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Segmental order of entangled polymer networks is controlled by monomer fluctuations along the confining tube MICHAEL LANG, JENS-UWE SOMMER, Leibniz Institute of Polymer Research, Hohe Strasse 6, 01069 Dresden, Germany, THEORY OF POLYMERS TEAM — The tube model of entangled chains is applied to compute segment fluctuations and segmental orientational order parameter in polymer networks. The latter is essential for interpreting NMR measurements of entangled polymer networks. The sliding motion of monomers along the tube axis leads to a non-homogeneous reduction of segmental order along the chain. For network strands of length N much larger than entanglement length N_e , the average segmental order decreases $\sim (N_e N)^{-1/2}$ in marked contrast to the $1/N_e$ contribution of entanglements to network elasticity. As consequence, network modulus is not proportional to segmental order in entangled polymer networks. Monte Carlo simulation results of polymer networks over a wide range of molecular weights are in quantitative agreement with the theoretical predictions. The impact of entanglements on these properties is directly tested by comparing with simulations where entanglement constraints are switched off.

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