

# Pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine-Schiff base ligands as new catalyst systems mediated atom transfer radical polymerization of (meth)acrylate monomers

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**Abstract** 2,6-bis[1-(*cis*)-myrtanylimino]ethyl]pyridineiron (II) chloride (**2**) and 2,6-bis[1-(1-phenylimino)ethyl]pyridineiron(II) chloride (**3**) were investigated as novel complexes for iron-mediated atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA) and *tert*-butyl acrylate (*t*BA) using toluene as the solvent, and ethyl 2-bromoisobutyrate as the initiator. A catalyst/initiator molar ratio as low as 0.1/1 was used in order to reduce catalyst contamination to the polymers. Both complexes produced PMMA and *Pt*BA polymers with controlled structures and very low molecular weight distributions as low as 1.07, in particular for complex **3**. High to moderate conversions (30–45%) were obtained in 20 h, although very diluted amount of catalyst was used and in the absence of any reducing agent which indicates an efficient catalyst system. The resulting polymers were characterized by NMR, GPC, and DSC. Syndio-rich atactic poly(*t*-BA) and poly(MMA) with relatively high  $[\text{rr}]$  diads (50%, 42%, respectively) were isolated.

**Keywords** ATRP · Bis(imino)pyridineiron(II) complexes · *tert*-Butylacrylate · Methyl methacrylate · Tacticity · Molecular weight distribution

## Introduction

Atom transfer radical polymerization (ATRP), a method for controlling free radical polymerizations, has recently developed into a versatile tool in polymer chemistry which has been applied to a wide range of vinyl monomers utilizing various initiators and catalyst systems. A special advantage of ATRP is that it requires less stringent conditions than ionic methods [1].

A steady effort has been directed toward designing ligands that display improved activity in ATRP, yet are still cost effective. In copper based ATRP, replacement of bipyridine ligands with alkyl amines lowers the redox potential of the copper halide catalyst and accelerates the polymerizations [2]. A similar phenomenon was also observed in ruthenium and iron [3] catalyzed ATRP when triphenylphosphine and bipyridine were replaced with tributylphosphine and tributylamine, respectively. Trialkyl- and triarylphosphine complexes of iron(II) and iron(III) halides gave promising results in direct and reverse ATRP of styrene and methyl methacrylate [4–6]. The research was thus addressed toward less toxic ligands which similarly permit a fine-tuning of the steric and electronic properties at the metal center. Four-coordinate iron(II) complexes bearing  $\alpha$ -diimine ligands with alkyl substituents were efficient catalysts for well-controlled ATRP of styrene [7]. However, the lowest value reached by the polydispersity index ( $\text{PDI} = M_w/M_n$ ) for the polystyrenes by these catalysts is 1.27, which is greater than the value of 1.1 typically obtained

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with the copper-based catalysts [8] and iron(II) complexes of tridentate salicylaldiminato ligands [9].

A series of ruthenium catalysts [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>, Ru(Ind)Cl(PPh<sub>3</sub>)<sub>2</sub>, Ru(Cp\*)Cl(PPh<sub>3</sub>)<sub>2</sub>] were also employed for MMA in conjunction with a series of bulky fluoroalcohols such as (CF<sub>3</sub>)<sub>3</sub>COH, (CF<sub>3</sub>)<sub>2</sub>C(Ph)OH and, *m*-C<sub>6</sub>H<sub>4</sub>[C(CF<sub>3</sub>)<sub>2</sub>OH]<sub>2</sub>. One of the advantages of the ruthenium catalysts in such alcoholic solvents is expected to be their high stability to these solvents due to the low oxophilicity of ruthenium [10].

Among the various ruthenium complexes, Ru(Cp\*)Cl(PPh<sub>3</sub>)<sub>2</sub> was the most effective in giving the narrowest MWD ( $M_w/M_n$ ) 1.07) in (CF<sub>3</sub>)<sub>3</sub>COH and (CF<sub>3</sub>)<sub>2</sub>C(Ph)OH, which were also efficient in enhancing the syndiotacticity to *rr* 80% and 77%, respectively, at 0°C [11].

