Synthesis of methacrylate macromonomers using silica gel supported atom transfer radical polymerization

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Introduction

Atom transfer radical polymerization (ATRP) has been developed as a new approach to the living polymerization. In contrast to the typical anionic, cationic or group transfer polymerizations, which are very sensitive to protonic species, ATRP has the advantage of great tolerance to water and other protonic species.

One of the important applications of living polymerization is to synthesize well-defined functional polymers of relatively low molecular weight, such as macromonomers. ATRP was successfully used to synthesize polymers bearing functional terminal groups, such as vinyl[7-9] and hydroxyl[10-12] groups. A subsequent problem for ATRP is its low catalyst efficiency and thus the high catalyst concentration required. In a typical ATRP procedure, the metal halide was about 0.1~1% (molar) of monomer, i.e., a monomer to catalyst ratio of 100 to 1000. The high catalyst residual gives the final product deep color. Therefore, after polymerization, an additional process is required to remove the catalyst from the product, usually by passing silica or alumina gel or acidic resins[13]. These post-treatments not only waste catalyst but also it is time-consuming and costly. A potential route to solve this problem is to support the catalyst onto solid, which can be easily removed from the final product, and ideally be recycled. Very recently, ruthenium(II) catalyst attached onto 3-aminopropyl-functionalized silica was successfully used for the ATRP of MMA. The polymerization displayed typical living characteristics.[14] However, ATRP mediated by CuBr supported on silica gel or crosslinked polystyrene particles via Schiff-base ligands produced polystyrene or PMMA with molecular weights much lower than those achieved with the silica gel supported catalyst system.

Full Paper: A silica gel supported CuBr-hexamethyl-triethylenetetramine (HMTETA) (SG-CuBr/HMTETA) catalyst system was developed for the synthesis of poly-(methyl methacrylate) (PMMA) and poly(dimethylaminoethyl methacrylate) (polyDMAEMA) macromonomers with terminal vinyl or allyl group by atom transfer radical polymerization (ATRP). Catalyzed by SG-CuBr/HMTETA and with vinylxyethl 2-bromoisobutyrate (VBIB) or allyl 2-bromoisobutyrate (ABIB) as initiator, the MMA polymerization showed first order kinetics up to a 60% monomer conversion. The polymerization rate slowed down at higher conversions due to a reduction in radical concentration. Gel permeation chromatography (GPC) results showed that the decrease in radical concentration was caused by the reaction of radicals with the initiator’s vinyl or allyl group moieties. In contrast, the DMAEMA polymerization was first order kinetics throughout the polymerization. The molecular weights of the resulting PMMA and polyDMAEMA increased linearly with conversion with low polydispersities. After the first run polymerization, the catalysts were recycled for second and third runs. The recycled catalysts still mediated a living polymerization of MMA or DMAEMA, producing polymers with controlled molecular weight and narrow polydispersity, but their catalytic activities decreased significantly. The reactivity reduction of the recycled catalyst was due to radical side reactions that yielded an extra amount of CuBr2 as well as the catalyst loss during recycling.
higher than predicated and high polydispersities.\textsuperscript{[15]} Copper bromide immobilized onto multidentate amine-functionalized silica gel was no longer found to mediate living polymerizations of MMA, MA and styrene.\textsuperscript{[16]} The copper bromide-hexamethyltriethylenetetramine (HMTETA) complex was an excellent catalyst for ATRP of MMA, DMAEMA, St and MA.\textsuperscript{[8,17]} Recently we observed that the complex absorbed on silica gel mediated a living polymerization of MMA\textsuperscript{[18]}. The supported catalyst retained 80\% activity for the first recycle and 50\% activity for the second. Most significantly, the reused catalyst allowed even better control over the molecular weight in the second and third run polymerization of MMA.\textsuperscript{[18]} The support catalyst was also suitable for packing column reactors as continuous ATRP processes with high stability.\textsuperscript{[19]} In this paper we extend our work to the synthesis of macromonomers by heterogeneous ATRP polymerization of MMA mediated by copper bromide-HMTETA complex adsorbed on silica gel.

**Experimental part**

**Materials**

Methyl methacrylate (MMA) and 2-dimethylaminoethyl methacrylate (DMAEMA) from Aldrich were distilled under vacuum and stored at $-15^\circ$C before use. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, ligand), CuBr and allyl 2-bromoisobutyrate (ABIB, initiator) also from Aldrich were used as received. Toluene was distilled over CaH$_2$. Silica gel with 230–400 mesh and average pore diameter of 60 Å was purchased from SiliCycle. It was boiled in deionized water for 5 h and then dried in the air and under vacuum. The chemical structures of the initiators and ligand used in this work are shown in Scheme 1.

