Polymer and polyelectrolyte brushes: the effect of macromolecular architecture on structural, elastic and tribological properties

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Polymer brushes are built up of neutral or charged (ionic) macromolecules grafted to a planar surfaces or to colloidal particles. We overview recent advances in theory of polymer brushes with the main focus on specific features arising due to branched or cyclic topology of the brush-forming macromolecules and its interplay with solvophilic/solvophobic and long range electrostatic interactions.

We present first a scaling approach for describing large-scale structural properties of brushes formed by branched macromolecules. This approach involves inevitably assumptions about intramolecular strain distribution. A more refined self-consistent field (SCF) analytical theory enables us to justify these assumptions and to get a better insight into intrinsic structure of brushes formed by branched macromolecules of arbitrary topology. This approach is coupled to the Poisson-Boltzmann approximation for analysis of structural properties of brushes formed by ionic branched macromolecules.

The SCF method enables us also to analyse structure of multi-component brushes. We demonstrate that branched and linear macromolecules with selected molecular weights and architectures can distribute their free ends all over the volume of a mixed brush and produce unified polymer density profiles which results in equal availability of terminal functional groups. This property is controlled solely by topology of the brush-forming chains irrespectively of the nature of intermolecular interactions.

Compared to brushes of linear chains, the brushes of branched macromolecules provide a sharper increase in the repulsive force when the brushes pushed to overlap. The branched polymer brushes decorating apposing surfaces exhibit weaker interpenetration than brushes of linear chains. We thus discuss the impact of branching on the tribological properties of the brush-decorated surface and colloidal stability of dispersions.