

Towards more controlled poly(*n*-butyl methacrylate) by atom transfer radical polymerization

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Abstract

The homogeneous controlled/‘living’ free radical polymerization of *n*-butyl methacrylate in toluene or *o*-xylene at 90 °C, in bulk and in solution, using the novel combination of the catalyst bis-triphenylphosphine iron(II)chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$) with ethyl 2-bromoisobutyrate ($((\text{CH}_3)_2\text{CBrCO}_2\text{Et})$) and α,α -dichloroacetophenone (CHCl_2COPh) as initiators has been investigated. The rate of polymerization initiated by the two initiators exhibited first-order kinetic with respect to the monomer. A linear increase of the number-average molecular weight (M_n) versus monomer conversion was observed for these systems. Among the two initiation systems, ethyl 2-bromoisobutyrate gave the fastest polymerization rate. A system with Fe^{3+} added at the beginning of the polymerization was examined and the lowest polydispersity ($M_w/M_n \sim 1.2$) was found when 10% Fe^{3+} , relative to Fe^{2+} was added.

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1. Introduction

Recently, several approaches to controlled/‘living’ free radical polymerizations have been reported [1]. The most efficient techniques seem to be degenerative transfer system (RAFT) and atom transfer radical polymerization (ATRP). These both methods have advantages as well as disadvantages. RAFT as well as ATRP can be used for a variety of different monomers. Nevertheless ATRP, in which the contribution of transfer and termination to the overall reaction are suppressed, seems the most successful and especially well suited for low molecular weight functional polymers [2–10].

Scheme 1 summarizes the general mechanism of ATRP, which involves the abstraction of a halogen from the dormant chain by a metal center (such as a complex

of Fe^{2+}) in a redox process. Upon halogen abstraction, the free radical formed (the active species) can undergo propagation as in conventional free radical polymerization. However, the free radicals are also able to abstract the halogen back from the metal, reproducing the dormant species.

These processes are rapid, and the dynamic equilibrium that is established favors the dormant species. The concentration of the active radicals is therefore very low, limiting radical–radical coupling/disproportionation reactions as the principal mode of termination.

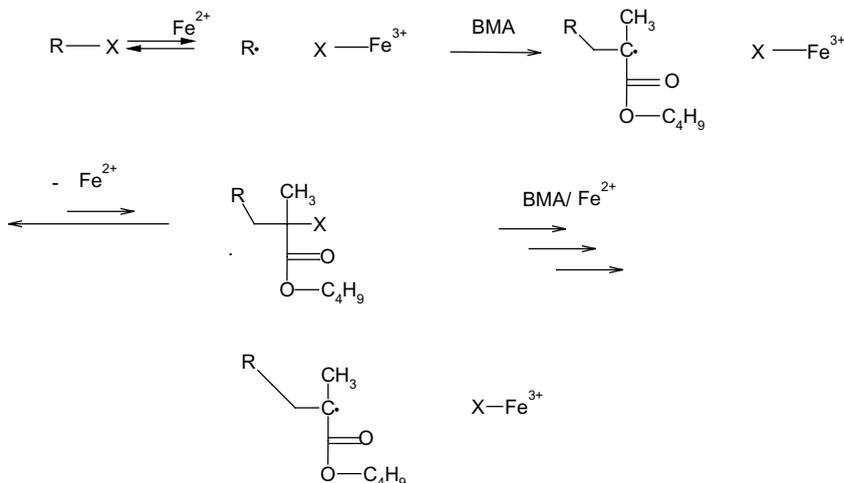
A fast dynamic equilibrium also allows each polymer chain to grow equally, resulting in low polydispersities.

Transition metal catalyzed atom transfer radical polymerization of *n*-butyl methacrylate (BMA) was of great interest to many researchers [11–13]. The results of polymerization they achieved by ATRP technique provide well-defined polymers with low polydispersities ($1.05 < M_w/M_n < 1.5$).

Here we present a study of the ATRP of BMA both in bulk and in solution in order to find the best conditions (initiator, solvent, and additive) for a more controlled

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Where :

Fe^{2+} : $FeCl_2 \cdot 4H_2O(PPh_3)_2$

R : $(CH_3)_2CBrCO_2Et$, $CHCl_2COPh$

Scheme 1. Basic concept of ATRP.

synthesis poly(*n*-butyl methacrylate) (PBMA) catalyzed by Fe^{2+}/PPh_3 complex.

