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ORIGINAL PAPER

Hexamethylenetetramine as both a ligand and a reducing agent in AGET atom transfer radical batch emulsion polymerization

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Abstract Cheap and commercially available hexamethylenetetramine (HMTA) as both a ligand and a reducing agent has been successfully applied in activator generated by electron transfer (AGET) atom transfer radical batch emulsion polymerization (ATREP) for the first time. Both methyl methacrylate (MMA) and butyl acrylate (BA) can be polymerized in a controlled way according to the kinetic studies. Block copolymer of MMA and BA (PMMA-*b*-PBA) has been prepared in one pot to further prove the living/controlled characteristics of the reaction. Hundred ppm levels of Cu(II) residue was left in the polymer product after 95% of Cu(II) was removed by simply decomposing HMTA-Cu(II) complex under acidic conditions. This method features use of cheap ligand/reducing agent, environmentally benign water-based reaction medium, fast reaction rate, and simple removal of undesired Cu(II) residue.

Keywords Hexamethylenetetramine (HMTA) · Ligand ·
Activator generated by electron transfer atom transfer radical polymerization (AGET ATRP) · Atom transfer radical batch emulsion polymerization (ATREP)

Introduction

Controlled/living radical polymerization (CRP) has been extensively studied in recent years because of its unique advantages over living ionic polymerization and conventional radical polymerization [1–4]. So far, there are mainly four kinds of living radical polymerizations, i.e., atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer radical polymerization (RAFT),

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nitroxide-mediated polymerization (NMP), and iodine transfer polymerization (ITP) [5–9]. Among them, atom transfer radical polymerization (ATRP) has attracted much attention due to its characteristics such as controllable polymer molecular weight, narrow molecular weight distribution, adaptability to most monomers, smartly designable molecular architectures (e.g., comb-like, star-like, telechelic, and gradient polymers, etc.), and many commercially available ATRP initiators [10–13]. However, normal ATRP method always requires air-sensitive low-valent metal catalysts (e.g., Cu(I)) and this drawback limits its many potential applications. Thanks to Matyjaszewski's research group for their pioneering work in developing activator generated by electron transfer (AGET) ATRP and activator regenerated by electron transfer (ARGET) ATRP approach, high-valent metal catalysts (e.g., Cu(II)) together with appropriate reducing agents (e.g., ascorbic acid) can be used directly in the living radical polymerization, thus solving the problem of air sensitivity to some extent [14–16].

ATRP can be conducted in bulk, solution, dispersion, or emulsion polymerization systems, but the environmental pressure in recent years has stimulated people to research environmentally benign reaction media for ATRP. For example, ATRP in supercritical CO_2 [17], ionic liquids [18], and poly(ethylene glycol) [19] have been reported. However, the above reaction media still suffer from high cost compared to common organic solvents, and many properties of ionic liquids such as toxicity and biodegradability are still unclear [20]. Water is a well known cheap and environmentally friendly medium for many reactions, therefore, ATRP under water-based polymerization conditions has been widely studied in recent years [21–26]. Although, ATRP has been performed successfully in miniemulsion polymerizations where polymerizing loci are similar to that of bulky polymerizations [24], direct emulsion polymerization of ATRP is still a challenging task due to the preferred partition of catalysts in aqueous phase. Fortunately, Matyjaszewski's research group has developed a one-pot, two-step procedure of emulsion polymerization system, which can convert a colloidally stable microemulsion to an emulsion polymerization by controlled feed of monomer [22, 23].

