Three Faces of Polymer Entanglements

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The confining tube model represents the collective topological effects of many neighboring polymers on a given one by a confining potential. The diameter of the confining tube and the conformations of network strands change non-affinely with macroscopic deformation. In contrast, the pairwise entanglements model identifies topological restrictions between a pair of chains. Such pairwise topological entanglements deform affinely with the macroscopic deformation of the polymer network and are therefore qualitatively different from confining tube entanglements. We show that the number of monomers in the affine strand increases upon network swelling due to the dis-interpenetration of network chains and saturates at a value corresponding to the pairwise entanglements determined by the primitive path analysis. This saturation corresponds to the collective-to-pairwise entanglement transition. Both collective and pairwise entanglements improve mechanical properties, such as the toughness of polymer networks, by re-equilibrating tension in network strands. The third type of topological interactions between polymers is observed upon polymer deswelling and is similar to entanglements, forcing non-concatenated rings into compact, loopy globular conformations. Such transient entanglements formed upon deswelling of polymer gels store the extra length of polymer strands in fractal loopy conformations and allow super-elasticity of de-swollen gels – their very large reversible deformability.