2. Experimental

2.1. Materials

BMA (purum grade from Fluka) was purified by washing with 5% sodium hydroxide aqueous solution, followed by washing with water. The organic portion was then dried for 24 h under anhydrous sodium sulfate, filtered, and finally distilled under reduced pressure. Toluene (analytical grade from Merck, Germany), was distilled over Na/benzophenone, deaerated by bubbling nitrogen, and stored under nitrogen. Ethyl 2-bromo-isobutyrate ($(CH_3)_2CBrCO_2Et$) and α,α -dichloroacetophenone ($CHCl_2COPh$) were dried under molecular sieves. All other reagents were used as received.

2.2. Synthesis of catalyst

$FeCl_2 \cdot 4H_2O(PPh_3)_2$ was prepared by stirring a mixture of hydrated $FeCl_2 \cdot 4H_2O$ (1.0 g, 5.03 mmol) and PPh_3 (2.9 g, 11.1 mmol) in acetone as a solvent under dry nitrogen for 24 h at room temperature, after which stirring was stopped after 3 h to allow sedimentation. The yellowish precipitate was dried under vacuum for 3 h.

2.3. Polymerization

Polymerization of BMA was carried out under dry nitrogen in a dried schlenk tube equipped with a mag-

netic stirring bar. The tube was charged with the required amount of $FeCl_2 \cdot 4H_2O(PPh_3)_2$ sealed with rubber septum, and then degassed to remove oxygen. Degassed BMA and degassed solvents (if used) were added using a nitrogen-purged syringe, and the tube was degassed and back-filled with nitrogen three times. The solution was stirred for 5 min. Finally, immediately after the initiator was added via nitrogen-purged syringe, the tube was immersed in a preheated oil bath heated to a desired temperature. After a given time, the reaction was stopped, and the reaction mixture was cooled to room temperature and diluted with tetrahydrofuran. The obtained polymer solution was passed over alumina to remove the catalyst, then the polymer was precipitated with an excess amount of methanol.

The dried product was then characterized by gravimetry, 1H -NMR, and GPC techniques.

2.4. Characterization

The percentage conversion of the BMA monomer was determined by weighing the dried polymer.

The molecular weights were determined by room temperature SEC (Waters System Interface model, Waters 510 HPLC Pumps, Waters Differential Refractometer, Waters 700 satellite Wisp, and four linear PL gel columns: 104, 105, 103 and 100 nm connected in series). Chloroform was used as a solvent and eluent. The samples were filtered through a 0.5 μm Millex SR filter. Injected volume was 200 μl and the flow rate was 1 $ml\ min^{-1}$. Monodisperse polystyrene standards were used for primary calibration.

The $^1\text{H-NMR}$ spectra of polymer were recorded using a Varian Inc. (Palo Alto, CA) Gemini 2000XL NMR spectrometer operated at 300 MHz. The polymer solution was prepared by dissolving about 50 mg of polymer in 3 ml of deuterated chloroform (CDCl_3).

3. Results and discussion

A similar system, as the one used by Wang et al. [14] was adopted. Wang and coworkers used 1,2 dichloroethane as the initiator for polymerization of BMA. The polydispersities they achieved were 1.5, although the targeted molecular weight was rather low degree of polymerization, ($\text{DP} = 33$).

In order to get a more controlled polymer with higher molecular weights ($\text{DP} = 100$ and 150), we chose other initiators for the polymerization.

3.1. Effect of initiator

The main role of the alkyl halide (R-X) initiator is to determine the number of initiated chains. The halide group, X, must rapidly and selectively migrate between the growing chain and the transition metal complex. It has been noted, however, that well-defined polymers can also be prepared in the presence of minor chain-breaking reactions, if molecular weights are low enough and the polymerization is initiated fast enough.

Since the initiator is a useful tool for fine-tuning ATRP, two initiators were examined. The kinetics of the bulk polymerization of BMA at 90°C initiated by ethyl 2-bromo isobutyrate and α,α -dichloroacetophenone are presented in Figs. 1 and 2.

The straight semilogarithmic kinetic plot $\ln([M]_0/[M]_t)$ versus time, t , (where M_0 is the initial concentration of the monomer, and M_t is the monomer concentration at any time) indicates that the concentration of growing radicals is constant. It also can be seen from

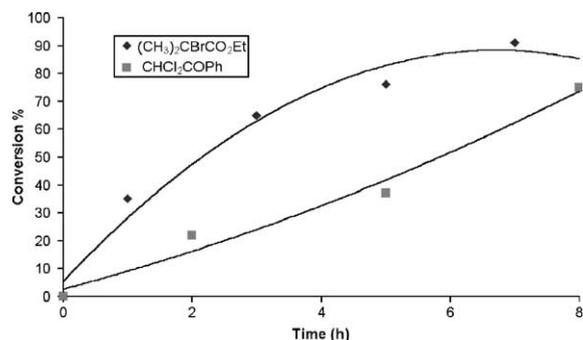


Fig. 1. Bulk polymerization of BMA with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} (\text{PPh}_3)_2$ as the catalyst ($[\text{monomer}]:[\text{initiator}]:[\text{catalyst}] = 150:1:1$) using $(\text{CH}_3)_2\text{CBrCO}_2\text{Et}$ and CHCl_2COPh as initiators at 90°C .

