Amphiphilic Polymeric Core-Shell Particles:

Novel Synthetic Strategy and Potential Applications of the Particles

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ABSTRACT

We have developed a novel and commericially viable route to a wide range of highly uniform, amphiphilic core-shell particles in nano- to micro-scaled sizes. Novel feature of this synthetic approach is that it combines graft copolymerization, *in situ* self-assembly of the resulting amphiphilic graft copolymers and emulsion polymerization in a one-step synthesis. This versatile methodology allows us to design and tailor-made particles for specific applications through selection of appropriate amino-containing water-soluble polymers and hydrophobic monomers.

Keywords: nanoparticles, core–shell, amphiphilic, well-define, uniform

INTRODUCTION

Core−shell polymeric particles that consist of two or more very different chemical components and have particle diameters in nano- to micro-size ranges often exhibit improved physical and chemical properties over their single-component counterparts in applications as diverse as biomedicine and surface coatings. In particular, amphiphilic particles that consist of well-defined hydrophobic cores and hydrophilic shells have attracted much attention because of their potential applications in diagnostics, bio-separation, drug delivery, gene therapy, enzyme immobilization, coatings, and catalysis [1, 2]. They are also of interest from a fundamental point of view in colloid and interface science [3-5].

Various synthetic approaches have been reported to synthesize amphiphilic core–shell particles based on polymerization and assembly methods. They include: (1) Graft copolymerization of a hydrophilic monomer onto a reactive seeded particle via either conventional or living radical polymerization [6, 7]. (2) Copolymerization of a reactive macro-monomer with a hydrophobic monomer [8]. (3) Emulsion polymerization in the presence of block copolymer [9] or comb-like copolymer [10] containing controlled free radicals moieties. (4) Ab initio emulsion polymerization by self-assembly using controlled radical polymerization [11]. (5) Self-assembly of amphiphilic block copolymers, followed by crosslinking the core or shell via covalent or ionic bonding [12]. (6) Stepwise deposition of polyelectrolytes onto charged particle surface [13].

METHODOLOGY

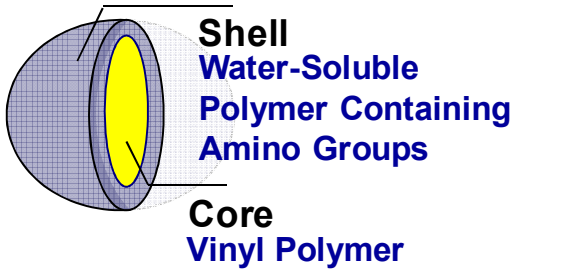
We have developed another route to synthesize well-defined, amphiphilic core–shell particles and hydrophilic microgels [14-17], based on the aqueous-phase redox reaction between alkyl hydroperoxide and amine functional groups of a water-soluble polymer. Initiation comes about when the amine-containing water-soluble polymers interact with a small amount of catalyst in water at between 70–80 °C to generate free radicals on the polymer backbone. The macroradicals subsequently initiate the graft polymerization of the hydrophobic monomer. The amphiphilic macro-radicals generated can *in situ* self-assemble to form polymeric micelle-like microdomains, which become loci for the subsequent polymerization of the monomer: a type of emulsion polymerization. Well-defined amphiphilic core–shell particles with diameters between 50 and 300 nm, thus can be produced in the absence of surfactant.

FEATURES

Novel feature of this synthetic approach is that it combines graft copolymerization, *in situ* self-assembly of the resulting amphiphilic graft copolymers and emulsion polymerization in a one-step synthesis. This versatile methodology allows us to design and tailor-made particles for specific applications through selection of appropriate amino-containing water-soluble polymers and hydrophobic monomers. Special features of this synthetic route and products include:

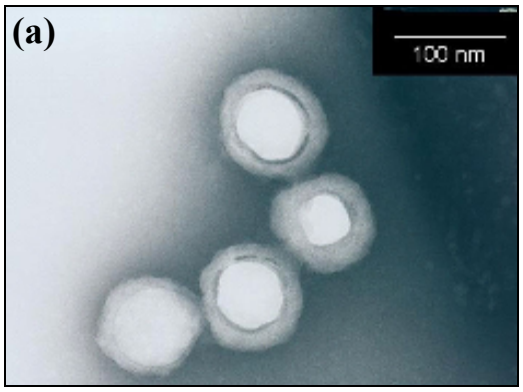
- The particles are easy to synthesize in high solids content (up to 30%) without using surfactant.
- The particles have well-defined core-shell nanostructure ranging from nano-to micro-scale with narrow particle size distribution.
- The process uses aqueous-based Chemistry, which is environmentally benign.
- The core property of the particle can be varied (e.g. hard, soft, temperature-sensitive and hollow).
- The shell component can use a wide range of amine containing water-soluble polymers such as synthetic and biopolymers
- Surface functionalities and properties can be easily altered.

