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# Synthesis of photo- and pH-responsive composite nanoparticles using a two-step controlled radical polymerization method

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ABSTRACT

We present a versatile synthetic method for photo- and pH-sensitive composite nanoparticles using a combined use of reversible addition-fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP). Crosslinked nanoparticles of a random copolymer composed of methyl methacrylate (MMA), 4-vinylbenzyl chloride (VBC) and divinylbenzene (DVB) were first synthesized using RAFT miniemulsion polymerization in aqueous solution. This was followed by solvent exchange through extraction and dialysis that allowed the nanoparticles to be transferred to and highly swollen in an organic solvent (anisole or THF). By dissolving a monomer of a stimuli-responsive polymer in the solution, subsequent ATRP grafting polymerization could be initiated by halide groups on the swollen nanoparticle, resulting in larger composite nanoparticles. Photosensitive poly-(*1*-pyrenylmethyl methacrylate) (PPyMA) and pH-sensitive poly(dimethylaminoethyl methacrylate) (PDMAEMA) were incorporated in the composite nanoparticles, and their photo- and pH-responsive behaviors were investigated. With this method, monomers soluble in organic solvents can be used in conjunction with emulsion polymerization in aqueous solution to design functional composite nanoparticles.

## 1. Introduction

Much effort has been devoted to the use of emulsion polymerization to prepare composite latex particles that combine properties of more than one polymer. The most used method consists in polymerizing a first monomer in aqueous solution, which leads to the formation of seed particles, and then adding a second monomer followed by its polymerization [1–5]. This procedure allows for the formation of core-shell particles of two polymers, with the actual morphology controlled by thermodynamic and kinetic parameters [6]. For instance, to reduce the interfacial tension between two immiscible polymers A and B, methods were developed in which a small number of graft [7] or block copolymer [6] composed of A and B can be formed during the reaction that acts as a compatibilizing agent for the two constituent polymers. However, this method generally requires that the two monomers be in the liquid form, which limits the number of usable monomers and renders the synthesis of stimuli-responsive composite nanoparticles difficult, because, for example, most monomers for photo-responsive polymers are solid under ambient conditions. Recent efforts in exploiting the controlled radical polymerizations offer possible solutions to this problem. Among many reports, Jhaveri et al. showed that particles of a polymer bearing bromine groups could be prepared using surfactant-free emulsion polymerization, collected and redispersed in an organic solvent due to the highly crosslinked nature (using a trimethacrylare monomer as the crosslinker); with bromine groups exposed on the surface, surface-initiated atom transfer radical polymerization (ATRP) could be used to graft a second polymer resulting in core-shell nanoparticles [8]. Zhang and Stöver used precipitation copolymerization to prepare lightly crosslinked and thus swellable microspheres that, after modification to introduce bromine groups, were served as ATRP macroinitiators to graft a second polymer from an outer layer and the surface of the microspheres (diameter ~ 4 μm for the composite particles) [9]. In this paper, we report a modified version inspired by these approaches, which is based on the use of swellable nanoparticles (not microspheres) to graft a second polymer from the inside, and show that it is a general and versatile method for the synthesis of photo- and pH-sensitive polymer composite nanoparticles.

The approach is schematically illustrated in Fig. 1a. Firstly, a reversible addition–fragmentation chain transfer (RAFT)

