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Gas Permeation in Thin Glassy Polymer Films

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The development of asymmetric and composite membranes with very thin dense "skins" needed to achieve high gas fluxes enabled the commercial use of membranes for molecular level separations. It has been generally assumed that these thin skins, with thicknesses of the order of 100 nm, have the same permeation characteristics as films with thicknesses of 25 microns or more. Thick films are easily made in the laboratory and have been used extensively for measuring permeation characteristics to evaluate the potential of new polymers for membrane applications. There is now evidence that this assumption can be in very significant error, and use of thick film data to select membrane materials or predict performance should be done with caution. This presentation will summarize our work on preparing films of glassy polymers as thin as 20 nm and characterizing their behavior by gas permeation, ellipsometry and positron annihilation lifetime spectroscopy. Some of the most important polymers used commercially as gas separation membranes, i.e., Matrimid® polyimide, polysulfone (PSF) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), have been made into well-defined thin films in our laboratories by spin casting techniques and their properties studied using the techniques we have developed. These thin films densify (or physically age) much faster than thicker films, and, as result, the permeability decreases, sometimes by several-fold over weeks or months for thin films. This means that the properties of these thin films can be very different from bulk films. The techniques, interpretations and implications of these observations will be discussed. In a broader sense, gas permeation measurements can be a powerful way of developing a better understanding of the effects of polymer chain confinement and/or surface mobility on the behavior of thin films.