RSC Advances

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Amide group-containing polar solvents as ligands for iron-catalyzed atom transfer radical polymerization of methyl methacrylate

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

A series of amide group-containing polar solvents, formamide (Fo), *N*-methylformamide (MFo), *N*,*N*-dimethylformamide (DMF), acetamide (Ac), *N*-methylacetamide (MAc), *N*,*N*-dimethylacetamide (DMAc), urea, tetramethyl urea (TMU), 2-pyrrolidone (2-Py), *N*-methyl-2-pyrrolidone (NMP), and 5-methyl-2-pyrrolidone (MPy), were used as both solvents and ligands for iron(II)-catalyzed atom transfer radical polymerizations (ATRPs) of methyl methacrylate (MMA) with ethyl 2-bromo-2-phenylacetate (EBPA) as initiator. Most of the polymerizations showed well controlled characters, and the structures of polar solvents had great effect on their catalytic activity. In addition, the living features of the systems remained in the presence of limited amount of polar solvents. Some of the polar solvents (MFo, TMU, and 2-Py) were also employed for iron(III)-catalyzed activators generated by electron transfer (AGET) ATRPs of MMA, and the results were well as those of ATRPs.

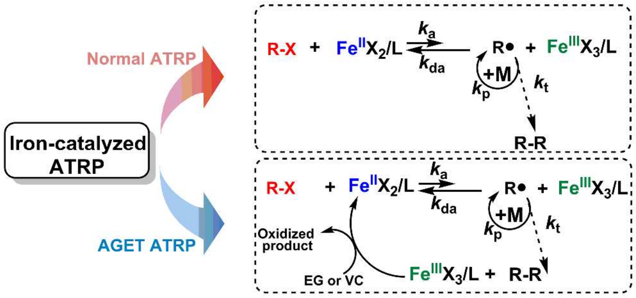
Introduction

Metal-catalyzed controlled radical polymerization (CRP), also known as atom transfer radical polymerization (ATRP) has been a versatile tool for synthesizing well-defined polymers[1-15] with controlled molecular weights (M_n) and narrow molecular weight distributions (MWDs, M_w/M_n) since it was first presented in 1995.[16-18] The catalyst used in ATRP is considered to be most essential and important issue for controlling a polymerization,[6,7,14,15] and a great deal of efforts were thus made to research the effect of various complexes on polymerizations, such as copper,[10,11,19-27] ruthenium,[2,6,28-35] and iron.[14,15,36-57]

On account of the environmental and sustainable aspects, the iron-based catalysts are one of the most promising catalysts for ATRP among those catalysts. Firstly, iron exists widely in the earth's crust as an extremely abundant metal, which can be obtained easily at a low price.Secondly, the iron metal has low toxicity and biocompatibility, which is significant for the application in industry.[2,6,7] What's more, the usually existed state iron(II) and iron(III) have empty orbitals to coordinate to many ligands, and form active complexes used in CRP in large scale. Compared with copper-based catalysts, iron complexes used in ATRP were generally less active. However, the development of environmentally benign and sustainable iron-based systems is becoming a trend of "green" chemistry or "green" reaction on the applications of organic chemistry,[58-61] polymer chemistry,[6,7,14,15,62] and electrochemistry.[63-68] Various ligands have been applied for complexing with iron salts to form iron-based catalysts,[14,15] such as the traditional phosphine (P), nitrogen (N), or P-N ligands. Notably, some organic acid- and salt-containing ligands were also developed for iron-catalyzed ATRP.[15] Although these catalysts are active for ATRP, the cost and separation of these iron complexes need to be paid more attentions for the potential practical application of ATRP technique.

Recently, $FeBr_2$-catalyzed ATRPs of methyl methacrylate (MMA) in polar solvents were reported by Matyjaszewski *et al.*[69,70] The resultant polymers had molecular weights agreed with the theoretical values, and the MWDs values remained low (M_w/M_n < 1.3) when conducted in *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), and acetonitrile (MeCN), but the polymers obtained in dimethyl sulfoxide (DMSO) had poor controllability (M_w/M_n > 2.0). The experiment results suggested that certain polar solvents act as ligands for iron species due to the coordination ability of solvents with $FeBr_2$. Actually, the polar solvents which have lone pairs of electrons (nitrogen, oxygen, or phosphorus atoms) can also coordinate with organoiron complexes, and their coordinating and catalytic properties have been studied in our previous study.[71, 72] To study the polar solvents' function for conducting CRP as ligand, Bulgakova *et al.*[73] and Xue *et al.*[74] reported the activators generated by electron transfer (AGET) ATRP of MMA using polar solvents (DMF, NMP, or MeCN) in the absence of additional ligands. Most of the polymerizations showed the typical characteristic of "living"/controlled radical polymerization. In addition, we also used alcohols, such as methanol, ethanol, ethylene glycol (EG), and glycerol as reducing agent for the iron-catalyzed AGET ATRP of MMA in the presence of polar solvents as ligands.[75] Very recently, Zhu and coworkers[76] also reported the iron-catalyzed AGET ATRP of

MMA using polyethylene glycol 400 (PEG-400) as both solvent and ligand.



