

<sup>a</sup>Department of Chemical Engineering, Kyoto University, A4-021, Katsura Campus, Nishikyo-ku, Kyoto, 615-8510, Japan. \*Corresponding author: taki@cheme.kyoto-u.ac.jp.

The control of pore-size distribution in porous films is essential in many applications. Here, we report the development of a process facilitating the production of polymeric porous films with bimodal or unimodal poresize distributions. High-pressure  $CO_2$  was homogeneously dissolved into a liquid film comprised of a UVcurable monomer and a photoinitiator solution. The  $CO_2$  pressure was released to atmospheric pressure, causing bubble nucleation via depressurization-induced phase separation. Simultaneously, UV light was applied to the film, causing bubble nucleation via photopolymerization-induced phase separation. During the nucleated bubbles expanded and coalesced, the UV light induced the photopolymerization of the monomer. Photopolymerization solidified and stabilized the transient porous (bubble) structure of the thin film. Interestingly, the timing of the UV irradiation altered the pore-size distribution in the film. When UV irradiation was applied prior to depressurization-induced phase separation, most of the bubble nucleation occurred via photopolymerization-induced phase separation, and the pore-size distribution was unimodal, with a mean pore diameter of 10 µm. However, when the UV irradiation was applied after depressurizationinduced phase separation, the pore size-distribution was bimodal, with two maxima at diameters of 10 and > 20µm, due to the dual modes of bubble nucleation (i.e., depressurization and photopolymerization) and subsequent bubble coalescence. This process facilitates the creation of films with either bimodal or unimodal pore-size distributions.