Continuous Atom Transfer Radical Block Copolymerization of Methacrylates

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A column reactor packed with silica-gel-supported copper bromide (CuBr)–hexamethyltriethylenetetramine (HMTETA) was developed for the continuous-transition–metal-mediated living/controlled radical polymerization [atom transfer radical polymerization (ATRP)] for homo- and block copolymerization of methyl methacrylate (MMA). The reactor showed good stability (> 100 h) in both catalyst activity and molecular weight of the poly(methyl methacrylate) (PMMA) produced. The MMA conversion decreased as the flow rate increased. The polymerization in the reactor was in first order with respect to monomer concentration. The molecular weight of the resulting PMMA increased linearly with MMA conversion, exhibiting the characteristic feature of living polymerization. Thus, simply changing the flow rate of MMA, which in turn determined the MMA conversion, readily controlled the molecular weight of PMMA. The block copolymerization of MMA with n-butyl methacrylate (nBMA) was carried out using two reactors connected in series. The block copolymers were slightly contaminated by PMMA prepolymer from the first column. The molecular weight of the nBMA block could be changed by the flow rate of the nBMA in the second reactor. This packed column reactor technology is feasible for continuously synthesizing polymers or block copolymers with controlled molecular weights that are readily adjustable by changing the monomer flow rates.

Introduction

Atom transfer radical polymerization (ATRP) is a transition metal complex mediated living radical polymerization based on an equilibrium of active and dormant propagating radicals, as shown in Eq. 1 (Matyjaszewski, 1997). Dormant polymer chains with terminal carbon–halide bonds (P–X) react with a catalyst to generate radicals to propagate monomers, while the radicals can also react with the catalyst at a higher oxidation state to return to the dormant state. Because the forward reaction is much slower than the reverse reaction, the polymer chains are in the dormant state the longest. Consequently, the radical termination reactions by coupling and/or disproportionation are kinetically suppressed in order to achieve a living/controlled polymerization (Matyjaszewski, ed. 1997). ATRP has been proven to be a versatile and robust method for synthesizing polymers with controlled molecular weight, low polydispersity (Wang and Matyjaszewski, 1995; Kato et al., 1995; Granel et al., 1996; Percec et al., 1997), and various functionalities (Haddleton et al., 1997; Matyjaszewski et al., 1998; Zeng et al., 2000; Shen et al., 2000a). Compared with living anionic polymerization, the obvious advantages of ATRP are its insensitivity to water, low reaction temperature (room temperature to 100°C), and versatility for various monomers.

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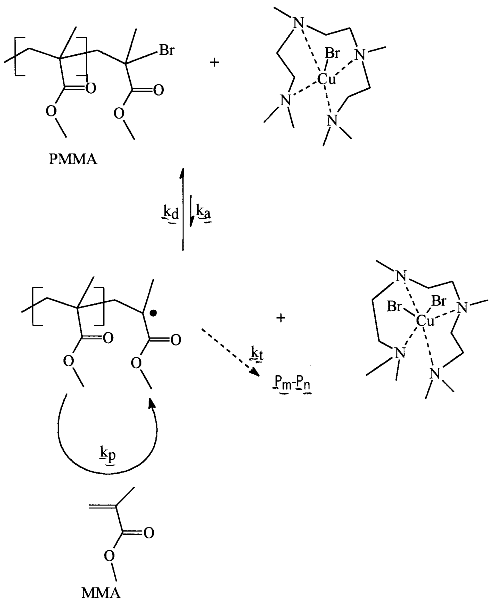


The major challenge that ATRP faces in industrial applications is the high concentration of residual catalyst and consequent color in its final products. Usually there is about 0.1–1% catalyst (w/w) in the products prepared by ATRP. Therefore, after polymerization, additional processes are required to remove the catalyst from the product mixture, usually by passing the mixture through silica or alumina gel or resins (Matyjaszewski et al., 2000) or by reprecipitation (Kasko et al., 1998) on a lab scale. This post treatment is not only time-consuming but is also costly due to catalyst waste.

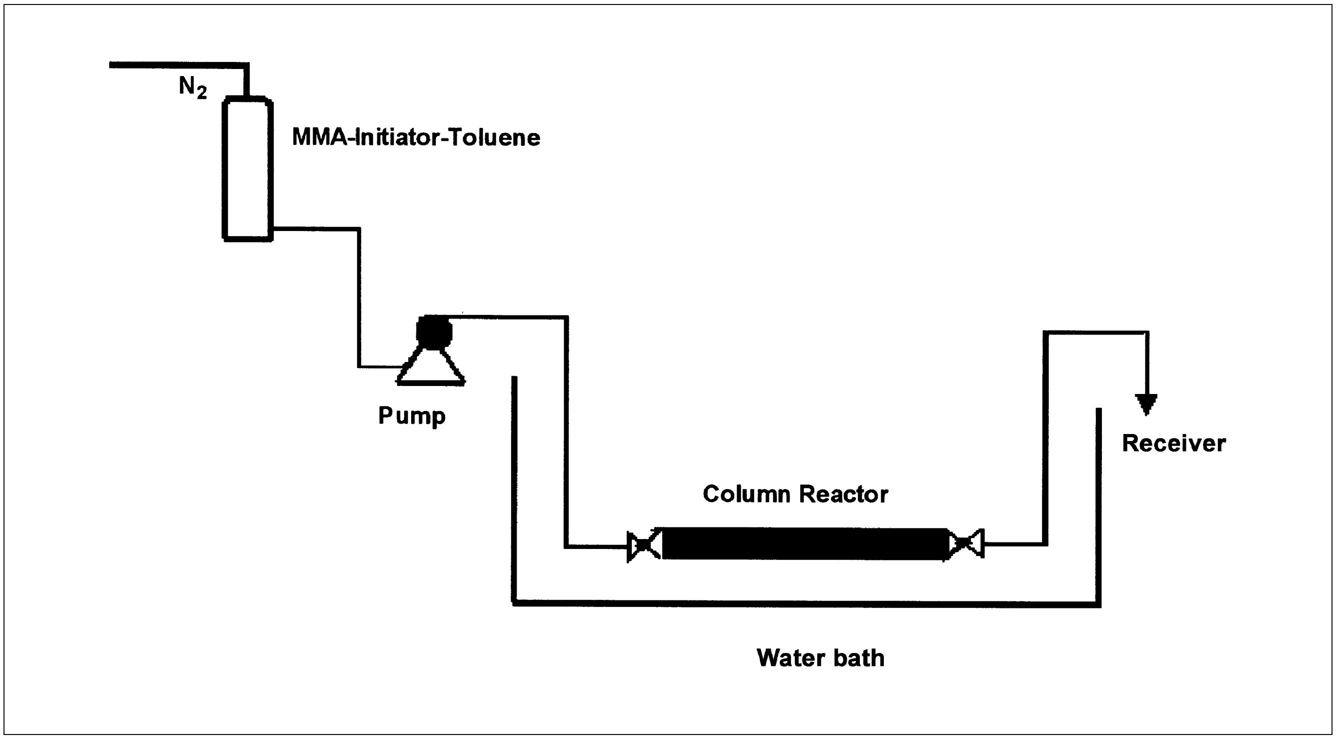
Efforts have been made to solve these problems by supporting the catalyst/ligand system onto solids that can be readily recovered and reused in subsequent polymerizations (Kickelbick et al., 1999; Haddleton et al., 1999; Shen et al., 2000b, 2001; Shen and Zhu, 2001). While this system can recycle the catalyst, the catalyst recycling by batch process is laborious. A continuous ATRP process to eliminate the recovering and recycling operations of the catalyst/ligand system is preferable.