Scheme 1 Mechanism of iron-catalyzed ATRP using amide group-containing polar solvents as ligands.

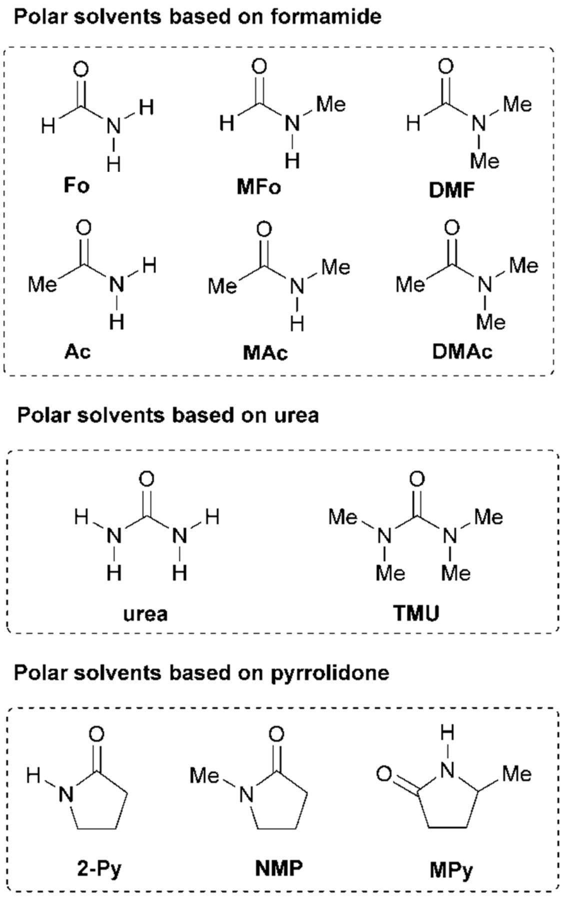
The polymerizations were well-controlled even when the concentration of PEG-400 was reduced to a catalytic amount. This system is much more environmental when compared with most traditional iron-catalyzed ATRP systems due to the “green” nature of PEG-400. Compared to the conventional iron-based catalytic systems, it is particularly significant that the polymerizations were found to be more environmentally friendly ATRP in the presence of polar solvents as ligands.

In consideration of polar solvents’ role acting as ligands in iron-catalyzed ATRP mentioned above, they have the electron donor groups, such as oxygen atom in DMF or NMP, and all of them are able to coordinate to iron(II) ([Ar]3d^{6}4S^0) or iron(III) ([Ar]3d^{5}4S^0) which have the empty orbitals. We expected that the coordination ability of polar solvents to iron salts and their universality enable them to apply in iron-catalyzed ATRP, and to be appropriate substitutes for traditional P ligands or N ligands. In this article, combining the various advantages of iron catalyst and polar solvent, the iron-catalyzed ATRP of MMA (Scheme 1) was investigated using polar solvents having amide groups as ligands. These amide group-containing ligands are classified to polar solvents based on formamide, polar solvents based on urea, and polar solvents based on pyrrolidone by their structures (see Scheme 2). They all have coordination ability with iron salt more or less based their structure. The majority of them are the first time used for ATRP. As expected, some of them showed well controllability on molecular weights and MWDs. In addition, the different structures of the polar solvents had great effect on their catalytic activity. It is significant for the optimization of polar solvents on the ATRP application. In order to ease the separation step of solvents from polymerization system for the purpose of environmental protection, we also reduced the concentration of polar solvents to catalyst amounts, and it was still feasible for ATRP. These amide group-containing polar solvents were also employed in the iron(III)-catalyzed AGET ATRP (see Scheme 1), and most of the systems showed controlled features.

Experimental

Materials

Methyl methacrylate (MMA, 98+%, Sinpharm) was passed through a column filled with neutral alumina, dried over calcium hydride (CaH$_2$), distilled under reduced pressure, and stored in a freezer under argon. Formamide (Fo, 99+%, Sinpharm), *N*,*N*-dimethylformamide (DMF, 99.5+%, Sinpharm), *N*-methylacetamide (MAc, 99+%, Sinpharm), *N*,*N*-dimethylacetamide (DMAc, 99+%, Sinpharm), and *N*-methyl-2-pyrrolidone (NMP, 95+%, Sinpharm) were dried over CaH$_2$ and distilled under reduced pressure. *N*-methylformamide (MFo, 99+%, Acros), acetamide (Ac, 98+%, Sinpharm), 2-pyrrolidone (2-Py, 99+%, Xiya), 5-methyl-2-pyrrolidone (MPy, 98+%, TCI), urea (99+%, Sinpharm), tetramethyl urea (TMU, 98+%, TCI), ethyl 2-bromo-2-phenylacetate (EBPA, 95%, Alfa Aesar), iron(II) bromide (FeBr$_2$, 98+%, Alfa Aesar), iron(III) bromide (FeBr$_3$, 98+%, Alfa Aesar), vitamin C (VC, 99+%, Sinpharm), sodium carbonate (Na$_2$CO$_3$, Sinpharm), and ethylene glycol (EG, 99+%, Sinpharm) were used without further purification.



