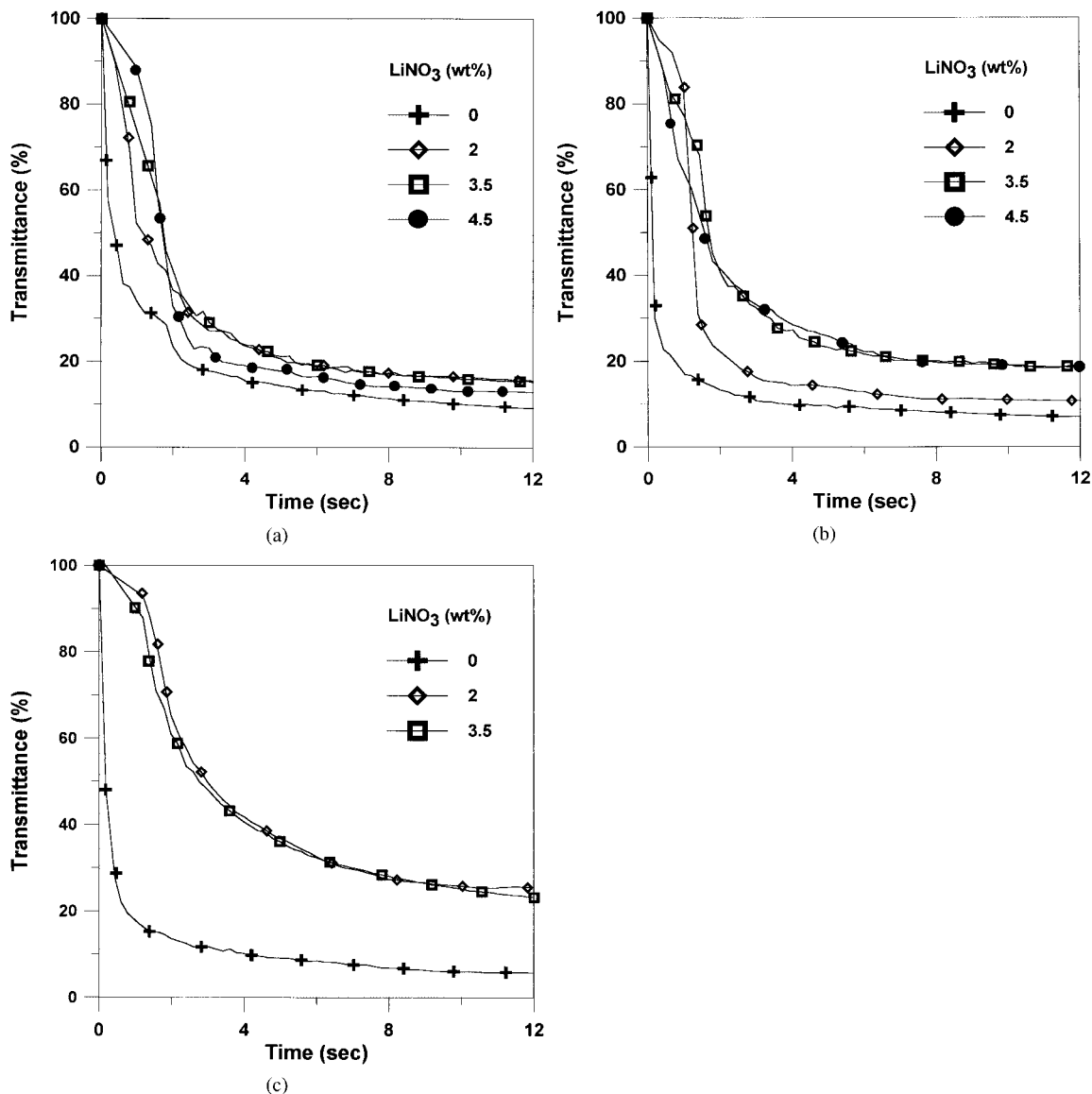
**Figure 12** Effect of LiNO$_3$ concentration on light transmission of solutions directly immersed into the nonsolvent bath: (a) 10 wt % PC, (b) 14 wt % PC, and (c) 18 wt % PC.

