

RAPID COMMUNICATION

Utility of Atom Transfer Radical Polymerization for the Preparation of Poly(methyl methacrylate) Beads in an Aqueous Suspension

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Received 5 August 2003; accepted 12 November 2003

Keywords: methyl methacrylate; atom transfer radical polymerization (ATRP); suspension polymerization; hexylated triethylene tetramine ligand; GPC

Copper-mediated atom transfer radical polymerization (ATRP) is one of the most important controlled/living polymerization methods.^{1–4} It has found widespread applications in the preparation of homopolymers and block or multiblock copolymers^{5–7} of styrene and acrylic ester monomers with low polydispersities. ATRP has been demonstrated to be very useful for creating graft⁸ and brush polymer architectures on solid surfaces⁹ with negligible amounts of homopolymer formation. Moreover, Percec et al.¹⁰ recently reported more complex structures such as the divergent synthesis of dendritic macromolecules from conventional monomers with suitable combinations of a terminator multifunctional initiator and ATRP. Despite the great versatility of copper-mediated ATRP for controlled/living chain growth under solution or emulsion conditions, it has not yet found an application in suspension polymerization, most likely because of the appreciable solubility of common copper complexes in water. Besides the economic peculiarities, suspension polymerization has unique advantages, such as bead particle products and easy control of the polymerization process.

There have appeared a few reports on the use of ATRP under suspension polymerization conditions. Matyjaszewski et al.¹¹ reported that the direct ATRP of methyl methacrylate (MMA) in an aqueous suspension proceeded with first-order kinetics in the presence of an oil-soluble ligand, 4,4'-di(5-nonyl)-2,2'-bipyridine, and

a nonionic surfactant. This result was ascribed to the suspension mechanism. The reverse ATRP took place in an emulsion fashion under the same conditions. They also presented the polymerizability of styrene by copper-mediated ATRP in a toluene/water mixture.¹² In addition, Percec et al.¹³ reported a method for ATRP of vinyl chloride in a two-phase system containing H₂O and tetrahydrofuran (THF) initiated with CHI₃ and catalyzed by Cu₂O/tris(2-aminoethyl)amine or Cu₂O/poly(ethyleneimine) at room temperature. They found that a combination of two processes, liquid–liquid emulsion and solid–liquid dispersion polymerization, was operative. More recently, the copper-mediated ATRP of MMA in an aqueous suspension of diphenyl ether was used to prepare crosslinked hollow polymer particles about 50–100 μm in diameter.¹⁴ Zhu et al.¹⁵ reported ATRP of MMA in an aqueous suspension and found a typical ATRP behavior under direct suspension conditions, although they used a water-soluble catalyst system (CuCl/bipyridine). However, this system was not found to be successful in reverse ATRP.

In view of these studies, we can conclude that the extension of ATRP to suspension conditions is highly critical. The final product of the suspension polymerization is expected to be in the form of 200–800-μm spherical beads, which has not been described by ATRP so far. This requires the proper selection of the suspension stabilizer. The suspension stabilizer must not be involved in the chain transfer, and the polymerization must also proceed with first-order kinetics as bulk and solution polymerizations do. This can be achieved with an organosoluble initiation system.

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 42, 1362–1366 (2004)
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