Scheme 2 Structures of amide group-containing polar solvents.

Polymerization Procedures

A typical polymerization procedure with the molar ratio of $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[solvent]_0/[Na_2CO_3]_0 = 200/1/1/20/2$ is as follows. A schlenk flask (25 mL) was charged with FeBr$_2$ (61 mg, 0.28 mmol) and Na$_2$CO$_3$ (60 mg, 0.57 mmol). The flask was sealed with a rubber septum and was cycled three times between vacuum and argon (Ar) to remove oxygen. Degassed polar solvents, MMA (6 mL, 56.3 mmol) were then added to the flask through degassed syringes. The solution was stirred for 30 min at room temperature. After three additional freeze-pump-thaw cycles, the initiator, EBPA (49.5 μL, 28.2 mmol) was added, and the flask was immersed in a thermostated oil bath at

60 °C. At timed intervals, samples were withdrawn from the flask with a degassed syringe. The monomer conversion was determined gravimetrically after removal of the unconverted monomer and solvent under reduced pressure, and the resulting residue was diluted with tetrahydrofuran (THF) and then filtered through a column filled with neutral aluminum oxide to remove the iron catalyst. The poly(methyl methacrylate) (PMMA) solution was then precipitated using an excess of *n*-hexane, and these polymers were dried under vacuum overnight at 80 °C for gel permeation chromatography (GPC) characterization. The same experimental procedures were carried out for the iron(III)-catalyzed AGET ATRP.

Table 1 $FeBr_2$-catalyzed ATRP of MMA using polar solvents based on formamide as ligands[a]

Entry	Solvent	$[M]_0/[solvent]_0$[b]	Base	Time (h)	Conv. (%)	$M_{n,th}$[c] (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	Ac (solid)	4:1		30	0	NA	NA	NA
2	Ac (solid)	100:1	Na_2CO_3	17	70	14250	23600	1.87
3	MAc	2:1 (v/v)		68	0	NA	NA	NA
4	MAc	2:1 (v/v)	Na_2CO_3	29	34	7050	6900	2.04
5	MAc	10:1	Na_2CO_3	1.5	56	11500	12600	1.28
6	DMAc	2:1 (v/v)		25	0	NA	NA	NA
7	DMAc	2:1 (v/v)	Na_2CO_3	3.5	57	11600	13600	1.23
8	DMAc	10:1	Na_2CO_3	1.5	42	8700	9360	1.31
9	Fo	2:1 (v/v)		30	0	NA	NA	NA
10	Fo	10:1	Na_2CO_3	1.3	25	5250	120000	3.5
11	MFo	10:1		43	0	NA	NA	NA
12	MFo	10:1	Na_2CO_3	3.2	50	10250	14200	1.43
13	DMF	2:1 (v/v)		7	15	3250	2300	1.27
14	DMF	10:1	Na_2CO_3	25	40	8250	10800	1.56

[a] $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[Na_2CO_3]_0$ = 200:1:1:2 or 0, 60 °C; [b] the ratio of $[M]_0$ to $[solvent]_0$ is molar ratio except for marking with "(v/v)" which stands for volume ratio; [c] $M_{n,th} = ([MMA]_0/[Initiator]_0) \times M_{MMA} \times conversion + M_{EBPA}$, M_{MMA} and M_{EBPA} represent the molecular weight of MMA and EBPA, respectively.

Chain extension experiment

A predetermined quantity of PMMA macroinitiator (PMMA-Br) obtained by ATRP of MMA with a molar ratio of $[MMA]_0/[PMMA]_0/[FeBr_2]_0/[TMU]_0/[Na_2CO_3]_0$ = 500/1/1/50/5 was added to a schlenk flask, and then a predetermined quantity of MMA, $FeBr_2$, TMU, and Na_2CO_3 was added. The rest of the procedure was the same as that described above. The chain extension polymerization was carried out under stirring at 60 °C.

Measurements

^1H NMR spectrum was performed by a Bruker AV400 NMR spectrometer with deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the standard. The number-average molecular weight ($M_{n,GPC}$) and M_w/M_n of the polymers were determined using Agilent 1100 gel permeation chromatograph (GPC) using PLgel 79911GP-104 (7.5 × 300 mm, 10 µm beads' size) column. THF was used as the eluent at a flow rate of 1 mL/min at 35 °C. Linear polystyrene standards were used for calibration.

Results and discussion

Some previous works[74-76] had been done to demonstrate that EBPA was the optimal initiator for the iron catalyzed ATRP of MMA because of both the phenyl and ester groups in EBPA contributing to the stabilization of the generated radicals. Therefore, all polymerizations were conducted with EBPA as the initiator in the following studies. The general amide group-containing polar solvents were chosen for our study as much as possible, and we classified them to polar solvents based on formamide, polar solvents based on urea, and polar solvents based on pyrrolidone by their structures.