In addition to reaction media, ligands also play important roles in ATRP for dissolving transition metal catalysts in organic media [27]. For example, Kotre synthesized a bipyridine amphiphilic macroligand and researched its usage in normal ATRP and reverse ATRP [28]. Dong and Matyjaszewski described ARGET ATRP of 2-(dimethylamino)ethyl methacrylate as both a monomer and a reducing agent [29]. Chen et al. [30] reported AGET ATRP of acrylonitrile using 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as both a ligand and a reducing agent. Kwak and Matyjaszewski researched systematically nitrogen-based ligands as reducing agents in ARGET ATRP [31]. Although many kinds of ligands have been developed and researched in recent years, the cost of ligands is still an unnegligible aspect for ATRP [6, 27, 32, 33]. Therefore, it is very significant and urgent to find and study new efficient, low cost ATRP ligands both in industry and academics.

The presence of metal residues in polymer products of ATRP will limit their use for many purposes such as drug encapsulation, biomedical, and food packaging materials. And many efforts have been made to remove metal residues after ATRP reactions. For instance, Brittain's research group has reported the use of precipitons and JandaJel resins for copper removal in ATRP [34, 35]. Recently, Munirasu et al. [36] described the application of hydrated natural clay to remove Cu residue. However, the above methods for Cu removal suffer from complicated ligand structures, tedious operation, and/or high cost. Up to now, the most acceptable metal removal method is still alumina or silica chromatography, though it has also high cost and tedious operation drawbacks [37, 38].

Herein, we report for the first time the use of cheap hexamethylenetetramine (HMTA) as both a nitrogen tetradentate ligand and a reducing agent in AGET ATRP under water-based emulsion polymerization conditions [39–42]. At least four aspects can reflect the importance of our work: the first one is commercial availability and very low cost of HMTA in AGET ATRP reactions, which will solve the problem of high cost ligands; the second is that HMTA functions as both a ligand and a reducing agent in AGET ATRP, thus avoiding the addition of another reducing agent and simplifying the reaction components; the third lies in that undesired Cu(II) residue can be easily removed from polymer products under appropriate acidic conditions; the last is that our method has used environmentally friendly water as the polymerization medium. Thus, our method makes it possible to prepare polymers very easily via AGET ATREP reactions, and has very promising practical and industrial applications.

Experimental

Materials

Monomers (methyl methacrylate (MMA) and *n*-butyl acrylate (BA)) were washed in 5% aqueous NaOH, and then distilled under reduced pressure to remove the inhibitor prior to use. Polyoxyethylene (20) oleyl ether (Brij-98), $CuBr_2$ (AR), 2,2′-bipyridyl (BPY) (AR), hexamethylenetetramine (HMTA) (AR), neutral Al_2O_3 (AR), ethylene diaminetetraacetic acid (EDTA, AR), 1-(2-pyridylazo)-2-naphthol (PAN, AR), HOAc (AR), and tetrahydrofuran (THF) (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC) and used directly without purification; ethyl 2-bromoisobutyrate (EBiB) (Alfa Aesar) was used directly as received. Deionized water was prepared by us.

Characterization

Gel permeation chromatography (GPC) was performed on an HP 1100 HPLC, equipped with a Waters 2414 refractive index detector and three Styragel HR 2, HR 4, HR 5 of 300 × 7.5 mm columns (packed with 5 mm particles of different pore sizes). The column packing allowed the separation of polymers over a wide molecular weight range of 500–1,000,000. THF was used as the eluent at a flow rate of 1 mL min^{-1} at 40 °C. PMMA standards were used as the reference. The average particle diameter (D_z) and particle size distribution (PSD) were determined on Rize-2008 laser particle size analyzer. The structure of the PMMA-*b*-PBA copolymer was characterized by ^{1}H-NMR spectroscopy on a Bruker AV 400 MHz spectrometer, with tetramethylsilane (TMS) as the internal standard. $CDCl_3$ was used as the solvent. Monomer conversions were determined by gravimetry.