Ruthenium complexes with chiral phosphane ligands such as Ru(Ind)Cl[(-)-DIOP] (DIOP=2,3-(isopropylidenedioxy)-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)-butane) were also employed in asymmetric halogen transfer radical addition and metal-catalyzed living radical polymerization reactions of methyl acrylate (MA), and methyl methacrylate (MMA). The above complexes induced asymmetric chiral addition reactions in high chemical yields and relatively high optical yields (10–30% *ee*) [12].

Earlier we reported four tetradentate nitrogen ligands, viz. dichloro{[*N,N'*-diphenyl-*N,N'*-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**I**), {[*N,N'*-dioctyl-*N,N'*-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**II**), {[*N,N'*-dibenzyl-*N,N'*-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**III**), and (1*R*,2*R*)-(-)-*N,N'*-di(quinoline-2-methyl)di-iminocyclohexane (**IV**), that were synthesized and used as complexing ligands in iron-mediated polymerization of methyl methacrylate [13]. High to moderate conversions (87%–43%) were obtained in relatively short times (90 min for **I** and 30 min for **II**), which indicates an efficient catalyst system. When the bulkiness of the substituents was significantly increased, as in ligand **III**, a decrease in polymerization rate and loss of control occurred. Ligand **IV** was less efficient than the other ligands, probably because the ethylene bridge was replaced by cyclohexane bridge. Very recently, we reported the synthesis of new pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine-, quinolinaldimine- and thiophenaldimine-Schiff base ligands. The complexes, after activation with MAO, were evaluated as catalysts for coordination polymerization of *tert*-butyl acrylate (*t*BA), methyl methacrylate (MMA) and *n*-vinyl carbazole (NVC) [14, 15]. Polymerization results showed that bis(imino)pyridyl-based complexes are more active than the complexes containing the aldimine ligands. In addition, the ketimine complexes having bulky aliphatic substituents have highest activities in *t*BA polymerizations while activity of the complexes with aromatic substituents, is in general lower and dependent on the substituents on the aniline. The potential of iron(II) complexes in homopolymer-

ization of various polar monomers has been demonstrated as polymerization experiments indicated that these complexes are also active towards the polymerization of methyl methacrylate, and *n*-vinyl carbazole. Herein we report the implementation of pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine, as catalysts for atom transfer radical polymerization of *tert*-butyl acrylate (*t*BA) and methyl methacrylate (MMA). In this report the initiator to catalyst molar ratio has been 1: 0.1 in the synthesis of all polymers under investigation with no reducing agents involved since a major drawback of this technique is the need for relatively high amounts of redox active transition metal (typically equimolar amounts to alkyl halide initiator), which makes product purification inevitable. The contamination of the polymer with the metal may be seen as a serious limitation to the industrial application of ATRP [16–20].

## Experimental

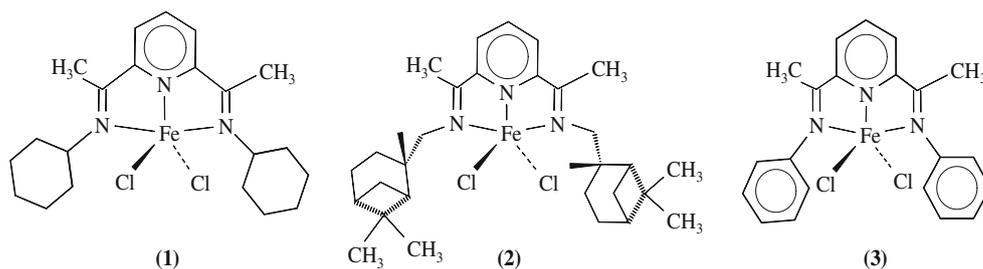
### Materials

*tert*-Butyl acrylate, (*t*BA), (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. Methyl methacrylate (MMA) (Aldrich, 99%) was purified by passing it through a column of activated basic alumina to remove inhibitor. It was then stored under nitrogen at -15°C. Toluene (Analytical grade from Merk, Germany), was distilled over Na/benzophenone, deaerated by bubbling nitrogen, and stored under nitrogen. Ethyl 2-bromoisobutyrate ((CH<sub>3</sub>)<sub>2</sub>CBrCO<sub>2</sub>Et) was dried under molecular sieves. The complexes, 2,6-bis[(1-cyclohexylimino)ethyl]pyridineiron(II) chloride (**1**), 2,6-bis[(1-*cis*)-myrtanylimino)ethyl]pyridineiron(II) dichloride (**2**), and 2,6-bis[(1-phenylimino)ethyl]pyridineiron(II) chloride (**3**) were prepared following literature procedures [14, 15]. All other reagents were used as received.