Polar solvents based on formamide as ligands

As mentioned in the section of Introduction, polar solvents (NMP, DMF, MeCN, and DMSO) can coordinate to iron salt, and be used as ligands for ATRP. As far as we know, the oxygen atom in the amide group can act as electron donor to coordinate to iron ion.[77, 78] To probe the role of amide group as a ligand, various of polar solvents based on formamide having linear structure (Fo, MFo, DMF, Ac, MAc, and DMAc) were used as ligands for the ATRP of MMA with a molar ratio of $[MMA]_0/[EBPA]_0/[FeBr_2]_0$ = 200:1:1 and $[MMA]_0/[polar\ solvent]_0$ = 2/1 (v/v) without additional ligand at 60 °C. As shown in the Table 1, no reaction occurred in the absence of Na_2CO_3 for almost all of the solvents (entries 1, 3, 6, 9, and 11) except for the DMF which was consistent with the work reported (entry 13).[69] Zhu's works[48, 79-81] suggested that the catalyst amounts base can signally accelerate the iron-catalyzed ATRP, and the controllability of the polymerizations could maintain as well. They considered that the increased value of pH can reduce the redox potential ($E_{1/2}$) of the polymerization. The lower redox potential induced a faster reversible cleavage (activation) of a carbon-halogen terminal and, in turn, generated more radical species, which resulted in the enhancement of rate and controllability of the polymerization. Moreover, the base (Na_2CO_3 or NaOH) was also applied for iron(III)-catalyzed AGET ATRP of MMA with FeX_3 (X = Br, or Cl)/polar solvent catalytic systems using different alcohols as reducing agents in our previous work,[75] and the results revealed the exciting rate-enhanced effect of base on polymerization. Likewise, Bai *et al.*[82] reported the Cu-catalyzed AGET ATRP using alcohol as a reducing agent. Cu(II) was changed to Cu(I), and the alcohol was oxidized to an aldehyde or ketone in the presence of base. The polar solvents studied in this article have lower coordination ability compared with the traditional P, or N ligands. The reactions may be carried out very slowly. Even no polymerization conversion was obtained after a long enough time in the absence of base (entries 1, 3, 6, 9, and 11 in Table 1). According to the above investigation, the base was added to our systems. As expected, most of them showed well controllability and relatively fast polymerization rate when the ratio of Na_2CO_3 to $FeBr_2$ was 2. What interested us was that the resulting PMMA obtained from DMAc system (entry 7) had number-average molecular weights (M_n) consistent with the predicted values and low MWDs value (M_w/M_n = 1.23). In the case of MAc system, the M_n matched he theoretical value well (entry 4). However, the PDI was a little bit high. When the polymerization was carried out in Ac or Fo (entries 2 and 10), the molecular weights were great bigger than the theoretical values and had high polydispersities (PDIs). The possible reason was the poor dissolubility of Ac or Fo in MMA.

Table 2 $FeBr_2$-catalyzed ATRP of MMA using polar solvents based on urea as ligands[a]

Entry	Solvent	$[M]_0/[solvent]_0$ [b]	Base	Time (h)	Conv. (%)	$M_{n,th}$ [c] (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	urea (solid)	4:1		30	0	NA	NA	NA
2	urea (solid)	100:1	Na_2CO_3	5	35.2	7290	92100	2.7
3	TMU	2:1 (v/v)		56	11	2400	NA[b]	NA[b]
4	TMU	2:1 (v/v)	Na_2CO_3	2	64	13000	12000	1.24
5	TMU	2:1 (v/v)	Na_2CO_3	3	78	16000	14000	1.24
6	TMU	10:1	Na_2CO_3	3	41	8450	7400	1.27

[a] $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[Na_2CO_3]_0$ = 200:1:1:2 or 0, 60 °C; [b] the molecular weight was too small and out of the range of the instrument.

