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# Microporous anisotropic phase inversion membranes from bisphenol-A polycarbonate: study of a ternary system

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**Abstract**

The aim of this work was to investigate anisotropic microporous membrane formation by phase inversion; using immersion precipitation technique and a ternary polymer system consisting of bisphenol-A polycarbonate, *N*-methyl-2-pyrrolidone as solvent and water as non-solvent to the polymer. Membrane morphology was observed by scanning electron microscopy (SEM) and related to some variables involved in membrane synthesis with the help of cloud-point measurements and precipitation kinetics, determined by means of light transmission experiments. The results show that the studied system presents a very small miscibility gap, which favors instantaneous demixing and the mechanism of nucleation and growth of the polymer lean phase, as well as macrovoid formation, yielding membranes with big macrovoids and low-pore interconnectivity, when directly immersed into a non-solvent bath. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords*: Microporous membrane; Polycarbonate; Phase inversion

## 1. Introduction

Since when Loeb and Sourirajan [1] developed the first anisotropic membranes by phase inversion using cellulose acetate by the end of the 1960s, the production of synthetic polymeric membranes has been widely investigated [2]. In the last 30 years, a large number of new polymeric materials was discovered and many of the new polymers have been used in membrane preparation. It also became clear that in membrane processes, the development of membranes with transport properties suitable to the desired separation is of fundamental importance [3]. These facts brought up the necessity of researches that investigate membrane formation by phase inversion using the newly formed systems, so that membrane morphology and transport properties can be efficiently controlled.

Many phase inversion membranes used in microfiltration and ultrafiltration processes use polymers that have high thermal and chemical resistance, such as polyethersulfone, polysulfone, polyetherimide, polyimide, etc. Polycarbonate (PC) is also a polymer with excellent properties and widely used in a great number of applications [4]. However, there are few works that study membrane formation by phase inversion technique using PC as base polymer. Most of these works involve dense anisotropic membrane preparation for gas permeation processes [5–11]. It is also reported that dense films of PC are used in the microfiltration membrane preparation by track-etching technique. However, membranes obtained in such a way show very low surface porosity [12–14].

Phase inversion is one of the most used techniques to prepare microporous membranes. It is based on turning a polymeric solution to become unstable, which can be accomplished by the modification of the solution temperature or by the introduction of another component to the solution, a non-solvent to the base polymer. In order to minimize the free energy of mixture, phase separation can occur and a new equilibrium state is reached [15–17].

In the phase separation process, formation of at least two new phases is possible: one rich and the other lean in polymer. Mass transfer between the two phases makes the new disperse phase to grow, until viscous effects, characteristic of the polymer systems, force this process to stop. Depending on the physicochemical nature of the system, different phenomena, such as crystallization, gelation or the crossing of glass transition of the system may occur. The competition of such phenomena during liquid–liquid phase separation leads to the formation of membranes with different morphologies. In order to obtain membranes suitable for different applications, which may vary from microfiltration to gas separation processes, membrane

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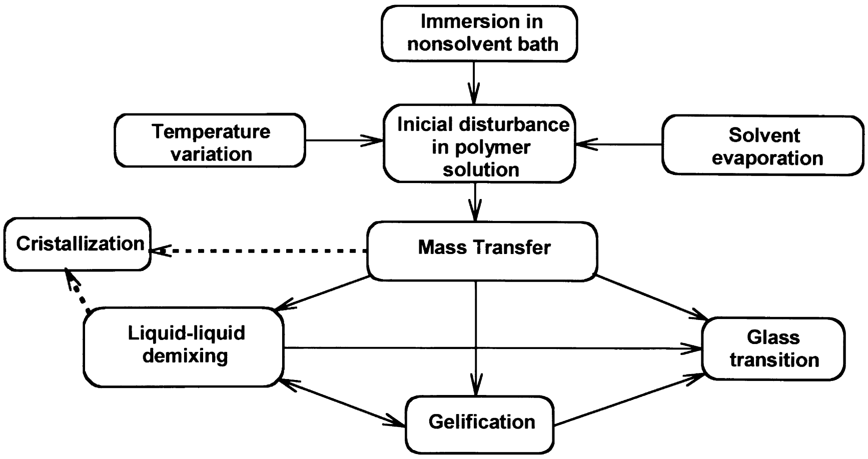

Fig. 1. Processes involved in membrane formation by phase inversion.

formation process must be controlled. Fig. 1 illustrates the overall processes and possible ways that are involved in membrane formation.