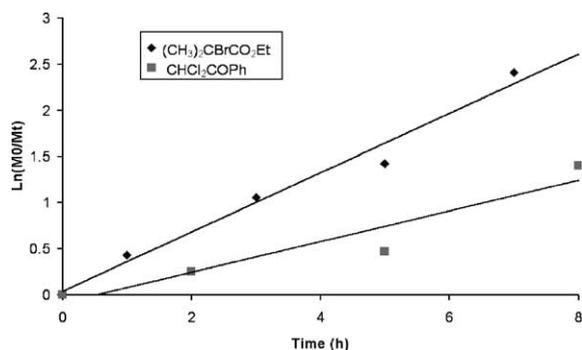


Fig. 2. First-order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in the bulk polymerization of BMA at 90°C using $(\text{CH}_3)_2\text{CBrCO}_2\text{Et}$ and CHCl_2COPh as initiators ($[\text{monomer}]:[\text{initiator}]:[\text{catalyst}] = 150:1:1$).

these figures that ethyl 2-bromoisobutyrate is a better initiator for BMA than α,α -dichloroacetophenone. This can be attributed to the more labile C–Br bond in the former initiator, compared to the C–Cl bond in the latter. Also, the structure of alkyl group in the ethyl 2-bromoisobutyrate is similar to the structure of the dormant polymer species.

Moreover, the experimental number average molecular weight, (M_n, exp) increases with monomer conversion (see Fig. 3) and matches the theoretical one, (M_n, theo) calculated from the following equation:

$$M_n = (\Delta[M]/[\text{R-X}]_0)(M_w)_0$$

where $\Delta[M]$, $[\text{R-X}]_0$, and $(M_w)_0$ present the concentration of consumed monomer BMA, the initial concentration of the initiator, and the molecular weight of BMA, respectively.

It should be noted here, that (M_n, exp) and (M_n, theo) values based on the above equation match well, even though the molecular weights obtained by SEC were

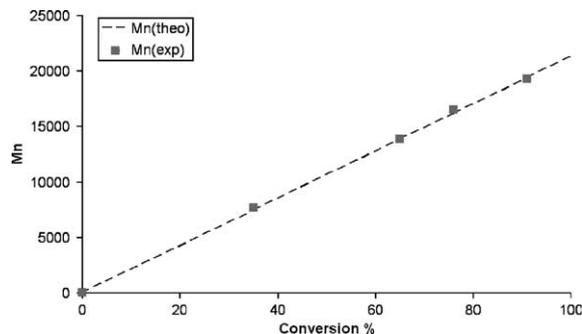


Fig. 3. Dependence of molecular weights on monomer conversion in the bulk polymerization of BMA at 90°C with $(\text{CH}_3)_2\text{CBrCO}_2\text{Et}$ as the initiator and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} (\text{PPh}_3)_2$ as the catalyst.

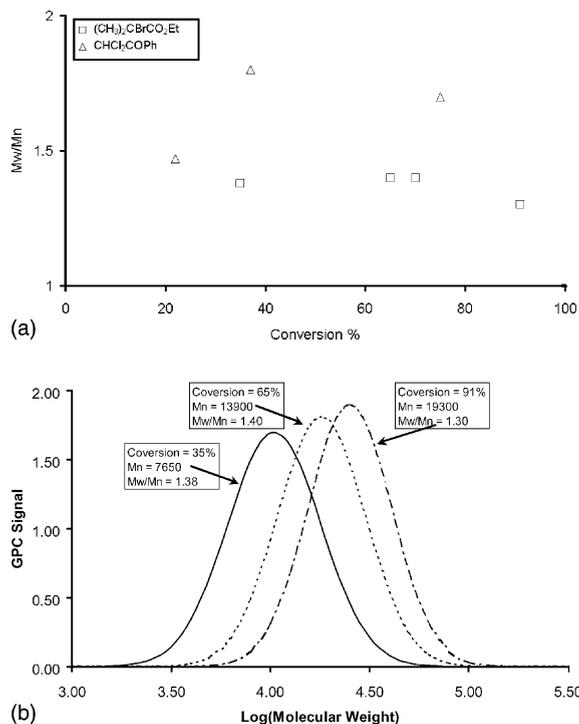


Fig. 4. (a) Dependence of polydispersities on monomer conversion of BMA under the same conditions as in Fig. 1. (b) GPC curves of PBMA prepared by ATRP using $(CH_3)_2CBrCO_2Et$ as initiator under the same conditions as in Fig. 1.

compared to those of polystyrene standards. This result indicates that an insignificant degree of transfer occurred during the polymerization [9,15].