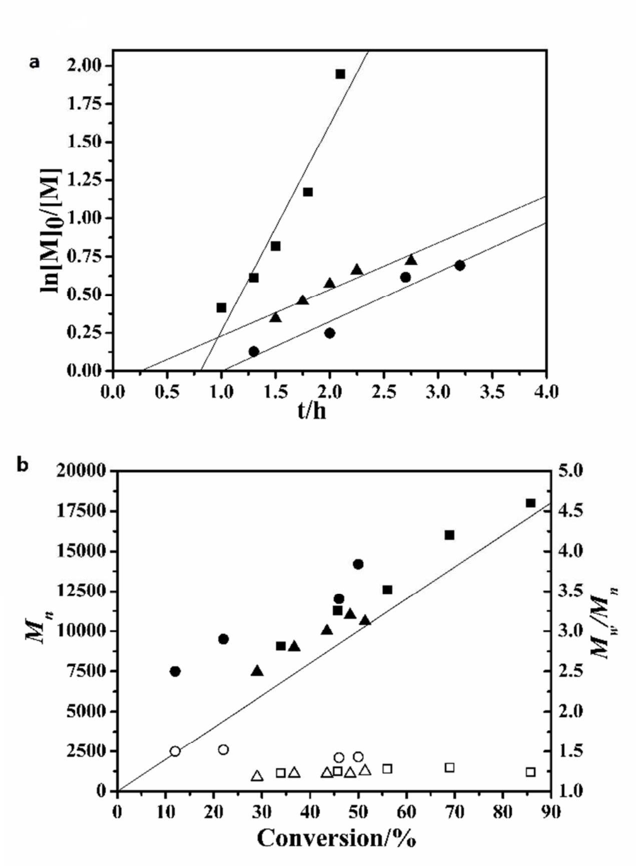


Fig. 1 (a) Kinetic plots of $\ln([M]_0/[M])$ verses time and (b) plots of M_n (filled symbols) and M_w/M_n (open symbols) values verses conversion for $FeBr_2$-catalyzed ATRP of MMA using polar solvents based formamide as ligands. $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[solvent]_0/[Na_2CO_3]_0$ = 200:1:1:20:2, 60 °C. ■ = MAc; ▲= DMAc; ● = MFo.

In addition, when the amount of solvents was reduced to the molar ratio of $[MMA]_0/[solvent]_0$ = 10:1, almost all of the reactions still expressed controlled characters (entries 5, 8, 12, and 14). It is very significant for the application of ATRP in environmentally friendly industry. Kinetic plots for the ATRP of MMA with a molar ratio of $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[solvent]_0/[Na_2CO_3]_0$ = 200/1/1/20/2 at 60 °C are depicted in Fig. 1a. Polymerizations proceeded with approximately first-order kinetics in all cases, indicating a constant concentration of growing radicals during polymerizations. The dependence of M_n and M_w/M_n on the monomer conversion within different polar solvents based on formamide is shown in Fig. 1b. The molecular weights of all PMMA increased linearly with the conversion. It is noted that all the experimental molecular weights were slightly higher than the corresponding theoretical ones, which may be attributed to the low initiator efficiency respectively. Other explanations need further study. The MWDs values of DMAc and MAc were relatively low (M_w/M_n = 1.18-1.28), but a little higher for MFA (M_w/M_n = 1.42-1.52). Even so, they still could be seen as "living"/controlled radical polymerization.

Polar solvents based on urea as ligands

Urea is generally used as nitrogenous fertilizer in agriculture production and exists extensively in nature. It has the amide group as same as polar solvents based on formamide discussed above. Moreover, urea has one more amidogen than the latter. This may endow the urea stronger coordinate ability to form catalyst complexes with iron salts. However, there was no reaction when the urea was added into the system with the ratio of $[MMA]_0/[urea]_0$ = 4/1 as shown in the entry 1 of Table 2. In view of the results of polar solvents based on formamide, it took a long time for the urea to coordinate with $FeBr_2$ to express activity. Thus, Na_2CO_3 was used to accelerate the polymerization. It can be seen from the Table 2 that the resulting polymer had a high experimental molecular weight and polydispersitiy (entry 2). The result indicated that the base's rate-enhanced effect had taken. Another reason for the poor controllability may be urea's weak solubility in MMA. The viscosity of the polymerization system increased along with the reaction, and lots of catalyst complex were formed at the bottom of the flask, resulting in nonuniformity of the system.

The results of TMU systems were quite different from those of urea (entries 3-6 in Table 2). When the initial volume ratio of MMA to TMU was 2, the reaction can be carried out in the absence of the base (entry 3). But the polymerization reached a low conversion of 11% in 56 h, that was extremely low comparing with the entries 4 and 5 ($[catalyst]_0/[Na_2CO_3]_0 = 1/2$). It can be seen that the polymerization reached a very high conversion of 64% with well values of molecular weight and MWD ($M_w/M_n = 1.24$) of the resultant polymers just in 2 h when using Na_2CO_3.The catalyst amount of base not only improved the rate of the polymerization, but also kept the "living" feature of the system (M_w/M_n = 1.24-1.27). Some differences can be seen when comparing the results of TMU with ones of polar solvents based on formamide as shown in Table 1. The polymerizations had higher rate and better controllability using the TMU as ligand especially with the ratio of $[MMA]_0/[solvent]_0$ = 2/1 (v/v). For example, when using MAc or DMAc as ligands, the conversions of monomers came to 34% and 57% in 29 h and 3.5 h respectively. But for TMU, the conversion reached 78% in just 3 h. Seeing from the structure of these solvents, the four methyl groups on TMU could enhance its coordination ability because that methyl group is a better electron donor (electron donating substituent) than hydrogen group, and can improve the electron cloud density of nitrogen or oxygen.[83] Thus, the $FeBr_2$/TMU complex showed better catalytic activity. The polymerization was still well-controlled when the molar ratio of the $[TMU]_0$ to $[MMA]_0$ reduced to 1:10, although the polymerization rate decreased a little (entry 6). The linear increase observed for the TMU in Fig. 2a indicated that the concentration of growing radicals remained constant during the polymerization process. A relatively long induction period existed. The evolution of M_n and MWDs values on the monomer conversion was shown in Fig. 2b. The molecular weights of all PMMA increased linearly with the conversion, and had little deviation compared with the theoretical molecular weights. In addition, the values of M_w/M_n remained relatively small (< 1.3). All of the conclusion suggested that TMU was suited to carry on the ATRP of MMA acting as ligand to from active complex with $FeBr_2$.

