

일반강연 A-8

**SALS를 이용한 고분자용액의 상전환 기구에 관한 연구
: C1-C4 알코올의 첨가에 따른 상분리 거동에 미치는 효과와
투과 특성**

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**The study of phase inversion of polymer solutions using
small angle light scattering (SALS): The effect of addition
of alcohol (C1-C4) on phase separation behavior and
hydraulic permeation**

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1. Abstract

Small angle light scattering and field emission scanning electron microscope have been used to quantify the kinetics of liquid-liquid separation behavior during water vapor(RH52% \pm 3%) at 27°C) quenching (non-solvent induced phase separation, NIPS) of polysulfone/NMP/Alcohol and CPVC/THF/Alcohol, respectively . Time dependence of the position of the light scattering maximum was observed at polysulfone dope solutions, confirming spinodal decomposition (SD). while CPVC dope solutions showed a decreased scattered light intensity with a increased q-value, indicating nucleation & growth (NG).

For the each system, domain growth rate in the intermediate and late stage of phase separation decreased with increasing the number of carbon of alcohol used as additive (non-solvent). Also, in the early stage for SD, the scattering intensity with time was in accordance with Cahns linear theory of spinodal decomposition,[1-3] regardless of types of non-solvent additive.

2. Experimental

The setup of small angle light scattering (SALS) apparatus was described in detail elsewhere [4,5] and only a brief account was given here. The scattering intensity, I , is measured as a function of the magnitude, q , of the scattering vector, denoted by $q = [4\pi \sin(\theta/2)]/\lambda$, where q is the magnitude of the scattering vector, θ is the scattering angle of the intensity maximum, and λ is the wavelength of the light (He-Ne 632.8nm, 10mW), respectively. A collimated laser beam impinges into sample, which is located in the rectangular glass chamber (30×30×25cm) connected with the humidity controller (JEIO Tech. Model SK-G001, Seoul, Korea). Both the transmitted and scattered light were projected on the opaque screen at the upper side of the rectangular glass chamber in whose focal plane a beam stop blocks the directly incident beam and the images of scattered light were recorded and digitized by the CCD (NTC/CCD-512-TK, Roper Scientific, Trenton, NJ, U.S.A.) with ST-133 controller. To obtain the scattered light intensity, $I(q)$, as a function of time, the CCD output (512×512 pixels) was averaged over rings of pixels centered about the optical axis of the apparatus, which correspond to the same magnitude, q , of the scattering vector. This setup allowed us to measure $I(q)$ over scattering vectors in the range of $0.398\mu\text{m}^{-1} < q < 3.72\mu\text{m}^{-1}$, corresponding to angles from 2.3° to 21.6° . The data from all angles can be recorded at a rate of 2msec/scan. In a typical experiment, the scattered light intensities at different angles were recorded in real time for up to several minutes to document the time evolution of light intensities. The experiments of SALS were conducted by quenching the polymer solutions in water vapor from the one-phase region to the two-phase region at a given concentration. Scattering cells prepared by casting a thin film (150 μm) of dope solution on microscope slide were located on circular aperture and were exposed the water vapor of RH52%(3%) at 27°C in the glass chamber. During the water vapor quenching, scattered light intensities and patterns were monitored as elapsed time.

The cross-sectional morphologies of the quenched films after SALS experiment were also determined using field emission scanning electron microscope (FE-SEM, JEOL-6340F, Kyoto, Japan) at an accelerating voltage of 15kV.

A dead-end stirred cell filtration system [6] was used to measure the flux of deionized water through the prepared specimens.

3. Results and discussion

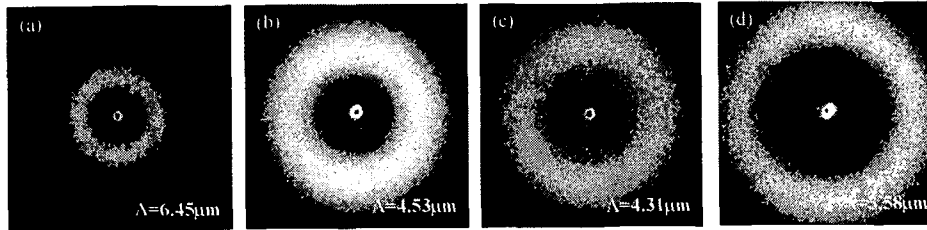


Fig. 1. Small angle light scattering patterns for proceeding phase separation of 20wt% Psf solution under RH52% ($\pm 3\%$) (a) 117.0 sec (without alcohol), (b) 120.0 sec (10wt% methanol), (c) 271.5 sec (10wt% n-propyl alcohol), and (d) 294.0 sec (10wt% n-butyl alcohol)

