Original article

Atom transfer radical polymerization of methyl acrylate, methyl methacrylate and styrene in the presence of trolamine as a highly effective promoter

Qiao Xu, Yi-Feng Zhu, Zhao Yuan, Hua-Dong Tang *

Institute of Industrial Catalysis, Zhejiang University of Technology, Hangzhou 310014, China

A B S T R A C T

Transition metal-mediated atom transfer radical polymerization (ATRP) is a "living"/controlled radical polymerization. Recently, there has been widely increasing interest in reducing the high costs of catalyst separation and post-polymerization purification in ATRP. In this work, trolamine was found to significantly enhance the catalytical performance of CuBr/N,N,N',N'-tetrakis(2-pyridylmethyl) ethylenediamine (CuBr/TPEN) and CuBr/tris[2-(dimethylamino) ethylamine] (CuBr/Me$_6$TREN). With the addition of 25-fold molar amount of trolamine relative to CuBr, the catalyst loadings of CuBr/TPEN and CuBr/Me$_6$TREN were dramatically reduced from a catalyst-to-initiator ratio of 1 to 0.01 and 0.05, respectively. The polymerizations of methyl acrylate, methyl methacrylate and styrene still showed first-order kinetics in the presence of trolamine and produced poly(methyl acrylate), poly(methyl methacrylate) and polystyrene with molecular weights close to theoretical values and low polydispersities. These results indicate that trolamine is a highly effective and versatile promoter for ATRP and is promising for potential industrial application.

1. Introduction

In 1995, atom transfer radical polymerization (ATRP) using transition-metal complexes as catalyst and organic halide as initiator was almost simultaneously reported by Sawamoto [1] and Matyjaszewski [2] independently. Thereafter, ATRP, as one of the most successful "living"/controlled radical polymerizations, has been widely used to prepare a large variety of well-defined macromolecules including graft [3], block [4–6], gradient [7], star [8,9], hyperbranch [10,11], and dendritic (co)polymers [12], and as well as functional polymeric materials with halogen [13], hydroxyl [14], epoxy [15], cyano [16], and amide groups [17]. Recently, ATRP has attracted extensive attention in industrial applications due to its broad range of applicable monomers, high initiation efficiency, precise control of molecular weights, and mild reaction conditions.

However, ATRP intrinsically suffers from a severe challenge on its road to full commercialization due to the high cost of catalyst loading at industrial scales. In many ATRP reactions, such as those mediated by CuBr/2,2′-bipyridine(CuBr/Bpy), CuBr/1,1,4,7,10,10-hexamethyltriethylene-tetraamine (CuBr/HMTETA) and CuBr/N,N,N',N',N''-pentamethyldiethylenetriamine (CuBr/PMDETA), a nearly equal amount of catalyst and initiator (catalyst/initiator ratio = 1) is usually applied to produce well-controlled polymerizations with appropriate reaction rates. Accordingly, the catalyst concentration in these systems is approximately in the range of 1000–10,000 ppm if the monomer-to-initiator ratio is normally set up between 50 and 500. These catalysts mostly remain in the polymer products after polymerization, consequently coloring, polluting, and poisoning the polymers and deteriorating their properties such as transparence, stability, and dielectricity. Therefore, post-polymerization purification [18,19] such as extraction, chromatography separation and ion-change as well as *in situ* catalyst separations (*e.g.*, liquid–liquid and solid–liquid biphasic polymerization) [20,21] have been explored to remove the catalyst residue in the polymer products, leading to high costs, environmental problems, and scale-up difficulties.

Many efforts have been made to develop highly active catalytic systems for the purpose of minimizing catalyst consumption and reducing purification costs. Matyjaszewski group reported activators regenerated by electron transfer ATRP (ARGET ATRP) [22] and initiators for continuous activator regeneration ATRP (ICAR ATRP) [23] with catalyst concentrations reduced to tens of ppm.

However, these two systems are only applicable to those highly active catalysts such as CuBr/tris[2-(dimethylamino)ethyl]amine (CuBr/Me$_6$TREN) and not suitable for many traditional ATRP catalysts (e.g., CuBr/Bpy, CuBr/PMDETA and CuBr/HMTETA). Many researchers found that the addition of a small quantity of promoter could improve the catalyst activity and shorten the polymerization time at low catalyst concentrations. For example, Haddleton et al. [24] reported that the ATRP of methyl methacrylate (MMA) catalyzed by CuBr/N-n-butyl-2-pyridylmethanimine was greatly enhanced with the addition of benzoic acid because the benzoic acid coordinated with the copper center. Matyjaszewski et al. found that the addition of copper powder, ascorbic acid, or stannous octoate accelerated the polymerization rates of MMA and styrene (St) due to the reduction of dormant copper(II) species to active copper(I) species by the additives [25–27]. Bai and co-workers [28] demonstrated that certain alcohols were efficient reducing agents for reduction of Cu (II) ions to Cu (I) ions in AGET-ATRP of methyl acrylate (MA) and styrene (St). Luo et al. [29] observed a significant enhancement of polymerization rate with the addition of tiny amounts of aluminum hydroxide, boric acid or isobutyl boronic acid in ATRP of St. Interestingly, Zhang et al. [30] found that certain polymerization inhibitors such as 2,4,6-trinitrophenol could speed up the polymerization of MMA catalyzed by FeCl$_2$/PPh$_3$.

