

# Synthesis of *tertiary*-butyl acrylate polymers and preparation of diblock copolymers using atom transfer radical polymerization

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## Abstract

The synthesis of *tert*-butyl acrylate by atom transfer radical polymerization (ATRP) is reported. This polymer was prepared using  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  catalyst system in conjunction with methyl 2-bromopropionate as initiator, in bulk and in solution using acetone as a solvent. The addition of solvent was necessary in order to decrease the polymerization rate and to afford low polydispersity polymers. The number-average molecular weights of the resulting polymers increased in direct proportion to the monomer conversion, and the polydispersities ( $M_w/M_n$ ) were as low as 1.2. In addition, the preparation of an AB diblock copolymer of poly (*n*-butyl methacrylate)–block–poly (*tert*-butyl acrylate) by ATRP is reported. The resulting polymers and copolymers were characterized by means of size exclusion chromatography and  $^1\text{H-NMR}$  Spectroscopy.

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## 1. Introduction

Living polymerization is considered to offer the best techniques for the preparation of polymers with controlled molecular weights and polydispersities [1,2]. These processes enable chemists to synthesize polymers with predictable molecular weights and block copolymers with high blocking efficiency [3].

Among these polymerization techniques is atom transfer radical polymerization (ATRP) [4,5], which requires less stringent conditions than ionic methods [6].

Scheme 1, summarizes the general mechanism of ATRP. This method utilizes a reversible halogen (X) abstraction step in which a lower oxidation state metal

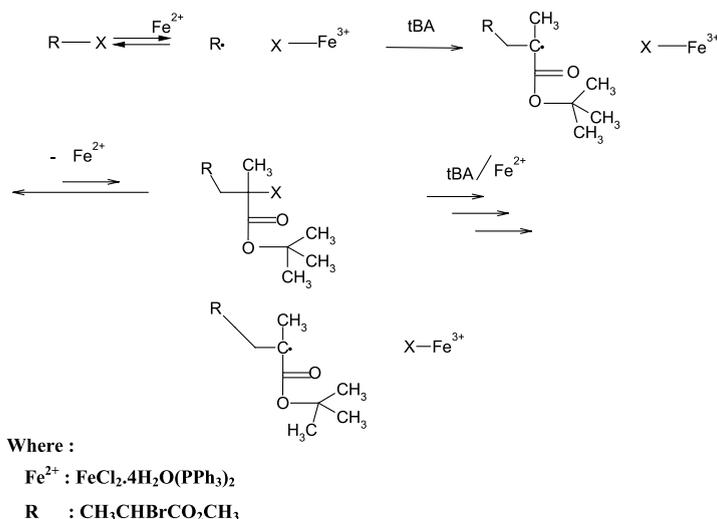
( $\text{Fe}^{2+}$  complexed by ligand  $\text{PPh}_3$ ) reacts with an alkyl halide ( $\text{R-X}$ ) to generate a radical ( $\text{R}^\cdot$ ) and a higher oxidation state metal complex ( $\text{X-Fe}^{3+}/\text{PPh}_3$ ). The radical then adds a monomer (i.e., *tert*-butyl acrylate, tBA) to generate the polymer chain. The higher oxidation state metal ( $\text{Fe}^{3+}$ ) can then deactivate the growing radical to generate a dormant chain and a lower oxidation state metal.

The molecular weight is controlled, since both initiation and deactivation are fast, allowing all the chains to begin growing at approximately the same time, while maintaining a low concentration of active species [3]. Thus, block copolymers containing quite different monomers may be synthesized successfully using technique.

Block copolymers of acrylates and methacrylate are not only challenging synthetically, but also interesting because of their morphological, phase, and mechanical properties. These properties are realized partly through

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Scheme 1. Basic concept of ATRP.

the combination of a high temperature block (methacrylate), with a softer, lower temperature block, (acrylate) [6].

We have studying iron-based catalysts for *n*-butyl-methacrylate polymerization [7], and became interested in iron-mediated ATRP. Iron is particularly attractive for use as an ATRP catalyst due to its low cost, and low toxicity.

This paper reports on the ATRP of tBA using the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  catalyst system. Additionally, we report the preparation of block copolymers of poly *n*-butyl methacrylate macroinitiator (PBMA) with tBA by ATRP.

## 2. Experimental

### 2.1. Materials

tBA (purum grade from Fluka) was purified by washing with 5% aqueous sodium hydroxide 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. Poly(butyl methacrylate) (PBMA) macroinitiator was dissolved in THF and precipitated in methanol (three times), filtered, and finally dried at room temperature for 48 h. Methyl 2-bromopropionate ( $\text{CH}_3\text{CHBrCO}_2\text{CH}_3$ ) was dried under molecular sieves. All other reagents were used as received.