Recently, we found that the CuBr–hexamethyltriethylenetetramine (CuBr-HMTETA) complex absorbed on silica gel mediated a living polymerization of MMA (Shen et al., 2000b). The recycled catalyst retained a high degree of catalytic activity. Most significantly, the reused catalyst had even better control over the molecular weight of the polymers produced in the second and third runs of MMA polymerization (Shen et al., 2000b). In order to overcome the drawbacks of the batch ATRP by the supported catalyst, we have developed a continuous polymerization process for ATRP (Zhu et al., 2000; Shen et al., 2000c). In this article, we report the experimental results of continuous polymerization and block copolymerization of MMA using the column reactors packed with a silica-gel-supported catalyst.

Experimental Section

Materials

MMA and *n*-butyl methacrylate (nBMA) from Aldrich were distilled under vacuum and stored at −15°C before use. *N*,*N*,*N*′,*N*″,*N*‴*N*‴-1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, ligand), CuBr, and methyl α-



Scheme 1. Column reactor for the continuous ATRP of MMA.

bromophenylacetate (MBP, initiator), also from Aldrich, were used as received. Toluene was distilled over CaH_2. Silica gel (100–200 mesh, Chromatographic Grade, Sargent-Welch Scientific Co.) was boiled in deionized water for 5 h and then air- and vacuum-dried.

Apparatus

The polymerization system is shown in Scheme 1. The pump, solution flask, and column reactor were connected with 1-mm-diameter stainless tubing. The metering pump was Gilson Model 302 with an adjustable flow rate at 0.01 mL/min. The flow rate was calibrated by a weight method. The column reactor was made from stainless metal tubing of 900-mm length and 4.0-mm inner diameter. The pressure in the storage flask was kept positive, relative to the atmosphere pressure by ultrahigh-purity nitrogen.

Catalyst preparation and column packing

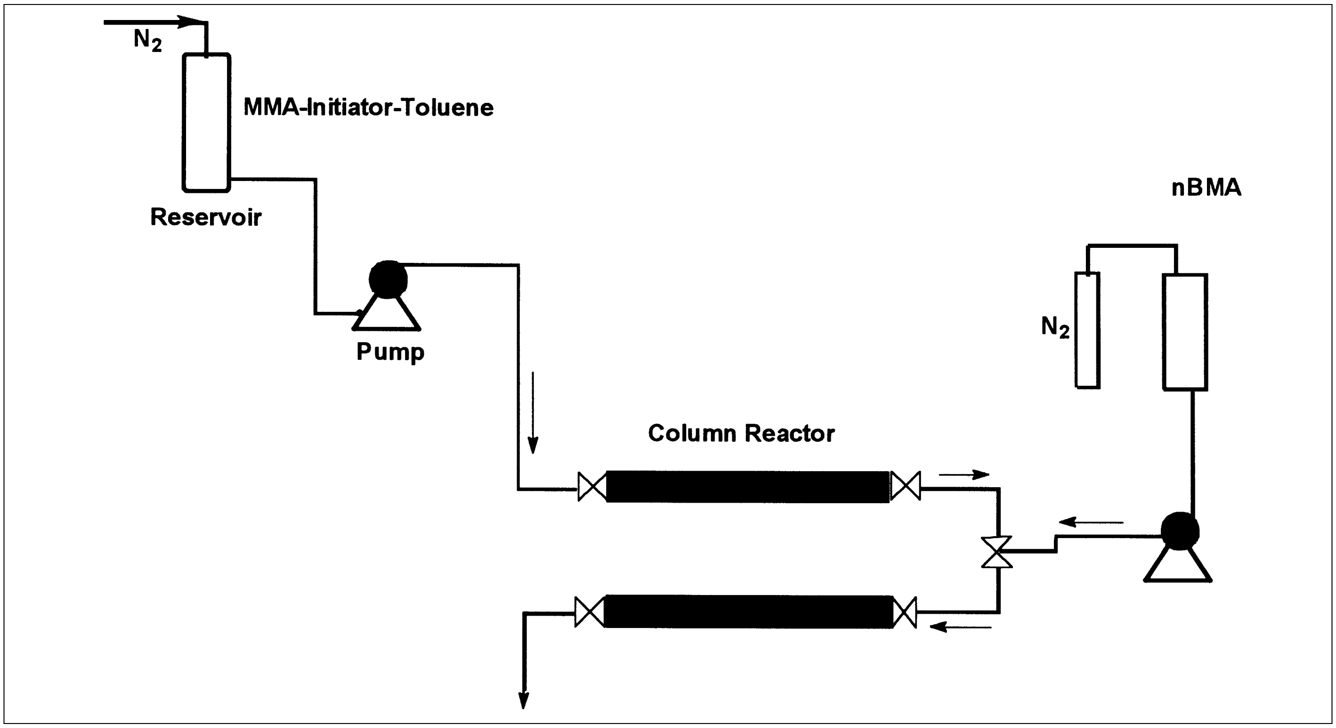
Boiled silica gel (12 g) was loaded into a Schlenk flask and was degassed by vacuum–nitrogen for five cycles. Toluene (100 mL), CuBr (0.6 g), and HMTETA (0.96 g) were then added to the flask under nitrogen atmosphere. The mixture was bubbled with ultrahigh-purity nitrogen for 10 min with efficient stirring. The mixture was then stirred for another 3 h at room temperature. After the stirring, the silica gel became blue (the unsupported Cu(I)Br-HMTETA complex has a green color, but the silica-gel-supported complex is blue; there was no change in its oxidation state), but the toluene solution was colorless. The blue silica gel was transferred and packed into the column reactor under a nitrogen atmosphere. The reactor was connected to the pump under a nitrogen atmosphere.

Polymerization

A typical polymerization process was as follows. A MMA–MBP–toluene polymerization solution [MMA/toluene $= 1/3$ (w/w), MMA/MBP $= 100$ (molar)] was degassed and added to the storage flask. The flow rate was set and the pump was turned on. The reactor was then immersed into the water bath, which had been set at the required temperature. The outlet solution was collected at different time intervals and weighted to calibrate the flow rate. After the polymerization ran for $2 \sim 3$ mean residence times (τ), three parallel samples of $0.2 \sim 0.5$ mL eluted out from the reactor were collected. The solution was diluted with $CDCl_3$. The MMA conversion was measured from the ^1H-NMR of the solution by calculating the intensity ratio of $OC\underline{H}_3$ signals in polymer (3.60 ppm) and monomer (3.75 ppm). A 50-μL sample of the solution was injected to GPC to measure the molecular weight and polydispersity of the resulting PMMA.