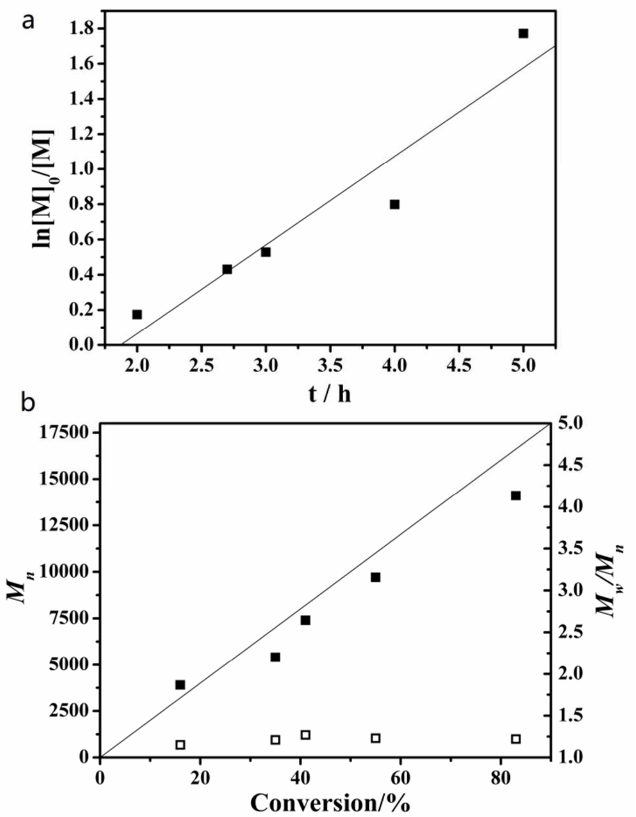


Fig. 2 (a) Kinetic plots of $\ln([M]_0/[M])$ verses time and (b) plots of M_n (filled symbols) and M_w/M_n (open symbols) values verses conversion for $FeBr_2$/TMU-catalyzed ATRP of MMA. $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[TMU]_0/[Na_2CO_3]_0$ = 200:1:1:20:2, 60 °C.

Polar solvents based on pyrrolidone as ligands

NMP had been reported to coordinate well to iron salt generally, and the generated catalyst complex expressed dramatic living characteristic when used in CRP both of ATRP[69] and AGET ATRP.[74, 75] To identify the activity of the ATRP of MMA

Table 3 $FeBr_2$-catalyzed ATRP of MMA using polar solvents based on pyrrolidone as ligands[a]

Entry	Solvent	$[M]_0/[solvent]_0$	Base	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	2-Py	2:1 (v/v)		27	0	NA	NA	NA
2	2-Py	2:1 (v/v)	Na_2CO_3	1.5	48	9800	19500	1.38
3	2-Py	2:1 (v/v)	Na_2CO_3	2	74	15000	20900	1.35
4	2-Py	10:1	Na_2CO_3	4.4	17	3650	4650	2.23
5	MPy	2:1 (v/v)		6	19	4050	7200	1.33
6	MPy	2:1 (v/v)		27	67	13650	16800	1.54
7	MPy	2:1 (v/v)	Na_2CO_3	2.3	54	11000	10500	1.93
8	MPy	10:1	Na_2CO_3	2	40	8250	10700	1.8
9	NMP	2:1 (v/v)		7	33	6850	4300	1.39
10	NMP	2:1 (v/v)		23	45	9250	5700	1.42
11	NMP	10:1	Na_2CO_3	3	33	6850	6700	1.21
12	NMP	10:1	Na_2CO_3	6.7	68	13850	12300	1.22

[a] $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[Na_2CO_3]_0$ = 200:1:1:2 or 0, 60 °C.

catalyzed by $FeBr_2$/NMP, some experiments were run at the same condition as above. From the entries 9 and 10 in Table 3, it can be seen that the conversion was up to 33% in 7 h with the ratio of $[MMA]_0/[NMP]_0 = 2:1$ (v/v). What's more, the PMMA obtained were well behaved ($M_w/M_n = 1.39$). The result confirmed the excellent activity of NMP in ATRP of MMA as a ligand especially compared with other amide group-containing polar solvents mentioned in this article. Some other polar solvents carried out polymerizations in the absence of base, such as DMF, TMU, and MPy, and they had conversions of monomers getting to 15%, 11% and 19% in 7 h, 56 h, and 6 h respectively, that were relatively slower compared with that using NMP as ligand. In order to further probe the ability for NMP as a ligand in ATRP. The same experiments were conducted in the presence of catalyst amount of NMP ($[MMA]_0/[NMP]_0 = 10/1$), and the base was also added into the reaction to compare with other systems. From Table 3, it can be seen that the resulting polymer reached a conversion of 33% just in 3 h, and had a value of $M_{n,GPC}$ as pretty similar as $M_{n,th}$, and a narrow MWD ($M_w/M_n = 1.21$) (entry 11). Thereafter, the conversion came to 68% in 6.7 h with well controlled result (entry 12).