### 2.2. Synthesis of catalyst

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  was synthesized according to the method described in details in our earlier paper [7].

### 2.3. Polymerization

Polymerization of tBA was carried out under dry nitrogen in a dried schlenk tube equipped with a magnetic stirring bar. The tube was charged with the required amount of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ , sealed with a rubber septum, and then degassed to remove oxygen. Degassed tBA 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 the 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. The reaction mixture was cooled to room temperature and diluted with tetrahydrofuran (THF). 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 characterized by gravimetry,  $^1\text{H-NMR}$ , and GPC techniques.

### 2.4. Synthesis of block copolymers

Block copolymerizations were performed in the same way as a typical polymerization at 110 °C, using 25% (v/v) acetone as a solvent, and PBMA as a macroinitiator instead of methyl 2-bromopropionate.

### 2.5. Characterizations

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

The molecular weights were determined by room temperature SEC (Waters System Interface module,

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  $\mu\text{m}$  Millex SR filter. The injected volume was 200  $\mu\text{l}$  and the flow rate was 1  $\text{ml min}^{-1}$ . Monodisperse polystyrene standards were used for primary calibration.

The  $^1\text{H-NMR}$  spectra of the 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 ( $\text{CDCl}_3$ ).

### 3. Results and discussion

#### 3.1. Synthesis of tBA polymer

tBA has been polymerized using several different methods, including ionic [8,9], nitroxide-mediated [10], and metallocene-mediated reactions [11]. ATRP has been used successfully for a variety of acrylate monomers, including methyl [12–15], *n*-butyl [16–19], ethyl [20], and 2-hydroxyethyl [21]. However, in most of these polymerizations bipyridine ligands were utilized.

The bulk polymerization of tBA using the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  catalyst system is heterogeneous. This type of system usually requires many experiments with different operating conditions (temperature, reaction time and monomer to initiator ratio) in order to achieve the best results.

We aimed at polymers with moderate molecular weights and optimized the number of experiments according to our goal. Table 1 summarizes the synthesis conditions and the characteristics of poly(tBA) (PtBA) obtained by ATRP.

Table 1 showed that at a high temperature the reaction was very fast (i.e. 90% conversion in 1 h, entry 1). Although the theoretical number average molecular weight,  $M_n$ , theo, is in quite good agreement with the experimental one,  $M_n$ , exp, obtained by gel permeation chromatography (GPC), the polydispersity ( $M_w/M_n$ )

was rather high. Though the temperature was reduced to slow down the reaction (Entry 2), the polydispersity was still high, which suggests a poor control of the polymerization.

Aiming at lower molecular weights by using a lower temperature (Entry 3) appeared not to work properly. Lower molecular weights with a higher temperature (Entry 4) at different time intervals slightly lowered the polydispersities of the resulting polymer and the experimental and theoretical molecular weights were in good agreement.

We believe that for the bulk polymerization of tBA using  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ , a high monomer-to-initiator ratio ( $\geq 200$ ) together with a high temperature ( $\geq 80$ ) are the best conditions to obtain polymers with defined molecular weights, though the polydispersities were high ( $\geq 1.5$ ). Matyjaszewski and co-worker [3] achieved polydispersities as low as 1.22 in the bulk polymerization of tBA with high targeted molecular weights (monomer-to-initiator ratio of 400) using  $\text{CuBr}_2/\text{PMDETH}$  as the catalyst system. In their polymerizations there was a significant deviation between experimental and theoretical molecular weights, particularly at higher conversions. This was due to differences in the hydrodynamic volumes between the PtBA and the linear polystyrene standards.

However, in order to improve the solubility of the catalyst, we conducted the polymerization in solution, using acetone as the solvent. This seemed to be an appropriate way to produce polymers with controlled molecular weights and low polydispersities.

In order to gain some information about the solution polymerization mechanism, we determined the ATRP kinetics of tBA using methyl 2-bromopropionate as initiator.

