Communication **Open Access**

XianRong Shen*, DengZhou Xia, YiXin Xiang and JianGang Gao

γ-valerolactone (GVL) as a bio-based green solvent and ligand for iron-mediated AGET ATRP

https://doi.org/10.1515/epoly-2019-0033
Received December 20, 2018; accepted January 25, 2019.

Abstract: In this paper, γ-valerolactone (GVL), a bio-based polar solvent, was applied as green solvent for iron(III)-catalyzed AGET ATRP without any external ligand. GVL is a fully degradable, non-toxic green solvent and has complex ability to iron halide complexes through −OCO- group. GVL as the solvent and the ligand for AGET ATRP of MMA in a controlled manner, as proved by kinetic study, the low PDI values and the increase in polymer molecular weight versus monomer conversion. Chain re-initiation experiments and ^{1}HNMR characterization were conducted to further confirm the living feature.

Keywords: green solvent; AGET ATRP; living radical polymerization; γ-valerolactone; ligand

1 Introduction

Transition metal complex catalyzed ATRP (Atom Transfer Radical Polymerization) for the synthesis of well-defined polymers was reported over 20 years ago (1-3). For achieving a controlled/living polymerization process, it should maintain low numbers of growth free radicals and large excess of dormant centers in the ATRP reaction medium to suppress chain termination reactions, and should quickly establish a balance between the transition metal complexes in the low oxidation state and the higher oxidation state complexes which acts as the deactivator. Metal complexes play an important role on this equilibrium in regulating the catalytic cycle associated with the efficiency of the catalytic system. Various metal catalysis such as copper, ruthenium, iron, other transition metals have been investigated (4). Among these metals, copper-based ATRP catalysts are the most deeply investigated metal for the synthesis of well controlled polymers (5). However, the development of iron-based catalysts remains of great attention due to its unique advantages of low toxicity, abundance, low cost, biocompatibility and environmental friendliness (6).

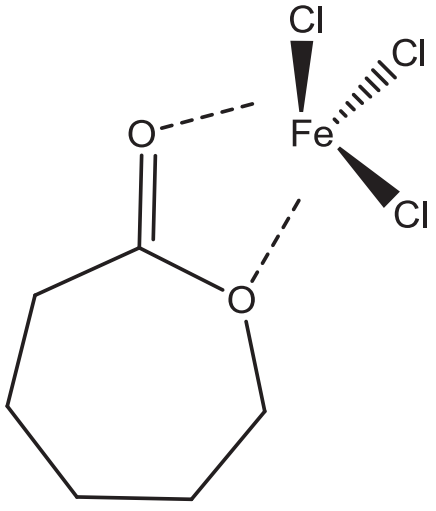
In a typical iron-mediated ATRP catalytic system, ligands should be added to complex with iron halide to form iron-based catalysts and to modulate the redox potential of metal centers to maintain proper reactivity and kinetics of atom transfer during ATRP. Phosphorus-based ligands and simple amines ligands have been widely tested in the iron mediated ATRP systems (7). However, due to the expensive or toxic problems, these ligands have been limited in some areas such as biological materials. For this reason, some cheap and relatively less toxic ‘‘green’’ organic acids ligands, such as, iminodiacetic acid (8), pyromellitic acid (9), isophthalic acid (10) and succinic acid (11), also have been considered in iron-mediated ATRP. Nowdays, biocatalysis has become a research hot topic in polymer chemistry field. Some proteins, such as hemoglobin (12), have the complex ability to iron species, these compounds have also been applied as ligands for iron-mediated ATRP of vinyl monomers. Interestingly, where iron-mediated ATRP conducted in some traditional polar solvent, such as DMF, MeCN, DMSO and NMP, use of external ligands becomes unnecessary; Polar solvent works as the dual functions of ligand and solvent (13,14). However, these traditional organic solvent are harmful to the environment for its hazardous, toxic. To avoid these unfavorable effects, it is urgent to select more environmentally friendly and inexpensive solvents to extend the application of iron catalysts. For this reason, Some ‘green’ solvents, such as water (15,16), poly (ethylene glycol) (17), crown ether (18) and ionic liquids (19) have been selected as reaction media for ATRP reaction, and some of these also could be worked both as solvent and ligand for iron-catalyzed ATRP (17-20).

