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A Nanotechnology Review

SURFACE ENGINEERING OF POLYMERIC NANOPARTICLES BY CONTROLLED RADICAL POLYMERIZATION

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Abstract

The design and synthesis of nano-engineered materials with precise control over material composition, architecture and functionality is integral to advances in diverse fields. Recent development in the techniques of functional polymeric nanomaterials such as controlled radical polymerization (CRP) has opened up a new horizon to provide cascades of novel hybrid nanomaterials for versatile applications. CRP, especially atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization, has been demonstrated as a powerful strategy for synthesizing well-controlled macromolecules. The resulted organic-inorganic hybrid nanostructures encompassed in this dissertation show their huge promise towards mechanical, electrical, optical, imaging, biomedical and actuating applications. Above all, these versatile techniques for surface functionalization of nanomaterials by polymers offer indispensible tools for the future development and application of these materials and structures.

Key words: Controlled Radical Polymerization, Polymer, Nanocomposites, Advanced Nanotechnology.

Introduction

Nanotechnology refers broadly to manipulating matter at the atomic or molecular scale and using materials and structures with nanosized dimension, usually ranging from 1 to 100 nm. Due to their nanoscale size, nanomaterials show unique optical, electronic, catalytic and chemical properties, and also because nanometer-size structures are appropriate for interfacing with biomacromolecules (proteins, DNA, and so forth) and probing intracellular environments. The nanoparticles (NPs) are usually coated with an organic or inorganic layer that provides solubility, long-term colloidal stability, and further modification. Nanohybrids adopt some unique characteristics from the components that compose it; synergistic effects can also produce properties not present in any of the parts.

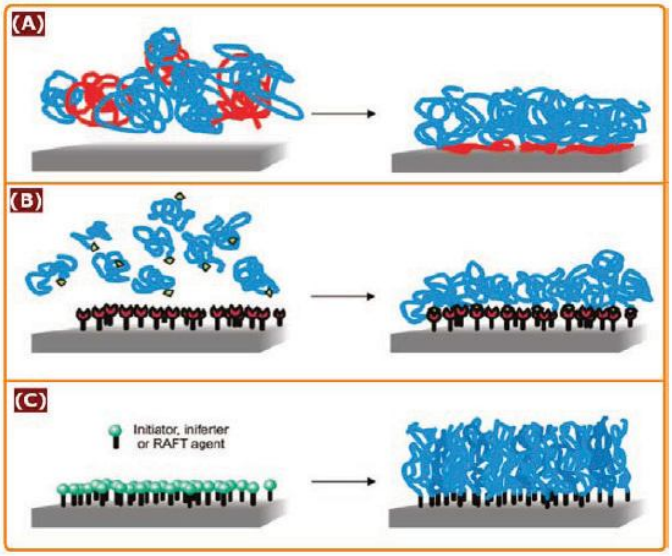
In recent years, there has been a considerable interest in the development of polymer nanocomposites because of their dramatically increased surface area to volume ratio, leading to a variety of unique properties. Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix with dispersed inorganic nanofillers. Polymer nanocomposite shows unique properties, combining the advantages of the inorganic nanofillers (e.g., rigidity, thermal stability) and the organic polymers (e.g., flexibility, dielectric, ductility, and processability). The inorganic nanofillers have large surface area, leading to a significant increase in interfacial area [1-5]. These nanofillers, even at very low concentrations, can strongly change the macroscopic properties of the polymer. Inorganic nanofillers include metal oxides (e.g., SiO2, TiO2, Al2O3, Fe3O4), nanotubes, layered silicates (e.g., montmorillonite, saponite), metalic NPs (e.g., Au, Cu), semiconductors (so called quantum dots, e.g., PbS, CdS, CdSe), and mesoporous silicas shows the different classes of nano-and microparticles which are all very general and multifunctional, but have applications in a very wide fields.

A great deal of motivation exists for the modification of these materials and surfaces to render these outstanding materials viable for potential applications in materials and bioscience. Nowadays, investigating the methodologies that can be employed to modify surfaces in a selective and efficient fashion is a prime goal to control the chemical composition at the material interface. The particle surface can be manipulated with a secondary metal or polymer to create core-shell structures. The outer shells function as protective layers for the inner inorganic NPs cores and alter the surface chemistry to enable post-synthetic functionalization of the surface chemistry. The nanosized structures afford polymers unique and superior properties differing from those of the bulk polymer, such as optical, magnetic, thermal, and electrical properties. Hence, a huge number of studies have been performed to control the size and shape of the NPs core and/or to choose the chemical structure of the stabilizing ligand shell. This allows the tailoring of the NPs specific properties towards the many foreseen applications in drug delivery, surface coatings, nanoreactors, catalysis and filtration [6-14].