**Synthesis of vinyloxyethyl 2-bromoisobutyrate (VBIB, initiator)**

10 g (0.113 mol) ethylene glycol vinyl ether (EGVE) and 19 ml (0.136 mol) triethylamine were dissolved in 250 ml THF. The solution was cooled in an ice-water bath. To this solution, 14.0 ml 2-bromoisobutyryl bromide (BIBB) (0.113 mol) in 50 ml THF was added dropwise. The mixture was stirred for another 2 h at room temperature (EGVE reacted with BIBB to yield VBIB and HBr; HBr was absorbed by triethylamine). Next, triethylamine hydroxy bromide salt was filtered off. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in CHCl$_3$ and washed three times with 50 ml water. The aqueous parts were combined and shaken with 50 ml fresh CHCl$_3$. The total CHCl$_3$ solution was then dried over anhydrous CaCl$_2$ overnight. After filtering off the drying agent, CHCl$_3$ was distilled under vacuum. A brown liquid was obtained and a further distillation under high vacuum gave a colorless liquid. Yield, 20.8 g.

**Polymerization**

A typical polymerization process is as follows: 0.0356 g CuBr and 0.071 g silica gel were added to a Schlenk flask and degassed by 5 vacuum-nitrogen cycles. Then 2.48 g MMA, 7.43 g toluene and 0.0570 g HMTETA, also degassed, were added and the mixture was bubbled with nitrogen for 5 min with stirring. The silica gel particles changed to a blue color. The degassed 42 ml VBIB was then introduced into the bottle dropwise with stirring. The bottle was subsequently heated to 70 °C in an oil bath with efficient stirring. At different time intervals, 0.2–0.5 ml of the reacting mixture was withdrawn from the bottle with a nitrogen-purged syringe. The solution was diluted with CDCl$_3$. The conversion was measured with $^1$H NMR by calculating the intensity ratio of OC$_3$H$_7$ (for MMA) or OCH$_2$ (for DMAEMA) signals in the polymer and the monomer. Part of this solution was used for GPC characterization.
**Catalyst reuse**

After the polymerization was complete, the mixture was left standing for some time at room temperature. The upper layer, which was a clear solution, was carefully removed via cannula under nitrogen atmosphere. The solid left in the bottle was washed twice with 20 ml degassed toluene under nitrogen. Then the same amount of degassed MMA toluene and initiator, as in the first polymerization run, was added to the bottle and reheated. The same procedure as the first polymerization run was repeated.

**Measurements**

Nuclear Magnetic Resonance (NMR) Spectroscopy: $^1$H NMR spectra were recorded on a Bruker ARX-200 spectrometer at 200 MHz. $^1$H NMR chemical shifts in CDCl$_3$ were reported downfield of 0.00 ppm with TMS as the standard.

Molecular weight measurements: Number- and weight-average molecular weights ($M_n$ and $M_w$, respectively) were determined by gel permeation chromatography (GPC, Waters 150) using THF-2% (v/v) trimethylamine as solvent at 25°C with an RI detector. Narrow polystyrene standards (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows based Millenium software package.

**Results and discussion**

The adsorption of the CuBr-HMTETA complex onto silica gel in toluene-monomer solution was investigated first. It was observed that once silica gel was added to toluene-MMA solution of the copper-HMTETA complex, the silica gel immediately turned blue, while the upper layer solution was colorless, suggesting the catalyst was adsorbed onto silica gel. When silica gel was added to the toluene-DMAEMA solution of the copper-HMTETA complex, the silica gel also turned blue. However, the upper layer solution still had some grey color. This indicates that the CuBr-HMTETA complex could not be completely adsorbed onto the silica gel in the presence of DMAEMA.

The adsorption of copper bromide complex onto silica gel was assumed by a physical interaction of a highly polar copper bromide-HMTETA complex with a highly polar silica gel surface. The low polarity of MMA-toluene solution made the CuBr-HMTETA complex stable on the silica gel surface. In contrast, high polarity and coordination ability (via the nitrogen atom) of DMAEMA monomer led to the copper bromide-HMTETA complex having a high partition in the solution. Therefore, the complex was only partially adsorbed onto the silica gel in the DMAEMA-toluene solution.

