Abstract Submitted
for the MAR11 Meeting of
The American Physical Society

Tuning the Dynamics of Penetrant Transport in Glassy Polymers through Network Structure Modification ADAM EKENSEAIR, NICHOLAS PEPPAS, Department of Chemical Engineering, The University of Texas at Austin — The relative rates of the diffusional and relaxational processes during the absorption of penetrant molecules in glassy polymers determine the nature of the transport process and lead to Fickian, Case II, and anomalous absorption behavior. While previous models account for anomalous behavior, there is still a disconnect between theory and experiment, as data must be fit to the model with previously determined independent parameters. With trends leading to smaller device scales and increasingly complex polymer structures, there is a need for a quantitative understanding of the manner in which a polymer's network structure alters both the rate and the mode of penetrant transport. To this end, the effects of the basic network parameters of PMMA, including the degree of crosslinking, polymer mesh size, and the crosslink interchain bridge length, on the integral sorption of methanol were studied utilizing gravimetric integral sorption studies. The effects of sub-T_g annealing/aging, temperature, and the presence of un-reacted monomer were also investigated. Controlling the relative timescale of the relaxational process by altering the polymer network structure was shown to directly influence the Case II front propagation velocity and control the overall nature of the observed transport behavior.

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Date submitted: 19 Nov 2010 Electronic form version 1.4