Recently, utilization of renewable resources derived organic solvents has attracted more attention around the chemical world. Some bio-based green solvents now have

*** Corresponding author: XianRong Shen,** School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu 241000, PR China, e-mail: 10929016@zju.edu.cn.
DengZhou Xia, YiXin Xiang and JianGang Gao, School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu 241000, PR China.

been successfully employed in several chemical reactions such as glycerol and ethyl lactate (21-23). Among these agricultural biomass derived solvents, γ-valerolactone (GVL) is a room temperature stable liquid and has very low toxicity (LD50 oral rats = 8,800 mg / kg) (24). Since Dumesic reported an industrially acceptable process to produce GVL from biomass lignocellulosic, it makes suitable for the replacements of petroleum-derived solvents on a large scale (25). GVL has many excellent properties making it an ideal choice to traditional polar solvent alternatives. The polarity of GVL and other common polar solvents is very similar; For example, the measured GVL dielectric constant is 36.47 at 25°C, while the dielectric constants of DMF, NMP, CH_3CN, and DMA are 36.7, 32.0, 37.5, and 37.8, respectively (26). Although many work has been reported to utilize GVL instead of common polar solvents in chemical processes. However, to date, there has never been a report of the application of γ-valerolactone to ATRP catalytic system (27,28).

It is well known that ROP of ε-caprolactone catalyzed by metal Lewis acid catalyst through coordination-insertion mechanism, and ε-caprolactone monomer has complex ability to metal chlorite through –OCO- group (Scheme 1) (29,30). These results mentioned us that ε-caprolactone and its derivatives which have lactones group could be act as solvent and ligand for iron-mediated ATRP. However, the ring of ε-caprolactone can be opened by a lewis acid catalyst; it is unsuitable candidate as solvent and ligand for ATRP reaction (31,32). The valerolactone ring has a lower tension and difficult to open polymerization, and may be applied as a solvent and ligand to iron-mediated ATRP (33).



Scheme 1: Coordination between ε-caprolactone and $FeCl_3$.

As mentioned above, lactones which have a seven-membered ring with high tension like ε-caprolactone can catalyzed by metal Lewis acid via ring open polymerization. For this reason, in this paper, we choose 'non-polymerizable' lactones with only five-membered ring like γ-valerolactone as solvent and ligand for Fe-mediated ATRP. Moreover, γ-butyrolactone, γ-caprolactone, γ-octanolactone which all have low tension five-membered ring also have been discussed as solvent and ligand to further confirm that bio-based γ-valerolactone was a high efficient solvent for this catalysis system.

2 Materials and methods

2.1 Materials

Methyl methacrylate (MMA, Aladdin Industrial Corporation (China)) (AR) was passed through a basic alumina column to remove the radical inhibitor in monomer before use. γ-valerolactone (GVL) (CP, Alfa Aesar), γ-butyrolactone (CP, Alfa Aesar), γ-caprolactone (CP, Alfa Aesar), γ-octanolactone (CP, Alfa Aesar), sodium ascorbate (Sinopharm Chemical Reagent Co. Ltd., SCRC, AsAc-Na), $FeBr_3$ (Alfa Aesar), and ethyl bromophenylacetate (98%, Alfa Aesar, EBPA) were used as received. All other solvents and reagents were used as received except as noted.

2.2 Typical procedure for the AGET ATRP of MMA in γ-valerolactone

In a typical ATRP experiment, $FeBr_3$ (21 mg, 0.07 mmol) was dissolved in 1.5 mL γ-valerolactone in a clean glass tube. Then, 28 mg AsAc-Na (0.14 mmol) and 3 mL MMA (28.2 mmol) were added, and the mixture was bubbled with nitrogen for 15 min and then sealed with a rubber septum. EBPA (25 μL, 0.14 mmol) was subsequently introduced via a syringe, then immersed in a thermostated oil bath at the designated temperature. After an expected time, the tube was opened to stop the reaction. The product PMMA was obtained after precipitation in large amounts of methanol and water mixture, filtered, and dried in vacuo to constant weight. The conversion of the monomer was determined gravimetrically.

2.3 Chain extension experiment

Chain extension was performed employing the above mentioned AGET ATRP technique in γ-valerolactone. In a

polymerization tube, 0.18 g (0.0475 mmol, M_n = 3800 g/mol) of PMMA macroinitiator was dissolved in 3 mL (28.2 mmol) MMA under stirring and nitrogen atmosphere. Next, 14 mg (0.0475 mmol) $FeBr_3$ and 18.7 mg (0.095 mmol) AsAc-Na were placed in 1.5 mL γ-valerolactone in another tube under stirring. Both solutions were then mixed, bubbled with nitrogen for 15 min, and sealed with a rubber septum. After an expected time, the tube was opened to stop the reaction. The chain-extended PMMA was obtained after precipitation in large amounts of methanol, filtered, and dried in vacuo to constant weight.