The synthesis of macromonomers by ATRP of MMA and DMAEMA mediated by the silica gel supported CuBr-HMTETA was assessed by using vinyl(VBIB) or allyl(ABIB) containing initiator. Fig. 1 shows the MMA polymerization using the two initiators at 70 and 90°C. There was no difference in the polymerization with ABIB and VBIB as initiator respectively, which is in agreement with the fact that the initiating moieties of the two initiators are the same in molecular structure. At 90°C, the polymerization with VBIB as initiator proceeded much faster and achieved higher conversion than that at 70°C.

Fig. 1 shows that the MMA polymerization proceeded in a first order kinetics with respect to the monomer up to ca. 60% conversion. After this, the polymerization slowed down and deviated from the first order kinetics, suggesting that the radical concentration decreased at high conversions. This observation is very different from the MMA polymerization catalyzed by the same supported catalyst but using initiator without unsaturated group (methyl α-bromo-α-phenylacetate, MBP), which was a first order reaction throughout the polymerization. This comparison suggests that the deviation of MMA polymerization with VBIB and ABIB from the first order kinetics at high conversion was caused by the initiator.

The GPC traces of the resulting PMMA are shown in Fig. 2 and 3. At the early stage, the GPC traces were of typical Gaussian distribution without any shoulder peak. When the conversion reached around 70%, a shoulder peak appeared at the high molecular region. The intensity of the shoulder peak increased with the polymerization. The shoulder peak became more significant when the polymerization was carried out at 90°C, as shown in Fig. 3. The high molecular weight population corresponding to the shoulder peak may be produced by the reaction of propagating radicals with terminal unsaturated moieties (Scheme 2, VBIB as initiator), which yielded polymer chains with doubled molecular weight. Because the bro-
mine in \(-\text{CH}_2\text{CH}--\text{O}\) was very difficult to be abstracted to generate the radical, the radical concentration subsequently decreased and thus induced a slower polymerization rate (see Fig. 1).

Fig. 4 shows the dependence of molecular weight and molecular weight distribution of PMMA on the MMA conversion. Before the conversion reached 60%, the molecular weights of PMMA resulting from all polymerizations increased linearly with conversion and were very close to the theoretical values. The molecular weight distributions at this stage were narrow, less than 1.2. But the molecular weight and molecular weight distribution increased sharply at conversions higher than 70%. This is particularly true for those polymerizations carried out at 90°C. This phenomenon coincided with the observation that the shoulder peak in the GPC traces appeared and became more significant at higher temperature.

The polymerization of DMAEMA with VBIB as initiator is shown in Fig. 5. In contrast to the MMA polymerization, the DMAEMA polymerization catalyzed by the catalyst proceeded smoothly up to 80% in a first order kinetics, indicating a constant radical concentration. The GPC traces of the resulting polyDMAEMA gradually moved to the high molecular weight region and only
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showed a sign of a shoulder peak at about 80% conversion, as shown in Fig. 6. The molecular weights of poly-DMAEMA increased with DMAEMA conversion and were very close to the theoretical values (see Fig. 7). The deviation of the experimental molecular weights of poly-DMAEMA at high conversions may be due to the different hydrodynamic volumes of the polystyrene standard and polyDMAEMA.

The improvement of the DMAEMA polymerization compared to that of the MMA with the same catalyst system may be derived from the catalyst that was not adsorbed onto the silica gel. As discussed above, in the presence of DMAEMA monomer, silica gel could not adsorb all the catalyst. Therefore the catalyst in solution mediated the radical concentration in the solution more efficiently and thus decreased the probability of radicals attacking the terminal vinyl groups in the polymer.

Catalyst recycling

After completion of the polymerization, the upper layer of the polymer solution was removed and green silica gel particles were recovered for the second polymerization run. Fig. 8 shows the MMA polymerization for the first and second uses of the catalyst. The recycled catalyst retained some activity, i.e. about 15% of its original activity (the difference in the curve slopes). This is very different from the MMA polymerization with the same catalyst but using MBP as initiator\(^{[18]}\). With MBP as initiator, the recycled CuBr-HMTETA supported on silica gel retained 80% of its original activity\(^{[18]}\).
The significant activity loss of the recycled catalyst with VBIB as initiator may be caused by the loss of catalyst during the recycling and produced extra CuBr$_2$. The polymer solution removed from the polymerization mixture after the catalyst had settled down was slightly green in color, suggesting some removal of the catalysts. During ATRP, the reaction of radicals with unsaturated groups in the initiator moieties produced highly unstable radicals (CH$_2$—C'—H—O—) (Scheme 2). These radicals easily proceeded side reactions such as the radical coupling reaction. The disappearance of radicals finally led to extra CuBr$_2$ being left in the system (Eq. 1). It was reported that a small amount of CuBr$_2$ could substantially decrease the polymerization rate by driving back the equilibrium (Eq. 1) and thus decreasing the radical concentration.$^{[20]}$

$$\text{Ph—X} + \text{CuX-Ligand} \xrightarrow{K} \text{Ph} + \text{CuBr}_2/\text{Ligand}$$

