SALS을 이용한 폴리술폰/NMP의 SD 산란 패턴의 관찰

이상훈, 강종석, 김대식, 이영무
한양대학교 공과대학 응용화학공학부

The Observation of Scattering Pattern by Spinodal Decomposition with Time Evolution using SALS

Sang Hoon Lee, Jong Seok Kang, Dae sik Kim, Young Moo Lee
School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

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 (/2)]/λ. 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 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 obtaine 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 0.398μm-1 < q < 3.72μm-1, corresponding to angles from 2.3 to 21.6.

Results

The existence of the fractal regime at very small scattering vectors (q ≪ 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

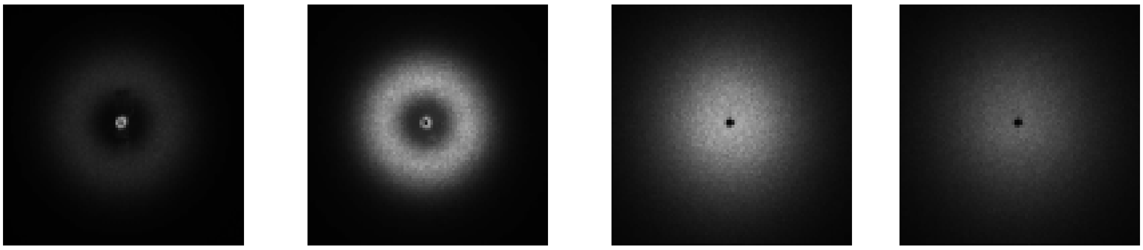

Fig. 1. Progression of scattering pattern with time from NIPS in PSF/NMP solution

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 Cahns linear theory 1-3 of spinodal decomposition, the exponential increase of the scattered intensity is described by $I(q,\mathrm{t})$ 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) = -Mq2(2f/c2 + 2kq2) (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 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)/q2 vs. q2 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 qm, qc, and D, describing the dynamic of phase separation. qc is the critical (maximum) wavenumber of fluctuations which can grow. qm is the most probable wave number of fluctuations having the highest rate of growth. According to eq. 2**,** qc is given by the intercept on the q2 axis. qm is calculated from the relation qm2 = (1/2) qc 2. The apparent diffusion coefficient D defined by D = -M(2f/c2) is given by the intercept on the vertical axis.

Conclusion

We have shown the combined results of the scattering patterns with time evolution and the cross-section morphology by field emission scanning electron microscopy to investigate the effects of alcohol on two phases domain growth, or concentration fluctuation of Psf/NMP solution during water vapor induced phase separation. In case of the scattering of dope solution containing 10wt% methanol or n-propanol, the intermediate and late stage of SD was predominantly observed. Meanwhile, in the case of 10wt% n-butanol, the characteristic scattering patterns progressed by three stages like the early, the intermediate, and the late stage of phase separation by SD were clearly observed. From the observation of the scattering patterns of each dope solution, as the scattering maximum occurred at the larger angles (larger *q*) in the order of n-butanol > n-propanol > methanol > no alcohol, the pore size of final morphology decreased. This result was quantitatively analyzed through the comparison of domain sizes from FE-SEM with size scales obtained from by SALS.

Table 1. Characteristic parameters describing spinodal decomposition of Psf/NMP/ alcohol solution. quenched under water vapor of RH53% at 27°C.

alcohol	q_m [b] (μm^{-1})	q_c [c] (μm^{-1})	$-D_{app} \times 10^{10}$ (cm^2/sec)	Λ [d] (μm)	Pore size [e] (μm)
- [a]	0.97	1.37	43.8	6.45	8.0-6.5
methanol	1.38	1.96	4.7	4.53	7.8-4.5
n propanol	1.46	2.06	8.1	4.31	4.5-3.9
n butanol	1.76	2.48	8.3	3.58	4.1-3.8

Footnote: [a] Used Psf/NMP solution without alcohol. [b] Calculated from the equation ($q_m^2 = 1/2q_c^2$). [c] Obtained from x intercept in Fig. 6. [d] Calculated from the equation, $\Lambda = 2\pi/q_m$, meaning the spacing between polymer-rich regions. [e] Results from FE -SEM measurement.

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