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Percolation¹ RICHARD Entanglement Theories: Packing vs. WOOL, University of Delaware — There are two emergent theories of polymer entanglements, the Packing Model (Fetters, Lohse, Graessley, Milner, Whitten, \sim '98) and the Percolation Model (Wool \sim '93). The Packing model suggests that the entanglement molecular weight M_e is determined by $M_e = K p^3$, where the packing length parameter $p = V/R^2$ in which V is the volume of the chain (V=M/ ρ Na), R is the end-to end vector of the chain, and K \approx 357 ρ Na, is an empirical constant. The Percolation model states that an entanglement network develops when the number of chains per unit area Σ , intersecting any load bearing plane, is equal to 3 times the number of chain segments (1/a cross-section), such that when $3a\Sigma = 1$ at the percolation threshold, $M_e \approx 31 M_j C_{\infty}$, in which M_j is the step molecular weight and C_{∞} is the characteristic ratio. There are no fitting parameters in the Percolation model. The Packing model predicts that M_e decreases rapidly with chain stiffness, as $M_e \sim 1/C_{\infty}^3$, while the Percolation model predicts that M_e increases with C_{∞} , as $M_e \sim C_{\infty}$. The Percolation model was found to be the correct model based on computer simulations (M. Bulacu et al) and a re-analysis of the Packing model experimental data. The Packing model can be derived from the Percolation model, but not visa versa, and reveals a surprising accidental relation between C_{∞} and M_i in the front factor K. This result significantly impacts the interpretation of the dynamics of rheology and fracture of entangled polymers.

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