Fig. 1 reveals a semi-logarithmic plot of the heterogeneous ATRP of tBA in 33%(v/v) acetone. The polymerization was initiated by methyl 2-bromopropionate, catalyzed by  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  and run at 110  $^\circ\text{C}$ . The plot of  $\ln([M]_0/[M]_t)$  versus time (where  $M_0$  is the initial concentration of the monomer, and  $M_t$  is the monomer concentration at any time) is linear (apparent rate constant,  $k_p^{\text{app}} = 10 \times 10^{-4} \text{ s}^{-1}$ , suggesting a

Table 1

ATRP of tBA using  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  catalyst system, initiated by methyl 2-bromopropionate under various conditions in bulk

Entry	[Monomer]/ [Initiator]	Temperature ( $^\circ\text{C}$ )	Time (h)	Conversion (%)	$M_n$ , exp	$M_n$ , theo <sup>a</sup>	$M_w/M_n$
1	200/1	110	1	90	22800	23000	1.98
2	200/1	90	2	60	13000	15400	2.17
3	150/1	70	2	80	18900	15400	2.14
4	150/1	110	0.5	30	10000	5800	1.80
			1	72	16300	13900	2.00
			2	90	17000	17300	1.90

<sup>a</sup>  $M_n$ , theo = 128 ( $([\text{tBA}]_0/[\text{methyl 2-bromo propionate}]_0 \times \text{conversion})$ ).

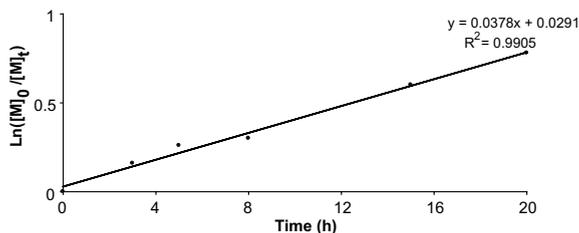


Fig. 1. First order kinetic plot of  $\ln([M]_0/[M]_t)$  versus time in solution polymerization of tBA with  $\text{CH}_3\text{CHBrCO}_2\text{CH}_3$  as the initiator and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  as the catalyst in (33%v/v) acetone at 110 °C. [Monomer]:[Initiator]:[Catalyst] = 200:1:1.

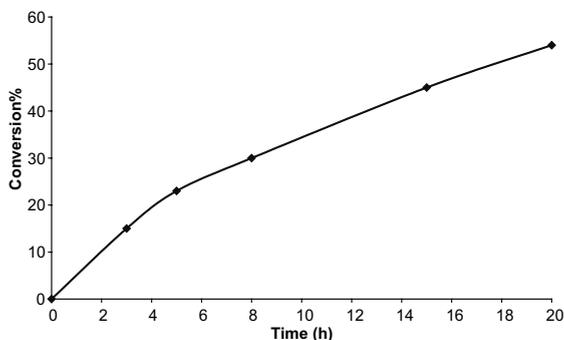


Fig. 2. Solution polymerization of tBA with  $\text{CH}_3\text{CHBrCO}_2\text{CH}_3$  as the initiator and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  as the catalyst in (33%v/v) acetone at 110 °C. [Monomer]:[Initiator]:[Catalyst] = 200:1:1.

constant number of propagating species throughout the reaction.

Fig. 2 illustrates a kinetic plot of conversion versus time, showing that monomer conversion increases with time, and that the reaction rate is slow (54% conversion in 20 h).

The linear increase of the number average molecular weight,  $M_n$ , exp, versus monomer conversion is demonstrated in Fig. 3. It can be seen that  $M_n$ , exp, values are

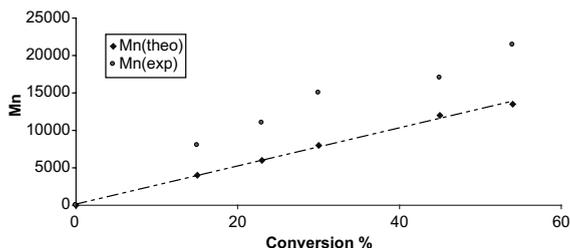


Fig. 3. Dependence of molecular weight on monomer conversion in (33%v/v) solution polymerization of tBA at 110 °C in acetone. [Monomer]:[Initiator]:[Catalyst] = 200:1:1.

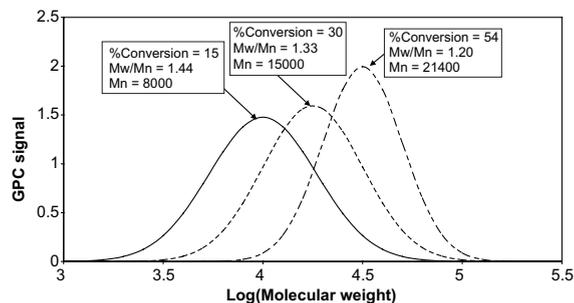


Fig. 4. GPC curves of PtBA obtained under the same conditions as in Fig. 1.

higher than the theoretical ones,  $M_n$ , theo, in particular at high conversion [3].