Recent developments in the techniques of polymer synthesis such as controlled radical polymerization (CRP) provide a feasible approach to prepare well-defined macromolecules with desired functionalities. CRP, especially atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization, nitroxide-medicated radical polymerization (NMP), has been demonstrated to be a powerful tool for synthesizing macromolecules with controlled molecular weight and desired architectures [15,16]. It is expected that these versatile techniques of polymer synthesis can be utilized as a useful resource for the development and application of exciting novel and improved materials and structures [17-19].

2. Synthesis of polymer brushes via surface grafting strategies

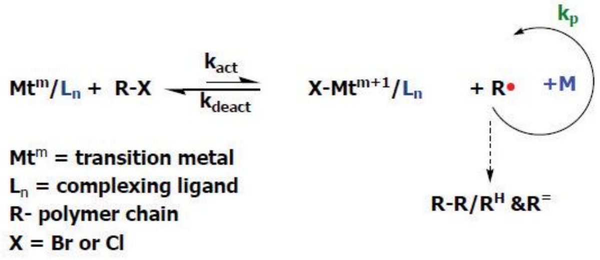
Nanohybrids comprising a polymer and an inorganic NP or surface can be generally prepared by physisorption or chemisorption attachment. In polymer physisorption, polymer chains with 'sticky' segments are adsorbed onto a suitable substrate. Non-covalent adsorption of polymers to surfaces is a reversible process and such polymer brushes are often unstable (Scheme 1A). Covalent tethering of polymer chains to substrates can be accomplished either by the 'grafting to' or 'grafting from' approaches [20-22]. In the 'grafting to' approach, polymer chains are attached directly on suitable surfaces via reaction between end-functionalized polymers and appropriate reactive groups on substrate surfaces (Scheme 1B). Although experimentally grafting to strategy is very straightforward, but it suffers from several limitations, which make it difficult to produce thick and very dense polymer brushes. Steric repulsions between polymer chains hamper the formation of dense polymer brushes. Furthermore, with increasing polymer molecular weight, the reaction between the polymer end-group and the complementary group on the substrate surface becomes less efficient. As a result of these limitations, "grafting from" method has become the preferred option for the synthesis of polymer brushes. This approach has attracted much interest in recent years because of its effectiveness in producing functional polymer brushes of large thickness and high density in a controllable manner. In the grafting from approach, the polymerization is directly initiated from initiator-functionalized surfaces (Scheme 1C). The substrate surface of choice is first modified with an initiator monolayer. The polymer chains grow directly from the reactive sites of the immobilized initiator layer. In order to achieve maximum control over brush length, density, polydispersity and composition on the surface, several 'grafting from' methods have been developed, including surface-initiated cationic polymerization, anionic polymerization, and ring-opening polymerization.



Sheme 1. Synthetic strategies for the preparation of polymer brushes

3. Atom transfer radical polymerization (ATRP)

Radical polymerization has been playing an important role in the development of nanotechnology because of its widespread applications in the preparation of polymer based functional nanomaterials. Of the CRP methods, ATRP has been considered as one of the most successful methods for the polymerization and block-copolymerization of a wide range of monomers in a controlled manner. ATRP involves the use of a transition metal halide and a suitable nitrogen-based ligand [23,24]. The control over radical polymerization is based on two principles. Firstly, initiation should be fast to provide a constant concentration of growing polymer chains. Secondly, the majority of the dormant polymer chains should retain the ability to grow, due to established dynamic equilibrium between the dormant species and the growing radicals. A general mechanism of ATRP is shown in Scheme 2. The catalyst complex establishes a reversible equilibrium between the growing radicals (active species) and dormant species. When the concentration of propagating radicals is sufficiently low in comparison to the dormant species, the proportion of terminated chains from biomolecular recombination can often be neglected (¡5%). Thus, by keeping the concentration of active species or propagating radicals sufficiently low, termination can be suppressed throughout the polymerization process to produce mostly well-defined polymer chains (¿95%). The ATRP process does not require stringent experimental conditions and can tolerate a wide range of functional monomers. Because of its controlled/'living' nature, ATRP allows the preparation of well-controlled polymers of narrow molecular weight distribution, predetermined by the concentration ratio of the consumed monomer to the introduced initiator. A large variety of multi-functional materials can be prepared by varying the polymer microstructure (e.g. linear, branched, hyperbranched, or multi-armed star-shaped polymers) and/or the composition (e.g. gradient copolymers, block copolymers, or grafts). Most importantly, ATRP can be easily initiated from various types of substrates (e.g. planar surfaces, inorganic particles/colloids, polymer chains, networks, and dendrimers) to produce well-defined functional polymer brushes for tailoring the surface properties.