of the polymer rich phase was the main mechanism of formation, characterizing liquid–liquid phase separation and precipitation below the critical line, near the surface ADD/S/NS. Solutions containing 10 wt % PC and 7 or 10 wt % PVP formed mechanically stable membranes, even though these showed big voids, as well as formation of big amounts of polymer latex during precipitation, with similar characteristics to the one described before. This fact suggests that these conditions were very near the critical line, favoring precipitation of part of the solution by nucleation and growth of the polymer rich phase. Membranes obtained from solutions with low concentration of PVP presented pores typical of polymer lean phase nucleation and growth mechanism, poorly interconnected.

**Inorganic additive (liNO$_3$)**

Miscibility gap

Tests to determine LiNO$_3$ solubility in water and in NMP were made by titration. Subsequently, PC/NMP solutions were titrated with a LiNO$_3$/NMP solution. The cloud-point curve is showed in the diagram presented in Figure 9.

The characteristic behavior of this curve, presenting an inflexion point and turning towards the PC/NMP axis, may be due to the fact that this curve stands for two different boundaries. The first (and lower) part of the curve may represent the binodal curve, while the upper part, the viscous effects boundary.
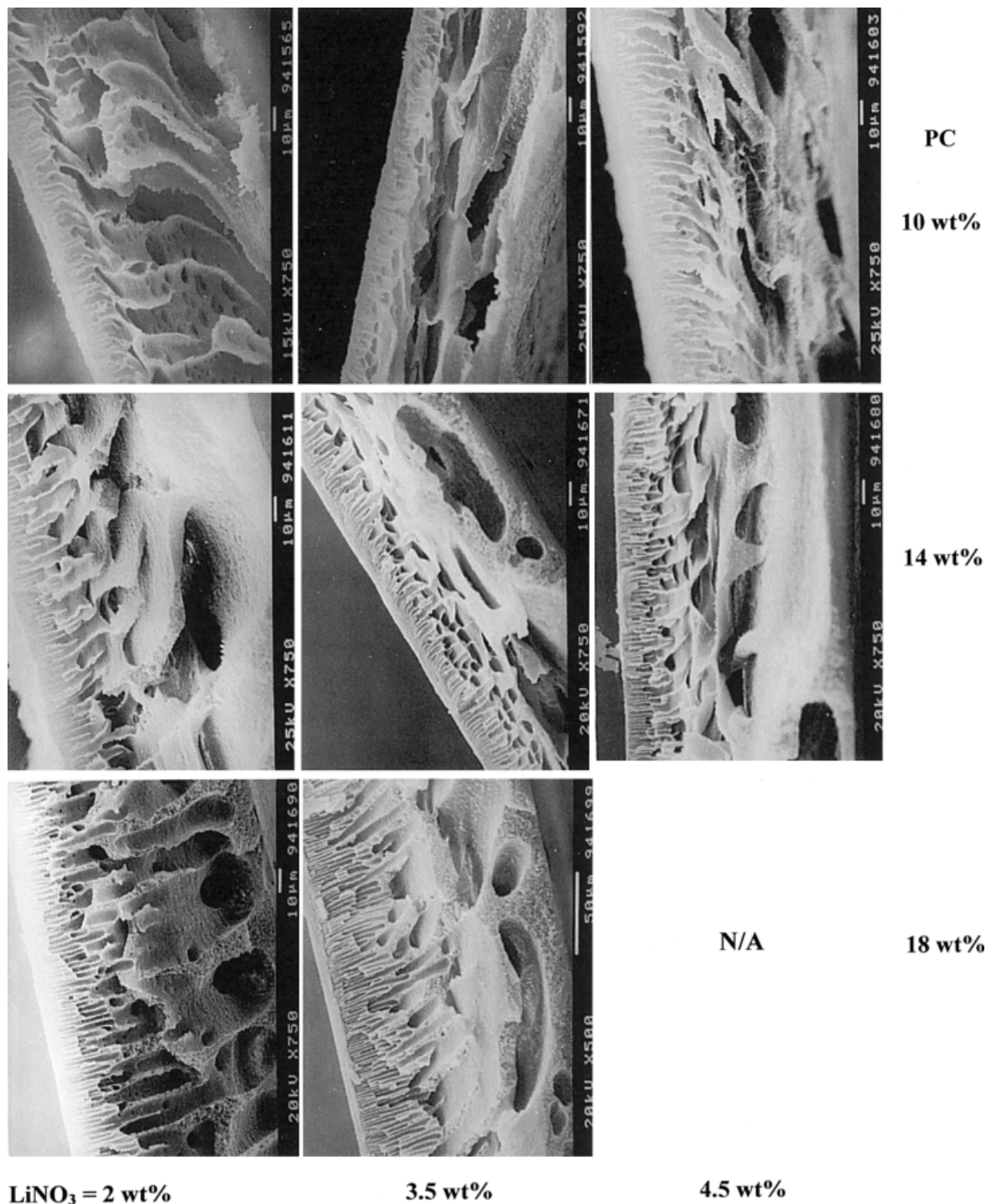
**Figure 13** Effect of LiNO$_3$ and PC concentration on membrane cross-sections morphology. Direct immersion into the nonsolvent bath. (N/A = unstable solution).

