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# Phase transitions of polysulfone solution during coagulation

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Coagulation of a polysulfone solution film was induced by water vapour sorption under atmospheric exposure, followed by water diffusion in a coagulation bath. Demixing in the skin region of the solution film can involve both equilibrium and non-equilibrium phase separation. Surface pore size of the solidified film is proportional to the duration of the liquid–liquid phase separation during vapour sorption.

**(Keywords: polysulfone; demixing; phase separation; vitrification)**

## *Introduction*

A polymeric solid film or a membrane can be prepared by the phase inversion process, which involves phase transition of a homogeneous polymer solution[1]. The phase transition or demixing phenomena at the top layer of a solution film plays an important role in the overall morphology and characteristics of a final solid film. The demixing rate of a solution film depends on both kinetic factors and thermodynamic factors[2–4]. From the thermodynamic factors, the phase equilibria or the possible phase transitions can be estimated. However, the possible transition in a thermodynamic phase diagram is not always found in a real coagulation system[2]. If the composition of a solution changes rapidly during coagulation, the demixing conditions can be far from the equilibrium state. The corresponding precipitated structures can be distinguished from the structure which is formed near the equilibrium state. Therefore, the kinetic factors, which are represented by mass transfer between components, determine the occurrence of the possible transitions[2].

Polysulfone (PS) is an amorphous polymer and is one of the most common materials for membrane preparation. Demixing mechanisms of a PS solution film consist of vitrification, liquid–liquid phase separation and thermo-reversible sol–gel transition[5]. If the solution film is demixed by the liquid–liquid phase separation due to the nucleation of the polymer-lean phase, growth of the separated phases is required for the polymer-rich concentrated phase to solidify as a solid film.

The purpose of this investigation is to find both evidence for equilibrium and non-equilibrium demixing in a PS solution film, and a relationship between the duration of equilibrium demixing and pore size on the surface of a solidified film. Phase diagrams of the ternary solutions (PS–dimethylformamide (DMF)–$H_2O$ and PS–*N*-methylpyrrolidone (NMP)–$H_2O$) can be obtained by solving the chemical potential equations with the Flory–Huggins solution theory[4–6].

## *Experimental*

The polymer (Udel P-3500) was supplied by Amoco Co. and the solvent was DMF of an analytical grade from Aldrich Chem. Cloud point data of the PS–DMF–$H_2O$ ternary system were obtained by titrating PS–DMF solutions with water at 21°C. The polymer and solvent were mixed in a flask with a rubber septum stopper. After 24 h, deionized water was added into the binary solution by a syringe through the septum, while thorough mixing was applied using a magnetic stirrer. Composition at the cloud point was determined by measuring the weight of the added water when a visual turbidity was achieved.

Using 15 wt% PS solution in DMF, solution films were cast to 0.21 mm clearance gap on $20 \times 20\,\mathrm{cm}^2$ glass plates at 21°C. The films were exposed at environments of 50% and 65% relative humidity, respectively. After exposure for specified times, the films were immersed into a deionized water bath at 21°C. Cross-sections and top surfaces of the prepared membranes were observed by using a scanning electron microscope (Hitachi S-800). Membrane samples were collected at the centre region of the solid membranes (fractures under cryogenic conditions), and dried at 21°C in atmospheric pressure. The fractured specimens were coated with gold–palladium alloy before SEM photographs were taken.

## *Results and discussion*

Cloud point experimental data indicated that a small amount (1–2 wt%) of water content is enough to phase separate the PS–DMF solutions up to 16 wt% of the polymer. As cast, the solution films were transparent. During the initial exposure to the atmosphere, composition of a cast film is varied by water vapour sorption rather than by evaporation of the solvent, since DMF is a highly hygroscopic and non-volatile (b.p. 152.8°C) solvent. A transparent cast film showed a cloudy feature