Fig. 1 shows a typical hollow-type scattering patterns of SD. The change of scattered intensity with time at various values of q was investigated. In the initial stage of phase separation, the scattered intensity increased exponentially with time. thereafter, the intensity deviated increasingly from the exponential curve. According to Cahns linear theory [1-3] of spinodal decomposition, the exponential increase of the scattered intensity is described by $I(q,t) \propto \exp[2R(q)t]$ (eq.1), where I is the scattered intensity, t is the time after the initiation of the spinodal decomposition, and $R(q)$ is the growth rate of concentration fluctuation having the wavenumber (q). $R(q)$ is given by $R(q) = -Mq^2(\alpha^2 f / \alpha c^2 + 2kq^2)$ (eq.2), where M is the mobility, k is the concentration-gradient energy coefficient, f is the free energy of mixing, and c is the concentration of the solution. According to eq. 1, a plot of $\ln I$ vs. t at fixed q should yield a straight line of slope $2R(q)$. A line relationship was realized for the initial stage of phase separation from a plot of $\ln I$ vs. t line. This indicates that the initial stage can be described by the linearized spinodal decomposition theory.

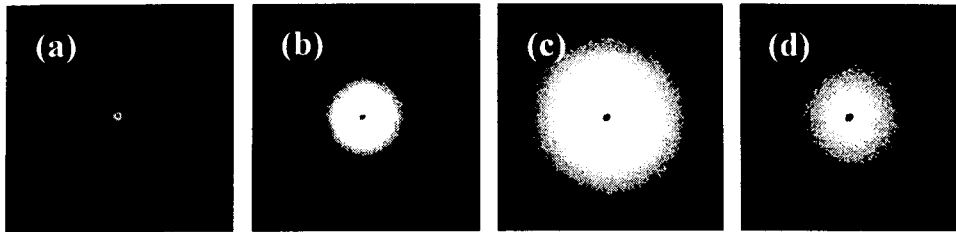


Fig. 2. The representative light scattering patterns with time evolution during phase separation under RH53% at 27°C: the result of 9wt% CPVC/THF solution with 30wt.% n-butanol, a) 117.0sec, (b) 120.0sec, (c) 271.5sec, and (d) 294.0sec.

For spinodal decomposition system, scattered light intensities increase with time and display a scattering maximum that also grows with time. However, in this system, the intensity of the scattered light increases with time, but there is never any sign of a maximum as shown in Fig. 2. The spinodal ring could not be observed. These results show reliable evidence that the mechanism of this system develop under Nucleation and Growth (NG).

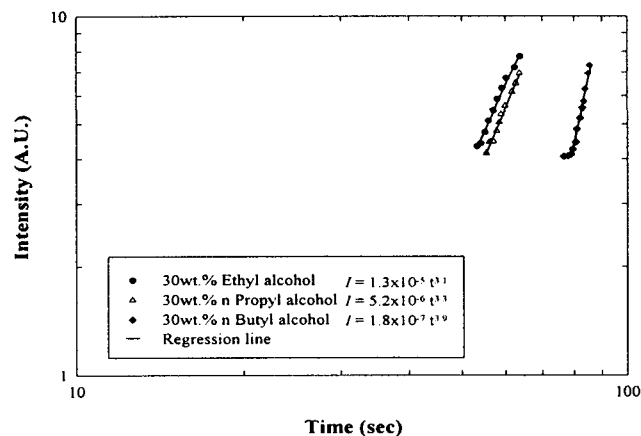


Fig. 3. Logarithmic plot of light scattering intensity as a function of time for CPVC solutions.

In the NG mechanism, intensity (I) at a fixed angle is related with time (t)

to a power law $I \propto (t-t_0)^n$, where t_0 is the time when nucleation starts.[7] Homogeneous NG gives 4.0 for n , whereas heterogeneous NG gives 3.0. [8] Logarithmic plot of I against t was shown in Fig. 3. Here, it was estimated that homogeneous and heterogeneous separation occurred in *n*-butanol system and ethanol/*n*-propanol system, respectively.

4. References

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