RAPID COMMUNICATION

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

NIYAZI BICAK, MUSTAFA GAZI, UMIT TUNCA, INAN KUCUKKAYA

Department of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

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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 copolymers⁵⁻⁷ 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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$$[CuBr]_{aq} + [L]_{org} - [CuBr - L]_{org}$$

$$K = \frac{[CuBr - L]_{org}}{[CuBr]_{aq} - [L]_{org}}$$

Scheme 1. Extraction of CuBr by H-TETA. K denotes the extraction equilibrium constant $[CuBr - L]_{org}$ denotes the amount of copper extracted by the ligand in the organic phase, $[CuBr]_{aq}$ denotes the initial concentration of CuBr in water, and $[L]_{org}$ denotes the concentration of the ligand in the organic phase.

In this study, we have targeted the preparation of spherical bead polymers by ATRP of MMA in aqueous suspensions. We believe that controlled/living chain growth can be achieved by ATRP under true suspension conditions. To extend ATRP to the suspension process, we have used a proper ligand, hexylated triethylenetetramine (H-TETA), that forms organosoluble copper complexes.

In this study, true suspension conditions have been established with H-TETA (prepared as described previously¹⁶) as a ligand and poly(N-vinyl pyrrolidone) (PVP) as a suspension stabilizer. It has been demonstrated that spherical beads of poly(methyl methacrylate) (PMMA) can be prepared by ATRP in an aqueous suspension.

For this reason, the extractabilities of CuBr (which was freshly prepared according to the literature¹⁷) and CuBr₂ by the ligand were inspected by the extraction of CuBr and CuBr₂ from aqueous solutions into the monomer phase. A series of aqueous solutions of CuBr and CuBr₂ were prepared by the dissolution of appropriate amounts of the corresponding salts in various concentrations $(3.5 \times 10^{-3} \text{ to } 41.8 \times 10^{-3} \text{ M})$. Each solution (50 mL) was mixed with 10 mL of MMA containing $0.325 \text{ g} (5.0 \times 10^{-4} \text{ mol})$ of H-TETA and was shaken in a separator funnel for 10 min. The organic layer became deep blue or green in less than 1 min. For distinct phase layers, 0.2 g of solid KBr was added to the mixtures. The aqueous phases were separated, and 5-mL samples were transferred into 100-mL volumetric flasks for the analysis of the residual copper contents. The copper contents were determined by a colorimetric method, with ethylenediamine used as a color reagent.¹⁸ The same procedure was followed for the analysis of Cu(I), except that the cuprous salts were oxidized with 1 mL of HNO₃ (65.0%) and neutralized with Na_2CO_3 before the analyses. The extracted amounts were calculated from differences in the initial and final copper contents of the aqueous solutions. Such an extraction can be considered chelate extraction (Scheme 1). Thus, the distribution of 0.5 mmol (0.717 g) of CuBr between a 10-mL monomer phase containing 0.5 mmol of the ligand and a 50-mL aqueous phase was determined by the analysis of the residual copper concentration $(1.83 \times 10^{-5} \text{ mol } \text{L}^{-1})$ in water after the extraction equilibrium.

The nonextracted part of the copper was 1.83×10^{-5} mol L⁻¹ \times 50 mL = 9.15×10^{-4} mmol. The extracted part of the copper was determined as follows:

Extracted copper = Total copper - Residual copper

$$= 0.5 \text{ mmol} - 9.15 \times 10^{-4} \text{ mmol}$$

= 0.499085 mmol

The concentration of the copper in the extracted phase was 0.499085 mmol/10 mL = 0.0499085 mol L⁻¹. The distribution coefficient (k_d) of the copper was

k_d=Copper concentration in the organic phase/

Copper concentration in the aqueous phase

 $= 4.99085 \times 10^{-2} \text{ molL}^{-1}/1.83$

 $imes 10^{-5} ext{ mol } ext{L}^{-1} = 2727$

The corresponding extraction coefficient (G) was

G = Extracted amount of copper/

Total amount of copper=0.499085 mmol/

 $0.5 \ mmol = 0.9997$

This means almost all CuBr was extracted into the monomer phase. This amount was quite satisfactory for conducting the polymerization in an organic phase. Similar experiments with different initial copper concentrations showed high percentages of extracted copper, as illustrated in Figure 1. Interestingly, the extracted amount of CuBr was proportional to its initial concentration in the aqueous phase. However, contrary to expectations, the extracted copper per mole of the ligand did not attain a maximum at [L]/[CuBr] = 1:1 (where [L] is the ligand concentration and [CuBr] is the CuBr concentration). Instead, a strict linearity was observed up to ratios of [CuBr]/[L] = 5:1. In another words, the G values of CuBr and CuBr₂ were always higher than 99%. This reveals that the extraction of CuBr into the organic phase deviated from typical chelate extraction. As a result, the high extractability of CuBr and CuBr, by H-TETA made it possible to fulfill true suspension conditions.