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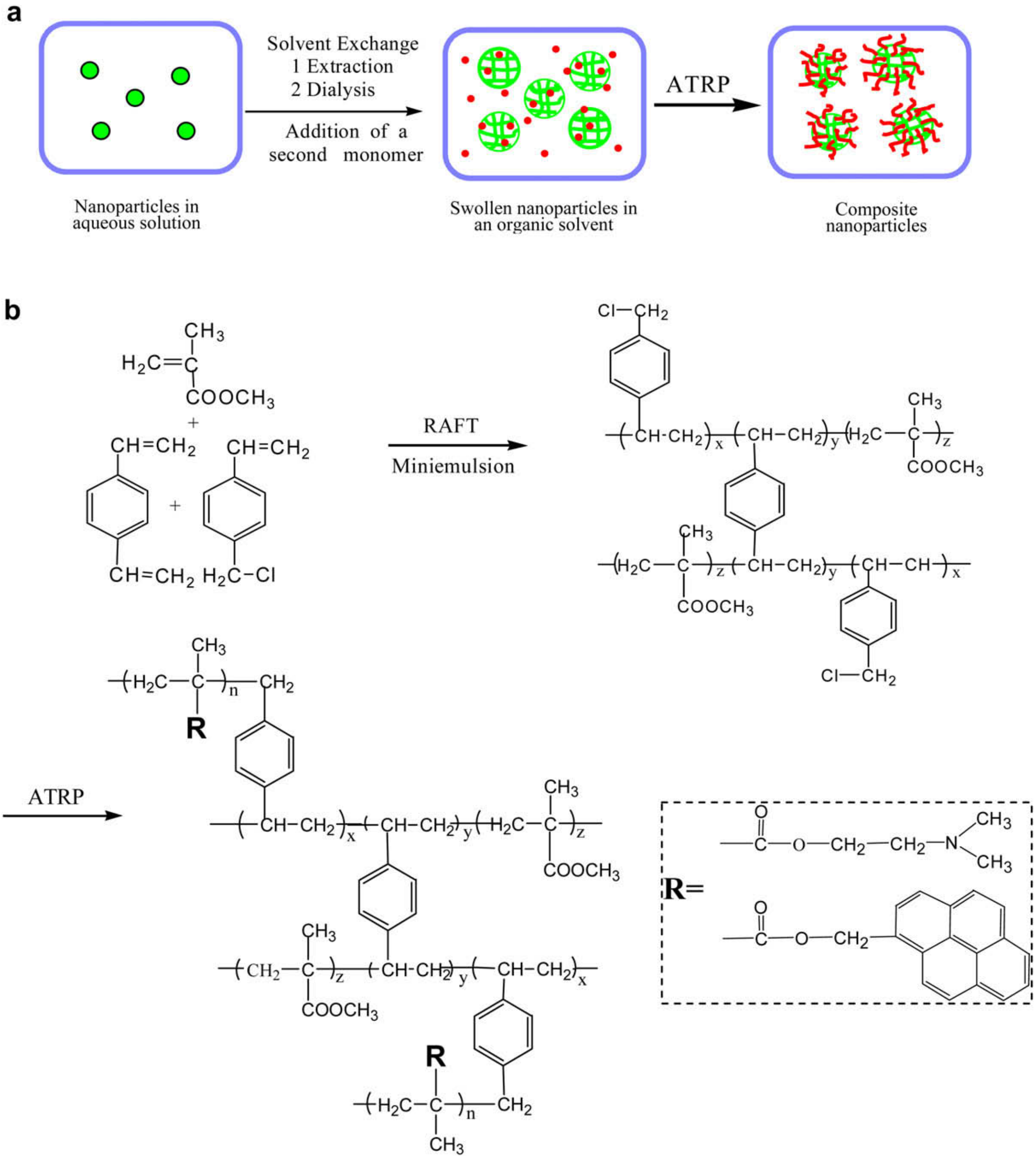

**Fig. 1.** (a) Schematic illustration of the synthetic approach based on solvent exchange and swelling of the seed nanoparticles prior to grafting polymerization. (b) General reaction scheme showing chemical structures of the stimuli-responsive composite nanoparticles.

miniemulsion polymerization is carried out in aqueous solution to produce crosslinked nanoparticles containing halide groups. This is followed by a solvent exchange process through extraction and dialysis against a chosen organic solvent, leading to solubilized and highly swollen nanoparticles. Then a second monomer is dissolved in the solution for polymerization through ATRP. Due to the swelling of the nanoparticles that exposes halide groups to the reactive solution, the ATRP is expected to start not only from the surface but also from the inside of the nanoparticles. In this way the resultant composite nanoparticles should have the second polymer emanate from the interior to surface. Given that the two polymers are immiscible, microphase separation should occur in the graft copolymer and allows for the compartmentalization of the nanoparticles. To demonstrate this method, we prepared photo- and pH-sensitive composite nanoparticles. As shown in Fig. 1b, the initial polymerization (RAFT miniemulsion) of methyl methacrylate (MMA), 4-vinylbenzyl chloride (VBC) and divinylbenzene (DVB) gives crosslinked nanoparticles dispersed in aqueous solution; after their transfer to and swelling in an organic solvent containing a second monomer, the subsequent polymerization (ATRP), enabled by VBC units [10–12], results in grafts of either photosensitive poly(*1*-pyrenylmethyl methacrylate) (PPyMA) or pH-sensitive poly-(dimethylaminoethyl methacrylate) (PDMAEMA). Note that although the crosslinked nanoparticles could be prepared using normal emulsion polymerization, RAFT was chosen with the purpose of investigating the combined use of two controlled radical polymerization methods in preparing such composite functional nanoparticles.