Fig. 4(a) shows that the values of the polydispersities of the resulting polymers obtained with the ethyl 2-bromoisobutyrate are lower than those obtained with α,α -dichloroacetophenone (e.g. $M_w/M_n = 1.42$ – 1.3 against 1.86 – 1.47) indicating a fast exchange between active and dormant species (see Scheme 1).

Fig. 4(b) shows GPC curves of PBMA which are single and symmetric peaks. Also it shows that there was almost complete initiation by the ethyl 2-bromo isobutyrate initiator, and that molecular weights progressively increased with time.

3.2. Effect of solvent

Typically, ATRP is conducted in bulk, but solvents may be used and are sometimes necessary when the polymer is insoluble in its monomer [4]. Two solvents were investigated for ATRP of BMA using $FeCl_2 \cdot 4H_2O(PPh_3)_2$ catalyst at $90^\circ C$, with a monomer concentration of 50% (v/v) for all reactions. Figs. 5 and 6 show the first-order kinetic plots of the polymerization of BMA using toluene and *o*-xylene as solvents.

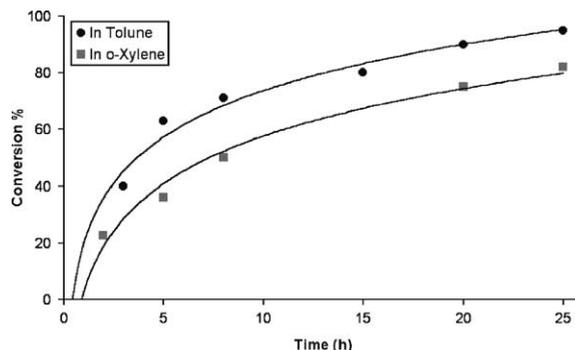


Fig. 5. Solution polymerization of BMA with $(CH_3)_2CBrCO_2Et$ as the initiator and $FeCl_2 \cdot 4H_2O(PPh_3)_2$ as the catalyst in (50% v/v) toluene, and in (50% v/v) *o*-xylene at $90^\circ C$. ([monomer]:[initiator]:[catalyst] = 200:1:1).

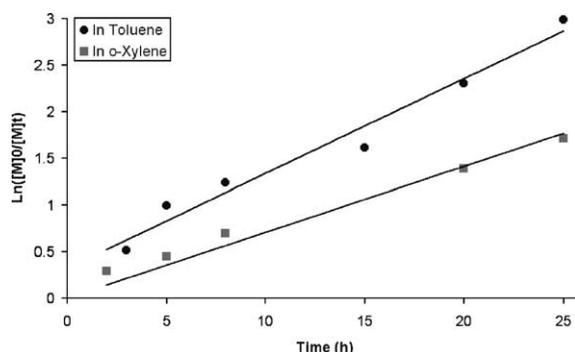


Fig. 6. First-order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in solution polymerization of BMA using the same conditions as in Fig. 5.

From these figures, it can be seen that both solvents yielded fast polymerization rates, but the polymerization in toluene was faster, plausibly due to the lower solubility of the catalyst system in *o*-xylene than in toluene.

Fig. 7 presents the linear evolution of number-average molecular weight, M_n , exp versus monomer conversion indicating controlled/'living' process with a negligible amount of transfer reactions.

This was further supported by the low polydispersities of the obtained polymers, as shown in Fig. 8, which also shows that polymerization of BMA can be conducted in solution using either toluene or *o*-xylene as solvents.