The suspension polymerization of MMA was carried out as follows (Scheme 2). To a 100-mL, three-necked flask attached to a reflux condenser and nitrogen inlet were added 50 mL of distilled water and 0.15 g of PVP (Fluka) as a suspension stabilizer. The flask was placed in a thermostated oil bath and stirred for about 30 min,



Figure 1. Extractability of copper by H-TETA (0.5 mmol) in MMA (10 mL) from aqueous solutions (50 mL) of CuBr and $CuBr_2$ at various concentrations.

until the stabilizer completely dissolved. KBr (0.2 g) was added to the solution to prevent the anion exchange of the complexed copper. The temperature of the bath was adjusted to 75 °C, and nitrogen was flushed through the solution. Under continuous stirring, 8 mL of MMA, 1 mL of a stock solution of precomplexed CuBr (0.5 mol L⁻¹) in MMA, and 1 mL of a 0.5 mol L⁻¹ initiator [ethyl 2-bromoisobutyrate (EBIB); Fluka] solution in MMA were added to the flask. The mixture was stirred at a constant stirring rate of about 500 rpm. Then, the contents of the reaction were poured into a mixture of 50 mL of methanol and 6 mL of acetic acid. The resulting light green, spherical bead particles were collected by filtration. The polymer was dried *in vacuo* at 40 °C for 24 h.

To follow the kinetics of the suspension polymerization, we repeated this procedure for different reaction times. In other words, we obtained each datum with a separate experiment to avoid the difficulties of sampling heterogeneous suspension mixtures. The data derived from the kinetic experiments were used to plot the graphs in Figures 2 and 3.

The first-order kinetic plot in Figure 2 indicates a rate constant of $1.52 \times 10^{-4} \ {\rm s}^{-1}$ (correction factor

= 0.9825). All the polymer products at conversions greater than 60% were beads. Although we did not attempt to optimize the size distribution, at a stirring rate of 500 rpm, 80–92% of the beads were 200–600 μ m. This reveals that PVP (Fluka; weight-average molecular weight = 24,000) is effective in stabilizing PMMA particles in a suspension.

The only drawback of this method is the light green color of the final bead products due to the copper complexes remaining inside the particles. We tried to remove the copper complexes in many ways. The most suitable way, we have found, is to leave the product in contact with an aqueous acetic solution (3 mL/g) for 24 h. The filtered bead products are still somewhat colored. A second treatment with the acid solution gives nearly white polymers.

Gel permeation chromatography (GPC) traces of the polymeric samples were taken with an Agilent 1100 with a refractive-index detector equipped with Waters Styragel columns (HR 5E, HR 4E, HR 3, and HR 2). THF was used as an eluent at a flow rate of 0.3 mL/min at 30 °C. The molecular weight of the polymers was calculated with the aid of PMMA standards. Before the manipulations, copper residues in the samples were



(Spherical Beads)

Scheme 2. ATRP of MMA in an aqueous suspension.



Figure 2. First-order kinetic plot of ATRP of MMA in an aqueous suspension at 75 °C $([MMA]_0/[EBIB]_0/[CuBr]_0/[H-TETA]_0 = 200/1/1/1; [MMA]_0/water = 10/50 v/v).$

removed by reprecipitation twice in an acetic acid/ethanol mixture (1/1). Thus, about 0.2 g of the light blue products was dissolved in THF (10 mL) and precipitated in 25 mL of an acetic acid/ethanol mixture. This procedure gave copper-free white polymers, which were pure enough to be used in GPC experiments. The linearity of the plot of the number-average molecular weight (M_n) versus the conversion in Figure 3 represents controlled chain growth in the polymerization. These results reveal typical ATRP behavior. However, the polydispersities of the polymers were somewhat higher and in the range of 1.3–1.5 up to 80% conversions;



Figure 3. Dependence of the molecular weights and polydispersities on the monomer conversion for ATRP of MMA in an aqueous suspension at 75 °C ([MMA]₀/[EBIB]₀/ [CuBr]₀/[H-TETA]₀ = 200/1/1/1; [MMA]₀/water = 10/50 v/v). The theoretical molecular weights are represented by the diagonal line. The triangles define the M_n and the squares define M_w/M_n .

at a 90% conversion, the polydispersity was 1.65. The $M_{\rm n}$ values (determined by GPC) were higher than the theoretical values usually observed in ATRP of MMA, and the initiator efficiencies were 0.79–0.73.

In conclusion, ATRP can be achieved under true suspension conditions with an organosoluble CuBr/H-TETA catalyst and with PVP as stabilizer. The first-order kinetics of the polymerization and the linearity of $M_{\rm n}$ -conversion plots indicate the typical ATRP behavior of the process. PMMA with moderate polydispersities can be obtained as spherical beads with polymerization yields of up to 60%. The overall results show that ATRP can be extended to suspension polymerization by the use of an oil-soluble catalyst and a proper stabilizing agent.

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