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Theoretical Modeling of Hydrogen Bonded and Metal-Ligand Associating Polymers[1]

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Applying analytical modeling in combination with Monte Carlo simulations we have studied the association behavior and properties of two types of supramolecular polymers employing 1) hydrogen bonded and 2) metal-ligand associative motifs. In the first case association between the hydrogen bonded arrays results in numerous donor-acceptor interactions between the complementary end groups of linear oligomers leading primarily to formation of linear chains or rings. Similar architectures of self-assembled polymers can also be obtained by reversible 1:2 complex formation between metal ions (such as Zn(+2), Cd(+2), Co (+2), etc.) and ligands of end-functionalized oligomers. In this case the association is strongly influenced by metal- ligand ratio. We analyze the chain-ring equilibrium and study the influence of the strength and type of association, rigidity of the complex and solution composition on the degree of association and the average molecular weight of the supramolecular polymers. For metal ions (such as La(+3), Nd(+3), Eu(+3), etc) capable of 1:3 complex formation with the ligands, self-assembly results in reversible polymers of more complex architecture, in particular a reversible network (in the percolation limit). Since the coordination sites of the metal possess unequal reactivity (having different energies of association with the first, second and third ligand) and due to the cooperativity of binding, network formation is influenced by different factors such as metal/ligand ratio, oligomer length and concentration. Predictions of an analytical model based on the equilibrium among different associating species and classical percolation theory compare favorably with simulation results for gel fraction and average molecular weight. Simulation results and theoretical predictions will be compared with available experimental data.

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