2.4 Characterization

Monomer conversion was determined by gravimetry and number average (M_n), and molecular weight distributions were determined by gel permeation chromatograph (GPC) on a PL GPC220 equipped with two PLgel 5-μm MIXED-C columns using a series of PMMA standards for calibrations. THF was used as the eluent at a flow rate of 1.0 mL/min at 40°C. The ^{1}H NMR spectrum of the obtained samples were recorded on a Bruker Avance III 400 MHz spectrometer using $CDCl_3$ as the solvent with TMS as an internal standard.

3 Result and discussion

3.1 Iron-mediated AGET ATRP in γ-valerolactone

In the previous experiment, we found that no polymer was formed with only γ-valerolactone, $FeBr_3$ deactivator and sodium ascorbate (i.e., in absence of MMA) after 72 h reaction time. The result indicated that γ-valerolactone cannot be polymerized under the AGET ATRP reaction condition. Subsbsequently, iron-mediated ATRP of MMA was conducted in γ-valerolactone and its derivatives, such as γ-butyrolactone, γ-caprolactone, γ-octanolactone (Table 1). The typical polymerization was performed at 75°C under the ratio [MMA]:[EBPA]:[$FeBr_3$]:[AsAc-Na]= 200:1:0.5:1 (EBPA:ethyl 2-bromo-2-phenylacetate, AsAc-Na: sodium ascorbate), $V_{MMA}/V_{solvent}$ = 3 mL/1.5 mL, in the absence of any external ligand. After 5 h reaction time, the monomer conversions had reached 70.1%, 66.1%, 59.8%, 61.2% in γ-valerolactone, γ-butyrolactone, γ-caprolactone, γ-octanolactone, respectively. All these catalytic system provided PMMA with low PDI values (M_w/M_n < 1.3) and controlled molecular weight. The structure of PMMA samples made using these solvent and γ-valerolactone itself were also characterized by ^{1}H NMR spectroscopy (supplementary material, Figures S1-S5). The calculated molecular weights were close to the values obtained by GPC analysis. The clear disappearance of GVL signals was further confirmed that the successful synthesis of PMMA polymer without any trace of ROP of the γ-valerolactone. The experiments results obviously indicated that the GVL and its derivatives could play a dual function both as green solvent and efficient ligand to mediate these iron catalysis system.

To expand the applicability of this catalytic system, a series of methacrylate monomer such as ethyl methacrylate, butyl methacrylate, benzyl methacrylate were also polymerized using $FeBr_3$/GVL as a catalyst. The results are shown in Table 2, ethyl methacrylate was well initiated and reached up to 60% conversion, yielded polymers with low dispersity (M_w/M_n = 1.24) and controlled molecular weight. The same polymerization behaviors were also observed in the butylmethacrylate, benzylmethacrylate were systems, indicating the well controllability.

3.2 Effect of concentration of $FeBr_3$ on AGET ATRP of MMA

It is desirable to conduct ATRP with small amounts of $FeBr_3$. However, sufficient catalysis dosage should be added to maintain a suitable control ability where using

Table 1: AGET ATRP of MMA in GVL and its derivatives.

Solvents	Conversion %	$M_{n,GPC}$	$M_{n,theo}$	PDI
γ-valerolactone	70.1	15900	14300	1.27
γ-butyrolactone	66.1	15200	13500	1.25
γ-caprolactone	59.8	13500	12300	1.25
γ-octanolactone	61.2	13800	12500	1.26

Experiment conditions: $[MMA]_0/[EBPA]_0/[FeBr_3]_0/[AsAc\text{-}Na]_0$ = 200/1/0.5/1 at 75°C, V_{MMA} = 3 mL, $V_{solvent}$ = 1.5 mL. Reaction time = 5 h.

Table 2: Polymerization for different monomers.

