Entanglement Density Changes in Free-Standing Thin Polymer Films JOSEPH STANZIONE, RICHARD WOOL, University of Delaware — The entanglement molecular weight M_e is obtained when a random walk chain crosses a plane three times to form a loop (R.P. Wool '83) such that for polymers with structure $–CH_2-CHX-$ where X is the side group, it is found that $M_e = 31\ C_\infty\ M_o/j$, where C_∞ is the characteristic ratio, M_o is the monomer mol weight and j=2 is the number of bonds per monomer. In thin films of thickness $d < 2R_g$, M_e behaves as $M_e \sim d$ and this behavior is confirmed by computer simulation of random walks in thin films with reflecting boundary conditions. Thus, the entanglement density $v \sim 1/M_e$ increases as d decreases and rheological properties such as plateau modulus change as $G_{N^\circ} \sim 1/d$ and plateau creep compliance $J_o \sim d$. The mechanical stiffening of thin films is in accord with recent experiments of McKenna et al (2012). The results are also in accord with the Packing model (Lin, Kavassil, Fetters 1983) where $M_e = 354\ p^3$ in which $p = M_o\ j/[C_\infty\ b_o^2]$. The packing model is exactly derived from the Wool entanglement model for these polymers since $C_\infty = 1.36\ [M_o/j]^{1/2}$. The empirical packing model with its excellent data correlation $M_e \sim p^3$ has been misinterpreted by many and such suggestions that v decreases due to nanoconfinement and $G_{N^\circ} \sim d$ are incorrect.

Richard Wool
University of Delaware

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