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**Self-Assembly of Polyoxometalate and Polyelectrolyte Macroions into Mechanically Strong Supramolecular Hydrogels** BENXIN JING, Y. ELAINE ZHU, Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, MI 48202 — Polyoxometalate (POM) macroions are the nanoclusters of transition metal oxide with size 1-10 nm and well-defined structure at the atom level. Because of their stoichiometric surface groups and high solubility in polar solvents to form thermodynamically stable solution, POMs are studied as excellent model macroions at nanoscale. In this work, we explore the electrostatic controlled self-assembly of anionic POMs and cationic or zwitterionic polyelectrolytes (PEs) in aqueous solution. Specifically we examine the complex formation of zwitterionic poly (3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide) (PSBMA) and cationic poly(diallyldimethylammonium chloride) (PDADMAC) with tungstate based POMs of varied valence. The phase diagram of POM/polyelectrolyte complexes is determined with varied POM/PE charge ratios. It is interesting to observe the coacervation of POMs with PSBMA. With cationic PDADMAC, hybrid POM-PDADMAC hydrogels can be formed. Nevertheless, POM-PDADMAC complexes exhibit much enhanced mechanical properties in comparison to polymer hydrogel. The viscoelastic properties of hybrid macroion complexes strongly depend on PDADMAC concentration, POM-to-PDADMAC molar ratio, the size and valence of POMs. At the intermediate range of POM-to-PDADMAC concentration ratio, shear thickening and strain hardening are observed with soft supramolecular hydrogels, which is resulted from the non-Gaussian stretching of polymer chains.

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