Monomor	Conversion %	$M_{n,GPC}$	$M_{n,theo}$	PDI
Methyl methacrylate	70.1	15900	14300	1.27
Ethyl methacrylate	60.1	16200	14000	1.24
Butyl methacrylate	50.6	16500	14600	1.25
Benzyl methacrylate	57.4	23800	20500	1.32

Experiment conditions: $[Monomer]_0/[EBPA]_0/[FeBr_3]_0/[AsAc\text{-}Na]_0$ = 200/1/0.5/1 at 75°C, $V_{solvent}$ = 1.5 mL. Reaction time = 5 h.

some polar solvent as solvent and ligand. Here, the polymerizations of MMA with different concentration of $FeBr_3$ catalyst (5000 ppm to 5 ppm) were investigated. The results (Table 3) indicated that the polymerizations were well controlled when $FeBr_3$ usage low to 50 ppm, which is reflected in the low molecular weight distribution and the designed molecular weight value. If the catalyst concentration is further lowered to 5 ppm, the polymerization reaction is out of control, giving PMMA a broad molecular weight distribution (PDI = 2.35). Anyway, $FeBr_3$/GVL here is a highly active catalyst system and can be successfully conducted at low catalysis concentration.

3.3 Effect of temperature on AGET ATRP of MMA

Figure 1a depicts the kinetic results of the AGET ATRP of MMA in GVL at different temperature (60°C, 75°C, 90°C respectively). As shown in Figure 1a, when polymerization performed at low temperature (60°C, 75°C), approximately first-order kinetics have been observed, these means a constant numbers of growth radicals during the whole reaction processes. Meantime, an induction period appeared in the cases of lower reaction temperatures (1h at 75°C, 2 h at 60°C). These may be caused by slow generation rate of $FeBr_2$ species in the initial stage of polymerization reaction, and needed enough time to build a dynamic equilibrium between the active species (iron(II)) and deactive species (iron(III)). Polymerization rate increased as the temperature increased from 75°C to 90°C, and the induction period was disappearance. The $\ln([M]_0/[M])$ plots versus reaction time is linear up until the reaction time was about 1 h (45.6% conversion) and a platform was observed. This means that the polymerizations is consistent with first order kinetics and indicates that the growth radical numbers was constant during the initial stage time of the reaction. At longer reaction period, the polymerizations slowed. The possible reason is that higher temperature can accelerate the reduction rates resulted in a higher concentration of iron(II) species and then increased the propagating radicals concentration, causing an increase proportion of termination reaction.

Table 3: AGET ATRP of MMA with different amounts of $FeBr_3$.

$[MMA]_0/[EBPA]_0/[FeBr_3]_0/[VC\text{-}Na]_0$	Fe (ppm)	Conversion %	$M_{n,GPC}$	$M_{n,theo}$	PDI
200:1:1:1	5000	63.9	11900	13000	1.15
200:1:0.5:1	2500	70.1	15900	14300	1.27
200:1:0.1:1	500	66.9	15200	13600	1.30
200:1:0.01:1	50	59.5	14600	12200	1.39
200:1:0.001:0.1	5	42.6	19800	8900	2.35

Experiment conditions: $[MMA]_0/[EBPA]_0/[FeBr_3]_0/[AsAc\text{-}Na]_0$ = 200/1/x/y at 75°C, V_{MMA} = 3 mL, $V_{solvent}$ = 1.5 mL. Reaction time = 5 h.

Figure 1b depicted the dependence of M_n and M_w/M_n versus the monomer conversion. It can be concluded that measured $M_{n,GPC}$ values of the obtained PMMA increased linearly with monomer conversion while maintaining relatively low PDI values (M_w/M_n < 1.35), however, these values were slightly higher than the calculated $M_{n,theo}$ values. Gel permeation chromatography (GPC) traces of polymers obtained at low reaction temperature shifted