Block copolymerization by two column reactors in series

Two reactors in series, as shown in Scheme 2, were used to carry out the block copolymerization of MMA and nBMA. The toluene solution with MMA and initiator (MMA/MBP = 30/1 in mole) was pumped into the first reactor, which was immersed in a 80°C water bath. The second monomer was



Scheme 2. Block copolymerization by two reactors connected in series.

pumped to the polymer solution eluted from the first reactor and the mixture was injected into the second reactor for polymerization. The solution eluted from the second reactor was collected and subjected to NMR and GPC measurements for the conversion and molecular weight data, respectively.

Measurements

Nuclear Magnetic Resonance Spectroscopy. Proton (^{1}H) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-200 spectrometer. ^{1}H NMR chemical shifts in $CDCl_3$ were reported downfield from 0.00 ppm using TMS as an internal reference. The conversion was measured with ^{1}H-NMR by calculating the intensity ratio of $OC\underline{H}_3$ signals in polymer (3.60 ppm) and monomer (3.75 ppm).

Molecular-Weight Measurements. Number and weight average molecular weights (M_n and M_w, respectively) were determined by gel permeation chromatography (pore size: 500 Å, 1500 Å, 10,000 Å) using THF-2% (v/v) triethylamine as the solvent at a flow rate of 1.0 mL/min at 25°C with an RI detector. Narrow dispersed polystyrene standards (Polysciences) were used to generate a universal calibration curve. Data were recorded and manipulated using the Windows-based *Millennium* software package. Narrow dispersed PMMA standards were also used. The differences from the PS standards in the molecular-weight range of this work were small. For example, for a PMMA sample having molecular weight of 2525 and PDI of 1.16, the molecular weight and PDI measured with the PS standards were 2557 and 1.12.

Measurement of Residence Time Distribution. The residence time distribution (RTD) of the column reactor was measured by pulse injecting narrow dispersed polystyrene ($M_n = 2800$, $M_w/M_n = 1.05$; $M_n = 10{,}000$, $M_w/M_n = 1.03$; Polyscience) and PMMA (synthesized according to Shen et al., 2000b; $M_n = 4000$, $M_w/M_n = 1.07$; $M_n = 14{,}000$, $M_w/M_n = 1.08$). The reactor was packed with the same silica gel as was used to support the catalyst. A refractive index detector was used to determine the polymer concentration eluted from the reactor. The signals were recorded and processed by Millennium Workstation for GPC and Microsoft Excel. The variance was calculated by

$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t)\,dt \tag{2}$$

Results and Discussion

Reactor stability

Silica-gel-supported copper bromide-HMTETA has been shown to be an excellent catalyst for supported ATRP in the batch process (Shen et al., 2000b). The system showed good stability. The catalyst was reclaimed after its first use by precipitation and a multiple washing procedure, and was recycled for second and third uses. The recycled catalyst remained 80% active in the second use and 50% in the third use relative to its initial activity. Therefore, for this work, this catalyst system was packed in a column reactor for the continuous ATRP of MMA.

The conversion of MMA was used as the indicator of the reactor activity. The activity stability of the column reactor was evaluated at 80°C by measuring the MMA conversion at a set flow rate. The reactor was run continuously at 1.2 mL/h, and the eluting solution was sampled at different intervals. Figures 1 and 2 show the stability of the packed reactors with different silica gel/CuBr ratios. The reactor activity with a silica gel/CuBr ratio of 20 or 30 was slightly low for the initial 10 h, but the system was stable up to 120 h. The solution

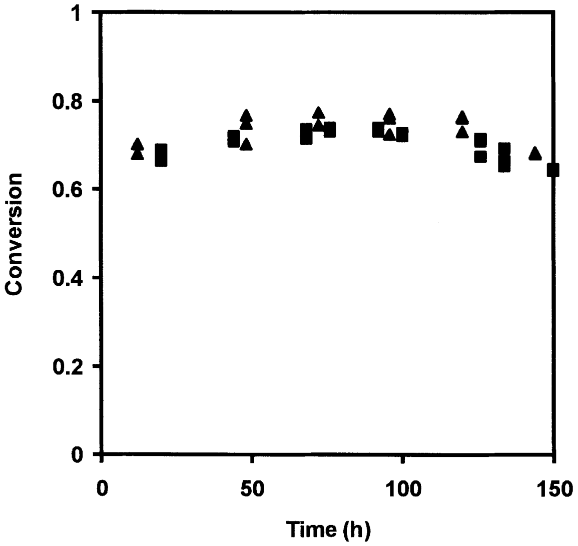


Figure 1. Stability of the reactors packed with catalysts of different silica-gel/CuBr ratios for the ATRP of MMA.

The MMA conversions at different polymerization times at the flow rate of 1.2 mL/h. MMA/toluene = 1/3 (w/w),; MMA/MBP = 100, 80°C; silica gel/CuBr = 20 (▲), 30 (■).

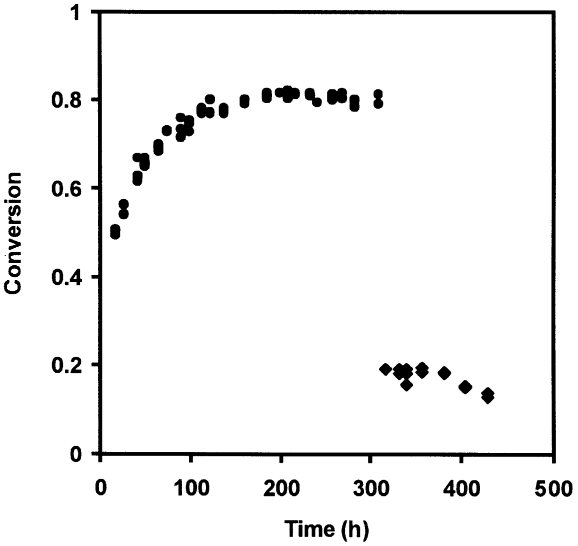


Figure 2. Stability of the reactor packed with catalyst of silica gel/CuBr = 10 for the ATRP of MMA.

The MMA conversions at different times at the flow rate of 1.2 mL/h (●) and 3.0 mL/h (◆). MMA/toluene = 1/3 (w/w); MMA/MBP = 100, 80°C; silica gel/CuBr = 10.

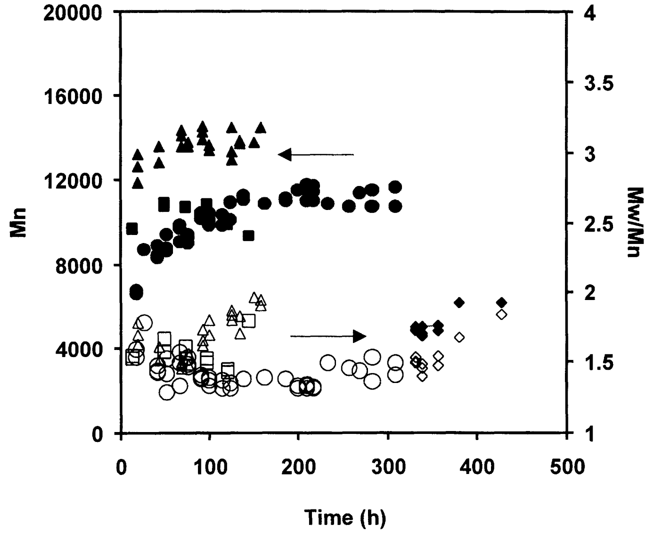


Figure 3. Molecular weight and polydispersity of PMMA produced at different times by the reactors packed with catalysts of different silica gel/CuBr ratios.

