

RHEOLOGY OF METALLO-SUPRAMOLECULAR POLYMER NETWORKS

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The class of supramolecular systems coined “metallo-supramolecular polymers” offer several advantages compared to their covalent counterparts, e.g. a “self-healing” mechanism due to the reversibility of the supramolecular bond. The present rheological study deals with transient networks from poly(ethylene-oxide) 4-arm-stars (4s-PEO) with terpyridine-functionalized end-groups. These specific systems for binding covalent macromolecular precursors are based on metal-bis-terpyridine complexes [Guillet et al. *Soft Matter* (2009) 5, 3409] and provide unique tunability and simplicity, thus making them ideal model systems to test supramolecular dynamics and stimuli responsive behavior on well-defined supramolecular architectures, such as stars or hierarchically branched structures.

The nature of the transition-metal ion determines the strength of the metal-ligand interactions e.g. iron and nickel being much stronger than zinc. Most interestingly the terminal time of the transient network is found to be not affected by the dilution with solvent, e.g. ethylene-glycol (EG), even in the highly diluted regime. The relaxation times and moduli increase with the addition of metal ions by several orders of magnitude compared to the unfunctionalized polymer, which demonstrates the unique tunability and simplicity of this kind of associations.