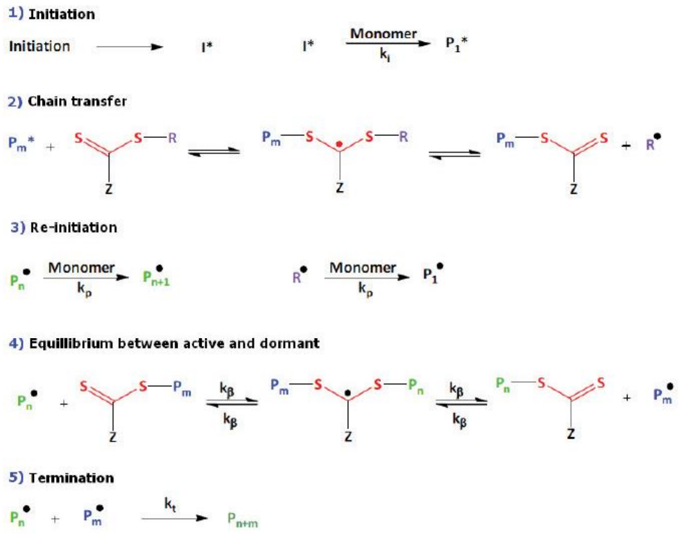


Scheme 2. A general mechanism for transition metal-catalyzed ATRP

During recent years, of the surface-initiated CRP techniques, surface-initiated ATRP has been recognized as the most versatile for various surfaces functionalization, including planar surfaces, and surfaces of inorganic particles, colloids and polymer networks, and even from dendrimers. In the preparation of functional polymer brushes via surface-initiated ATRP, the presence of a uniform monolayer of initiators on the target substrate surfaces is indispensable. Several immobilization methods of ATRP initiators have been developed for a wide range of biomedical substrates, including inorganic surfaces of silicon, silica, titanium, gold, Fe_3O_4, and surfaces of films such as polypropylene (PP), aromatic ring containing polymers, cellulose, and nylon. The synthesis of organic/inorganic hybrid materials using surface-initiated ATRP technique has gained increasing attention for emerging applications as sensors, imaging agents, storage media, and catalysis in biotechnology and microelectronics.

4. Reversible addition fragment chain transfer (RAFT) polymerization

RAFT polymerization, first reported in 1998 by Moad, Rizzardo and Thang at CSIRO in Australia, is a living radical polymerization (LRP) technique, a free radical polymerization technique which is observed to be a robust method suitable for different reaction media such as bulk, solution, emulsion, and miniemulsion, in ionic liquids and supercritical carbon dioxide, and at high pressure [25,26]. Several narrow polydispersity block copolymers have been prepared from a wide range of monomers with varying reactivity including functional monomers. Because of the above reasons, RAFT is the choice of interest for the synthesis of well controlled polymer architectures - in particular functional hydrophilic and amphiphilic (co)polymers - with a strong potential for applications in polymer-metal and polymer mineral hybrid nanoparticle fabrication [27,28].



The commonly accepted mechanism of the RAFT polymerization is demonstrated in Scheme 3. In RAFT polymerization a thiocarbonylthio group containing compound, with a general structure of Z-C(=S)S-R (step 2), is added to an otherwise conventional free radical polymerization in order to obtain a controlled radical polymerization. These controlling agents are reversible chain transfer agents (CTAs) or RAFT agents. First, the free-radical source is identical to that used in conventional free radical polymerization (thermoinitiator, photoinitiator). The transfer reaction between the active species and the thiocarbonylthio-containing CTA leads to the formation of dormant species (equilibrium I, sometimes called pre-equilibrium) and to the release of a fragment radical, Ro, able to initiate a new polymer chain (re-initiation). The dormant species, which also bear a thiocarbonylthio function (macroCTA), induce other reversible addition-fragmentation equilibrium (equilibrium II). The active species can also propagate and terminate like in a conventional free radical polymerization. However, in a RAFT polymerization, the amount of initiator (the only free-radical source), and thus the concentration of active species, is lower and the termination reactions are minimized. The polymer chains successively pass from a dormant state to an active state during which they can add monomer units. In contrast to a conventional free radical polymerization, chains grow in parallel during the whole polymerization process.

Currently, the CRP techniques, especially the RAFT processes, have been widely employed for the construction of new and well-defined nanohybrids. RAFT polymerization has been successfully used to grow polymer brushes from a wide variety of different substrates via surface-initiated polymerization. The well-defined complex macromolecules made by RAFT can be used to build nanostructures such as silicon oxide, silicon, metal oxide, clay mineral, gold, metal and semiconductor, carbon, and polymer surfaces [29]. RAFT is an emerging candidate for answering both the increasing need of modern scientific community to employ highly functional polymeric materials and the global requirements for developing sustainable chemicals and processes.

5. Conclusion

The main thrust of this review has been drawn to synthesize inorganic-organic nanocomposite materials due to their promising applications in many fields. Intercalation of organic species into layered inorganic solids represents one of the useful approaches to design and synthesize multifunctional materials useful in fabricating optical, electric, magnetic, sensors, imaging agents, storage media, and catalysis in biotechnology and biomaterials applications. The synthesis of organic/inorganic hybrid materials using surface-initiated ATRP, RAFT technique can be employed in preparing novel nanomaterials and molecular devices with tailor-made structures and properties for the future development and application of these materials and structures.

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