See Figures 1 and 2 for other experimental conditions. Silica gel/CuBr = 10 (●, ○), 20 (■, □), 30 (▲, △) at the flow rate of 1.2 mL/h; silica gel/CuBr = 10 (◆, ◇) at the flow rate of 3.0 mL/h, 80°C.

eluted from the reactor was slightly greenish when the column reactor started running, but later became very light in color or almost colorless. During this time interval, the change in the activity was within 7%. The polymerization at 90°C had very similar results (Shen et al., 2000c). This suggests that the reactor had a good retention of the catalyst activity.

After the stable period, the activity gradually decreased. This reduction in the reactor activity may be caused by an accumulation of copper dibromide Cu(II)Br_2 due to radical termination reactions and by a gradual wash out of the catalyst during polymerization. In an ATRP system, copper dibromide is generated to equilibrate with copper bromide (Eq. 1) (Matyjaszewski, 1997). If some radicals are consumed by side reactions such as radical coupling, the equilibrium shifts and generates an excess of $CuBr_2$ (Eq. 1). Figure 3 shows that the molecular weights of PMMA were always higher than the theoretical values ($M_{n\ \mathrm{Theoretical}}$ = the conversion × MW of MMA × MMA/MBP ratio, that is, the conversion data in Figures 1 and 2×10^4), that is, the initiator efficiencies ($M_{n\ \mathrm{Theoretical}}/M_{n\ \mathrm{Experimental}}$) were less than 1. These data indicate that some initiators were consumed by side reactions, leading to the gradual buildup of a $CuBr_2$ concentration, in the reactor. It has been demonstrated that $CuBr_2$ can shift the equilibrium and result in a lower radical concentration, and, thus, a slower polymerization rate (Matyjaszewski, 1997). At the same time, the catalyst in this reactor was supported onto the silica gel surface by physical adsorption. After a lengthy continuous operation, some catalyst may be washed out of the reactor. We found that the eluting solution had a very slight greenish color, particularly at the start of the polymerization operation. This loss of catalyst, thus, also contributed to the reduction in the reactor activity.

The reactors packed with different silica gel/CuBr catalysts had quite different stability characteristics at 80°C, as shown in Figures 1 and 2. The activity of the reactor packed with silica gel/CuBr = 20 or 30 was slightly lower at the early stage, but increased quickly to constant activity. The activity was stable up to 120 h before it started to decrease. However, with silica gel/CuBr = 10 (Figure 2), the initial activity of the reactor was much lower (50% conversion) than that of silica gel/CuBr = 20 or 30. It then took about 100 h for the system to gradually reach the stable activity. Once stabilized, the reactor remained constantly active for about 200 h at a flow rate of 1.2 mL/h and an additional 80 h at 3.0 mL/h. The molecular weight of the PMMA produced given in Figure 3 showed the same trend as the reactor activity. For silica gel/CuBr = 20 and 30, the molecular weight of PMMA increased slightly with time during the early stage of polymerization and became stable within 120 h with less than 7% variance in molecular weight of PMMA. For the silica gel/CuBr = 10 system, the molecular weight of PMMA increased gradually in the first 100 h, and then became stable for 200 h at a flow rate of 1.2 mL/h and a subsequent 80 h at a flow rate of 3.0 mL/h, corresponding to the MMA conversion.

It was unexpected that the reactor packed with silica gel/CuBr = 10, which meant more catalyst in the reactor than in the reactor packed with silica gel/CuBr = 20 or 30, would have a much lower activity at the beginning. The calculation of the catalyst/initiator ratio indicates that when the MMA–toluene–MBP solution flowed through the column reactor, each initiator molecule encountered more than one catalyst molecule. For silica gel/CuBr = 10, 20, 30, the corresponding CuBr/MBP was 23.2, 11.6, and 7.7, respectively.

The effect of CuBr/MBP on the polymerization was, thus, evaluated by batch process, as shown in Figure 4. The polymerization rate initially increased as the CuBr/MBP ratio was increased from 1 to 5, because more CuBr produced more radicals (Eq. 1), thus, increasing the polymerization rate. However, increasing the CuBr/MBP ratio further decreased the polymerization rate. This was caused by the fact that when there was too much excess copper bromide for each initiator, the equilibrium in Eq. 1 shifted to generate an excessively high concentration of radicals at the beginning. The radical termination reactions, thus, became significant. As indicated earlier, this radical consumption produced a high concentration of $CuBr_2$ in the system (Eq. 1), which can greatly suppress the polymerization (Matyjaszewski, 1997).

Therefore, when the reactor was packed with a catalyst of silica gel/CuBr = 10, the excess catalyst caused the generation of a high concentration of $CuBr_2$ in the reactor, which resulted in the low reactor activity. However, by gradually but continuously washing out the catalyst, the catalyst concentration decreased, and, thus, the activity increased.

Effect of flow rate and temperature on reactor activity

The data of MMA conversion vs. flow rate at 80 and 70°C are shown in Figure 5. At both temperatures, the MMA conversion decreased with increasing flow rate, as in the polymerization at 90°C (Shen et al., 2000c). For example, at 80°C, the MMA conversion reached 77% at 1.2 mL/h, but declined

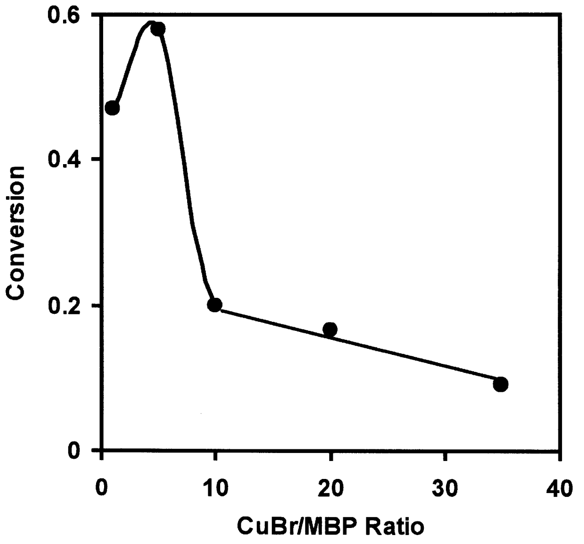


Figure 4. Effect of CuBr/MBP ratio on the activity of the catalyst.

Batch polymerization experiments: MMA/MBP = 100, MMA/toluene = 1/3, 80°C, 4 h.

to 22% at 4.8 mL/h. It is expected that at a higher flow rate, the polymer chains more quickly flowed out of the reactor, and, thus, had a shorter residence time. At the same flow rate, a lower temperature resulted in lower activity.