2-Py or MPy contains an amide group (see Scheme 2), and has ringed structure as similar as NMP. They were chosen to test the activity as ligands as well. Seen from the entries 1-8 in Table 3, when the polymerization was carried out with the ratio of $[MMA]_0/[\text{polar solvent}]_0 = 2:1$ (v/v) in the absence of Na_2CO_3, there was no polymerization in 27 h for 2-Py, but for MPy, the conversion was up to 19% in 6 h. The possible explanation for this is that the methyl group at MPy increases the ability of amide group to coordinate to iron salt, and makes it express higher "living" feature. The explanation is also applied to NMP. The polymerizations using 2-Py showed poor controllability presumably caused by its bad dissolution in MMA. In the absence of base, the resulting polymers using MPy showed some higher $M_{n,GPC}$ values than the theoretical molecular weights that may come from the low initiator efficiency. When the base was added into the polymerizations, the experimental molecular weights behaved well, but the values of M_w/M_n were a little higher. A suitable amount of base needs to be chosen for the ATRP of MMA using MPy as ligand.

The obtained results above demonstrated the potential of amide group-containing polar solvents used for Fe(II)-catalyzed ATRP of MMA. The addition of base was essential for most of the systems. The base's role had been stated above. The selected polar solvents act as ligands that increase the dissolubility of $FeBr_2$ in MMA, and also adjust the catalytic activity, which resulting in the well living feature of the polymerization. It's particular interesting that the polymerization can be carried out in the absence of base when using DMF, TMU, NMP and MPy. As mentioned above, all of them have the electron donor (methyl group) near or on the amide group, and it can increase the activity of the solvents by enhancing the solvents' coordination to iron salts. Especially for TMU, the four methyl groups around the atom oxygen greatly heighten the activity. As a result, the polymerizations have higher rate and well-controlled resultant polymers in the presence of TMU. This conclusion has potential application on the choice of suitable polar solvents for CRP. Besides, the configurations of the different solvents molecular may also influence their activity, and that needs further investigation.

Iron(III)-catalyzed AGET ATRP

AGET ATRP is easier to operate than normal ATRP on account of using high oxidation state catalyst, and has the similar "living" characters as ATRP when suitable reducing agents (RAs) are added. The iron(III)-catalyst AGET ATRP of MMA using difference reducing agents in the presence of some polar solvents (DMF, NMP, and MeCN) has been reported in my previous works,[74, 75] and most of them showed well-controlled features. To identify the activity of other polar solvents based on amide group in this article, three solvents (MFo, TMU, and 2-Py) were selected for the $FeBr_3$-catalyzed AGET ATRP of MMA using ethylene glycol (EG) or vitamin C (VC) as reducing agent. It can be seen from the Table 4 that all of the polymerizations were conducted successfully with additional limited amount of base. The polymerization rate with VC was faster than that with EG obviously, because of the stronger reducing ability for VC compared with EG. Some of the resulting polymers showed well-controlled features such as the entries 2, 3, and 4 with the MWDs values to be 1.38, 1.23, and 1.37, respectively, and little deviation of $M_{n,GPC}$ with respect to $M_{n,th}$ at the same time. As for other instances shown in Table 4 (entries 1, 5, and 6), the difference between the molecular weights of experiment and theory was a

Table 4 $FeBr_3$-catalyzed AGET ATRP of MMA using amide group-containing polar solvents as ligands[a]

Entry	Solvent	RA[b]	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	MFo	EG	6.1	80	16300	27580	1.59
2	MFo	VC	2.7	70	14250	16500	1.38
3	TMU	VC	15	53	10850	8600	1.23
4	2-Py	EG	8.5	17	3650	3550	1.37
5	2-Py	EG	12	77	15650	21850	1.46
6	2-Py	VC	1.1	62	12650	24250	1.55

[a] $[MMA]_0/[EBPA]_0/[FeBr_3]_0/[Na_2CO_3]_0 = 200:1:1:2$, 60 °C; [b] the ratio of RA to catalyst is 3:1 for EG, and 1:1 for VC.

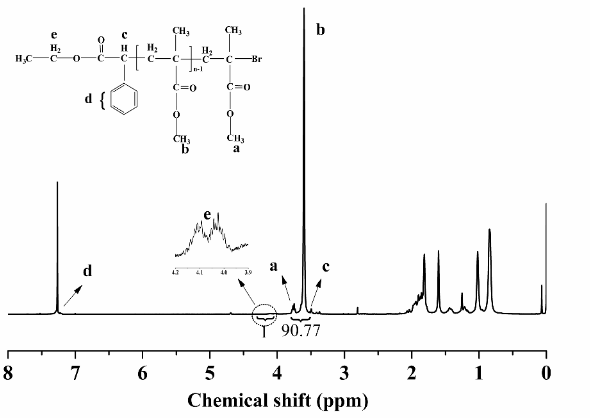


Fig. 3 ^{1}H NMR spectrum of PMMA ($M_{n,GPC}$ = 7200, M_w/M_n = 1.45) with $CDCl_3$ as the solvent. $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[TMU]_0/[Na_2CO_3]_0$ = 200:1:1:20:2, 60 °C.