Typical procedure for AGET ATREP of MMA with HMTA as a ligand and ascorbic acid as a reducing agent

In a typical experiment, $CuBr_2$ (0.0446 g, 0.2 mmol) and HMTA (0.0561 g, 0.4 mmol) were dissolved in degassed MMA (0.5 g, 5 mmol), followed by adding Brij-98 (0.8 g, dissolved in 7 mL of deionized water) and EBiB (0.0780 g, 0.4 mmol). The resulting microlatex was thoroughly purged by vacuum and flushed with nitrogen (three cycles) to eliminate oxygen. Then the reaction flask was sealed and placed in an oil bath thermostated at 80 °C. Ascorbic acid (0.0176 g, 0.1 mmol) dissolved in deionized water (5 mL) was injected to the mixture with a syringe to initiate the polymerization. Twenty minutes later, the left degassed MMA (1.5 g, 15 mmol) was added to undergo emulsion polymerization. During the reaction, samples were withdrawn periodically to determine the monomer conversion by gravimetry. The products PMMA were obtained after precipitation in ethanol, filtration, washing, and drying in vacuo at 60 °C to constant weight.

Before gel permeation chromatography (GPC) analysis, the polymer products are chromatographed with neutral alumina to remove the undesired Cu(II), using THF as the eluant.

Typical procedure for AGET ATREP of MMA with HMTA as both a ligand and a reducing agent

In a similar manner, $CuBr_2$ (0.0446 g, 0.2 mmol) and HMTA (0.4208 g, 3.0 mmol) are formed a complex in degassed MMA (0.5 g, 5 mmol), followed by adding Brij-98 (0.8 g, dissolved in 7 mL of deionized water) and EBiB (0.0780 g, 0.4 mmol). Then the reaction flask was sealed and placed in an oil bath thermostated at 80 °C. Twenty minutes later, the left degassed MMA (1.5 g, 15 mmol) was added to undergo emulsion polymerization. During the reaction, samples were withdrawn periodically to determine the monomer conversion by gravimetry.

Removal of Cu(II) residue from PMMA products under acidic conditions

After emulsion polymerization of MMA, the resulting green latex (containing 0.0446 g of $CuBr_2$) is divided into two equal parts: one part is acidified by adding glacial acetic acid (HOAc) till the pH value becomes 4–5, and the resulting mixture is stirred for 20 min. The two parts of latex are then treated in the following same way: they are demulsified by adding ethanol, filtered, and the two parts of filtrate are titrated by EDTA (0.02 mol L^{-1}) using 1-(2-pyridylazo)-2-naphthol (PAN) as an indicator. The analytical results are as follows: the acidic filtrate contains 0.0212 g of $CuBr_2$, accounting for 95% of total amount of $CuBr_2$; the neutral filtrate contains 0.0051 g of $CuBr_2$, accounting for only 23% of total $CuBr_2$.

Results and discussion

Hexamethylenetetramine (HMTA) is a nitrogen-containing ligand that can coordinate with various metal ions including Cu ion [43, 44]. Therefore, we firstly carried out an AGET ATREP experiment using HMTA only as a ligand and ascorbic acid (AA) as a reducing agent. Table 1 illustrates the polymerization results of MMA under AGET ATREP conditions. The results clearly show that HTMA is an effective ligand in AGET ATREP reaction system with $CuBr_2$ as the catalyst. The reaction rate is faster with HMTA ligand than that with BPY, which may result from the larger activation reaction rate constant of the HTMA tetradentate ligand than that of the corresponding BPY bidentate ligand [27].

Many kinds of tertiary amines can be used as reducing agents according to literature [31]. It is reasonable to deduce that HMTA with four tertiary amine moieties could be used as a reducing agent in AGET ATRP. The subsequent experiments prove our deduction right, and HMTA can be used as the sole reducing agent while BPY as the ligand. However, HMTA is a weak reducing agent compared to ascorbic acid and tetramethylethylenediamine (TMEDA) [19]. This result is consistent with the rule concluded by Kwak and Matyjaszewski, that is, the linear bidentate ligand has high reducing potential followed by the linear tri- and tetradentate ligands, and BPY that lacks in aliphatic amines has no reducing ability [31].