3.3. Effect of additives

Since ATRP is a catalytic process, the proportion of radicals and the polymerization rate can be controlled easily by adjusting the amount and activity of the transition metal components, including Fe^{2+} catalyst and Fe^{3+} deactivator. A series of reactions using different amounts of $FeCl_3$ (relative to Fe^{2+}) were carried out at $90^\circ C$ for 7 h to investigate the effect of the added

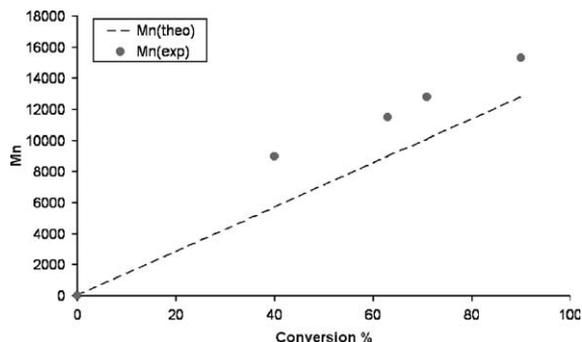


Fig. 7. Dependence of molecular weights on monomer conversion in (50% v/v) solution polymerization of BMA at 90 °C in toluene. ([monomer]:[initiator]:[catalyst] = 200:1:1).

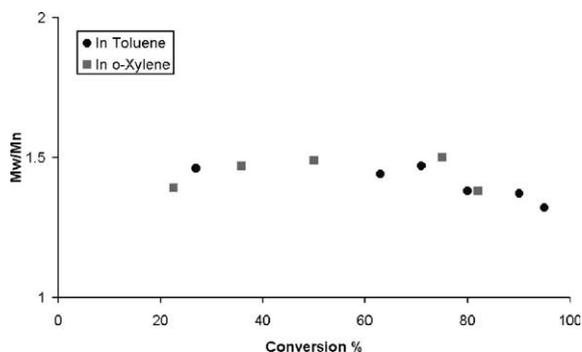


Fig. 8. Dependence of polydispersities on monomer conversion in the solution polymerization of BMA under the same conditions as in Fig. 5.

deactivator on the kinetics of the ATRP. At the beginning of the reaction 0%, 5%, 10%, and 15% (by mass) of FeCl_3 relative to the mass of Fe^{2+} was added.

Table 1 shows the effect of the additional amounts of deactivator on monomer conversion and on polydispersities of the polymers produced. From this table it is clear that, the proportion of radicals was reduced and the polymerization rate was consequently decreased with increasing amounts of deactivator FeCl_3 .

Also increasing the amount of deactivator resulted in polymers with low polydispersities up to a certain limit (10%) after which polydispersity started to slightly in-

Table 1

Dependence of the added amount of FeCl_3 on conversion in the solution polymerization of BMA in (50% v/v) toluene ([monomer]:[initiator]:[catalyst] = 200:3:1)

% (By mass) FeCl_3 added	% Conversion	Polydispersity
0	77	1.4
5	72	1.32
10	62	1.23
15	60	1.28

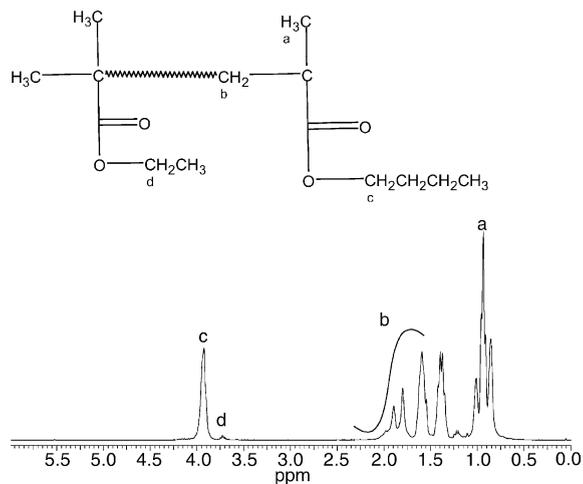


Fig. 9. ^1H NMR of PBMA obtained with $(\text{CH}_3)_2\text{CBrCO}_2\text{Et}/\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ in bulk.

crease. This is presumably caused by a limited solubility of Fe^{3+} in the reaction mixture, because if the amount of the added FeCl_3 is too much, the $\text{FeCl}_3/\text{PPh}_3$ complex will disperse heterogeneously, making polymerization difficult to be controlled.

3.4. End-group analysis

The polymer end-groups were analyzed with ^1H -NMR spectroscopy. The spectrum (Fig. 9) shows signals characteristic for the oxymethylene protons (d) of the ethyl ester group at the α -end, along with the large absorptions of the main-chain poly (BMA) units (e.g. oxymethylene protons adjacent to the *n*-butyl ester, (c)).

4. Conclusion

BMA was successfully polymerized using $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ catalyst, and in particular, ethyl 2-bromo isobutyrate as the initiator in both bulk and solution. A more controlled form of PBMA (higher molecular weight with low polydispersity) was thereby obtained. The addition of small amounts of FeCl_3 as deactivator decreased the rate of polymerization and lowered the polydispersity of the final polymer.

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