Polymer blend films have drawn considerable attention for numerous technological applications in the fields of coating techniques, adhesives, lubrication, microelectronics and biophysics in the past decades. Their performance in these applications depends on structures in blend films, which are mainly controlled by phase behaviors, e.g. phase separation of polymer blend, dewetting of the film and interplay between them. It is reasonable to imagine the complex phase behaviors when phase separation and dewetting take place in the same system. Such polymer blend films may involve the competition between them upon thermal or solvent annealing. Obviously, the relative rates of phase separation and dewetting dominate the competition between the two processes. Furthermore, the occurrence of one process (e.g. phase separation) affects the other one (dewetting) if they do not take place at the same time [1].

The competition between “dewetting” and “phase separation” behaviors in polymer blend films attracts significant attention. The simultaneous phase separation and dewetting in PMMA/SAN [poly(methyl methacrylate) and poly(styrene-ran-acrylonitrile)] blend ultrathin films upon solvent annealing have been observed for the first time in our previous work [2]. In this work, composition dependence of phase behaviors in the same system has been investigated using atomic force microscopy (AFM) and grazing incidence small-angle X-ray scattering (GISAXS). Both phase separation and dewetting processes were observed over the whole composition ratio investigated. Moreover, the evolution of film structures during solvent annealing was found to be much dependent on the composition of the blend. Basically, the solvent annealing leads to the complex structures in which the upper part (small spots, bicontinuous structures or a large continuous droplet) and the lower part (mimic-films) are composed of phase-separated SAN-rich phase and PMMA-rich phase, respectively. With increasing SAN weight fraction in the blend, on one hand, the diameter of lower part (PMMA-rich mimic-film) decreases monotonously. On the other hand, the upper part (SAN-rich phases) changes from small spots (SAN10, SAN30) to bicontinuous structures (SAN50), and finally a large continuous droplet (SAN70, SAN90) on top of PMMA mimic-film.

Figure 1. Snapshots of topography images [2.5×2.5μm²] for SAN10, SAN30, SAN50, SAN70 and SAN90 in the vapor of acetic acid at early (1), medial(2), later (3) stages, final stable structures and linecut of them (4). The z-axes is 109nm. (A) and (B) are the common double logarithmic presentations from GISAXS of SAN30 (A) and SAN70 (B).

References