### Polymerization

Polymerization of methyl methacrylate and *tert*-butyl acrylate were 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 monomer, initiator, and catalyst, sealed with a rubber septum, and degassed to remove oxygen. Degassed methacrylate monomer and degassed solvents were added with 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 an oil bath

**Fig. 1** Structures of the complexes (**1–3**) used in meth (acrylate) polymerization: **1**: 2,6-bis[(1-cyclohexylimino)ethyl]pyridineiron(II) chloride, **2**: 2,6-bis[1-(*cis*)-myrtanylimino]ethylpyridineiron(II) dichloride, and **3**: 2,6-bis[(1-phenylimino)ethyl]pyridineiron(II) chloride



preheated to the desired temperature. After a given time, the reaction was stopped and the reaction mixture was cooled to room temperature and diluted with tetrahydrofuran (THF). The obtained polymer solution was passed over basic alumina to remove the catalyst, and the polymer was precipitated with an excess amount of methanol. The dried product was characterized by NMR, DSC, and GPC techniques and the conversion was determined by gravimetry.

### Characterization

The percentage conversion was determined by weighing the dried polymer.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra ( $\text{CDCl}_3$ ) of the polymer were recorded using a Bruker (av 300) operated at 300 MHz. 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  $10^4$ ,  $10^5$ ,  $10^3$ , and 100 nm connected in series). Chloroform was used as solvent and eluent. The samples were filtered through a 0.5  $\mu\text{m}$  Millex SR filter. Injected volume was 200  $\mu\text{l}$  and the flow rate was 1  $\text{ml min}^{-1}$ . Nearly monodisperse polystyrene standards in the range  $2 \times 10^6$ –150  $\text{g/mol}$  were used for primary calibration. Thermal gravimetric analysis was performed on a NETZSCH STA 409 PC LUX instrument (heating rate 10  $\text{K/min}$ ).

## Results and discussion

Pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine are depicted in Fig. 1. These complexes were prepared with good to moderate yields. The synthetic route to the ligands and to the corresponding complexes under investigation have been reported by us elsewhere [14, 15].

In the above mentioned reports, it can be concluded that in the polymerization of *t*BA and MMA after activation with methyl aluminoxane (MAO) the activity and the molar masses of polymers were clearly influenced by the ligand structure and the choice of the metal center. It was also seen in the study that in the beginning of the polymerization iron(II) complex **1** bearing the cyclohexyl terminals was the most active, but rapidly the activity was decreased and after 1 h the activity reached a constant value. Polymerization results of *t*BA and MMA showed that the activity of the iron complexes increases with increasing the bulkiness of the substituents on the terminal groups of the ligand. Complex **2** [ $\text{Fe}(\text{BMyEP})\text{Cl}_2$ ] (BMyEP: 2,6-bis[1-(*cis*)-myrtanylimino]-ethyl]pyridine), where the ligand carries the bulky aliphatic myrtanyl substituents, exhibited the highest activity ( $54.9 \times 10^3$   $\text{g polymer/mol catalyst h}$ ) and produced the highest molar mass polymer ( $201.3 \times 10^3$   $\text{g/mol}$ ). For these interesting findings, one intention of this study is to implement these complexes in ATRP method for the polymerization of MMA and *t*BA. Other intention is to use a minimum amount of the catalyst since the major drawback of ATRP is the large amount of catalyst which is usually required to promote the polymerization control [21].