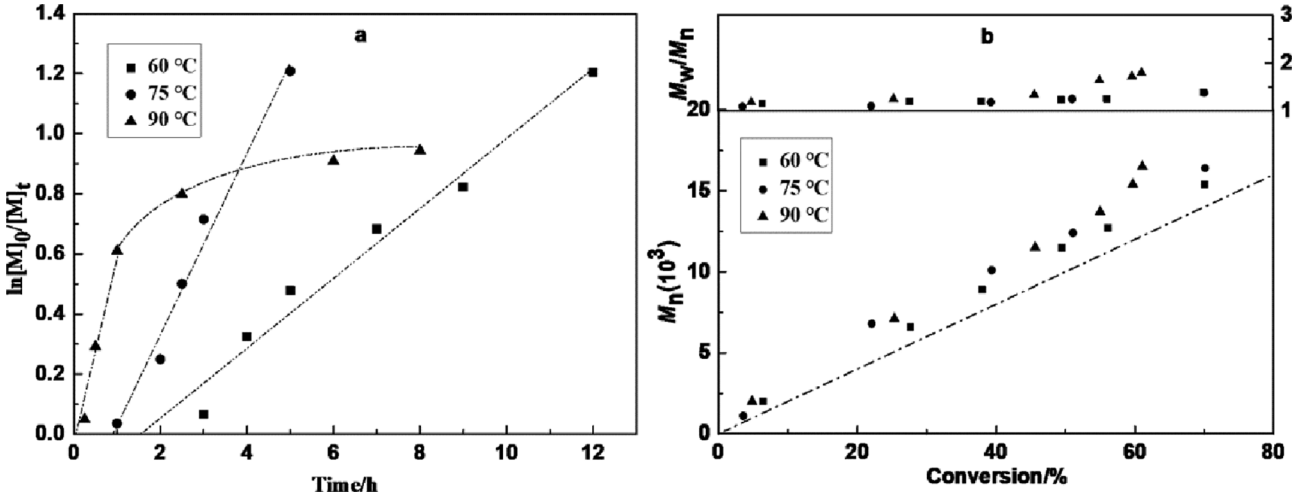


Figure 1: (a) Kinetic plots of $\ln([M]_0/[M])$ versus time and (b) $M_{n,GPC}$ and M_w/M_n versus conversion for the AGET ATRP of MMA in GVL at different polymerization temperatures without any external ligands. Experiment conditions: $[MMA]_0/[EBPA]_0/[FeBr_3]_0/[AsAc\text{-}Na]_0$ = 200/1/0.5/1, V_{MMA} = 3 mL, $V_{solvent}$ = 1.5 mL.

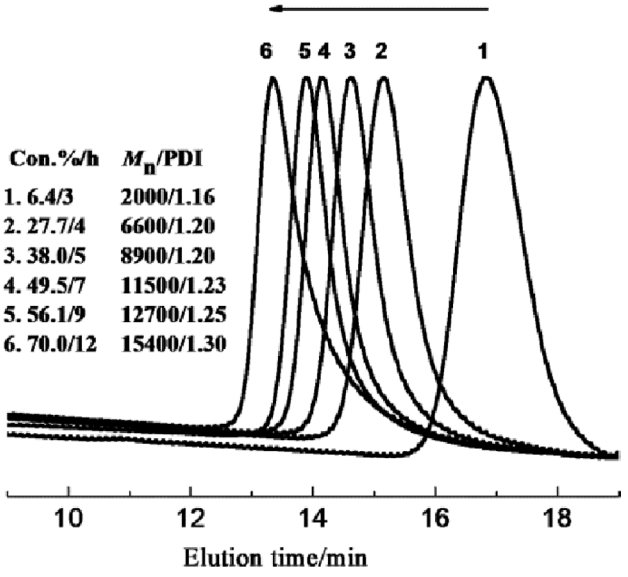


Figure 2: GPC traces for the polymerization of MMA in GVL at 60°C. Experiment conditions: $[MMA]_0/[EBPA]_0/[FeBr_3]_0/[AsAc\text{-}Na]_0$ = 200/1/0.5/1, V_{MMA} = 3 mL, $V_{solvent}$ = 1.5 mL.