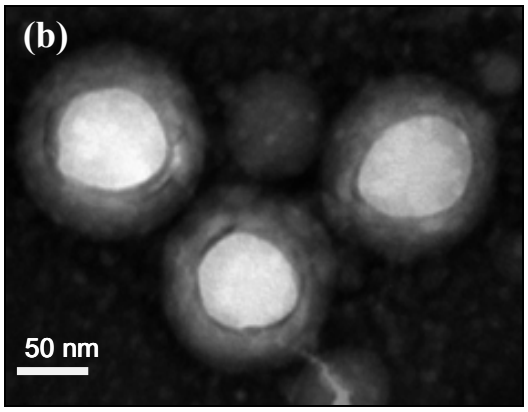
This process offers a commercially viable route to a wide variety of novel core-shell particles with different sizes, compositions, structures and functions (examples are shown in Figure 1). Applications of these unique particles in gene and drug deliveries, enzyme immobilization, bioseparation, water treatment, antibacterial and functional coatings have been demonstrated. This presentation will show the synthetic methodology that allows for tuning of the internal core and external shell compositions and properties for selected applications.

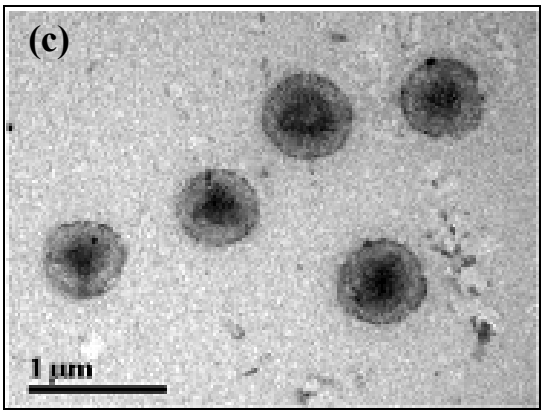


Hydrophobic core + hydrophilic shell
(Amphiphilic core-shell particle)

Hydrophilic core and shell
(Core-shell microgel or smart microgel)







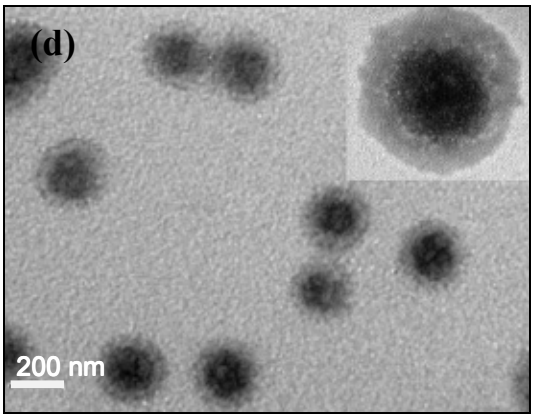


Figure 1. TEM images of particles (a) poly(methyl methacrylate) cores with polyethyeneimine shells; (b) polystyrene cores and polyethyeneimine shells; (c) poly(*n*-butyl acrylate) cores and chitosan shells: (d) poly(*N*-isopropylacrylamide) cores with chitosan shells.

POTENTIAL APPLICATIONS

These core–shell particles have been applied in various fields. For example, particles with PMMA cores (~ 90 nm in diameter) and hairy poly(ethyleneimine) shells have been successfully used as carriers in gene and drug deliveriers [18-20]. Particles with biopolymer shells such as chitosan and soft poly(n-butyl acrylate) cores have been applied onto cotton fabrics as a biocompatible antibacterial finishing [21, 22]. Particles with PMMA cores coated with either polyethylenimine or chitosan shells (~150 to 500 nm in diameter) have been applied as effective nanosorbents to remove heavy metals and organic contaminants in wastewater treatment [23]. The core-shell particles can be used for multiple times via a process of regeneration. For application in enzyme immobilization, novel one-step immobilization of celluase onto a non-porous nanoparticle has been developed [24]. The core-shell nanoenzyme particles show many advantages over the conventional immobilization methods. Furthermore, modification of the core-shell particles to hollow particles allows us to create novel materials such as nanotubes, nanofibers and rods in nano- and micro-size ranges [25, 26]. Magnetic-responsive, biocompatible core-shell particles with magnetic nanoparticles encapsulated inside the core have also been prepared [27] for usage in bio-separation, targeted drug and gene delivery and immobilization of enzyme.

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