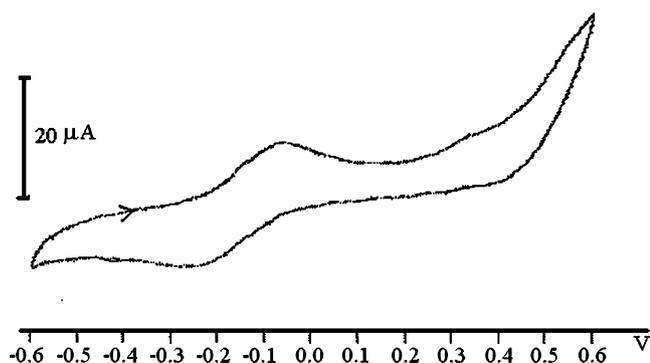
Table 1 shows the polymerization results of MMA and *t*BA utilizing penta-coordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine with molar ratio of catalyst/initiator as 0.1/1. Well-defined molecular weights and very low molecular weight distribution ( $M_w/M_n$ ) were obtained for all polymers except for complex **1** (entry 1) which produced a bimodal molecular weight distribution, plausibly because propagation of MMA was faster than initiation [8, 22, 23].

In one of our studies [13] we reported that polymerization results using ( $[N,N'$ -diphenyl- $N,N'$ -di(quinoline-2-methyl)]-1,2-ethylene diamine/ $\text{FeCl}_2$  catalytic system) were clearly best when the molar ratio of catalyst to initiator was 1.

**Table 1** Results of the ATRP polymerization of MMA and *t*BA using complexes (**1–3**)<sup>a</sup>

Entry	Complex	Monomer	Conversion %	$M_n \times 10^3$ g/mole	$M_w/M_n$	$T_g$ ( $^\circ\text{C}$ )
1	1	MMA	35	34.1	bimodal	108
2	2	MMA	20	33.5	1.25	108
3	3	MMA	45	52.2	1.07	114
4	3	<i>t</i> BA	30	72.5	1.07	60

<sup>a</sup> conditions:  $T=90^\circ\text{C}$ , solvent, Toluene (33% (v/v), [monomer]: [initiator]:[catalyst] = 200:1:0.1, reaction time = 20 h



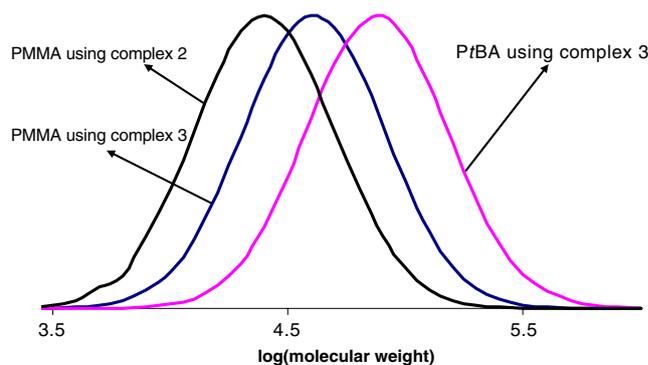
**Fig. 2** Cyclic Voltammetry of bis(amino)pyridine based complexes 2 and 3

Decrease in the catalyst to initiator molar ratio from 1.0 to 0.25 resulted in slower polymerization and broader molecular weight distribution, perhaps due to more frequent termination reactions during the early stage of the polymerization. Moineau et al. [24] studied the effect of decreasing the catalyst/initiator molar ratio from 1.0 to 0.05. They used Ni( $\text{PPh}_3$ ) $_2\text{Br}_2$  catalyst for the polymerization of methyl methacrylate (MMA) by ATRP technique. Their results were a slower polymerization, a larger polydispersity, and a smaller initiation efficiency.

By using 2,6-bis[1-(*cis*)-myrtanylimino]ethylpyridine iron (II) chloride complex (2, entry 2, Table 1) for the polymerization of MMA and the complex 2,6-bis[(1-phenylimino)ethyl]pyridine iron(II) chloride (3, entries 3 and 4, Table 1) for the ATRP polymerization of both MMA and *t*BA, polymers with controlled molecular weight poly(methyl methacrylate) (PMMA) (entry 3, Table 1) and poly(*tert*-butylacrylate) (PtBA) (entry 4, Table 1) with very narrow polydispersities (as narrow as 1.07, entries 3 and 4) have been synthesized. Moreover, the monomer conversion has been reasonably acceptable, despite the fact that diluted amount of catalyst has been used which indicates high catalyst efficiency, in particular for complex 3. We believe that increased electron donicity of the ligands play an important role in the activity of ATRP catalysts. The high Lewis basicity of the 2,6-bis[(imino)ethyl]pyridine may lower the redox potential of the iron(II) complexes facilitating halide abstraction from dormant polymer chains. This would shift the equilibrium toward growing polymer radicals and therefore increase the rate of polymerization. Due to its reversible one-electron redox (Fe(II)-Fe(III)), the complexes 2 and 3 were studied electrochem-

