

특별강연 III

INVESTIGATION OF DEMIXING PHENOMENA OF A POLYMER SOLUTION DURING THE PHASE INVERSION PROCESS

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ABSTRACT

Polysulfone (PS) membranes were prepared by the phase inversion process using water or isopropanol as nonsolvent. The Flory-Huggins theory for a ternary system nonsolvent/solvent/polymer is applied to describe the thermodynamic equilibria of the components. The calculated ternary phase equilibria show that demixing of a PS binary solution with n-methylpyrrolidone (NMP) will be fast in a water coagulation bath and will be delayed in an isopropanol bath. The prepared membranes were characterized by SEM, gas adsorption-desorption measurement, and permeability test. The membrane, which is precipitated by fast demixing in a water bath, has nodular structures in the skin region and includes finger-like cavities in the sublayer. The membrane coagulated by isopropanol has a very dense and thick skin structure, which is formed by delayed demixing. The membrane coagulated by isopropanol showed considerably lower pore volume and surface area compared to that observed with water coagulation method. With dimethylformamide (DMF) as solvent and 2-3 wt% of water, the solution can show the liquid-liquid phase separation due to agglomeration of the polymer-lean phase from the homogeneous solution. The membranes, which were coagulated near an equilibrium state, show the large (micron size) round pores in the whole membranes. The pores do not contribute the permeation characteristics.

INTRODUCTION

The phase inversion process is one of the best known techniques for the preparation of synthetic polymeric membranes. It involves casting of a film of a homogeneous and concentrated solution on an appropriate plate and precipitating the film in a coagulation bath of nonsolvent. The precipitated membranes generally have an asymmetric structure, where a dense skin region is distinguished from a porous sublayer.

In a coagulation bath, demixing of the polymer solution film is induced by the exchange of solvent with nonsolvent. During the exchange, various types of phase or structural transitions can cause demixing of the film. The possible transitions involve phase separation, gelation, crystallization, and/or chemical reaction. The progress of a transition is influenced by two factors^{1,2,3}. One is related to the thermodynamic equilibria of a ternary system of nonsolvent/solvent/polymer from which the binodal curve or the boundary between two-phase and one-phase regions can be obtained. The other consists of kinetic factors including mass transfer between components during coagulation. It is impossible to coagulate a condensed polymer solution such as the membrane casting solution in a thermodynamic equilibrium state¹. Demixing rate, which determines the final membrane structure, can be established by correlating both factors. According to Ziabicki¹, the possible transition, which can be described by the thermodynamic relationships in a multicomponent system, is not always found in practice because of kinetic factors. Therefore, the membrane structure, which is precipitated by the phase inversion process, will be determined by demixing rate of the cast film.

The purpose of this research was to investigate the phase equilibria of ternary systems containing PS as polymer in a membrane casting solution, and to obtain morphology and performance data for the phase inversion membranes. Also, the relationship between the membrane structures and the kinetic factors is investigated by changing the rate of solvent-nonsolvent exchange⁴. Ternary phase equilibria were obtained by using the Flory-Huggins theory. The solidified membranes were characterized by SEM, gas adsorption-desorption technique⁵, and permeability measurement.

RESULTS AND DISCUSSION

The calculated phase diagram of two ternary systems nonsolvent/solvent/polymer is presented in Figure 1. The two systems are water/NMP/PS and isopropanol/NMP/PS. The location of the binodal curve for isopropanol coagulation is far from the binary mixing line of polymer and solvent. On the other hand, the binodal curve or the demixing region for water coagulation is located very close to the composition of the cast film or the binary mixing line. These results indicate that at the equilibrium conditions, a very small amount of water can phase separate the cast film, and the demixing of the film will be induced by a relatively large amount of

isopropanol. The positions of the tie lines at the ternary phase equilibria including water show that the polymer concentration in the polymer-rich concentrated phase is very sensitive to the degree of the phase separation. The tie lines for isopropanol coagulation manifest a moderate variation of the polymer concentration in the concentrated phase according to the progress of the phase separation. The diagram also shows that the major contribution to the difference between the two ternary phase diagram comes from the variation of g_{13} , since the variation of g_{12} indicating the compatibility between nonsolvent and solvent is relatively small. From the above results, it can be suggested that isopropanol as nonsolvent can cause delayed demixing of the cast film, which can be compared to fast demixing caused by water as nonsolvent.

Cross sections of the prepared membranes were observed using SEM photographs. As shown in Figure 2, the membrane precipitated in a water bath has nodular or granular structures at the skin region and has finger-like structures in the whole cross section of the membrane. The finger-like structures may be induced by fast penetration of nonsolvent into the cast film. The graded pore structures from the skin to substructure is also found. On the contrary, the membrane precipitated in a nonsolvent bath has relatively uniform cell type structures underneath the thick and dense skin region. The magnified picture of the cross section indicates the absence of separated nodule in the skin region.

The two different structures indicate that in the skin region, the membrane coagulated by fast demixing via phase separation and the membrane coagulated by isopropanol is induced by delayed demixing via gelation. The corresponding skin structures are distinguished from each other. The phase separated structure consists both of the polymer aggregates and of the gaps between the coalesced aggregates. The membrane structure formed by gelation shows a three dimensionally homogeneous polymer network. The thick and dense skin of the membrane contributes to low permeability and high rejection performance.