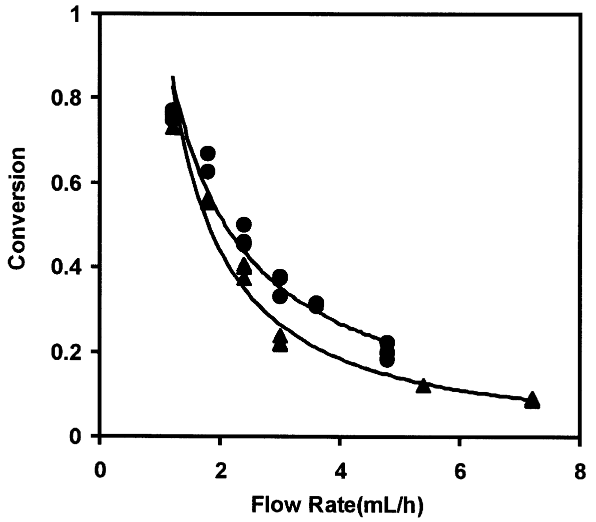


Figure 5. MMA conversion as a function of flow rate for the polymerization of MMA in the reactor at different temperatures.

MMA/toluene = 1/3 (w/w), MMA/MBP = 100, silica gel/CuBr = 20, 80°C (●) and 70°C (▲).

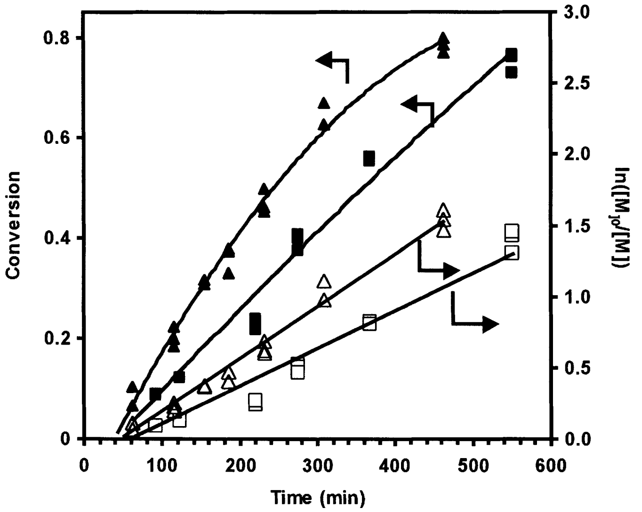


Figure 6. MMA conversion and kinetic plots as a function of residence time for the polymerization of MMA in the reactor at different temperatures.

See Figure 5 for experimental conditions: 80°C (▲, △) and 70°C (●, ○).

Figure 6 shows the dependence of MMA conversion on the mean residence time τ (that is, the liquid column volume over the volumetric flow rate). The MMA conversion increased smoothly with the residence time. The $\ln([M]_o/[M])$ vs. time plots were linear at both temperatures, indicating that the MMA polymerization in the column reactor was in first-order kinetics with respect to the monomer concentration, which is typical for an ATRP process. However, unlike the polymerization at 90°C, which had no induction period (Shen et al., 2000c), the polymerization runs at 80 and 70°C had induction times of ca. 50 min at 80°C and 60 min at 70°C. The induction period may be caused by the presence of impurities, such as oxygen trapped in the silica gel. This induction period was observed in batch ATRP processes. In addition, we carried out batch experiments where, if we used only nitrogen to purge the silica gel–toluene suspension without vacuum degassing, the polymerization slowed down very quickly.

Figure 7 shows the dependence of the molecular weight and molecular-weight distribution of PMMA on the MMA conversion. The molecular weight of the resulting PMMA at 80 and 70°C increased linearly with the conversion, a characteristic of the living polymerization process. Similar results were also obtained at 90°C (Shen et al., 2000c). This further confirms that the continuous polymerization inside the reactor underwent via the ATRP mechanism. The dormant polymer chains grew by reacting with catalytic centers on the silica gel surface and propagating monomers (Eq. 1) while passing through the column reactor.

The molecular weights of the resulting PMMA were higher than their theoretical values. The initiator efficiency of the polymerization was about 70% at 80°C and about 50–60% at 70°C. This deviation from the theoretical prediction was typical when a high silica gel/CuBr ratio system was used (Shen et al., 2000b). The reason is that the slow deactivation by the immobilized catalyst on the silica gel surface promoted radical side reactions such as coupling, and, thus, consumed some initiator molecules. The lower initiator efficiency at 70°C suggests a more severe radical coupling reaction at this temperature, probably because of the lower catalyst activity.

Since the molecular weight of PMMA is a linear function of the MMA conversion (Figure 7), while the conversion is determined by the flow rate (Figure 5), the molecular weight

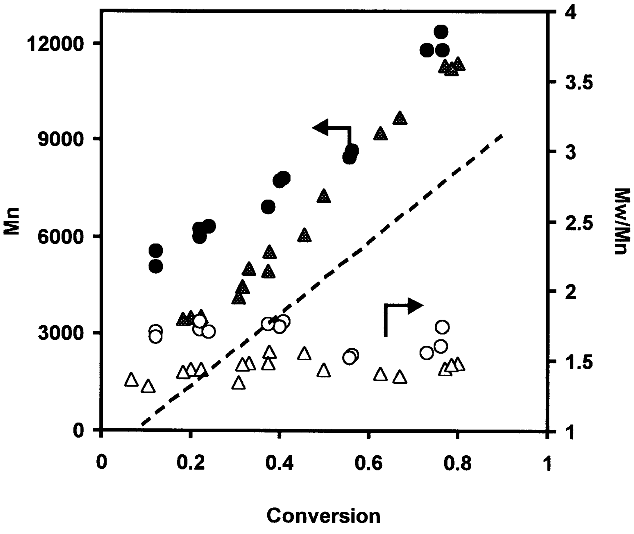


Figure 7. Molecular weight and molecular-weight distribution of PMMA produced in the reactor as a function of MMA conversion.

See Figure 5 for the experimental conditions: 80°C (▲, △) and 70°C (●,○), theoretical (—).

of PMMA can be readily controlled by the flow rate, as shown in Figure 8. At 80 and 70°C, the PMMA molecular weight decreased with increasing the flow rate. At the same flow rate, the polymerization at 70°C produced polymers with a higher molecular weight because of lower initiator efficiency. The continuous ATRP process is thus advantageous in preparing polymer products with different molecular weights. The simple operation of adjusting the flow rate produces various polymer grades of different molecular weights.

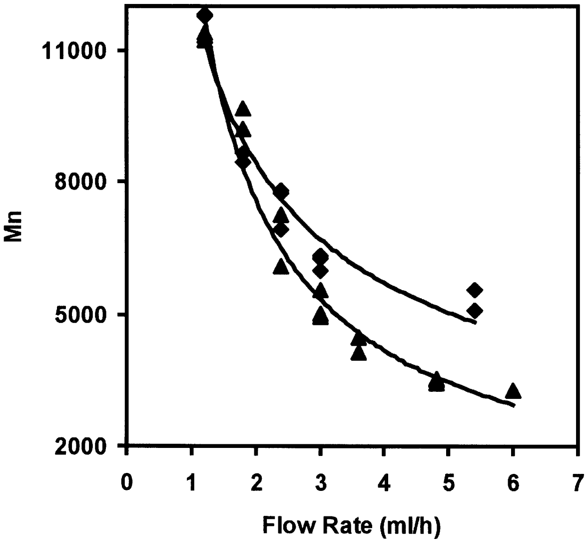


Figure 8. Molecular weight of PMMA produced in the reactor at 80°C and 70°C as a function of the flow rate.