Many techniques can bring on a polymer solution to phase inversion. Immersion precipitation technique is one of the most used in the microporous anisotropic membrane preparation. This technique is rather simple and is based on the immersion of a polymer film, cast onto a suitable support, into a non-solvent bath as illustrated in Fig. 2. The solution will separate into two phases due to the solvent diffusion out of the polymer film to the precipitation bath and to the non-solvent diffusion from the precipitation bath to the film. This technique is very flexible and allows to obtain a great sort of morphologies, depending on the choice of the polymer (P), solvent (S), non-solvent (NS) and precipitation bath composition [13–15].

The diffusion of non-solvent and solvent in and out of the polymer solution film results in the formation of a ternary system, consisting of P, S and NS. Such a system can be represented by a ternary composition diagram schematically presented in Fig. 3. In this diagram, the binodal curve represents the projection of the equilibrium compositions and separates single-phase and two-phase regions. The spinodal curve separates the metastable and unstable composition regions. The shadowed area stands for the composition region where the viscous effects characteristic of the polymer solution may occur. Depending on S and NS mass transfer rates, the polymer solution will achieve the two-phase region or will go into the viscous effect region. When the binodal is first reached, the polymer solution demixes into two liquid phases, rich and lean in polymer. During membrane formation, the rich phase composition continues to increase until it reaches the viscous effect region. The polymer rich phase will originate the membrane matrix, while the polymer lean phase will form the membrane pores. By varying the parameters involved in membrane preparation different morphologies can be obtained.

In this context, the main objective of this work was the study of microporous membrane formation by phase inversion, using immersion precipitation technique and polycarbonate as base polymer. As very little information about membrane formation by phase inversion from polycarbonate systems was available, it was proposed to begin the investigation from a ternary system, consisting of polycarbonate, a solvent and a non-solvent to the polymer [18]. The behavior of this system and some of the phenomena associated to membrane formation were studied. The observed morphology was related to variables involved in membrane preparation.

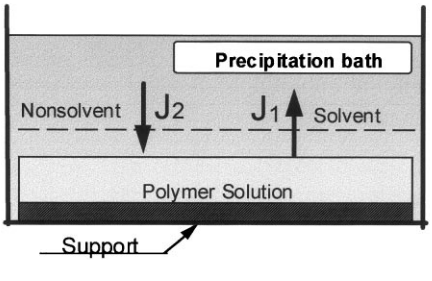

Fig. 2. Schematic diagram of the immersion precipitation technique.

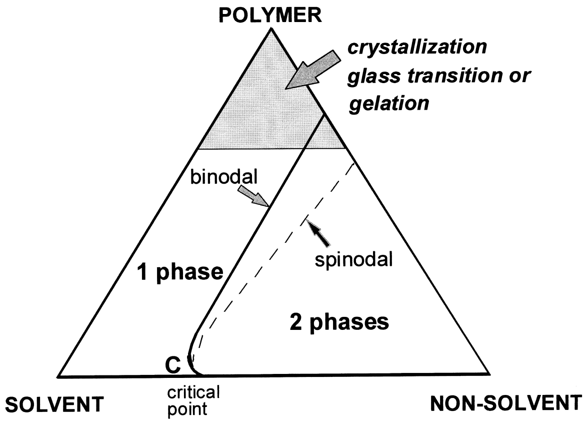

Fig. 3. Schematic representation of a ternary phase diagram.

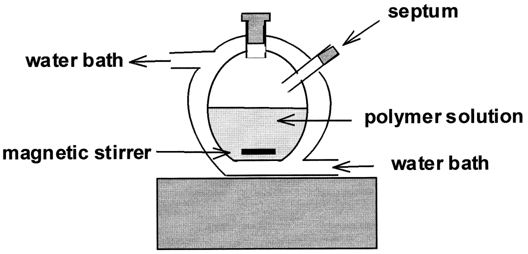

Fig. 4. Experimental apparatus for cloud-points determinations.

