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**Controlling Free Volume for Permeability enhancement in Polymer-Grafted Nanocomposites** CONNOR BILCHAK, EILEEN BUENNING, SANAT KUMAR, CHRISTOPHER DURNING, Columbia University, BRIAN BENICEWICZ, University of South Carolina — Significant advances in polymer membrane technology have been made by exploring glassy materials with intrinsically high ‘free volume’, allowing for diffusion selectivity. However, the permeability of these materials is restricted by the Robeson Upper Bound and exhibits long-term aging. While nanofiller have been used to avoid the deleterious effect of aging, they further limit transport properties and can result in non-equilibrium structures that phase-separate. We here show that 14nm silica nanoparticles grafted with rubbery Poly(Methyl Acrylate) (PMA) chains form hexatic lattices, solving a common difficulty in this class of membrane constructs of controlled dispersion morphology. In addition, our results show that these materials have permeabilities elevated relative to the neat polymer matrix, offering surprising beneficial gas transport properties. We also show that the ‘free volume’ available for diffusion can be adequately controlled by tuning polymer chain length and graft density. We propose the morphology of these grafted nanoparticle systems may be manipulated to optimize these composites for a wide variety of vital gas separations.

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