See Figure 5 for the experimental conditions: 80°C (▲) and 70°C (◆).

The polydispersities (M_w/M_n) were about 1.5 for the PMMA samples prepared at 80°C, and were higher (~ 1.8) for those prepared at 80 and 90°C (Shen et al., 2000c). These distributions were much broader than the polymers prepared with the same supported catalyst system in batch processes (about 1.1) (Shen et al., 2000b). This broadening in molecular-weight distribution may be caused by different residence times of individual polymer chains inside the reactor. The RTD of the reactor was measured by the pulse injection of monodispersed polystyrene (PS) and PMMA. The RTD of the reactor was rather broad. The variance σ^2 was 450 min^2 at a flow rate of 1.2 mL/h, and 110 min^2 at a flow rate of 3.0 mL/h. This large difference in the residence times caused some fractions of polymer chains to reside in the reactor for long time and, thus, grow to a high molecular weight, while other fractions of polymer chains exited the reactor too quickly and had short chain lengths. The Peclet number, calculated by

$$\frac{\sigma^2}{\tau^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2}\left(1 - e^{-Pe_r}\right) \qquad (3)$$

(Levenspiel, 1972), was 550 at a flow rate of 1.2 mL/h, and 700 at a flow rate of 3.0 mL/h. This indicates that there was little dispersion, due to the low diffusion of the polymer molecules. Efforts are currently being made to narrow the RTD of the reactor to improve the polydispersity of the resulting polymers.

The high viscosity of the polymerization solution also contributed to the broadening of the molecular weight distribution. It was observed that even with 25% monomer concentration (w/w) and at moderate conversions, the reaction solution eluted from the reactor was very viscous. This high viscosity imposed diffusion limitations on polymer chains (P-Br or $P^{\cdot}$) and made it difficult for the polymer chains to enter the catalytic sites on the silica gel surface. Consequently the propagating radicals ($P^{\cdot}$) were not deactivated fast enough, and, thus, propagated many monomer units in each activation/deactivation cycle (Eq. 1). The modeling work has shown that fast radical deactivation, so that a radical propagates only a few monomer units in each activation/deactivation cycle, is essential for producing polymers of low polydispersity by ATRP (Matyjaszewski, 1997; Zhu, 1999).

Polymerization with different monomer/initiator ratios

In addition to the flow rate, the monomer/initiator ratio was also used as a parameter to control the molecular weight of the PMMA produced. Figure 9 shows the MMA conversion as a function of flow rate with the monomer/initiator ratios of 100 and 200, respectively. The polymerization with MMA/initiator = 200 was slower than that of MMA/initiator = 100. This was because of the lower initiator concentration in the former system. A lower initiator concentration resulted in a lower propagating radical concentration, as shown in Eq. 1.

Figure 10 shows that the molecular weight of PMMA increased linearly with MMA conversion. The MMA/initiator = 200 system yielded double molecular weight compared to that of MMA/initiator = 100. For example, the Mn was 12,800

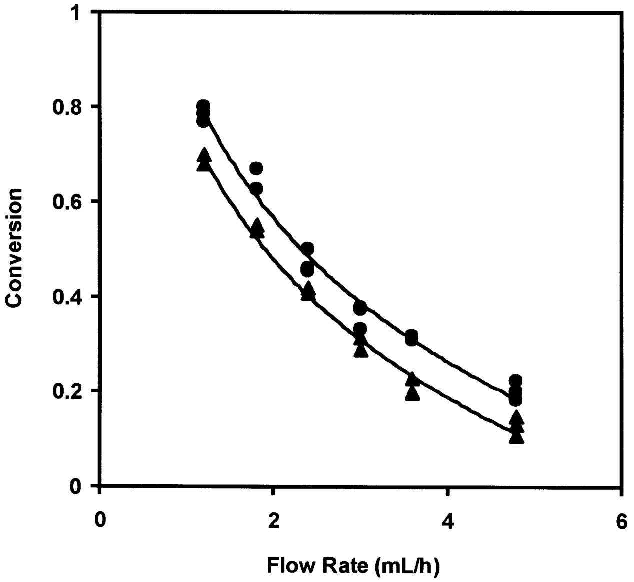


Figure 9. MMA conversion as a function of the flow rate for the polymerization in the reactor at MMA/Initiator ratio of 100 and 200.

MMA/toluene = 1/3 (w/w), silica gel/CuBr = 20, 80°C; MMA/MBP = 100 (●), 200 (▲).

for PMMA produced with MMA/initiator = 200 at 42% conversion, while it was 6,100 for MMA/initiator = 100 at 45% conversion. Plotting the PMMA molecular weight vs. (MMA/MBP)×conversion for these two systems gave a good linear function, as shown in Figure 11, strongly confirming the livingness of the polymerization in the reactor. This also provides another approach for designing polymer molecular weight, in addition to the flow rate method (Figure 8).

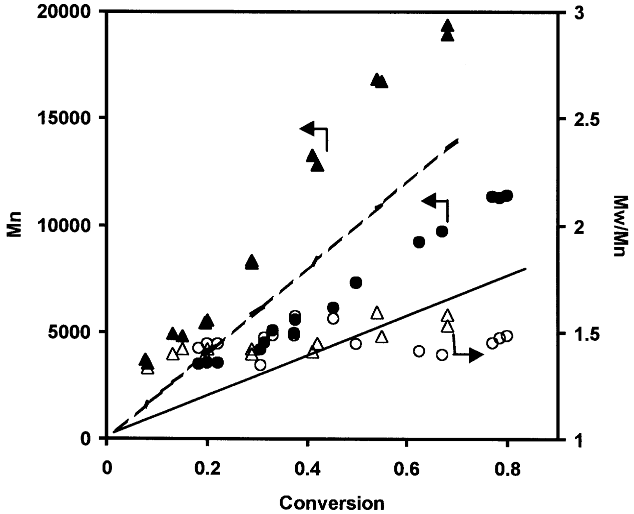


Figure 10. Molecular weight and polydispersity of PMMA as a function of MMA conversion for the polymerization of MMA at MMA/initiator ratio of 100 and 200.

See Figure 9 for the reaction conditions. MMA/MBP = 100 (●,○), 200 (▲,△). Theoretical Mn: MMA/MBP = 100 (—), 200 (.....).