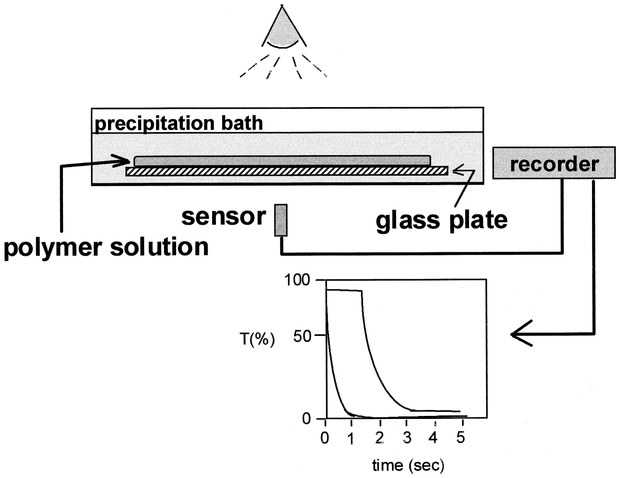

Fig. 5. Experimental equipment for observing the precipitation kinetics of polymer solutions.

## 2. Experimental

Polycarbonate (Durolon® I-2700, $M_w = 40,000$, Policarbonatos do Brasil), PC, dried for at least 24 h at 60°C, was dissolved in *N*-methyl-2-pyrrolidone (Riedel de Haën), NMP, in a concentration range of 10–25 wt%. Distilled water was also added to the cast solutions in a range of 0.5–2.0 wt%. Cloud-points of each solution were determined visually, at 25°C, using the device presented in Fig. 4. Water was added through a septum using a syringe and the solution was constantly stirred. The cloud-point was determined when turbidity of the solution persisted over 24 h. The polymer solution viscosity was measured at 25°C by a rotational viscometer (Brookfield).

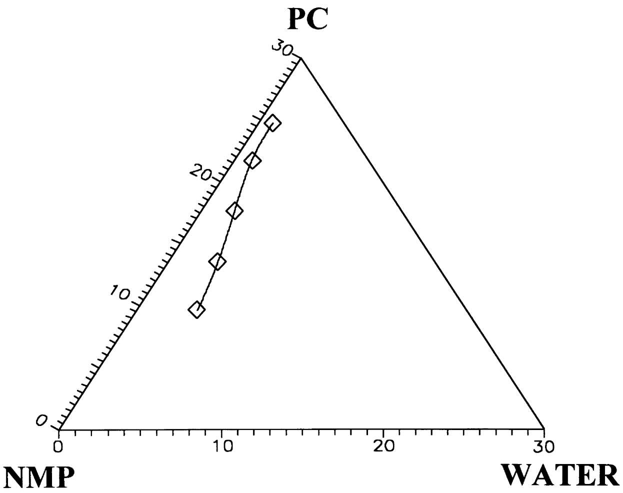

Fig. 6. Cloud-point curve for the system PC/NMP/water.

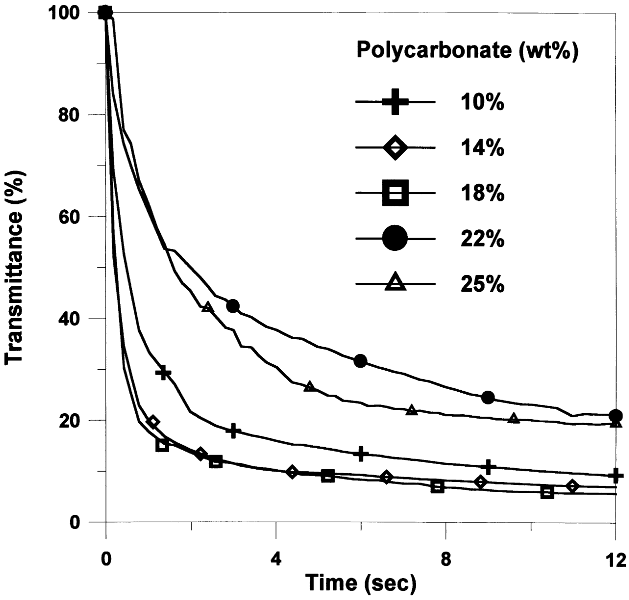

Fig. 7. Effect of polymer concentration on the precipitation kinetics of the polymer solutions—direct immersion into non-solvent bath.