Based on the above results, AGET ATREP reactions are then conducted with HMTA as both the ligand and the reducing agent. In this case, the amount of HMTA plays a crucial role in the whole polymerizations. The AGET ATREP reaction proceeds very slow or even does not occur without enough HMTA (Exp B1 and B2, Table 2). This may be ascribed to the weak reducing ability of HMTA that can not effectively convert Cu(II) to Cu(I) to initiate the living radical polymerization. The AGET ATREP reaction can not proceed normally until the ratio of HMTA to catalyst is elevated to 15/1 (Exp B3, Table 2).

Table 1 AGET ATREP of MMA with HMTA or BPY as the ligand

Exp	MMA (wt%)	Ligand	Reducing agent	Time (min)	Convn (%)[a]	$M_{n,th}$ (g mol^{-1})[b]	$M_{n,GPC}$ (g mol^{-1})[c]	PDI[d]
A1	13.8	HMTA	AA	20	6.5	310	520	1.13
				40	20.5	1,030	1,370	1.21
				60	68.4	3,020	4,810	1.32
				120	85.3	4,270	7,120	1.26
A2	13.8	BPY	AA	120	79.4	15,700	47,520	1.30
				180	84.5	16,620	66,590	1.44

The catalyst is $CuBr_2$

[a] Conversion was determined by gravimetry

[b] $M_{n,th}$ represents the corresponding theoretical number-average molecular weight, which is calculated by the mass of polymer divided by the mole of EBiB initiator

[c] $M_{n,GPC}$ is the number-average molecular weight determined by gel permeation chromatography (GPC)

[d] PDI is polydispersity index of the polymers

Table 2 AGET ATREP reactions with HMTA as both the ligand and the reducing agent

Exp	Monomer (wt%)	[HMTA]/[catalyst]	Time (min)	Convn (%)	$M_{n,th}$ (g mol^{-1})	$M_{n,GPC}$ (g mol^{-1})	PDI	ln([M_0]/[M])[a]	D_Z/nm[b] (PSD)
B1	MMA (20.0%)	2/1	240	~0	–	–	–	–	–
B2	MMA (20.0%)	5/1	240	<10	–	–	–	–	–
B3	MMA (19.4%)	15/1	10	~0	0	–	–	0	–
			20	26.2	3,370	2,440	1.29	0.30	–
			40	31.3	4,540	4,640	1.21	0.38	–
			60	38.7	5,610	6,530	1.16	0.49	–
			90	64.5	9,350	10,810	1.29	1.04	–
			120	71.7	10,400	14,590	1.34	1.26	–
			240	83.1	12,050	18,520	1.31	1.78	186 (0.24)
B4	BA (17.8%)	15/1	20	14.8	1,899	1,750	1.06	0.16	–
			40	30.6	3,930	4,610	1.24	0.37	–
			60	52.0	7,963	9,370	1.27	0.73	–
			90	70.0	8,989	11,760	1.22	1.20	–
			120	80.4	10,330	19,710	1.35	1.63	163 (0.20)
B5	Styrene (15.0%)	15/1	240	<10	–	–	–	–	–

The catalyst is $CuBr_2$

[a] [M_0] is the initial concentration of the monomer MMA, and [M] means the concentration of MMA at a certain reaction time