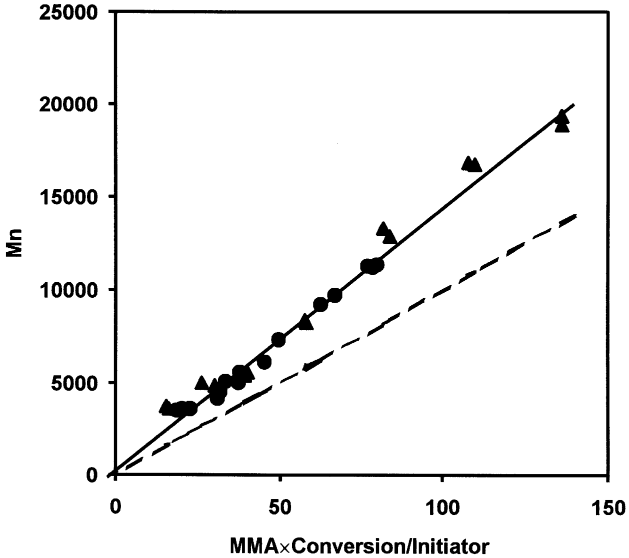


Figure 11. Molecular weight of PMMA as a function of MMA×conversion/MBP ratio for the polymerization.

See Figure 9 for the reaction conditions. MMA/MBP = 100 (●), 200 (▲). Theoretical Mn (......).

Scale-up

The polymerization of MMA was also carried out using two column reactors (500 cm long and 7.8 mm in diameter) in a series packed with 2 g of CuBr supported on 40 g silica gel (compared to 0.6 g CuBr on 12 g silica gel). Figure 12 shows that the polymerization in the larger reactor had the same trend of MMA conversion vs. flow rate as that in Figure 5. The molecular weight of the PMMA produced also increased with conversion (Figure 13), similar to that of the smaller reactor. These results indicate that the continuous ATRP can be scaled up to have higher productivity by using larger reactors.

Reproducibility

The reproducibility of the data was examined by repeating experiments with two sets of column reactors packed with the catalyst of silica gel/CuBr = 20 at 80°C. Figure 14 shows that the rate curves of the two experiments were almost identical. The difference in the apparent rate constants was 5.2% (3.8×10^{-3} min^{-1} and 3.6×10^{-3} min^{-1}, respectively). The molecular weights of the PMMA prepared by the two experiments were also very similar (see Figure 15). These results indicate that the continuous ATRP process had a very good reproducibility.

Block copolymerization

The block copolymerization by supported ATRP in a batch process has been studied (Davis et al., 2000, 2001). The continuous block copolymerization of MMA with nBMA was attempted in two column reactors connected in series, as shown

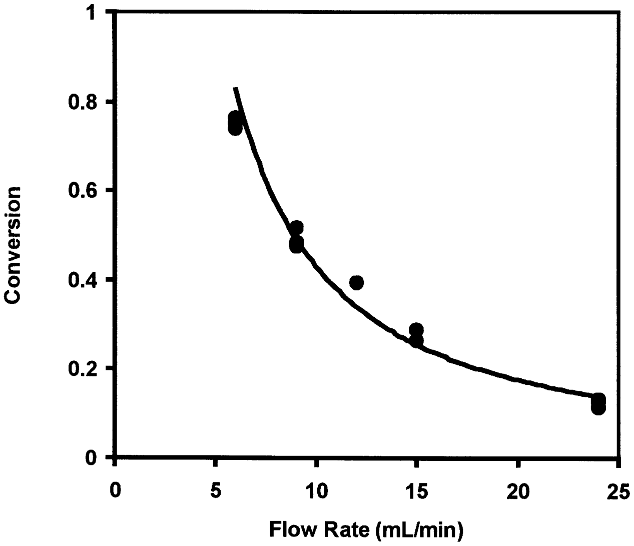


Figure 12. MMA conversion as a function of flow rate for the polymerization of MMA in two larger column reactors in series.

MMA/toluene = 1/3 (w/w), MMA/MBP = 100, silica gel/CuBr = 20; 80°C. Reactor: 500 mm in length; 7.8 mm inner diameter.

in Scheme 2. The MMA and initiator (MMA/initiator = 30) were delivered to Reactor I to produce PMMA prepolymer. The PMMA prepolymer chains eluted from Reactor I were mixed with the second monomer nBMA, and the mixture was pumped into Reactor II for block copolymerization. The resulting block copolymers were analyzed by GPC (see Figure 16), and their compositions were analyzed by NMR spectra (Table 1).

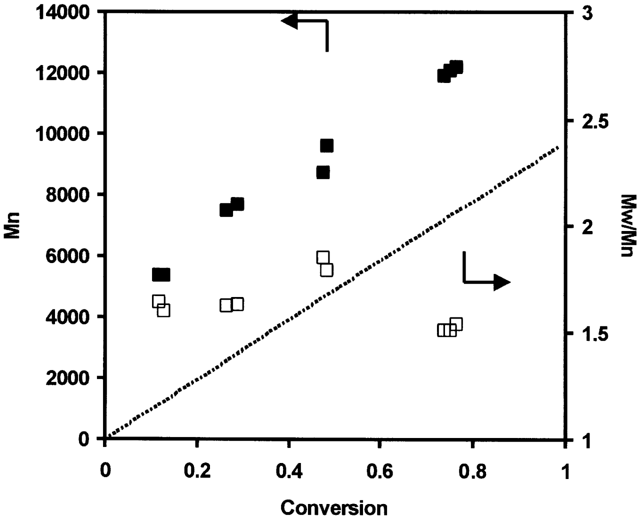


Figure 13. Molecular weight and polydispersity of PMMA as a function of MMA conversion for the polymerization in the larger reactor.

See Figure 12 for the reaction conditions. Theoretical Mn (......).

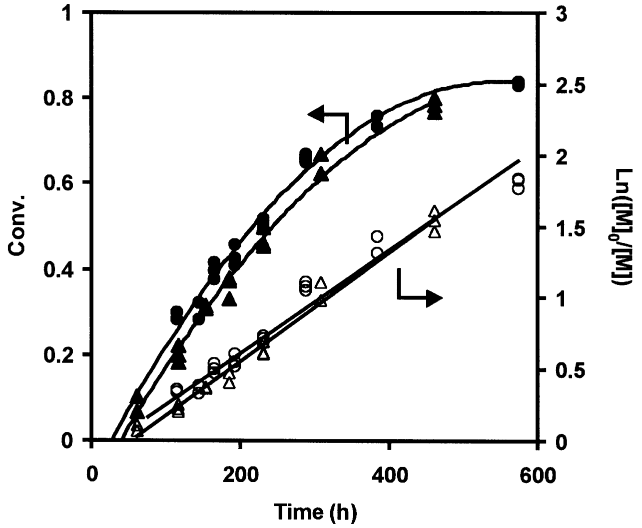


Figure 14. Reproducibility study: the MMA conversion vs. time in different runs using the reactor.

MMA/toluene = 1/3 (w/w), MMA/MBP = 100, silica gel/CuBr = 20; 80°C. Run 1 (●, ○), run 2 (▲, △).