In order to prepare flat membranes, polymer solutions were cast with the thickness of 0.13 mm upon a glass plate. They were immersed in a water bath after 30 s of

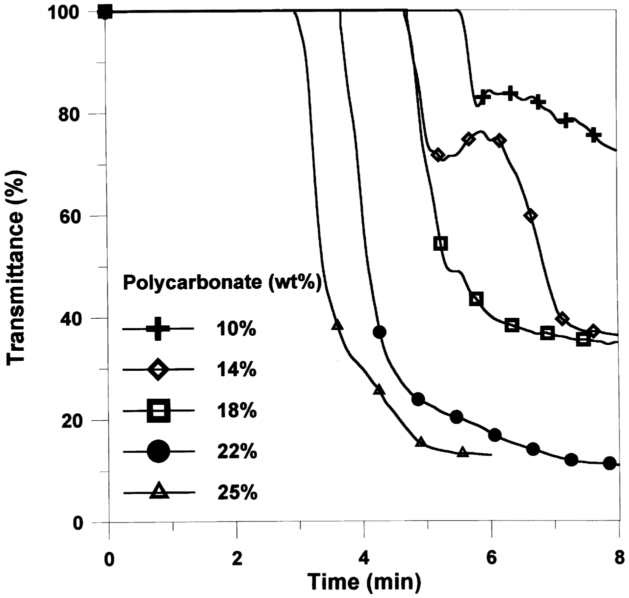

Fig. 8. Effect of polymer concentration on precipitation kinetics of polymer solution—long exposure time experiments.

