

THERMALLY INDUCED PHASE SEPARATION IN TERNARY POLYMER SOLUTION

Bumsuk JUNG^{*a}, Yong Soo KANG^a, and Richard A.L. JONES^b

Polymer Hybrid Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea, 130-650^{*a}

Fax: +82-2-958-6869 E-mail: bjung@kist.re.kr

Department of Physics, University of Sheffield, Hounsfield Road, Sheffield, S3 7RH, UK^b

ABSTRACT

Using Small Angle Light Scattering (SALS), the effect of quench depth on the kinetics of phase separation for ternary solution blends was investigated. The system was composed of two polymers (polystyrene and polybutadiene) and a solvent (toluene). The analyses of the early stage of phase separation were based on the Cahn-Hilliard theory [1,5]. Apparent diffusion coefficients and the fastest mode of fluctuations were evaluated, when quench depths of the system were varied near the critical composition of polymer. In the late stage of phase separation, the domain growth showed a power law with the 1/3 exponent, i.e. $q_m(t) \sim t^{1/3}$. For comparison between real images and scattering profiles with time, the image of phase domains with time were obtained by using Laser Confocal Scanning Microscopy (LSCM).

INTRODUCTION

Thermally Induced Phase Separation (TIPS) process [1] has been widely accepted as a new technology to prepare porous membranes. By lowering the temperature of a polymer solution below phase boundary, phase separation is able to be induced, and the size of phase domains can be controlled when the size of the domains reaches an aiming size. By leaching out the solvent with a non-solvent (or diluent), a tailor-made membrane is finally obtained in practice.

Lots of studies on the mechanism of kinetics of phase separation, using TIPS process have been carried out, and the process has already utilized for various membrane fabrications in industry. It is well known that the control of pore size in the final structure of membranes depends on the kinetics of phase separation. Therefore, the

most important subjects in membrane fabrication is to understand the kinetics of phase separation. Further, recent trends in the application of the TIPS process is restricted to polymer solution systems, because it is simple and easy-to-access. However, a new challenge for better methods of membrane preparation is extended to more complex systems such as polymer blends and ternary polymer systems. In order to testify the usefulness and the universality in the mechanism of phase separation in the TIPS process using a ternary system, the study of kinetics of phase separation, in particular ternary polymer solutions, as a preliminary and potential application to the membrane preparation is needed.

A detailed study of the kinetics of phase separation was investigated by using SALS and LSCM as a complementary tool. Acquiring scattering patterns from SALS and real images from LSCM with time, the mechanism of phase separation can be explored.

RESULTS AND DISCUSSION

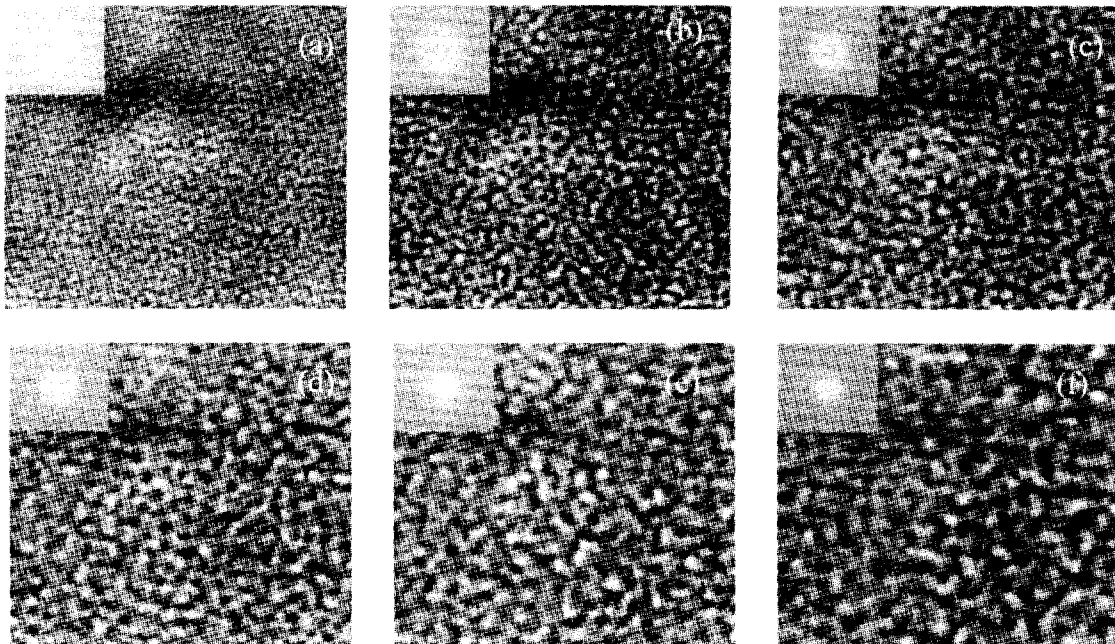


Figure 1. LSCM images of PS/PB/Toluene system with time after quenching, (a) 8 sec; (b) 41 sec; (c) 82 sec; (d) 164 sec; (e) 245 sec; (f) 368 sec. Quench depth (ΔT) is 5 °C. Total size of images are $115.2 \times 115.2 \mu\text{m}^2$. The insets show the power spectrum of 2D-FFT from the images.