The morphology of both membranes was measured by gas adsorption method using nitrogen gas. Even though data from the gas adsorption-desorption method cannot distinguish the active membrane pores at the membrane skin from the pores in the sublayer, these data can give information to overall membrane morphology. The surface area and the pore volume and distribution were obtained by using BET theory and Cranston-Inkley method, respectively. The sorption isotherms in Figure 3

show that at any relative pressure, the membrane coagulated by water has much higher volume of adsorbed nitrogen than the membrane coagulated by isopropanol.

CONCLUSION

The thermodynamic equilibria in ternary systems indicate that the demixing of PS solution including NMP as solvent will be fast in a water coagulation bath and will be delayed in an isopropanol bath. The demixing of the former progresses by the fast phase separation at the skin region. The corresponding membrane has nodular polymer aggregates in the skin region and large surface area and pore volume. On the other hand, the delayed demixing by isopropanol as nonsolvent induces gelation of the skin region. The precipitated membrane has a very dense and thick skin structure, and low surface area and pore volume.

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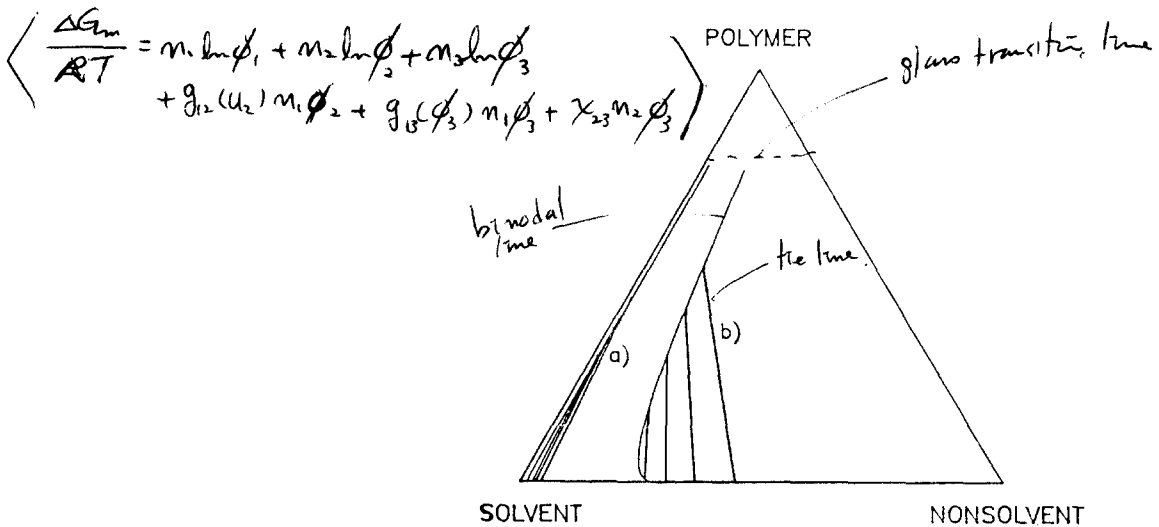


FIGURE 1. Binodal and tie lines in ternary systems including PS, NMP as solvent, and water (a) or isopropanol (b) as nonsolvent.

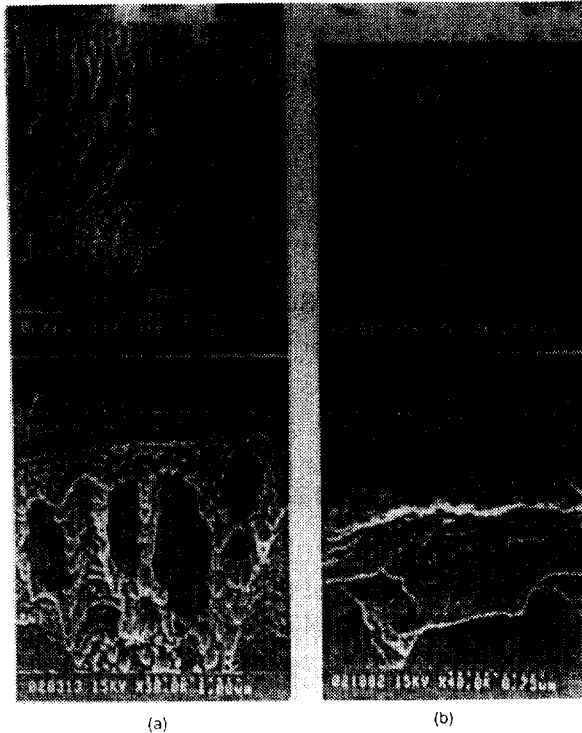


FIGURE 2. Cross sections (top) and cross sections of top region including top surface (bottom) of membranes; coagulated by immersion into a water bath (a) and coagulated by immersion into an isopropanol bath (b).

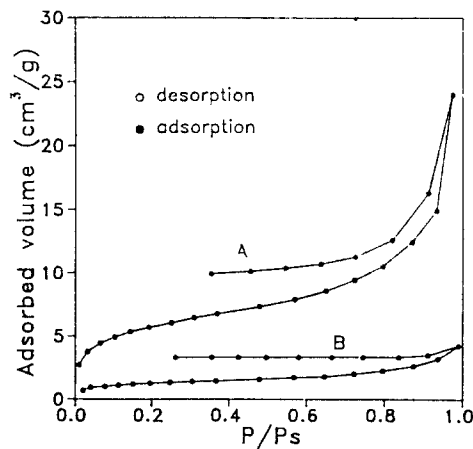


FIGURE 3. Nitrogen adsorption isotherms at 77 K for PS membranes; the membrane coagulated by water (A) and the membrane coagulated by isopropanol (B).