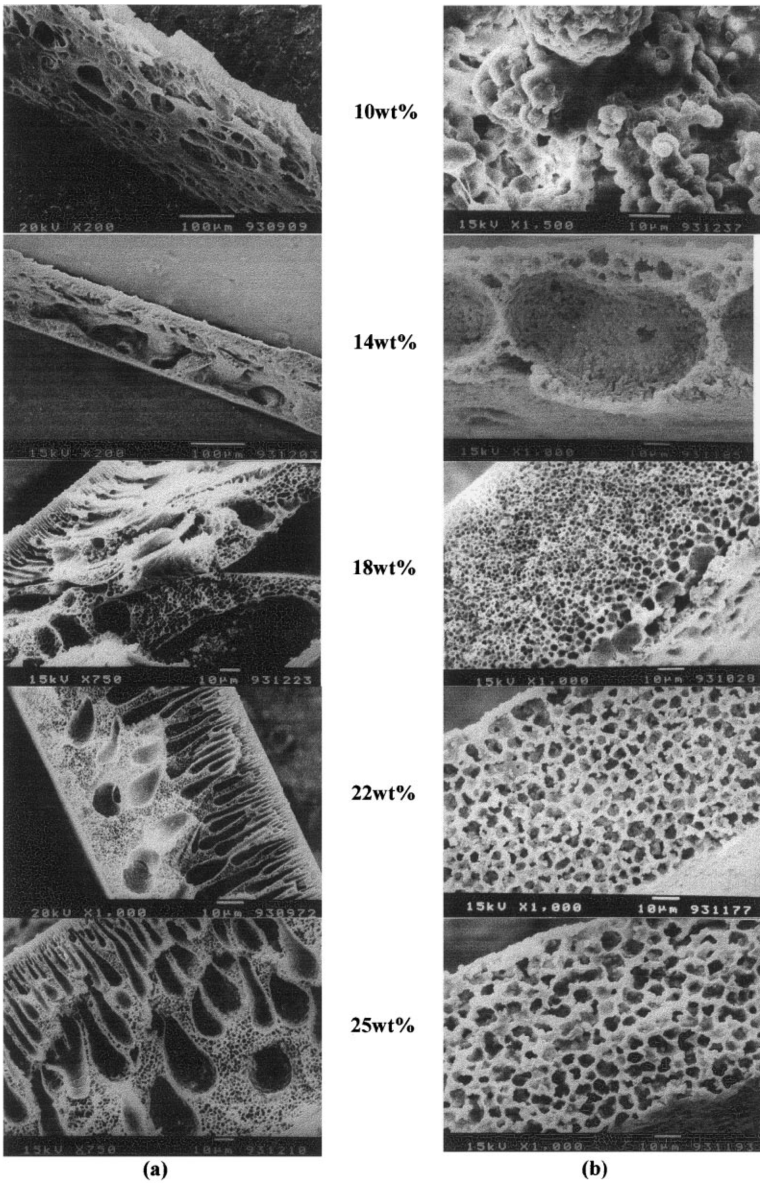

Fig. 9. Effect of PC concentration on the cross-section morphology of membranes obtained by: (a) direct immersion; and (b) precipitation by long exposure time.

exposition to the room environment. The local relative humidity was in the range of 65–75%. The precipitation of the solution could be followed using the equipment presented in Fig. 5. The precipitation of each polymer solution was followed three times, in order to test the reproducibility of the method. No significant difference or no change at all between the kinetics measurements for each condition was observed. Measurements using long exposure time to the room environment were carried out by placing the glass plate directly above the detector, without immersion into the water bath. The precipitation, in this case, occurs due to water absorption from air. After precipitation, the membranes were kept in a water bath at 60°C for 24 h, then dried, at room temperature, after solvent replacement (ethanol and hexane). The membrane samples were broken into liquid nitrogen, metalized and observed using a scanning electron microscope, SEM (Jeol 5300).

## 3. Results

The cloud-point curve is represented in the ternary diagram of Fig. 6. The PC/NMP/water phase diagram shows a very limited miscibility region. The maximum amount of water soluble in this system is about 3.7 wt%, which favors phase separation. It was also observed that the curve shows a slight inflection with the increase in polymer concentration. Due to the relatively low polymer concentration ($<25$ wt%), it may be assumed that this is a typical behavior of gelation (or crystallization). Therefore, for

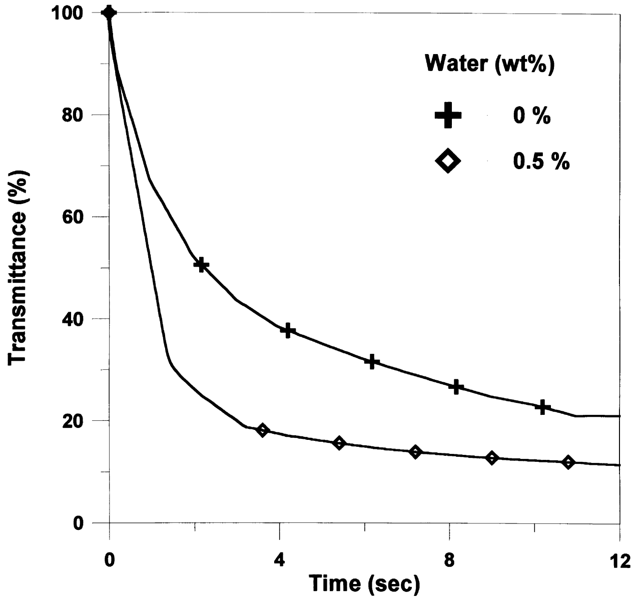

Fig. 10. Effect of water concentration on precipitation kinetics of polymer solutions containing 22 wt% PC—direct immersion into non-solvent bath.

lower PC concentrations (<ca. 15 wt%) the cloud-point curve may represent the binodal curve trend, as well as the gelation or crystallization boundary, for higher polymer concentrations (>ca. 15 wt%).

Light transmission experiment results show that all solutions present instantaneous demixing, when directly immersed into a water bath. In instantaneous demixing the top layer of polymer solution precipitates as soon as it contacts the precipitation bath. Fig. 7 shows the effect of PC concentration on the precipitation kinetics of binary solutions. First, it is observed an increase in the initial precipitation rate with polymer concentration, which may be explained by the reduction of miscibility. However, a strong reduction in the initial precipitation rate can be detected when the polymer concentration increases from 18 to 22 wt%, although from 22 to 25 wt% the precipitation rate decreases again. One possible hypothesis to this behavior is the presence of two antagonistic and competing effects. The increase in polymer concentration leads the solution to approach the two-phase boundary, accelerating the precipitation. On the other hand, when polymer concentration increases, its concentration on the interface precipitation bath–polymer solution also increases, leading to a higher resistance to mass transfer, decreasing the initial precipitation rate of the sublayers from the polymer solution film. However, it was observed that a further increase in the polymer concentration (from 22 to 25 wt%) leads again to an increase in the precipitation rate, indicating that the effect of proximity with two-phase boundary is, at this concentration, stronger than the effect of resistance at the interface.