(1)

The DMAEMA polymerization catalyzed by the catalyst recycled from its first run polymerization is shown in Fig. 9. Similar to the first polymerization run, the second and third runs were also in first order kinetics, but the activity of the recycled catalyst substantially decreased. Each time, the recycle catalyst retained only 25% of its activity. This activity loss of the catalysts recycled from the DMAEMA polymerization was mainly caused by the loss of catalyst during recycling. As discussed above, only partial catalyst was adsorbed on the silica gel in the presence of DMAEMA. Therefore, a high portion of catalyst was lost during catalyst recovery.

The dependence of molecular weight of PMMA and polyDMAEMA obtained by the recycled catalysts are shown in Fig. 10 and 11, respectively. The molecular weights of PMMA or polyDMAEMA increased with the conversion. The molecular weight distributions of the resulting polymers were around 1.2. The GPC traces showed no shoulder peak in the polymer samples prepared by the recycled catalysts. These results indicate that the recycled catalysts still mediated living polymerization of MMA or DMAEMA, even though the reactivity of the recycled catalysts was low.
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Macromonomer characterization

The PMMA and polyDMAEMA prepared with VBIB and ABIB as initiators were characterized by NMR. Fig. 12 shows that, besides the polymer backbone, there were signals ascribed to the terminal groups. For both PMMA and polyDMAEMA prepared with VBIB, there was a same tetrad signal at 6.50–6.30 ppm attributed to the methine proton of the vinyl group (–CH=–). The methylene proton signals of the vinyl group (–CH=–CH=–) were also found at around 4.0 ppm in PMMA polymer, but were overlapped by those of the ester group (–COOCH=–) in poly-DMAEMA. For PMMA prepared by ABIB as initiator, the signals of the allyl group were observed at 5.8 ppm (m, CH=CH–CH=–), 5.2 ppm (t, CH=CH–CH=–) and 4.45 ppm (d, CH=CH–CH=–). These observations proved that the prepared polymers contained the vinyl or allyl group from the initiator moieties.

The molecular weight of the polymers can also be calculated from the signal intensity ratio of the polymer backbone to the terminal unsaturated group. When the polymerization was terminated at relatively low conversion, the calculated $M_n$ values by NMR were agreeable to

Fig. 12. The $^1$H NMR spectra of PMMA and polyDMAEMA. (A): PMMA: (1) VBIB and (2) ABIB as initiator, 70 °C, 60 min, see Fig. 1 for the experimental conditions. (B) polyDMAEMA: VBIB as initiator, 70 °C, 70 min, see Fig. 5 for the experimental conditions.
the theoretical ones. For example, with VBIB as initiator, the $M_n$ of PMMA from 1 h polymerization (yield, 38.6%) was 4200 (Fig. 12, A (1)), close to theoretical value of 3860 ($M_n$Theor = MMA/Initiator $\times$ 100 $\times$ yield). But if the polymerization was pushed to high monomer conversion, the calculated $M_n$ values from NMR were much higher than the theoretical, which is consistent with the GPC results.

**Conclusion**

Silica gel supported CuBr-HMTETA was successfully used for the ATRP of MMA and DMAEMA for the synthesis of PMMA and polyDMAEMA macromonomers using allyl- (ABIB) and vinyl- (VBIB) containing initiators. In the MMA polymerization, the vinyl or allyl group survived when the conversion was less than 60%. At higher MMA conversion, the vinyl or allyl group began to react with radicals and thus the polymerization rate decreased. The DMAEMA polymerization showed first order kinetics throughout the polymerization without destroying the allyl or vinyl group. The molecular weights of PMMA and polyDMAEMA increased linearly with conversion giving narrow polydispersities. The recycled catalysts still showed catalytic activity and mediated a living polymerization of MMA or DMAEMA, but the reactivities of the recycled catalysts were relatively low because of the radical side reaction and catalyst loss.

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