After determination of cloud-point compositions of the ternary system PC/NMP/LiNO$_3$, the pseudoternary diagram was determined. The results are represented in Figure 10. Each curve in this diagram represents the intersection of planes of constant LiNO$_3$ concentration with the quaternary diagram. This figure shows that the addition of LiNO$_3$ to the polymer solution decreases strongly the miscibility gap of the system, possibly due to interactions of the solvent with this additive.

Viscosity

Viscosity of the studied solutions are presented in Figure 11 and compared to PVP increase in viscosity. As expected, the addition of the salt to the polymer
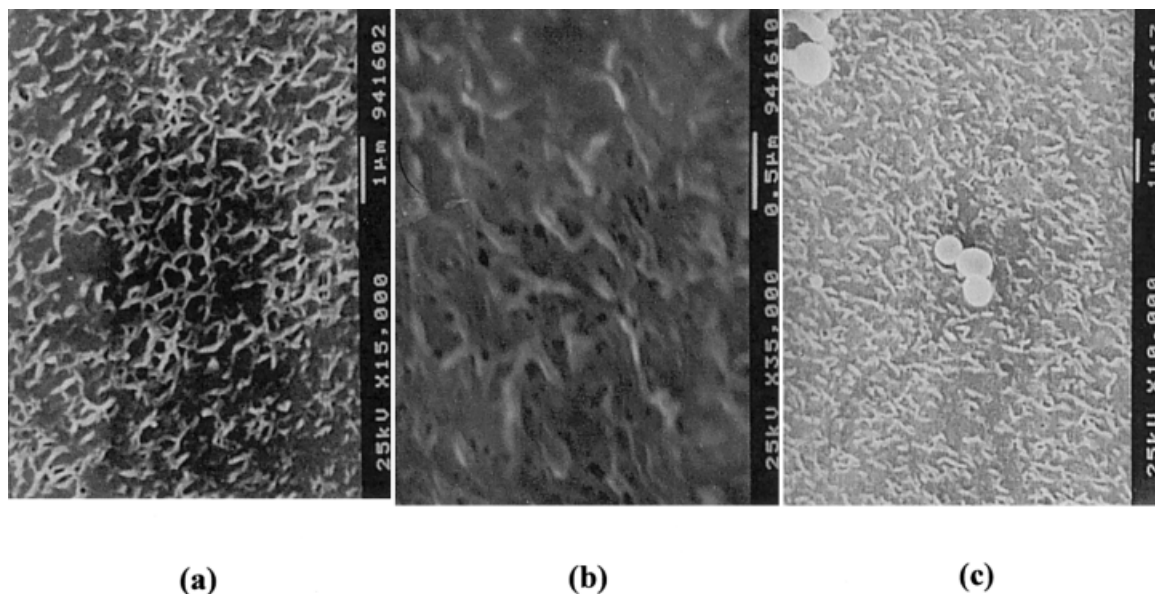
**Figure 14** Top surfaces of membranes obtained by direct immersion into the nonsolvent bath: (a) 10 wt % PC and 3.5 wt % LiNO$_3$, (b) 10 wt % PC and 4.5 wt % LiNO$_3$, and (c) 14 wt % PC and 2.0 wt % LiNO$_3$.

solutions increases the viscosity, due to the complex formation with the solvent, but this increase is much lower than that obtained with the addition of PVP, because this is a polymeric additive.