[b] D_Z is the particle size, and PSD means particle size distribution

The kinetic characteristics of the AGET ATREP reaction of MMA with HMTA as both the ligand and the reducing agent are illustrated in Fig. 1a. The plot of ln([M_0]/[M]) versus reaction time is almost linear, indicating that the radical polymerization follows first order kinetics. The reaction rate is quite high in the emulsion media, and 80% monomer conversion can be achieved within 2–4 h, while 8–10 h are required to reach the similar conversion in solution system [30]. This may be ascribed to the “compartmentalization effect” of the emulsion polymerization system, in which the reaction proceeds in independent micelles and the possible radical termination among different micelles is effectively avoided. Figure 1b shows the dependence of number–average molecular weight and polydispersity index (PDI) on the monomer conversions. With the increasing monomer conversion, the experimental number-average molecular weight ($M_{n,GPC}$) increases almost linearly, indicating that the number of chains is constant, and the value of $M_{n,GPC}$ is primarily consistent with the corresponding theoretical number-average molecular weight ($M_{n,th}$), especially at early stage of the polymerization. The deviation of $M_{n,GPC}$ from $M_{n,th}$ in the late of the reaction is probably attributed to high solubility of HMTA in aqueous phase. In the whole polymerization process, PDI is generally lower than 1.3, meaning high initiating efficiency and nearly all the chains begin to grow simultaneously. Thus, AGET ATREP of MMA with HMTA as both the ligand and the reducing agent has approximate controlled/living characteristics from the kinetic data and plots.

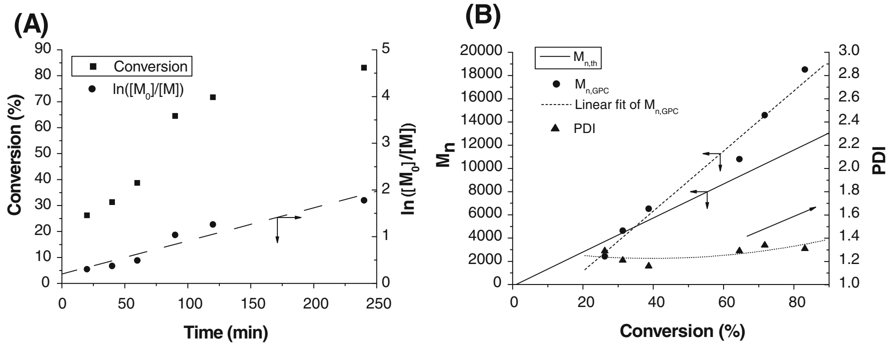

Fig. 1 **a** Dependence of MMA conversion and ln($[M_0]/[M]$) on the polymerization time with HMTA as both a ligand and a reducing agent; **b** Dependence of $M_{\mathrm{n,GPC}}$, $M_{\mathrm{n,th}}$ and polydispersity index (PDI) on the conversion of MMA with HMTA as both a ligand and a reducing agent

To verify the scope of the method, *n*-butyl acrylate (BA) and styrene monomers are also polymerized under the similar AGET ATREP conditions. The BA monomer can be polymerized normally while styrene doesn't work (B4 and B5, Table 2). The failure of polymerizing styrene may be attributed to more hydrophobic property of styrene than MMA and BA, thus making HMTA-Cu catalyst partition preferably in aqueous phase, which is undesired for water-based ATRP reactions. Figure 2 shows the kinetic plots of BA emulsion polymerization. Ln($[M_0]/[M]$) increases almost linearly with reaction time, and $M_{\mathrm{n,GPC}}$ has an approximate linear relationship with monomer conversion together with relatively low PDI. All of these prove controlled/living properties of the polymerization of BA.

The resulting microlatex after the first step is an almost transparent system with the particle size of 30–40 nm, meaning the microemulsion polymerization process. After the second step, the average diameters of the latex particles range from 100 to 200 nm with relatively broad particle size distributions (PSD), indicating nano to