Fig. 8 shows the precipitation kinetics for long exposure time experiments. The precipitation onset was dependent on polymer concentration, i.e. the more concentrated solutions precipitated first, since they need less water to become unstable. Comparing with the direct immersion, the effect of mass transfer resistance at the interface is minimized and no inversion in the precipitation behavior is observed. This fact also confirms that the two effects are present during precipitation, as mentioned before. It is interesting to point out that no difference in the precipitation onset of the solutions containing 14 and 18 wt% of PC could be observed. This behavior and the membrane cross-section photomicrographs, presented in Fig. 9, suggest a change in the phase separation mechanism. Another observation in Fig. 8 is the increase in the transmittance after the precipitation onset for the solution containing 14 wt% of PC. This seems to be related to the coalescence of polymer-poor phase nuclei, as it could be observed by SEM (Fig. 9b).

The precipitation by long exposure time for a 10 wt% PC solution results in a membrane with very poor mechanical resistance, which cracked thoroughly when it was tried to be removed from the glass plate. Precipitation below the critical point was discarded, because it is characterized by the nucleation of rich polymer phase and the exclusive formation of polymer spheres, which was not the situation.

Fig. 9 presents the photomicrographs of membranes cross-sections and illustrates the effect of PC concentration on membrane morphologies obtained by direct immersion into water bath (Fig. 9a) and by long exposure time to the room environment (Fig. 9b). The membranes obtained from solutions with higher polymer concentration by direct immersion into the water bath showed more oriented macropores in their sublayers. This result illustrates the effect of miscibility reduction due to higher polymer concentration, which restricts nuclei growth and, consequently, reduces macrovoids size. The membrane prepared from

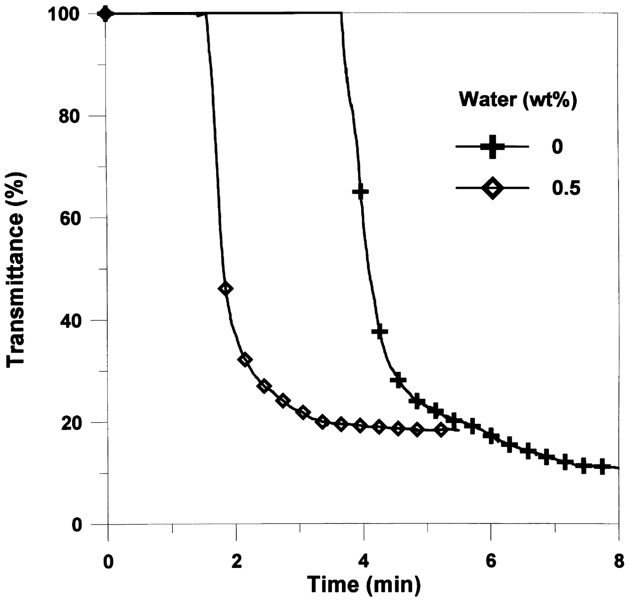

Fig. 11. Effect of water concentration on precipitation kinetics of polymer solutions containing 22 wt% PC—long exposure time experiments.