### Light transmission experiments and membrane morphology

Figure 12 shows the effect of lithium nitrate concentration on light transmission during precipitation, for different PC concentrations. The light transmission measurements show that the addition of LiNO$_3$ to the solution leads to a decrease in precipitation rate, which is more intense as PC concentration increases. As it was already presented, an increase in LiNO$_3$ concentration makes the miscibility of the solution to decrease and the viscosity to increase. The higher viscosity may reduce the mass transfer rates between the polymer solution and the bath, what reduces the precipitation rates. However, faster precipitation at the interface bath/solution, due to the reduction of the miscibility gap, could develop a resistance to mass transfer at the interface between the bath and the polymer film, also reducing the precipitation rate. An increase in PC concentration amplifies these effects.

Figure 13 shows the effect of PC and LiNO$_3$ concentration on the cross section of membranes obtained by direct immersion of the film into the nonsolvent bath. In general, the addition of LiNO$_3$ to the polymer solution causes membrane sublayers to become well arranged, and the increase of LiNO$_3$ concentration does not significantly affect the membrane morphology. Differently from PVP additive, LiNO$_3$ addition was not able to suppress macrovoid formation.

Top surface of membranes precipitated from solutions composed of 10 wt % PC and 3.5 and 4.5 wt % of LiNO$_3$ and 14 wt % PC with 2.0 wt % LiNO$_3$ showed some rugged structures (Fig. 14). Membranes obtained from solutions composed of 14 wt % PC with 3.5 and 4.5 wt % of LiNO$_3$ and of 18 wt % PC did not show such structures, suggesting that this morphology is related to low concentrations of polycarbonate and additive. Possibly the origin of such microstructures are tightly related with gelation or even crystallization of PC, which has already been observed in other studies of the authors.[30] DSC (differential scanning calorimetry) and X-ray diffraction were performed in all membranes and no residual solvent neither lithium nitrate could be detected.

