Ordering of Polymers – From the molecular to the macroscopic scale

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Polymers are typically very long chain-like molecules that are entropically driven to adopt a random coil conformation; coercing them to adopt a specific "folded" conformation is a major challenge that has confronted polymer chemists for a long time. In contrast, biological functions are most often accomplished with remarkable ease because giant biological macromolecules are gently guided to one specific three-dimensional folded structure using a variety of weak intra-chain non-covalent interactions, most important of which are H-bonding and electrostatic interactions. These relatively strong non-covalent interactions are often gently nudged by even weaker interactions, like π–stacking, hydrophobic interactions, etc. Clearly, biological structures often mockingly tease synthetic chemists who are faced with a herculean task when trying to mimic these elaborate, yet beautiful, biological macromolecules, even if it were just at the structural level.

During the past decade, we have developed some interesting approaches to coerce synthetic polymer chains to adopt specific, but rudimentary-type of folded conformations, such as pleated structures; these were accomplished using a variety of weak intra-chain interactions, such as charge-transfer interactions, metal-ion complexation, solvophobic effects, etc.[1] More recently, we have been exploring selective segment crystallization as a possible driver to fold synthetic polymers into single-chain nano-particle type entities; these were accomplished, in one case, by designing suitable periodically grafted amphiphilic graft copolymers,[2] while in the other by generating *Janus*-type amphiphilic hyperbranched structures.[3] The central theme in both these systems is the exploitation of the strong tendency for long alkylene segments to crystallize in a paraffinic-type crystalline lattice. I shall discuss these new designs to control the conformation at a single-chain level, provide evidences for their formation and discuss the consequences of such molecular-level control on their bulk morphology.

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3. Raj Kumar Roy, E. Bhoje Gowd and S. Ramakrishnan, "Periodically Grafted Amphiphilic Copolymers: Nonionic Analogues of Ionenes" *Macromolecules* 45*,* 3063 (2012).