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Colloidal polymers from inorganic nanoparticle monomers

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ABSTRACT

The use of preformed inorganic nanoparticles as “colloidal monomers” has received recent attention for the formation of one-dimensional (1-D) mesostructures, or “colloidal polymers.” These colloidal monomers form linear assemblies through attractive, directional, interparticle interactions, which are similar to covalent or supramolecular interactions in classical polymer science. However, in contrast to the high degree of structural control available in the synthesis of classical molecular polymers, methods to control fundamental structural features such as chain length (DP), composition (copolymers), and architecture (linear, branched, etc.) are still being developed for NP-based colloidal polymer systems. We therefore review the colloidal polymerization of inorganic nanoparticle monomers by applying the conceptual framework provided by polymer science to categorize these novel systems. The descriptive nomenclature used for classical polymers is applied to NP assembly to define more explicitly the types of colloidal polymers formed in terms of DP, architecture, and composition (for binary NP assemblies). This review includes descriptions of inorganic nanoparticle types useful for the formation of colloidal polymers with examples chosen to demonstrate control over mesoscopic structure and composition. The various emergent optical, electrical and electrochemical properties from these materials are also reviewed and correlated with structural control achieved in various colloidal polymer systems.

Contents

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1. Introduction

The use of well-defined inorganic nanocrystals as reagents for the construction of novel colloidal compounds or assemblies is an emerging approach for the preparation of complex materials with hierarchical structure. A number of reports have described the concept of using inorganic nanoparticles (NPs) as "artificial atoms" for the formation of colloidal crystals and superlattices, as pioneered by Murray and coworkers [1–3]. Shape control of inorganic NPs later extended the structural complexity of these systems by introducing intricate nanocrystalline architectures in the form of nanorod, tetrapod, and dendritic morphologies, as first demonstrated for cadmium chalcogenide NPs [4–9]. Chemical transformations also exist which enabled the formation of "artificial molecules" containing two or more discrete nanoparticle domains within a single nano-object. Examples of these heterostructured nanomaterials include inorganic heterodimer NPs by Xu [10,11], Teranishi [12], Sun [13,14], and Hyeon and coworkers [15], which have been comprehensively reviewed elsewhere [16–18]. More recently, a "nanoparticle total synthesis" approach was developed for the formation of complex trimers, tetramers, and oligomeric species by sequential nanoparticle formation and bond forming reactions, which expanded the use of preformed nanocrystals as reagents for synthetic transformations [19–21].

Building on the concept of using nanoparticles as chemical precursors, the use of preformed nanoparticles as "colloidal monomers" has received recent attention for the formation of one-dimensional (1-D) mesostructures, or "colloidal polymers" (also termed "nanopolymers" or "nanochains"). These colloidal monomers form linear assemblies through attractive, and directional, interparticle interactions (e.g., electrostatic interactions, chemical bonds, magnetic interactions). *A key challenge in the synthesis of colloidal monomers is in developing synthetic methods to embed anisotropic character to nanoparticle materials to enable strongly associative 1-D interactions.* The formation of *colloidal polymers* requires that these interparticle associations be strong enough to overcome thermal fluctuations, and that these anisotropic interactions be highly efficient with minimal side reactions to form linear assemblies with reasonable degrees of polymerization (DP).

In contrast to the high degree of structural control afforded from the synthesis of classical molecular polymers, methods to tune fundamental structural features, such as, chain length (DP), composition (copolymers), and architecture (linear, branched, etc.) are still being developed for NP-based colloidal polymer systems. Applying these "principles of polymerization" [22] to the assembly of inorganic nanoparticles is expected to enable access to complex nanocomposite materials that cannot be fabricated via current synthetic methods. However, to the best of our knowledge, the use of inorganic nanoparticles to form colloidal polymers has not been reviewed in terms of monomer types, polymerization mechanisms, or methods for controlling fundamental polymer structural parameters.

Herein, we classify and review the colloidal polymerization of inorganic nanoparticle monomers by applying the conceptual framework provided by polymer science to these mesoscopic systems. The descriptive nomenclature used for classical polymers is used to define more explicitly the types of colloidal polymers that have been prepared in terms of DP, architecture, and composition (for binary or complex NP assemblies). This review includes descriptions of inorganic nanoparticle types useful for the formation of colloidal polymers with examples chosen to demonstrate control over key structural parameters, and correlation with emergent optical, electrical and electrochemical properties.

1.1. Types of colloidal polymerizations

We propose a classification scheme which divides colloidal polymerizations into categories by the interparticle interactions between NP monomers directing the formation of colloidal assemblies (Scheme 1). In classical polymer science, polymers are typically classified by their respective polymerization mechanisms (e.g., step-growth versus chain-growth) which further provides insight into the processes affecting the degree of polymerization (DP), polydispersity (M_w/M_n) and polymer structural features [22]. To date, the vast majority of colloidal polymers are formed via step-growth type processes. Furthermore, the preparation of colloidal polymers has been achieved by harnessing either permanent chemical bonds, or supramolecular associations between NP units [23–28]. However, fundamentally different colloidal monomer types and interparticle binding motifs have been used to form colloidal polymers that deviate from classical polymerization reactions of small molecule monomers. Colloidal polymers are synthesized by harnessing interparticle associations of nanoparticle monomers, and these associations depend greatly on features such as crystal phase, morphology, and ligand functionalization of the colloidal monomers utilized. Hence, the classification of existing colloidal polymers can best be described by the

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