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SALS를 이용한 polysulfone/NMP 상분리 관찰 및 투과실험

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The study of phase separation of polysulfone/NMP using small angle light scattering (SALS) and flux test

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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 quenching (non-solvent induced phase separation, NIPS) of polysulfone in NMP solution. Time dependence of the position of the light scattering maximum was measured by following various water vapors. For quenching to appropriate water vapor, domain growth rates increased with increasing quenching depth and the content of alcohol used as additive. Light scattering and microscopy shows that solutions quenched to water vapor showed ring-type scattering patterns. Also, in the early stage of phase separation, the scattering intensity with time was in accordance with Cahns linear theory of spinodal decomposition, regardless of types of non-solvent additive.

Experimental: Scattering techniques provide information on the conformation and organization of macromolecules in solution. The

scattering intensity, I , is measured as a function of the magnitude, q , of the scattering vector, denoted by $q = [4 n \sin (\theta/2)]/\lambda$. Where n is the refractive index of the solvent, q is the magnitude of the scattering vector, λ is the wavelength of the light (He-Ne 632.8nm) in the solutions and θ is the scattering angle, respectively. The small angle light scattering apparatus is described in detail elsewhere and only a brief account will be given here. A collimated laser beam impinges into sample, which is contained in flat cell. Both transmitted and the scattered light are projected on the screen in whose focal plane a beam stop blocks the transmitted beam, and collected by the CCD (NTC/CCD-512-TK, Roper Scientific, Trenton, NJ, U.S.A.) with ST-133 controller. To obtain the scattered light intensity, $I(q)$, the CCD output is averaged over rings of pixels centered about the optical axis of the apparatus, which correspond to the same magnitude, q , of the scattering vector. Care is taken to correct the data for the contribution of the CCD dark noise and for that of the stray light. The setup allows us to measure $I(q)$ over almost 2 decades of scattering vectors, in the range $0.398\text{mm}^{-1} < q < 3.72\text{mm}^{-1}$, corresponding to angles from 2.3 to 21.6.

Results: The existence of the fractal regime at very small scattering vectors ($q \ll R^{-1}$) reveals the existence of structures on length scales larger than R ; this can result from the presence of large aggregates or from entanglements in concentrated solutions. The fractal dimension at low q provides a measure of the supramolecular organization of the solution. In these cases, a roll-off may be visible at low q , indicating the correlation length (in a network of entangled polymers), or the size of aggregates in solution.

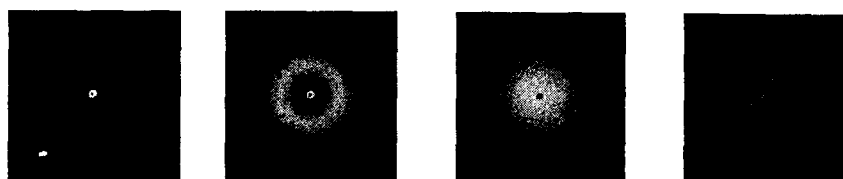


Fig. 1. Progression of scattering pattern with time from NIPS in PSF/NMP solution

Figure 1 shows the change of scattered intensity with time at various values of q . In the initial stage of phase separation, the scattered intensity increases exponentially with time. In the later stages, the intensity deviates increasingly from the exponential curve. According to Cahn's linear theory 1-3 of spinodal decomposition, the exponential increase of the scattered intensity is described by $I(q,t) = \exp[2R(q)t]$ (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 $R(q) = -Mq^2(2f/c^2 + 2kq^2)$ (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 linear relationship is 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. Linear results could be also obtained for other water vapor. From $R(q)/q^2$ vs. q^2 expected from eq. 2, the plots are straight lines, indicating again that the initial stage can be described within the framework of the linear theory. From the plots, one could obtain such characteristic parameters as q_m , q_c , and D , describing the dynamic of phase separation. q_c is the critical (maximum) wavenumber of fluctuations which can grow. q_m is the most probable wave number of fluctuations having the highest rate of growth. According to eq. 2, q_c is given by the intercept on the q^2 axis. q_m is calculated from the relation $q_m^2 = (1/2) q_c^2$. The apparent diffusion coefficient D defined by $D = -M(2f/c^2)$ is given by the intercept on the vertical axis.

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