



# Efficient one-pot synthesis of uniform, surface-functionalized, and “living” polymer microspheres by reverse atom transfer radical precipitation polymerization



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## ABSTRACT

A facile, general, and efficient one-pot approach to obtain uniform, highly cross-linked, surface-functionalized, and “living” polymer microspheres by reverse atom transfer radical precipitation polymerization (RATRPP) is described for the first time, which is easily realized by introducing reverse atom transfer radical polymerization (reverse ATRP) mechanism into precipitation polymerization system. The polymerization parameters including stirring rate, polymerization temperature, monomer loading, initiator concentration, and polymerization scale and time showed considerable influence on the yields and morphologies of the polymer microspheres, which makes it convenient to tailor the particle sizes by tuning polymerization conditions. The general applicability of RATRPP was verified by preparing some uniform functional copolymer microspheres with incorporated 4-vinylpyridine, glycidyl methacrylate, and 2-hydroxyethyl methacrylate. Moreover, the resulting polymer microspheres proved to be “living” by their direct grafting of hydrophilic polymer brushes via surface-initiated ATRP. Furthermore, a mixed particle growth mechanism is proposed for RATRPP (i.e., a combined “grafting from” and “grafting to” mechanism works prior to the consumption of the conventional initiator and a “grafting from” mechanism is dominant afterwards), which is quite different from the “grafting to” particle growth mechanism in the traditional precipitation polymerization and “grafting from” mechanism in the normal ATRPP.

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## 1. Introduction

Narrow or monodisperse, highly cross-linked, and micrometer-sized spherical polymer particles have attracted considerable attention in recent years due to their great potential in a wide range of applications [1–7]. Precipitation polymerization has proven to be an efficient approach for such purpose because of its easy operation and no need for any surfactant or stabilizer [7–21]. A large

number of uniform highly cross-linked polymer microspheres have been readily prepared by this versatile approach with different monovinyl monomers and divinyl cross-linkers, where uniform functional polymer microspheres are particularly interesting because they are highly promising in various advanced application areas [5–7].

Uniform highly cross-linked functional polymer microspheres can be directly prepared via the precipitation polymerization of a monovinyl functional monomer and a divinyl cross-linker, but rather time-consuming optimization of polymerization parameters is normally required [11,14,20]. In comparison, surface modification of polymer

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microspheres prepared via precipitation polymerization by their grafting of functional polymer shells allows more flexible and efficient synthesis of functional polymer microspheres [22–30]. In particular, the controlled “grafting from” approach permits growing dense and well-defined functional polymer brushes from the initiating groups on the particle surfaces by using various surface-initiated controlled/“living” radical polymerizations (CRPs) such as iniferter-induced living radical polymerization (ILRP) [31], nitroxide-mediated radical polymerization (NMP) [32], atom transfer radical polymerization (ATRP) [33,34], and reversible addition-fragmentation chain transfer (RAFT) polymerization [35–37]. Under such conditions, the presence of CRP-“living” groups on the surfaces of polymer particles is necessary. The polymer microspheres prepared by traditional precipitation polymerization, however, normally do not have such “living” groups, which makes their further surface modification necessary to introduce the required “living” groups prior to their surface functionalization [22–25]. Therefore, the development of facile and versatile approaches for the one-pot synthesis of uniform highly cross-linked polymer beads with surface-bound “living” groups is of significant importance for more efficiently obtaining advanced functional polymer particles.

Recently, a new kind of polymerization technique named controlled/“living” radical precipitation polymerization (CRPP) has been developed for the above purpose by introducing CRP mechanism into the precipitation polymerization system [6,7]. It combines the advantages of the traditional precipitation polymerization and CRP and can thus be performed in a diluted reaction solution in a controlled manner without need for any surfactant and stabilizer. Several different kinds of CRPP approaches have been developed for the synthesis of narrow or monodisperse, highly cross-linked, and “living” polymer microspheres up to now, including atom transfer radical precipitation polymerization (ATRPP) [38–40], RAFT precipitation polymerization (RAFTPP) [41,42], and iniferter-induced “living” radical precipitation polymerization (ILRPP) [43,44].