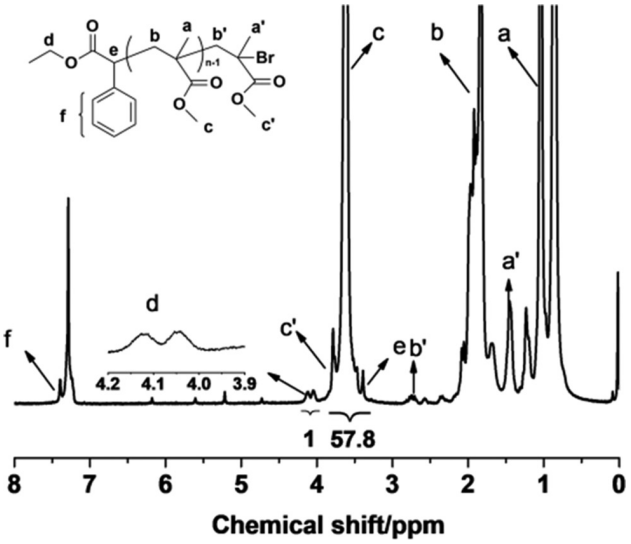


Figure 3: ^{1}H NMR spectrum of PMMA ($M_{n,GPC}$ = 3.8 ×10^3 g/mol, M_w/M_n = 1.21) with $CDCl_3$ as the solvent. Experiment conditions: $[MMA]_0/[EBPA]_0/[FeBr_3]_0/[AsAc\text{-}Na]_0$ = 200/1/0.5/1 at 60°C, V_{MMA} = 3 mL, $V_{solvent}$ = 1.5 mL. Reaction time = 3.5 h. Conversion = 17.1%.

clearly and completely to higher M_w with conversion (Figure 2). These results all strongly suggest that the polymerization of MMA was well-controlled in GVL solvent at low polymerization temperature.

3.4 Analysis of chain end and chain extension

^{1}H NMR spectrum of the PMMA ($M_{n,GPC}$ = 3800 g mol^{-1}, M_w/M_n = 1.21) was measured for analyzing chain end structure (Figure 3) and calculating $M_{n,NMR}$ valure.

The chemical shift at 3.8 ppm (c' in Figure 3) was corresponded to the methyl ester group at the chain end, as mentioned by Sawamoto et al. (34), the signal at 3.60 ppm (c in Figure 3) attributed to other methyl ester groups in main PMMA chains. The chemical shifts at 3.9–4.2 ppm (d in Figure 3), 3.4 ppm (e in Figure 3), and 7.1–7.4 ppm (f in Figure 3) belonged to the protons of methylene, methane, and phenyl derived from the initiator EBPA respectively. The molecular weight ($M_{n,NMR}$) of the PMMA can be calculated from the integrals in the ^{1}H NMR spectrum, according to equation:

$$M_{n,\mathrm{NMR}}\left(\mathrm{g/mol}\right) = \left(I_c/3\right)\times 100.12/\left(I_d/2\right) + 243.1 \qquad (1)$$

The calculated molecular weights ($M_{n,NMR}$ = 4100 g mol^{-1}) was in full agreement with the values obtained by GPC analysis ($M_{n,GPC}$ = 3800 g mol^{-1}), indicating that the PMMA obtained was end capped by the

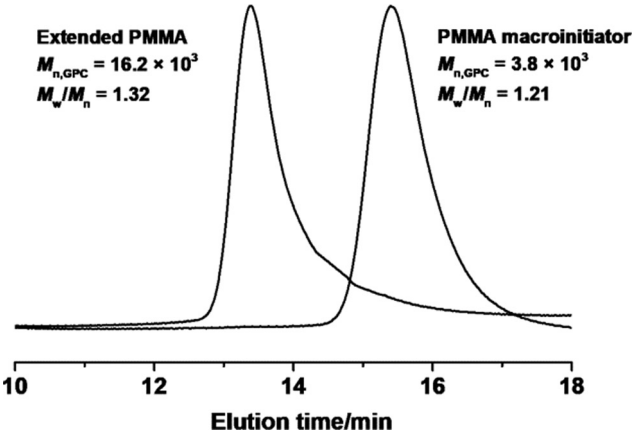


Figure 4: GPC traces of the PMMA before (right curve) and after the chain extension (left curve) experiment. Reaction conditions: $[MMA]_0/[PMMA\text{-}Br]_0/[FeBr_3]_0/[\,AsAc\text{-}Na]_0$ = 600/1/1/1, reaction temperature = 75°C.

EBPA moieties with high fidelity. Additionally, according to the mechanism of AGET ATRP, the obtained PMMA with Br end groups could be applied as macroinitiators to operate chain re-initiation polymerization. Therefore, the same PMMA sample ($M_{n,GPC}$ = 3800 g mol^{-1}, M_w/M_n = 1.21, reaction condition shown in Figure 3) was applied as a macroinitiator in chain extension experiments to further confirm the mechanism of the AGET ATRP.

As shown in Figure 4, the GPC curves shown a peak shift from the original polymers to the chain extended PMMA with $M_{n,GPC}$ = 16200 (M_w/M_n = 1.32). However, a slight increase in the value of Mw/Mn has been observed, which

may be attributed to a slight polymer loss of its activity in the polymer. The successful re-initiation experiment further confirms that the AGET ATRP of MMA in GVL solvent catalyzed by $FeBr_3$ was a high efficient ''living'' radical polymerization process.

