

Stimuli-responsive Pt⁽⁰⁾ containing metallosupramolecular polymers

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Supramolecular polymers (SPs) are macromolecules formed by self-assembly of monomeric units via non-covalent interactions such as H-bonding, metal-ligand complexation or ion pairing.^[1] SPs combine the physical properties of polymers and the advantages of dynamic supramolecular interactions, which also can impart stimuli-responsive behavior. Metallosupramolecular polymers (MSPs) represent a subclass of this materials family, in which chain extension takes place through coordination of multifunctional macroligands with metal salts.

Building on previous work on cross-linked Pt⁽⁰⁾-containing MSPs,^[2] we have recently developed a synthetic framework for the synthesis of MSPs in which chain extension takes place through Pt⁽⁰⁾(alkyne)₂ complexes. These materials are prepared by fast ligand exchange between Pt⁽⁰⁾(styrene)₃ and a diphenyl acetylene-terminated telechelic core; for this study the low-glass-transition cores poly(ethylene-co-butylene) and poly(tetrahydrofuran) were selected.

Homogeneous films of the new polymer were solvent cast and characterized by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS) and Fourier transform infrared spectroscopy (FTIR). Collectively, the techniques revealed nanophase segregation with no long range order and adequate stability under ambient conditions. Heating these materials over a characteristic threshold temperature causes the dissociation of the Pt⁽⁰⁾(alkyne)₂ complex, which leads to the formation of Pt⁽⁰⁾ nanoparticles in the polymer matrix as confirmed by TEM. The decomplexation kinetics were studied using a model compound that mimics the thermally labile polymeric Pt⁽⁰⁾(alkyne)₂ complexes and it was observed that the threshold temperature for thermal decomplexation depends strongly on the ligand structure. Overall, this procedure presents a new approach to the preparation of Pt nanoparticles, which has significant practical advantages over previous protocols that involve the *in situ* reduction of a metal salt.^[3]

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