28g Solvation Forces Due to Multiply Attachable Copolymers: a Density Functional Approach

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Abstract: Multiply attachable copolymers such as hydrophobically modified polyethylene glycol (hm-PEG) have been recently proposed for the stabilization of fusogentic liposomes and other liposomal colloids useful for drug delivery. The performance of these copolymers depends on their molecular architecture in particular the strength and the frequency of surface anchoring sites along the backbone of highly soluble polymer chains. In this work, we investigate theoretically the interactions between two planar surfaces mediated by multiply attachable copolymers with various frequencies of anchoring sites and chain lengths using a polymer density functional theory [Cao and Wu, Macromolecule, 38(3), 971, 2005]. We find that the cooperativity of anchoring sites is highly sensitive to the architecture of copolymer molecules. For ‘W'-type chains that have dangling tails, the increase of chain length at the fixed ratio of the non-binding to binding segments leads to stronger repulsive barrier in the surface potential and thus more efficient for surface protection. This prediction conforms to the experimental observation that increasing the number of hydrophobic anchors on a PEG polymer results in cooperativity of the polymer adsorption and steric stabilization of colloidal suspensions. For ‘M'-type copolymers that are free of dangling tails, however, the theory predicts that the copolymer with 2 binding sites (i.e. telechelic copolymer) is most efficient for the stabilization of colloidal particles. At fixed overall polymer molecular weight, the addition of anchoring sites gives rise to the stronger repulsion barrier in the solvation potential, i.e. copolymers with alternating short non-stick blocks between two binding sites provide higher level of surface protection than those with long non-stick blocks.