Cross-sections from membranes obtained by long exposure to the air are presented in Figure 15. Membranes obtained from solutions containing 10 wt % PC, differently from those obtained with solutions containing 14 wt %, showed an irregular cross-section, with macrovoids and large holes through the membrane. Spherical pores can be encountered in all cross-sections, which suggests that liquid–liquid demixing by nucleation and growth of polymer rich-phase is the predominant mechanism in these conditions. The increase in PC concentration on the solution leads to a higher uniformity of membrane morphology and reduces the pore size in membrane sublayers once again. This behavior is probably due to the reducing of miscibility region when polymer concentration is increased. This way, the nuclei growth is not favored, because the polymer solution becomes close to instability.
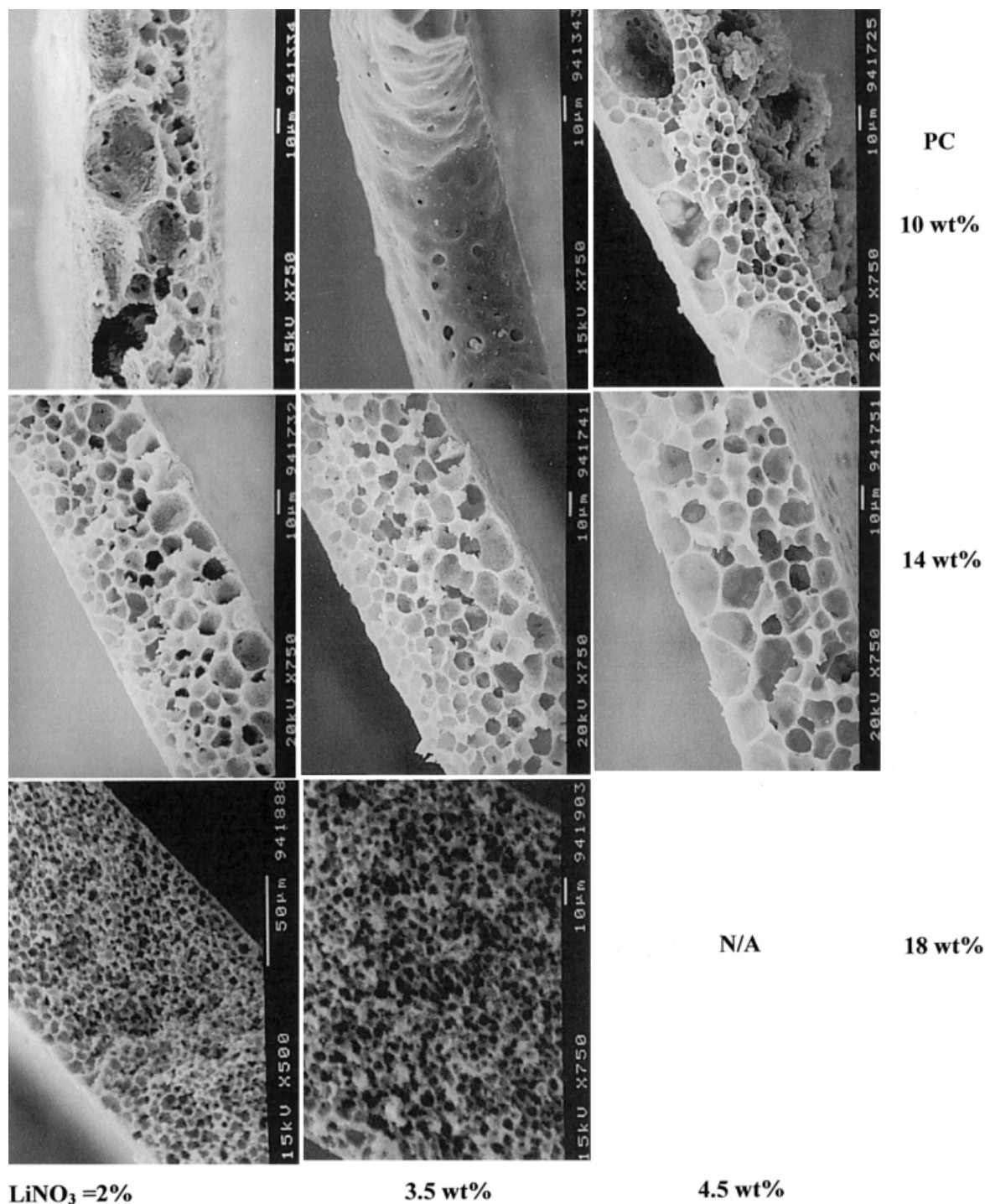
**Figure 15** Effect of LiNO$_3$ and PC concentration on membrane cross-section morphology. Precipitation by long exposure time to the air (N/A = unstable solution).

## CONCLUSIONS

The present work showed that Bisphenol-A Polycarbonate can be used as a base polymer to prepare phase inversion microporous membranes and a great sort of morphologies could be obtained. The addition of LiNO$_3$ to the polymer solution proved to be a good way to increase solution viscosity without leaving residues of the additive in the final membrane. This additive was also able to increase the regularity in sublayer pores. This latter effect was related with the complex formation between the Li$^+$ ion and the solvent (NMP) and consequent reduction of the miscibility gap. Another effect of the addition of the salt was the increase in pore interconnectivity and increase in pore size on membrane

surface. Addition of polyvinylpyrrolidone (PVP) to the polymer solution changed membrane morphology more markedly than the inorganic additive. PVP induced high pore interconnectivity and could even suppress macrovoid formation, depending on the amount added to the polymer solution.

In general, it could be pointed out that the decrease in the miscibility region and increase in mass transfer resistance are determining factors during polymer solution precipitation. The correct manipulation of he variables involved in phase inversion process allows obtaining different types of membranes, suitable to many applications.

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