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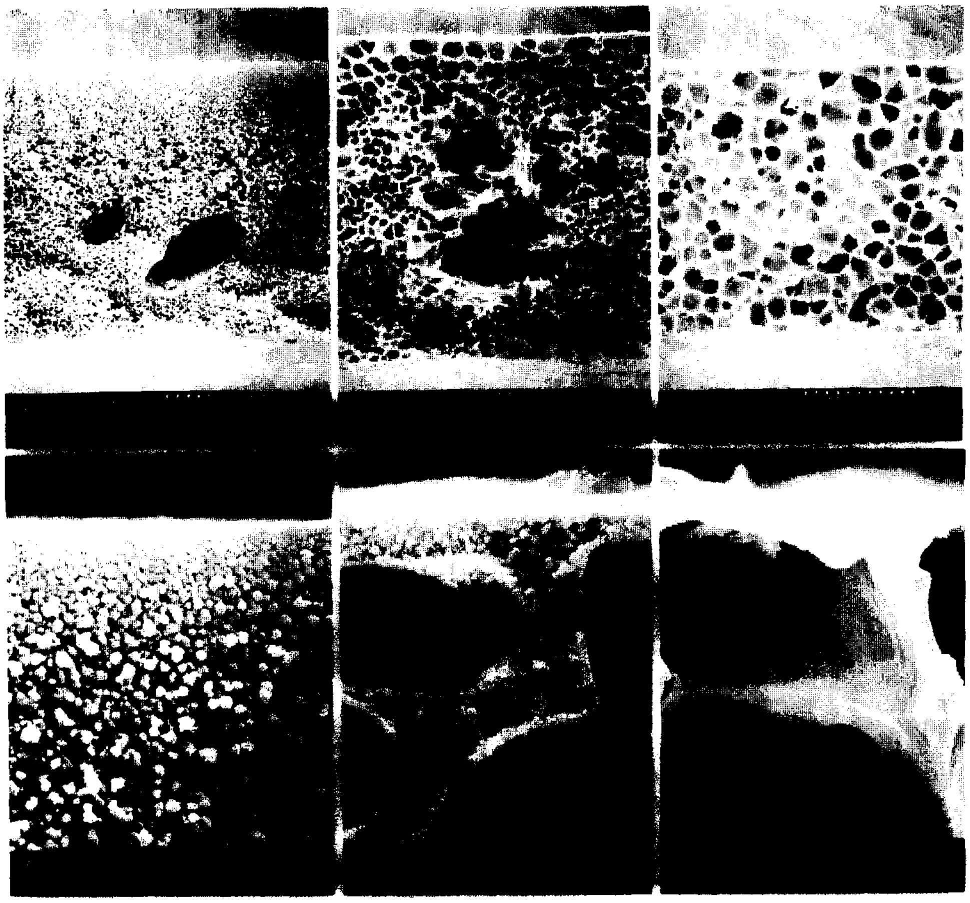

(a) (b) (c)

**Figure 1** Cross-sections of PS membranes (top) and cross-sections of skin regions of PS membranes (bottom) coagulated by immersion into a water bath after exposure to 50% relative humidity. Exposure times: (a) 30 s, (b) 120 s, and (c) 600 s

after 100 s at 50% humidity and after 50 s at 65% humidity. These phenomena indicate that the PS–DMF binary solution is sensitive to relative humidity in the atmosphere during vapour exposure. However, when the transparent cast films of 30 s exposure at both the 50% and 65% humidity condition were immersed into a water bath, the films developed cloudy features very rapidly, regardless of the humidity.

Cross-sections of the solidified membranes show that the membranes of *Figure 1a* and *Figure 2a* involving 30 s exposure have graded pore structures from the skin layer to the sublayer. The skin region of the membranes consists of nodule structures which are formed by aggregated polymer molecules. These structures are induced by the non-equilibrium demixing due to the rapid composition change through the exchange between water and DMF in a water bath. The binary diffusivity of water and DMF has been calculated to be $1.25 \times 10^{-5}$ cm s$^{-1}$ (reference 6). On the contrary, the membranes (b) and (c) of *Figure 1* and *Figure 2* include cell-like structures on the whole cross-section as well as the skin region. These membranes represent the cast films immersed into a water bath in a cloudy state. The change from a transparency to a cloudy feature during vapour exposure indicates the possible equilibrium demixing due to formation of the nucleation of the polymer-lean phase by the water sorption, which can be identified from the round surface pores and the round voids in the cross-sections.