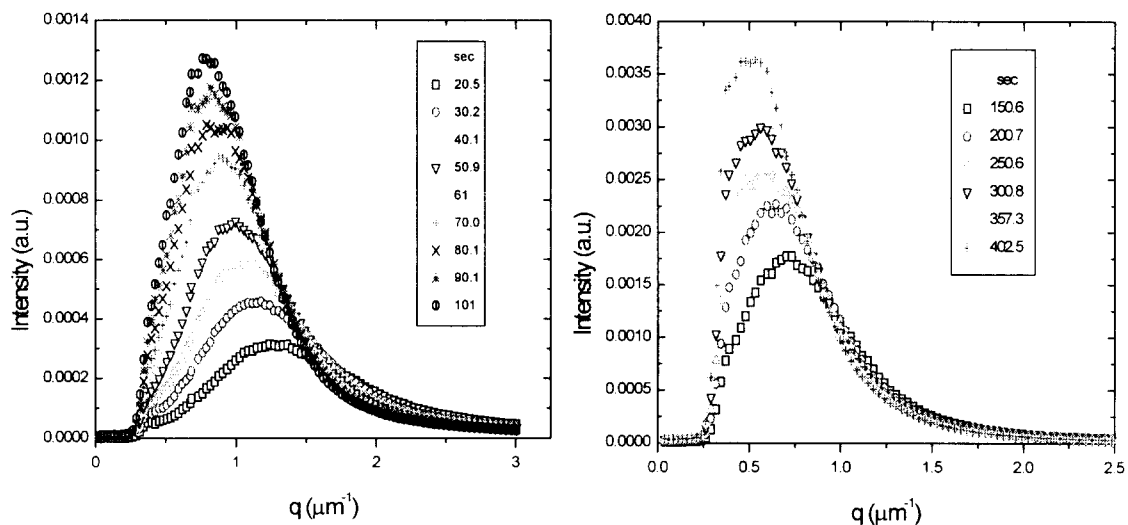


Figure 2. Intensity of peak increase and $q_m(t)$ decrease with time at the late stage of phase separation in the PS/PB/toluene system. The concentration of polymers is 5.2 Vol% at $\phi_{PS} = 0.5$. The quench depth is 5°C .

Figure 1 shows typical changes of LSCM images of phase domains at the critical composition of PS/PB in toluene with time. After quenching by 5°C below phase boundary, successive images with time were collected. The images show that the interconnected domains observed grow with time. Due to low contrast between the two phase domains, it is not quite noticeable to decide the initial domain shape and the size at earlier time, but the domain growth keeps increasing with time later. Through 2-Fast Fourier Transform (2-FFT) of images (see insets of Figure 1), the power spectra of real images were calculated. From the maximum value of correlation length ($q_m^{\text{FFT}}(t)$), most probable length of phase domains were evaluated.

Likewise, the changes of scattering profiles with time shown as in Figure 2 also represent the growth of phase domains. The characteristic behaviors of scattering profiles with time in the late stage of phase separation are that the scattering maximum ($q_m(t)$) move to low q and the intensity of peak ($I_m(t)$) increase with time, because the correlation length is bigger and the scattering contrast increases with time as the ripening of domains proceed.

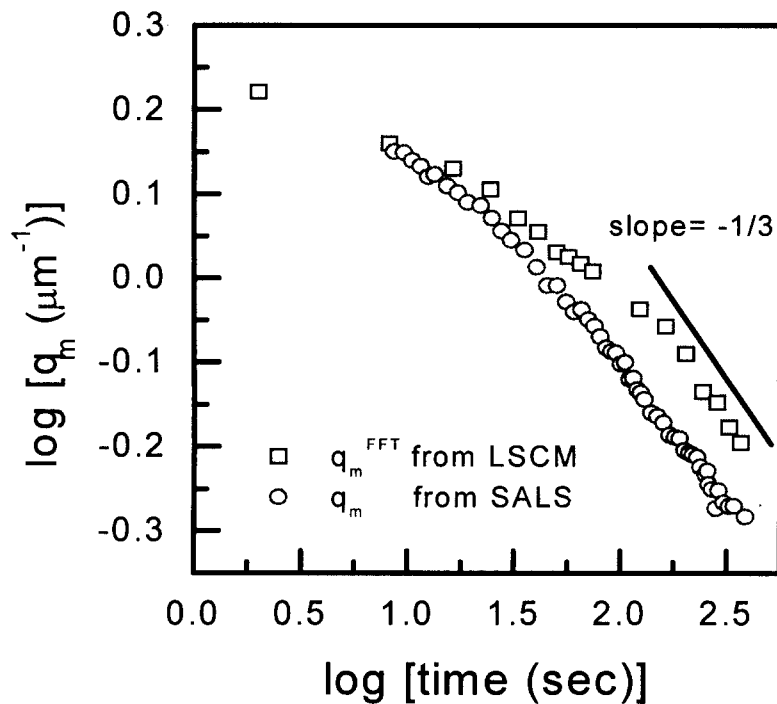


Figure 3. Double logarithmic plot of q_m from light scattering and q_m from FFT as a function of time. The quench depth is 5 °C.

As shown in Figure 3, both $q_m^{\text{FFT}}(t)$ from image analysis and $q_m(t)$ from the results of the light scattering experiment for the same quench depth ($\Delta T = 5$ °C) hold the 1/3 power law in the late stage of phase separation as Lifshitz and Slyozov [3], and Binder and Stauffer [4] predicted. Thus, it should be noted that the domain growth in the ternary system are also fitted to the classical model of coarsening as found in binary systems such as polymer blends and binary fluids.

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