Since its first discovery in 1995 [45–47], ATRP has attracted considerable attention for its versatility in the controlled design of macromolecular structures. According to their different initiating species used, two kinds of ATRP methods are available, which are normal ATRP and reverse ATRP [33]. In the normal ATRP system, the initiating radicals typically stem from the reaction between an alkyl halide (or arenesulfonyl halide) and a transition metal complex in its lower oxidation state (e.g., Cu(I) halide/ligand); while in the reverse ATRP system, conventional radical initiators (e.g., AIBN) are employed to generate primary radicals in the beginning of the polymerization, which are either directly deactivated by a transition-metal complex in its higher oxidation state (e.g., Cu(II) halide/ligand) or first reacted with monomer to provide propagating radicals and then deactivated, leading to the dormant species (i.e., alkyl halide) and the transition metal complex in its lower oxidation state (e.g., Cu(I) halide/ligand). In the subsequent steps, the resulting transition-metal complex in its lower oxidation state promotes exactly the same

ATRP process as normal ATRP. In comparison with the normal ATRP, the reverse ATRP has such advantages as the use of less toxic and cheap free radical initiators (compared with alkyl halides) and stable transition-metal complexes in their higher oxidation states (while the transition-metal complexes in their lower oxidation states are sensitive to oxygen). Although the normal ATRP mechanism has been introduced into precipitation polymerization system and the resultant normal ATRPP has proven highly efficient for preparing narrowly dispersed, highly cross-linked, surface-functionalized, and “living” copolymer microspheres [38–40], the reverse ATRPP (or briefly RATRPP) combining the reverse ATRP and precipitation polymerization has never been reported. Therefore, the development of RATRPP will not only provide a powerful new ATRPP approach but also enrich the family of CRPP.

In this paper, we have demonstrated for the first time that RATRPP is a facile and efficient approach for the one-pot synthesis of uniform, highly cross-linked, surface-functionalized, and “living” polymer microspheres. The effects of the polymerization parameters (including stirring rate, polymerization temperature, monomer loading, initiator concentration, and polymerization scale and time) on the morphologies and yields of the polymer particles were systematically studied. In addition, the general applicability of RATRPP, the “livingness” of the obtained polymer microspheres, and the particle growth mechanism in RATRPP were also investigated.

## 2. Experimental

### 2.1. Materials

4-Vinylpyridine (4-VP, Alfa Aesar, 96%) and ethylene glycol dimethacrylate (EGDMA, Alfa Aesar, 98%) were purified by distillation under vacuum. Glycidyl methacrylate (GMA, Tianjin heowns Biochemical Technology, China, 97%) was purified by passing it through a neutral aluminum oxide column. 2-Hydroxyethyl methacrylate (HEMA, Tianjin Institute of Chemical Reagents, China, chemical pure (CP)) was purified by washing its aqueous solution (25 vol% of HEMA) with hexanes (4 times), salting it out of the aqueous phase by addition of sodium chloride (NaCl), drying over anhydrous magnesium sulfate (MgSO<sub>4</sub>), and distilling under reduced pressure. *N*-Isopropylacrylamide (NIPAAm, Acros, 99%) was purified by recrystallization from hexane. Azobisisobutyronitrile (AIBN, Tianjin Jiangtian Chemicals, China, CP) was recrystallized from ethanol and stored at –18 °C prior to use. Acetonitrile (Tianjin Jiangtian Chemicals, analytical grade (AR)) was distilled over calcium hydride. *N,N*-Dimethylformamide (DMF, Tianjin Jiangtian Chemicals, 99.5%) was dried with anhydrous MgSO<sub>4</sub> and then distilled under vacuum. Copper(I) chloride (CuCl, Tianjin Jiangtian Chemicals, AR) was purified by stirring it with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried under vacuum at 75 °C for 3 days. Tris[2-(dimethylamino)ethyl]amine (Me<sub>6</sub>TREN) was prepared by a one-step synthesis procedure from commercially available tris(2-aminoethyl)amine (Acros, 97%) according to a reported

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