We recently reported CuBr/N,N,N′,N′-tetrakis-(2-pyridylmethyl)ethylenediamine (CuBr/TPEN) as a highly active catalyst with triethylamine (TEA) as a promoter for ATRP of MA, MMA and St [31–33]. The addition of TEA significantly increased the catalytic performance of CuBr/TPEN and consequently the catalyst concentration in these systems was reduced to ppm level. Nevertheless, TEA is a toxic, volatile, and highly flammable liquid with strong pungent odor and harmful irritation to human mucous membranes, skin, and eyes. The addition of TEA as a promoter may bring many adverse consequences (e.g., bad smell, toxicity and flammability) to polymer products. We herein report a novel non-toxic and biodegradable compound, trolamine, as a highly effective promoter combined with CuBr/TPEN or Me$_6$TREN for ATRP of MA, MMA and St. Based on Regulation (EC) No. 1907/2006 of the European Parliament and of the Council, trolamine is a non-hazardous substance without corrosion and irritation to human skin and has been widely used in cosmetics and medicines. The strong promotion effects of trolamine on the catalytic performance of CuBr/TPEN and CuBr/Me$_6$TREN were investigated, and the kinetics of polymerization as well as the underlying mechanism for the promotion effect are also discussed in this work.

2. Experimental

2.1. Materials

Methyl acrylate (MA, 99%, Aladdin), methyl methacrylate (MMA, 99%, Aladdin), styrene (St, 99%, Aldrich) were washed with 5% (w/w) NaOH solution, dried over molecular sieve, vacuum distilled, and stored in a refrigerator. Copper(I) bromide (CuBr, 98%, Sigma–Aldrich) was purified according to a published procedure [34]. Ligands N,N,N′,N′-tetrakis(2-pyridylmethyl) ethylenediamine (TPEN, 98%), tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN, 97%) was purchased from Sigma–Aldrich and directly used as received. Ethyl 2-bromoisobutyrate (EBiB, 99%), trolamine, tetrahydrofuran (THF) and methanol were from J&K Scientific and used as received without any further treatment.

2.2. Characterization

^{1}H NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer using CDCl$_3$ as a solvent. Chemical shift δ was given in ppm based on internal standard tetramethylsilane (TMS) (δ = 0 ppm). The monomer conversions of St, MA and MMA were determined using a gravimetric method [35]. The weight-average molecular weight (M_w), number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and polystyrene (PS) were detected on a Shimadzu Prominence gel permeation chromatography (GPC) system equipped with a Waters Styragel HR-4E solvent-saving column (molecular weight range: 500–100,000 g/mol) and a Shimadzu RID-10A refractive index detector. The eluent was THF with a flow rate of 0.3 mL/min at 35 °C. The GPC calibration curve and universal calibration curve were generated by a series of polystyrene standards (American Polymer Standards Corporation, molecular weight range: 1030–570,000) and used to calculate the M_n, M_w and M_w/M_n of PS, PMA and PMMA. UV–vis spectra of CuBr$_2$/Me$_6$TREN and CuBr/Me$_6$TREN were measured in methanol with a TU-1900 UV–vis spectrophotometer.

ATRP of MA, MMA and St: A typical procedure for ATRP of MA, MMA or St with CuBr/TPEN as a catalyst was as follows: a magnetic stirring bar and predetermined amounts of TPEN and CuBr were placed in a dry Schlenk tube. Oxygen was removed from the tube by applying high vacuum and backfilling with high purity nitrogen (5 cycles). A certain quantity of degassed monomer (e.g., MA, MMA or St) was added via a gas-tight syringe under the protection of nitrogen. The tube was transferred to a thermostable oil bath and equilibrated to a desired temperature. Then, required amounts of degassed initiator EBiB and trolamine were added via nitrogen-purged syringes. At timed intervals, samples were withdrawn via degassed gastight syringes, charged into hermetic vials, and stored in a freezer for GPC, ^{1}H NMR analysis, and gravimetric measurement. After the polymerization, a certain amount of polymer product was dissolved in THF and precipitated by cold methanol. The precipitates were collected, dried under vacuum at 80 °C, and characterized by ^{1}H NMR and ICP-MS.

3. Results and discussion

3.1. Promotion effect of trolamine on ATRP of MA catalyzed by CuBr/TPEN

For many ATRP catalysts such as CuX/BPY, CuX/PMDETA, and CuX/HMTETA (X = Cl or Br), a reasonable catalyst-to-initiator (catalyst/initiator) ratio of 0.5–1 is generally required to mediate a smooth polymerization. If the catalyst concentration is too low (e.g., catalyst/initiator <0.1), the polymerization will proceed very slowly and even stop at low conversions. For example, at catalyst/initiator = 0.01 (CuBr/EBiB = 0.01), the polymerization of MA catalyzed by CuBr/TPEN failed to proceed completely and the monomer conversion stopped at 25% in 3 h (Fig. 1(a), trolamine/CuBr = 0). Nevertheless, at the same catalyst/initiator ratio of 0.01, the addition of 5-fold molar amount of trolamine relative to CuBr (trolamine/CuBr = 5) significantly promoted the polymerization and increased the monomer conversion up to 95.1% in 6 h and 94.7% in 2.5 h if more trolamine was added (trolamine/CuBr = 25). In the presence of trolamine, the ln([M]$_0$/[M]) vs. time plots of the corresponding polymerization were linear, demonstrating that the radical concentration during the polymerization remained essentially constant and the ATRP reaction still kept first-order kinetics with respect to monomer concentration. These results clearly indicated that the addition of trolamine markedly improved the catalytical performance of CuBr/TPEN and promoted the polymerization to reach high conversion even at low catalyst concentration.

In the absence of trolamine, the number-average molecular weights of the obtained PMA were very low (M_n < 2000) and the molecular weight distributions were rather broad (M_w/M_n > 2), as shown in Fig. 1(b) (trolamine/CuBr = 0). While in the presence of five times the amount of trolamine relative to CuBr (trolamine/CuBr = 5),