4 Conclusions

In summary, we here reported that bio-based polar solvent GVL can be applied as an efficient reaction medium for the AGET ATRP. Well controlled polymers could be synthesized by using a nontoxic and inexpensive iron catalyst, and the use of external ligands become unnecessary. The GVL can play the dual function both of solvent and ligand. Well polymerization behavior also observed in other 'non-polymerizable' lactones like γ-butyrolactone, γ-caprolactone, γ-octanolactone. These results indicated that GVL is an excellent green solvent and we believe that its application in lager scale is very promising. Further investigations are ongoing to extend the scope of its use as universal solvent to other polymerization condition.

Acknowledgments: This work was supported by the Natural Science Foundation of the Anhui Higher Education Institutions of China (KJ2016A059), the Key Program in the Youth Elite Support Plan in Universities of Anhui Province (gxyqZD2018051) and Pre-Research Project for National Natural Science Foundation supported by Anhui Polytechnic University (KZ00417052).

References

1. Wang J.S., Matyjaszewski K., Controlled/"living" radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes. J. Am. Chem. Soc., 1995, 117(20), 5614-5615.
2. Percec V., Barboiu B., "Living" radical polymerization of styrene initiated by arenesulfonyl chlorides and CuI (bpy)nCl. Macromolecules, 1995, 28(23), 7970-7972.
3. Kato M., Kamigaito M., Sawamoto M., Higashimura T., Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris-(triphenylphosphine) ruthenium (II)/methylaluminum bis (2, 6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization. Macromolecules, 1995, 28(5), 1721-1723.
4. Matyjaszewski K., Atom transfer radical polymerization (ATRP): current status and future perspectives. Macromolecules, 2012, 45(10), 4015-4039.
5. Ribelli T.G., Fantin M., Daran J.C., Augustine K.F., Poli R., Matyjaszewski K., Synthesis and Characterization of the Most Active Copper ATRP Catalyst Based on Tris [(4-dimethylaminopyridyl) methyl] amine. J. Am. Chem. Soc., 2018, 140(4), 1525-1534.
6. Xue Z., He D., Xie X., Iron-catalyzed atom transfer radical polymerization. Polym. Chem., 2015, 6(10), 1660-1687.
7. Wang Y., Kwak Y., Matyjaszewski K., Enhanced activity of ATRP Fe catalysts with phosphines containing electron donating groups. Macromolecules, 2012, 45(15), 5911-5915.
8. Zhang L., Cheng Z., Shi S., Li Q., Zhu X., AGET ATRP of methyl methacrylate catalyzed by $FeCl_3$/iminodiacetic acid in the presence of air. Polymer, 2008, 49(13-14), 3054-3059.
9. Wang G., Zhu X., Cheng Z., Zhu J., Reverse atom transfer radical polymerization of methyl methacrylate with $FeCl_3$/pyromellitic acid. Eur. Polym. J., 2003, 39(11), 2161-2165.
10. Chen H., Yang L., Liang Y., Hao Z., Lu Z., ARGET ATRP of acrylonitrile catalyzed by $FeCl_3$/isophthalic acid in the presence of air. J. Polym. Sci. Pol. Chem., 2009, 47(12), 3202-3207.
11. Hou C., Qu R., Ji C., Wang C., Sun C., ATRP of acrylonitrile catalyzed by $FeCl_2$/succinic acid under microwave irradiation. J. Appl. Polym. Sci., 2006, 101(3), 1598-1601.
12. Silva T.B., Spulber M., Kocik M.K., Seidi F., Charan H., Rother M., et al., Hemoglobin and red blood cells catalyze atom transfer radical polymerization. Biomacromolecules, 2013, 14(8), 2703-2712.
13. Wang Y., Matyjaszewski K., ATRP of MMA in polar solvents catalyzed by $FeBr_2$ without additional ligand. Macromolecules, 2010, 43(9), 4003-4005.
14. Yang D., He D., Liao Y., Xue Z., Zhou X., Xie X., Iron-mediated AGET ATRP of methyl methacrylate in the presence of polar solvents as ligands. J. Polym. Sci. Pol. Chem., 2014, 52(7), 1020-1027.
15. He W., Zhang L., Miao J., Cheng Z., Zhu X., Facile iron-mediated AGET ATRP for water-soluble Poly (ethylene glycol) monomethyl ether methacrylate in water. Macromol. Rapid. Comm., 2012, 33(12), 1067-1073.
16. Cao J., Zhang L., Jiang X., Tian C., Zhao X., Ke Q., et al., Facile iron-mediated dispersant-free suspension polymerization of methyl methacrylate via reverse ATRP in water. Macromol. Rapid Comm., 2013, 34(22), 1747-1754.
17. Ding M., Jiang X., Peng J., Zhang L., Cheng Z., Zhu X., An atom transfer radical polymerization system: catalyzed by an iron catalyst in PEG-400. Green Chem., 2015, 17(1), 271-278.
18. Peng J., Ding M., Cheng Z., Zhang L., Zhu X., Iron-mediated AGET ATRP with crown ether as both ligand and solvent. RSC Adv., 2015, 5(127), 104733-104739.
19. Deng Z., Guo J., Qiu L., Zhou Y., Xia L., Yan F., Basic ionic liquids: a new type of ligand and catalyst for the AGET ATRP of methyl methacrylate. Polym. Chem., 2012, 3(9), 2436-2443.
20. Wu J., Zhang L., Cheng Z., Zhu X., Photocatalyzed iron-based ATRP of methyl methacrylate using 1, 3-dimethyl-2-imidazolidinone as both solvent and ligand. RSC Adv., 2017, 7(7), 3888-3893.
21. Gu Y., Jérôme F., Bio-based solvents: an emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry. Chem. Soc. Rev., 2013, 42(24), 9550-9570.
22. Sheldon R.A., Green and sustainable manufacture of chemicals from biomass: state of the art. Green Chem., 2014, 16(3), 950-963.