Fig. 4 shows the GPC curves of poly(*tert*-butyl acrylate), PtBA, which are single and symmetric peaks. A decrease in polydispersities with conversion, which is exhibited by this figure, suggests a controlled PtBA and, at the end of the reaction, molecular weight distributions are unimodal and narrow ( $M_w/M_n = 1.2$ ).

Finally, Fig. 5a shows the  $^1\text{H-NMR}$  spectra of the synthesized PtBA. The peak at  $\delta = 1.4$  is attributed to the *tert*-butyl resonance.

### 3.2. Block copolymerization of tBA using PBMA macroinitiator

Block copolymerization of BMA-*b*-tBA was performed using a two-step ATRP method. The first step is the synthesis of macroinitiator (PBMA). The polymerization of BMA has already been verified as a “Living” free radical polymerization with ethyl 2-bromo isobutyrate as the initiator in conjunction with  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$  as the catalyst system [7].

In the preparation of a block copolymer, we used a low conversion PBMA macroinitiator (conversion = 35%) and a high conversion PBMA macroinitiator (conversion = 76%) to verify the effect of loss of halogen during ATRP. Fig. 6 shows the unimodal GPC curves of PBMA and PBMA-*b*-PtBA using the following feed ratio: [tBA]:[PBMA]:[ $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}(\text{PPh}_3)_2$ ]:1000:1:1 at 110 °C in 25% (v/v) acetone (reaction time 15 h) with 35% conversion PBMA macroinitiator. From this figure it is clear that the GPC curve of macroinitiator PBMA is almost absent and completely shifted to a new higher molecular weight position. This indicates that the molecular weight can be controlled, and almost all PBMA macromolecules participated in the initiation, leading to the formation of diblock copolymer, PBMA-*b*-PtBA [21].

The  $^1\text{H-NMR}$  spectrum of PBMA-*b*-PtBA was measured and is shown in Fig. 5b. The signal at  $\delta = 3.9$  is attributed to the ester methyl protons in the PBMA unit,

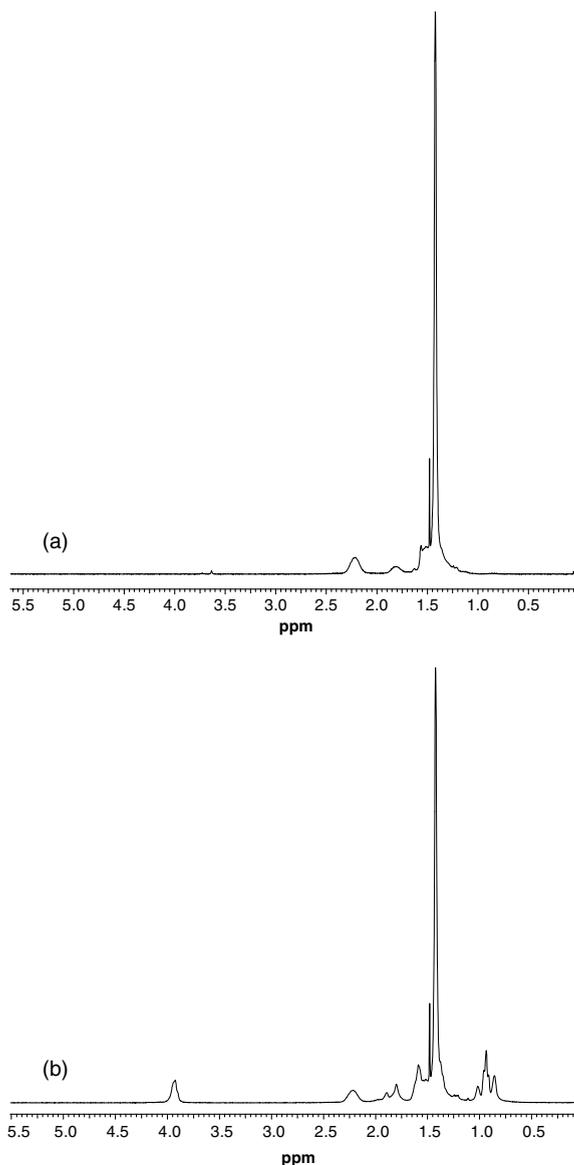


Fig. 5. (a)  $^1\text{H-NMR}$  spectra of tBA prepared by ATRP. (b)  $^1\text{H-NMR}$  spectra of PMMA-b-PtBA prepared by ATRP.

whereas the signal  $\delta = 1.4$  is due to the PtBA resonance in the ester group.

