Modulation of Fractional Free Volume (FFV) in Polymer Membranes Utilizing High-Pressure Carbon Dioxide

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Dense carbon dioxide has attracted much interest as a novel solvent, for its solvent properties may be tuned by manipulating the pressure and temperature. Whereas processes utilizing high-pressure carbon dioxide as a bulk solvent are challenged by the limited solvent quality of carbon dioxide for most hydrocarbons and the high cost for high-pressure equipments, the phenomenon of polymer swelling by carbon dioxide may be realized as viable processes with smaller apparatus under relatively low pressures. In order to understand phenomena of polymer swelling by dense carbon dioxide and the effects on fractional free volume, both equilibrium and meta-stable properties were assessed from ellipsometric measurements of polymer membrane thickness and the refractive index before and after the dense membranes are treated with high-pressure carbon dioxide. A process is developed to induce metastable increase in FFV of polymer membranes by gradually releasing disolved carbon dioxide from swollen polymer at low temperatures. This process is expected to provide a method to control FFV, thus the permeability of gases in dense polymer membranes.