23. Horvath I.T., Solvents from nature. Green Chem., 2008, 10(10), 1024-1028.
24. Alonso D.M., Wettstein S.G., Dumesic J.A., Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. Green Chem., 2013, 15(3), 584-595.
25. Wettstein S.G., Alonso D.M., Chong Y., Dumesic J.A., Production of levulinic acid and gamma-valerolactone (GVL) from cellulose using GVL as a solvent in biphasic systems. Energ. Environ. Sci., 2012, 5(8), 8199-8203.
26. Aparicio S., Alcalde R., Characterization of two lactones in liquid phase: an experimental and computational approach. Phys. Chem. Chem. Phys., 2009, 11(30), 6455-6467.
27. Ismalaj E., Strappaveccia G., Ballerini E., Elisei F., Piermatti O., Gelman D., et al., γ-Valerolactone as a renewable dipolar aprotic solvent deriving from biomass degradation for the Hiyama reaction. ACS Sustainable Chem. Eng., 2014, 2(10), 2461-2464.
28. Strappaveccia G., Luciani L., Bartollini E., Marrocchi A., Pizzo F., Vaccaro L., γ-Valerolactone as an alternative biomass-derived medium for the Sonogashira reaction. Green Chem., 2015, 17(2), 1071-1076.
29. Abraham G.A., Gallardo A., Lozano A.E., San Roman J., ε-Caprolactone/$ZnCl_2$ complex formation: Characterization and ring-opening polymerization mechanism. J. Polym. Sci. Pol. Chem., 2000, 38(8), 1355-1365.
30. Kricheldorf H.R., Mang T., Jonté J.M., Polylactones. 1. Copolymerizations of glycolide and iε-caprolactone. Macromolecules, 1984, 17(10), 2173-2181.
31. Hege C.S., Schiller S.M., Non-toxic catalysts for ring-opening polymerizations of biodegradable polymers at room temperature for biohybrid materials. Green Chem., 2014, 16(3), 1410-1416.
32. Gowda R.R., Chakraborty D., Environmentally benign process for bulk ring opening polymerization of lactones using iron and ruthenium chloride catalysts. J. Mol. Catal. A Chem., 2009, 301(1-2), 84-92.
33. Houk K.N., Jabbari A., Hall H.K., Alemán C., Why δ-valerolactone polymerizes and γ-butyrolactone does not. J. Org. Chem., 2008, 73(7), 2674-2678.
34. Fujimura K., Ouchi M., Sawamoto M., Ferrocene cocatalysis for iron-catalyzed living radical polymerization: Active, robust, and sustainable system under concerted catalysis by two iron complexes. Macromolecules, 2015, 48(13), 4294-4300.