Even though the membranes coagulated by immersion into a water bath in the cloudy state consist of cell-like structures, the morphology of the top layer in the membranes varies depending on the duration of vapour exposure. In the skin region including the spherical void phases, the membranes (b) of *Figures 1* and *2* have nodular structures surrounding phases, but the membranes (c) of both figures show dense polymer structure. The round void phase represents the polymer-lean phase which is formed during liquid–liquid phase separation due to the nucleation of the polymer-lean phase. The nodular structures in the membranes (b) of both figures represent a non-equilibrium demixing in the polymer-rich concentrated phase. Therefore, the structures of the membranes (b) indicate that the top layer of the membranes are possibly coagulated by the equilibrium demixing followed by the non-equilibrium demixing. In the substructure underneath the skin region, the cell-like structures in the membranes (b) of *Figures 1* and *2* can also be distinguished from those in the membranes (c) of both figures in that the latter shows more developed cell-like structures than the former.

Top surfaces (the air sides during the cast) of the membranes coagulated by immersion into a water bath after 65% humidity exposure are shown in *Figure 3*. The surface of the membrane in *Figure 3a* precipitated without equilibrium demixing consists of a non-porous surface. For this type of membrane,

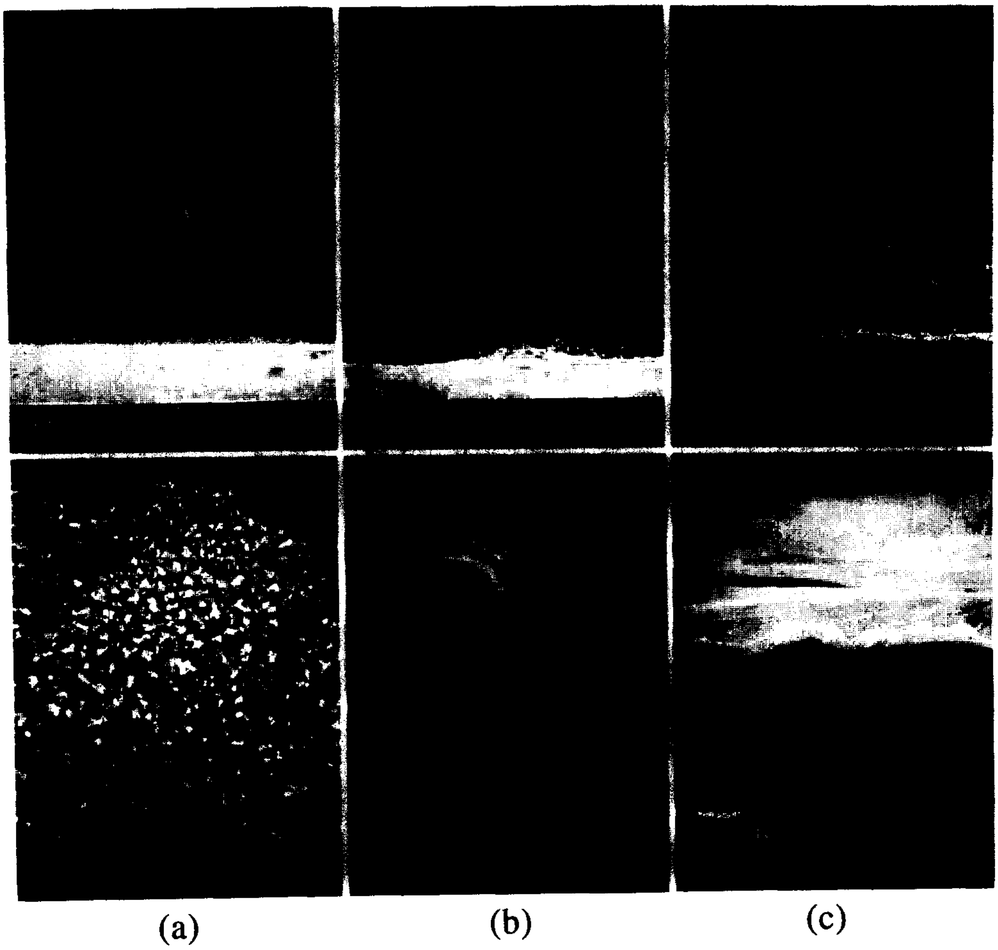

**Figure 2** Cross-sections of PS membranes (top) and cross-sections of skin regions of PS membranes (bottom) coagulated by immersion into a water bath after exposure to 65% relative humidity. Exposure times: (a) 30 s, (b) 60 s, (c) and 180 s

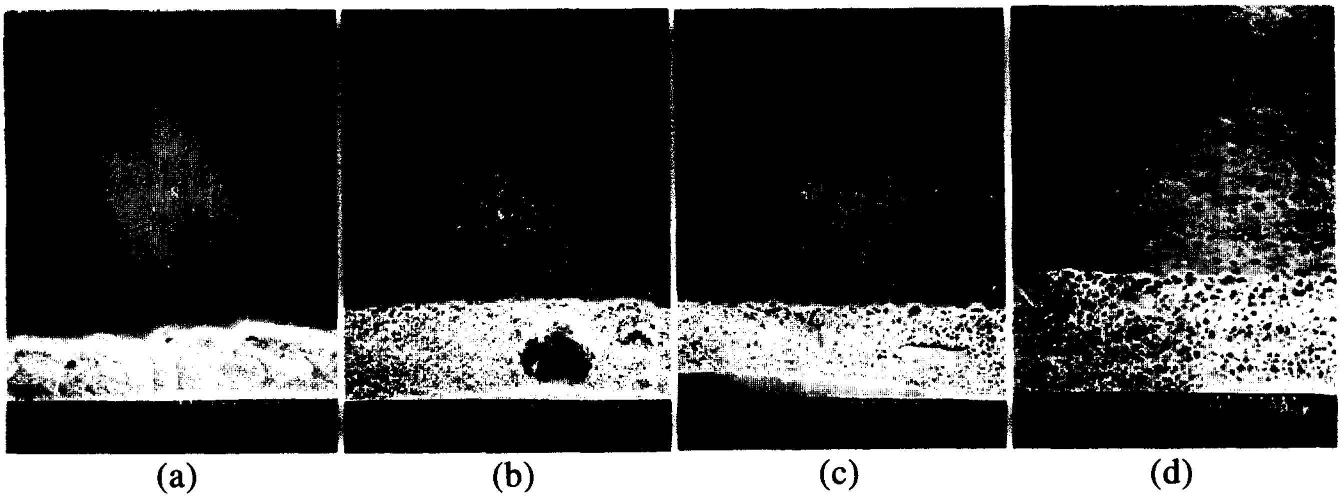

**Figure 3** Top surfaces of membranes coagulated by immersion into a water bath after exposure to 65% relative humidity. Exposure times: (a) 30 s, (b) 60 s, (c) 180 s, and (d) 600 s

coagulated by non-equilibrium conditions, crack-like gaps between the collapsed nodular structures were observed on the membrane surface at very high magnification[6]. On the contrary, membranes (b), (c) and (d) in *Figure 3* coagulated by immersion into a water bath after showing a cloudy feature have round pores up to 10 $\mu$m on the surface. Also, the pore sizes on membrane (d) are larger than those on membranes (b) and (c). These results indicate that the duration of the liquid–liquid phase separation during exposure is proportional to the pore size of the top surface of the membrane. The increase of the pore size is caused by the growth of the polymer-lean phase, which is set by immersion coagulation.

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