When 76% conversion of PBMA is used, diblock PBMA-b-PtBA is well-formed,  $M_n$ , exp, of PBMA = 16507 g/mol to  $M_n$ , exp, diblock PBMA-b-PtBA = 26930 g/mol, but polydispersity was higher (from  $M_w/M_n = 1.4$  of PBMA-Br to  $M_w/M_n = 1.8$  of PBMA-b-PtBA) using the same operating conditions and the same feed ratios. So, in order to synthesize well-defined copolymers, low conversion macroinitiator is preferable to avoid loss of the terminal halogen [22].

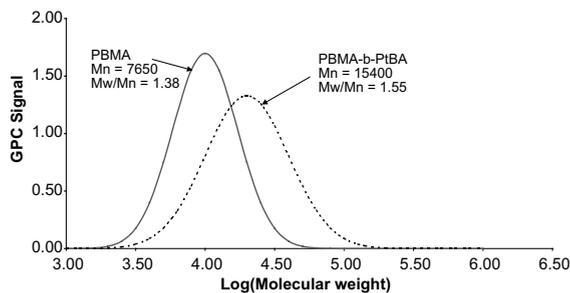


Fig. 6. Molecular weight distributions of PBMA macroinitiator and PBMA-b-PtBA diblock copolymer.

#### 4. Conclusion

Bulk and solution polymerization of tBA were conducted. The heterogeneity of the system forced us to prepare PtBA in acetone, which improved the solubility of the catalyst and produced polymers with well-defined molecular weights and relatively low polydispersities.

PBMA-b-PtBA was synthesized using both low conversion PBMA macroinitiator and a high conversion one. Low conversion PBMA macroinitiator yielded better results due to retention of the terminal bromine.

A simple triphenyl phosphine ligand could have been used for our ATRP of (meth)acrylate on the basis of relatively low cost and commercial availability. This ligand is good for ATRP, but it is not the best, so we are working on better ligands for ATRP in our laboratories.

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#### References

- [1] Klemm E, Schulze T. *Acta polym* 1999;50:1.
- [2] Baily WJ, Ni Z, Wu S-R. *Macromolecules* 1982;15:711.
- [3] Davis K, Matyjaszewski K. *Macromolecules* 2000;33:4039.
- [4] Wong J-S, Matyjaszewski K. *J Am Chem Soc* 1995;117:5614.
- [5] Kato M, Kamigaito M, Sawamoto M, Higashimura T. *Macro Mol* 1995;28:1721.
- [6] Shipp D, Wang J-L, Matyjaszewski K. *Macromolecules* 1998;31:8005.
- [7] Ibrahim K, Lofgren B, Seppala Y. *Eur Polym J* 2003;39:939.
- [8] Ishizone T, Yoshimura K, Hirao A, Nakahame S. *Macromolecules* 1998;31:8706.
- [9] Ishizone T, Yoshimura K, Yanase E, Nakahame S. *Macromolecules* 1999;3:95.
- [10] Goto A, Fukuda T. *Macromolecules* 1970;3:618.

- [11] Deng H, Soga K. *Macromolecules* 1996;29:1847.
- [12] Davis K, Paik H-J, Matyjaszewski K. *Macromolecules* 1999;32:1767.
- [13] Woodworth B, Metzener Z, Matyjaszewski K. *Macromolecules* 1998;31:7999.
- [14] Uegaki H, Kotani Y, Kamigaito M, Sawamoto M. *Macromolecules* 1998;31:6756.
- [15] Wang J-S, Matyjaszewski K. *Macromolecules* 1995;28:7901.
- [16] Matyjaszewski K, Nakagawa Y, Jaszczek C-B. *Macromolecules* 1998;31:1527.
- [17] Garcia M, de la Fuente J, Fernandez-sanz M, Madruga E. *Polymer* 2001;42:9405.
- [18] Ueda J, Kamigaito M, Sawamoto M. *Macromolecules* 1998;31:6762.
- [19] Shen Y, Zhu Sh, Zeng F, Peton R. *Macromolecules* 2000;33:5399.
- [20] Wootthikanokkhan J, Peesan M, Phinyocheep P. *Eur Polym J* 2001;37:2063.
- [21] Coca S, Jaszczek C-B, Beers K-L, Matyjaszewski K. *J Polym Sci Part A: Polym Chem* 1998;36:1417.
- [22] Yuan J-Y, Pan C-Y. *Eur Polym J* 2002;38:1565.