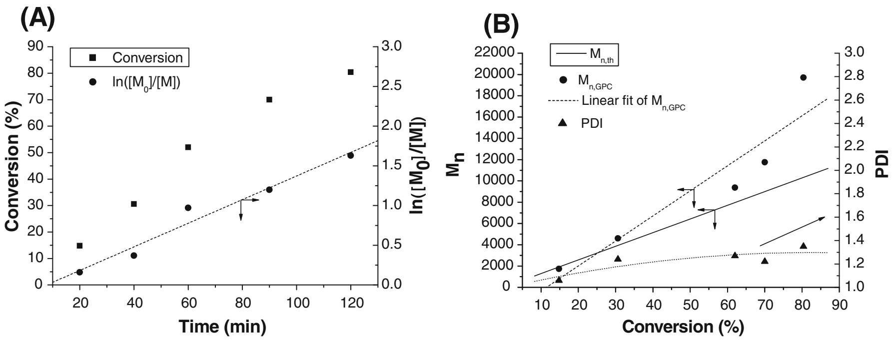

Fig. 2 **a** Dependence of BA conversion and ln($[M_0]/[M]$) on the polymerization time with HMTA as both a ligand and a reducing agent; **b** Dependence of $M_{\mathrm{n,GPC}}$, $M_{\mathrm{n,th}}$ and polydispersity index (PDI) on the conversion of BA with HMTA as both a ligand and a reducing agent

submicrometer size of the particles. The final latex is quite stable and can stand for more than a month without visible phase separation.

Chain extension experiment is also performed to further verify the controlled/living characteristics of the emulsion polymerization. First, MMA is polymerized under AGET ATREP conditions for as long as 6 h in order to consume nearly all the MMA monomer. Then, BA monomer is added to proceed another polymerization based on PMMA macroinitiator. The final PMMA-*block*-PBA polymer is characterized by GPC and ^{1}H-NMR, respectively (Figs. 3, 4). Figure 3 shows that the molecular weight increases from 4,210 to 6,230 after chain extension, with PDI becoming a little higher.

^{1}H-NMR spectrum of PMMA-*block*-PBA is shown in Fig. 4. The number of H_a proton at the end of the polymer is "1" which is designated as a standard. Then the number of H_b is about 14 that represents $7CH_2O$ signal on butyl group of BA, so, there are seven BA units in the polymer chain, i.e., $n \approx 7$. The singlet peak at

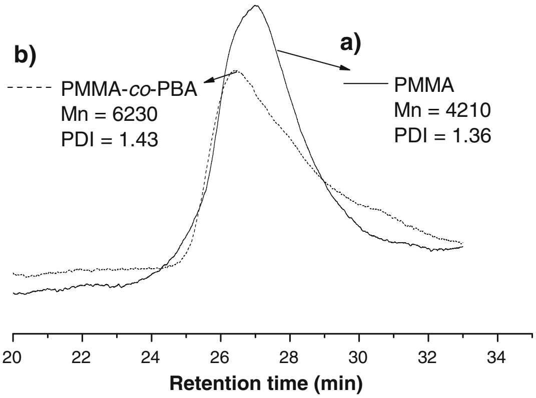

Fig. 3 GPC curves of (*a*) before chain extension and (*b*) after chain extension

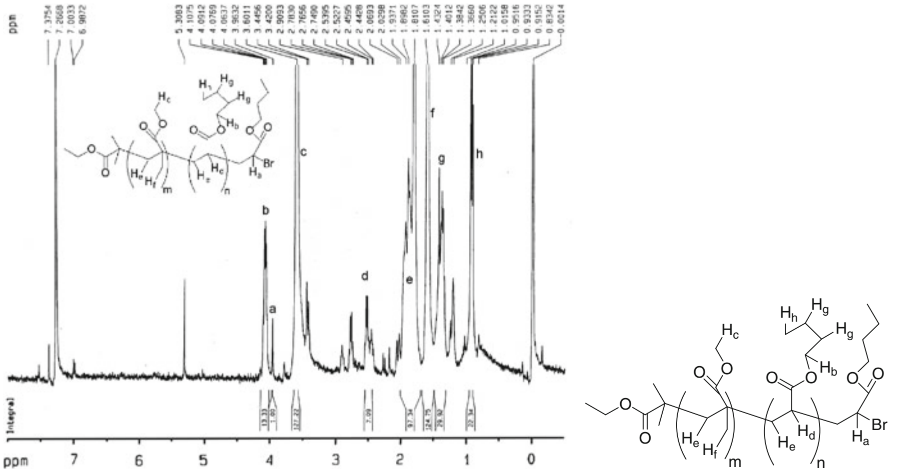

Fig. 4 ^{1}H-NMR spectrum of PMMA-*block*-PBA copolymer by sequential AGET ATREP reactions