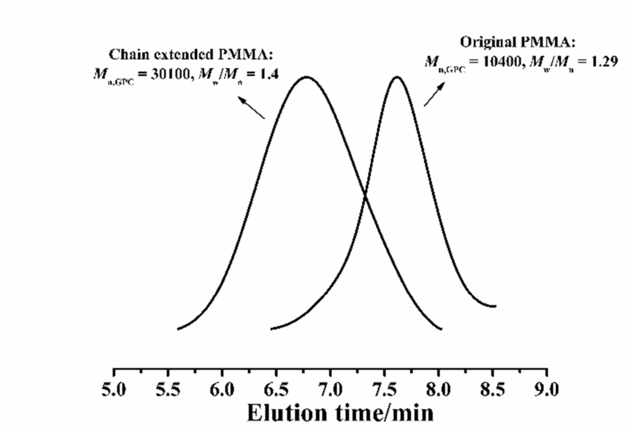


Fig. 4 GPC curves for chain extension experiment.

little big. All of them had the phenomenon that some precipitates formed during these reactions, which caused the nonuniformity of the systems. In spite of this, the chosen amide group-containing polar solvents have the potential for conducting iron(III)-catalyzed AGET ATRP. The results here further express the universality of the selected polar solvents used for CRP.

Chain end analysis and chain extension experiment

The chain end of the PMMA prepared from the $FeBr_2$-catalyzed ATRP in presence of limited amount of TMU was analyzed by ^{1}H NMR spectroscopy, as shown in Fig. 3. The signal of a (3.77 ppm) was attributed to the methyl ester group at the chain end, and the signal of b (3.60 ppm) came from the other methyl ester groups in PMMA. The signals of c (3.38 ppm), d (7.17-7.37 ppm) and e (3.97-4.17 ppm) corresponded to the protons derived from EBPA with methine, phenyl, and methylene. The molecular weight ($M_{n,NMR}$) can be determined by the integrals in the ^{1}H NMR spectrum based on the equation (1):

$$M_{n,NMR}\ (\text{g/mol}) = (I_{a,b}/3) \times 100.12/(I_e/2) + 243.1 \quad (1)$$

The calculated molecular weight of PMMA from the ^{1}H NMR spectrum ($M_{n,NMR}$ = 6300), which is in agreement with GPC result ($M_{n,GPC}$ = 7200). The result suggested that the end of the obtained PMMA was end-capped by the EBPA moieties.

In order to futher confirm the mechanism of ATRP carried out using polar solvents as ligand, the chain extension experiment was done using the resuliting polymers as macroinitiator. The macroinitiator (PMMA-Br, $M_{n,GPC}$ = 10400, M_w/M_n = 1.29) came from the ATRP with a ratio of $[MMA]_0/[EBPA]_0/[FeBr_2]_0/[NMP]_0/[Na_2CO_3]_0$ = 200:1:1:20:2 at 60 °C with a conversion of 61%, and the chain extended polymer (PMMA-*b*-PMMA-Br) was obtained from the ATRP with a ratio of $[MMA]_0/[PMMA\text{-}Br]_0/[FeBr_2]_0/[NMP]_0/[Na_2CO_3]_0$ = 500:1:1:50:5 at 60 °C in 1 h. As shown in Fig. 4, a peak shift can be seen from the macroinitiator to the chain extended PMMA with $M_{n,GPC}$ = 30100 and M_w/M_n = 1.40. The increased value of M_w/M_n may owe to a little polymer out of activity in the macroinitiator. The successful chain extension reaction confirms the controlled features of the polymerizations.

Conclusions

In summary, the iron(II)-catalyzed ATRPs of MMA were carried out in a series of amide group-containing polar solvents without additional ligand. Most of the systems showed characters of "living"/controlled radical polymerization in the presence of catalyzed amount of base. The results here confirmed the coordination potential of polar solvents with amide group to iron salt, and the formed catalyst complexes showed well activity. The structures of the polar solvents had great effect on their coordination ability, which is very important for the activity of the polymerization. The addintion of electron donor (methyl group) in the structures can improve the solvents' activity significantly, that can be seen from the results of DMF, TMU, MPy and NMP. It is particularly interesting that the polymerizations kept controlled, even when the polar solvents were reduced to a limited amount (the initial molar ratio of catalyst to solvent is 1:20), which is of great significance for green application. Some polar solvents were also employed for iron(III)-catalyzed AGET ATRP of MMA, as expected, they behaved well as similar as for ATRP. More details about the mechanism of the coordination between polar solvents and metal salt, and the work expanding the scope of polar solvents applied for CRP are still needed to do in future studies.

Acknowledgements

We are grateful to the National Natural Science Foundation of China (21304036, 51210004, 51433002, and 51473056), and the Specialized Research Fund for the Doctoral Program of Higher Education (20120142120024) for support of this work.

Notes and references

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