The molecular weight of PMMA prepolymer obtained from the first reactor was 4,000 with 80% conversion. When nBMA was injected at a flow rate of 1.2 mL/h, a block copolymer of molecular weight 11,000 was produced. Increasing the nBMA flow rate to 1.8 mL/h yielded a block copolymer of molecular weight of 18,000. There were no significant prepolymer shoulder peaks in the GPC traces of the block copolymer samples, indicating negligible contamination of the PMMA prepolymer and that the prepolymer PMMA chains eluted from the first reactor initiated the nBMA polymerization in the second reactor. These results further confirmed that the continuously supported ATRP in the reactor proceeded in a living manner. This work also demonstrated that the series

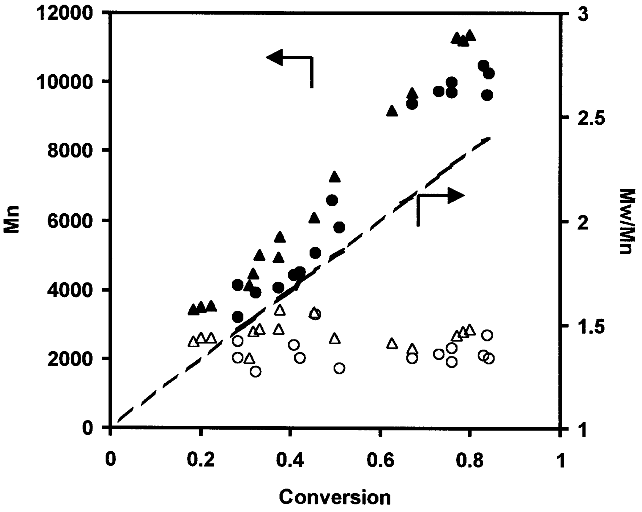


Figure 15. Molecular weight and polydispersity of PMMA produced in different runs.

See Figure 14 for experimental conditions. Run 1 (●, ○), run 2 (▲, △), theoretical Mn (........).

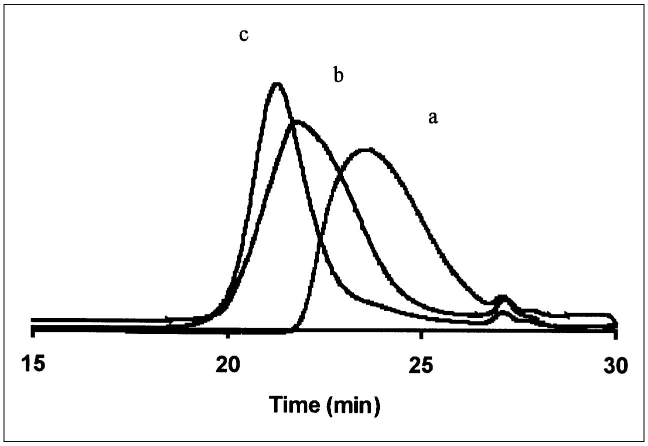


Figure 16. GPC traces of the block copolymerization of MMA and nBMA by two reactors in series.

PMMA prepolymer (a) produced in the first column: MMA/toluene = 1/4 (w/w), MMA/MBP = 30, silica gel/CuBr = 20; 80°C, flow rate = 1.2 mL/h; second column: silica gel/CuBr = 20; 80°C, pure nBMA, flow rate = 1.2 mL/h (b), 1.86 mL/h (c).

column reactor system is a feasible technology for synthesizing block copolymers with their block molecular weights readily adjusted by changing the two monomer flow rates.

It should be pointed that some challenges still remain to be solved for this newly developed continuously supported atom-transfer radical polymerization technology (C-SATRP Tech). First, the conversion of the second monomer was low. This was caused by the high flow rate in the second reactor due to the combined flows from the first reactor and that of nBMA. There was also some percentage of MMA units in the second block due to the presence of residual MMA in the flow eluted from the first reactor. Further developments should be directed at using a reactor having higher mean residence time to increase the second monomer conversion and to remove the unreacted MMA from the prepolymer solution to avoid its contamination of the second block composition.

Summary

In summary, a column reactor system packed with silica-gel-supported CuBr−HMTETA catalyst was shown to be very useful for continuous homo- and block copolymerization of MMA. The system had good stability with respect to both reactor activity and PMMA molecular weight. Various product grades of polymers with different molecular weights can be readily prepared by adjusting the monomer flow rate and/or by changing the monomer/initiator ratio. The block copolymerization of MMA with *n*BMA using two column reactors connected in series was useful for preparing block copolymers with controlled molecular weight and block distribution.

Acknowledgment

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Table 1. Block Copolymerization of MMA with *n*BMA in the Two Column Reactors Connected in Series

*n*BMA Flow Rate	MMA Conv. (%)	*n*BMA *n*Conv. (%)	Mn Copolymer	Mw/Mn Copolymer	MMA/nBMA in Copolymer
0	82	—	4,000	1.38	100/0
1.2	85	40	11,000	1.70	57/43
1.8	86	40	18,000	1.84	68/32

Note: See Figure 16 for the reaction conditions.

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Errata

For the article titled, "Electromagnetics, Heat Transfer, and Thermokinetics in Microwave Sterilization" by H. Zhang, A. K. Datta, I. A. Taub, and C. Doona (pp. 1957–1968, September 2001), the authors require a second reproduction of Figures 7 and 16 for clarification of details.

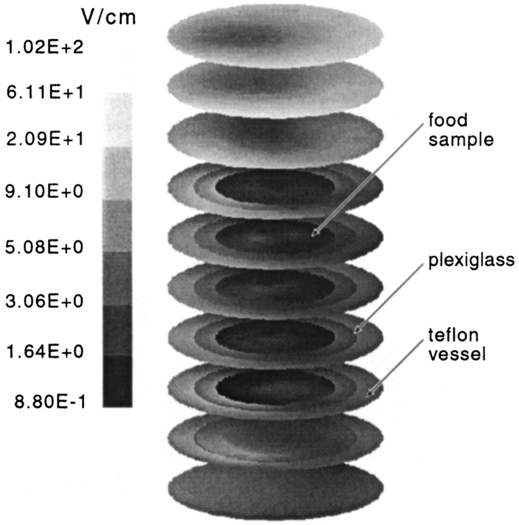

Figure 7. Electric fields in food sample, plexiglass, and teflon vessel for the assembly in Figure 2 during heating stage 1 of 0.7% salt ham.

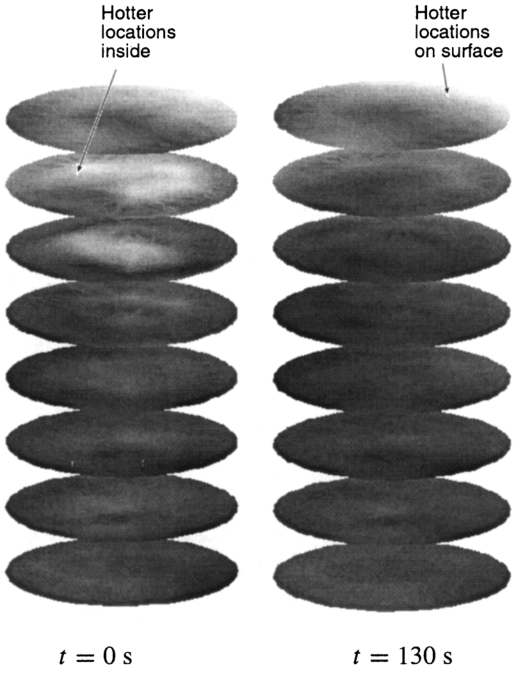

Figure 16. Horizontal section of cylindrical food at equal vertical intervals showing the change in heating potential from initial time to after 130 s of continuous heating.

Lighter shades of gray represent increased magnitude of heating potential.