3.60 ppm (H_c) results from the CH_3O of MMA unit, and the 126 H_c divided by 3 gives the number of CH_3O as 42, thus, the number of MMA unit is 42, i.e., $m \approx 42$. Other proton signals are distinguished as follows: the number of H_d from CH of BA unit is around 6; H_e signal at 1.81–1.89 ppm represents the 98 protons of CH_2 both from MMA and BA units; the singlet peak H_f is the CH_3 signal of MMA unit and H_g means the CH_2 signal of butyl group of BA; the triplet peak at 0.93 ppm is ascribed to the CH_3 information of butyl group of BA, and the total 21 of H_f is another proof that there are 7 BA units in the polymer chain. Therefore, the number-average molecular weight of the block copolymer can be calculated as follows:

$$\begin{aligned} M_{\mathrm{n,NMR}} &= M_{\mathrm{EBiB}} + m \times M_{\mathrm{n,MMA}} + n \times M_{\mathrm{n,BA}} = 195 + 42 \times 100 + 7 \times 128 \\ &\approx 5290 \end{aligned}$$

This value of $M_{\mathrm{n,NMR}}$ is consistent with that measured by GPC ($M_{\mathrm{n,GPC}} = 6{,}230$).

The presence of heavy metal (e.g., Cu) residues in the final polymer product of ATRP reaction is a drawback of this method and has limited its many potential applications. Therefore, easy removal of undesired metal residues is very important in ATRP [45]. As we know, hexamethylenetetramine (HMTA) is an acid-unstable compound that will be decomposed into NH_3 and HCHO under acidic conditions. This property has been applied by us to remove the undesired Cu(II) residue from the polymer. Under acidic conditions, the complex of Cu and HMTA is destroyed to release the Cu(II) ion into the aqueous phase [46]. Thus, after demulsification of the latex by adding low molecular alcohol, the polymer is precipitated from the mixture, with Cu(II) left in the liquid. However, correct selection of acids and acidification time is very important in this operation. For example, when pH value is adjusted to 3–4 by adding dilute aqueous HCl, followed by instant demulsification and precipitation, only around 80% of Cu(II) residue can be removed; on the other hand, after pH value adjustment is completed, the mixture is stirred for 20 min in order to remove more copper ion, but unfortunately, the latex turns from an emulsion to a semi-transparent mixture, indicating partial hydrolysis of PMMA to polymethacrylic acid under such acidic conditions. Therefore, strong acids are inappropriate in this metal removal process. After several experiments, weak acid HOAc proves to be a good choice. When the pH value is adjusted to 4–5 by adding HOAc, the acidic system is stirred for 20 min followed by other similar operations, about 95% of Cu(II) residue can be removed, and the left 5% of Cu(II) accounts for about 500 ppm of the polymer product. In fact, the PMMA polymer treated by this method looks transparent without green color, while that untreated shows green color of complex HMTA-Cu.

Conclusion

Cheap and commercially available hexamethylenetetramine (HMTA) as both a ligand and a reducing agent has been successfully used to polymerize MMA and/or BA under environmentally friendly AGET ATREP conditions. The kinetic data of the polymerizations of both MMA and BA indicate the controlled/living characteristics of the reactions, especially at the early stage of the polymerizations. Chain extension is also conducted to further prove the controlled/living property of the polymerization, and the block copolymer PMMA-*block*-PBA has been characterized by ^{1}H-NMR. The number-average molecular weight calculated by ^{1}H-NMR is consistent with that determined by GPC. Nearly 95% of the undesired Cu(II) residue can be removed by simply acidifying the latex, and only 500 ppm of Cu(II) residue is left in the product. This method will undoubtedly promote the practical applications of ATRP in many areas.

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