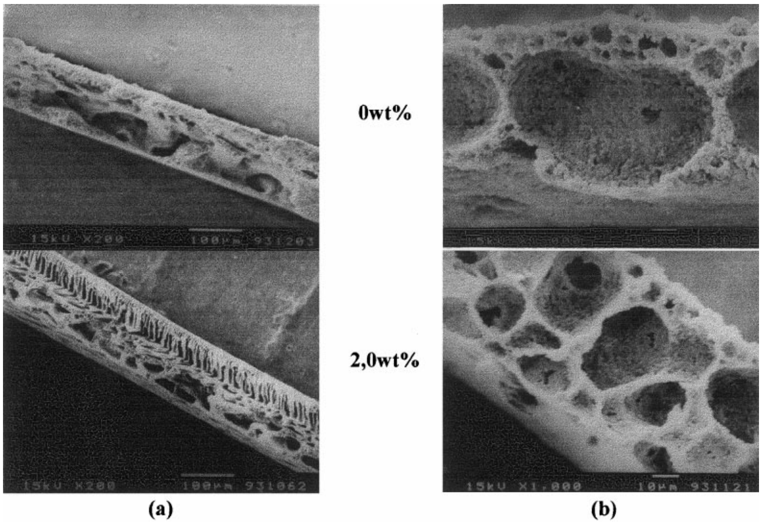

Fig. 12. Effect of water concentration on the cross-section morphology of membranes obtained by: (a) direct immersion; and (b) precipitation by long exposure time; PC concentration = 14 wt%.

10 wt% PC solution and direct immersion into the precipitation bath exhibits a totally different morphology with a highly interconnected pore structure, suggesting that another mechanism, such as gelation, occurs.

The membranes obtained by long exposure time from solutions with PC concentration higher than 18 wt% show a structure consisted of round and interconnected pores, with comparable size along the cross-section. This is an indication that reduced miscibility and a reduced inflow of NS leads to a rather uniform precipitation path. The membrane obtained from 18 wt% solution shows pore that increases in size along the membrane cross-section. It is probably related to increase in the system miscibility that turns water absorption longer before the precipitation onset. The main consequence is the development of a water concentration profile along the membrane cross-section causing the difference in nuclei growth. In more diluted solutions, the precipitation should be slower and the water absorption higher, these two facts favors the nuclei growth and coalescence, as well as nucleation and growth of polymer rich phase. As can be observed in the membrane cross-section photomicrographs, these effects may be occurring in the membranes obtained from 14 and 10 wt% PC solution, respectively.

Fig. 10 shows that addition of water accelerates the precipitation rate for solutions containing 22 wt% of PC, directly immersed in the water bath. This behavior reinforces the former hypothesis, since water addition to the polymer solution reduces miscibility and accelerates precipitation. The addition of water to the polymer solution also reduces the precipitation onset for long exposure time experiments, as could be seen in Fig. 11, for solutions containing 22 wt% of PC. As it was already discussed, the solution with water has a smaller miscibility region and needs less water to become unstable.

The effect of water addition to the polymer solution on membrane cross-section morphology could be observed in Fig. 12, for membranes obtained from solutions containing 14 wt% PC, by means of direct immersion into the water bath (Fig. 12a) and long exposure time to the environment (Fig. 12b). The increase in water content in the polymer solution leads to higher order of the membrane sublayer. This effect may be also correlated to the approaching of the two-phase region with the addition of water, restraining the nuclei growth of the polymer lean phase during precipitation.

## 4. Conclusions

Some aspects of the ternary system that consisted of PC/NMP/water were investigated. A remarkable fact is the low miscibility gap of the system, which could be noticed by cloud-points measurements. The low miscibility has important effects on membrane formation, because it favors instantaneous demixing and the mechanism of nucleation and growth of polymer lean phase, as well as macrovoids order.

In general, it could be concluded that increase in polymer concentration accelerates the precipitation of the ternary solutions. Nevertheless, changes on this behavior may occur depending on the action of contrary effects, as the acceleration of precipitation due to the phase separation boundary approximation, and the decrease of the precipitation rate due to the formation of an interfacial resistance between the NS bath and the polymer solution. The membrane obtained from a 10 wt% PC solution presented structures that suggests the presence of another phase separation mechanism, such as gelation, although a deeper investigation is still necessary for better comprehension. Water addition to the polymer solution allowed, in most of conditions, formation of more regular membranes.

Long exposure time to room environment leads to a slow water absorption by the polymer solution, allowing the diffusion front to reach deeper layers of the polymer solution film, leading to more isotropic membranes. Nevertheless, the membranes obtained in such a way, using 14 wt% of PC solution presented macrovoid in their cross-section structure, with extremely porous walls. The occurrence of such macrovoids may be due to the coalescence of polymer lean phase growing nuclei, as the precipitation kinetics results suggest.

## Acknowledgements

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