**Table 2** Results of the cyclic voltammogram of complexes 2 and 3

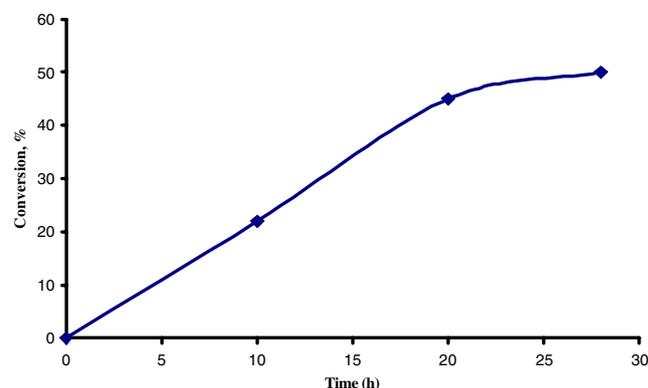
Complex	$E_p^a$ (V)	$E_p^c$ (V)	Conversion %	$M_n \times 10^3$ g/mole
1	0.08	0.41	35	34.1
2	-0.22	-0.08	20	33.5
3	0.45	0.72	45	52.2



**Fig. 3** GPC curves of PMMA and PtBA using complexes 2 and 3. Conditions are the same as in Table 1

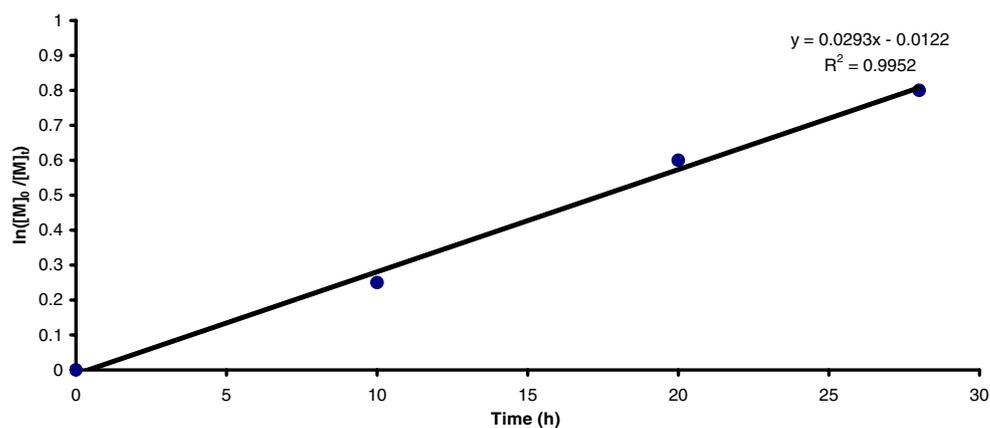
ically. Substituents (cycloaliphatic or aromatic) on the bis(imino)pyridine ligands affect the electron density and redox properties of the iron(II). The cyclic voltammogram of complex 2 is shown in Fig. 2. The results are tabulated in Table 2. The study showed that the oxidation potential of the phenyl substituted bis(imino)pyridine)-based complex (3) is more positive than that of the cycloaliphatic, myrtanyl substituted based complex (2). This could be due to the difference in basicity of the tridentate nitrogen ligands. The bulkiness of the aliphatic myrtanyl substituents on the nitrogen could be the reason for the lower basic properties of the nitrogen donor atom in the ligand of complex 2. The cyclic voltammogram of 2 (Fig. 2) is quasi-reversible with a one-electron transfer for the Fe(II)-Fe(III) redox couple of the central iron atom. Complex 2 showed the oxidation and reduction waves at -0.22 and -0.08 V, respectively. While 1 at 0.08 and 0.41 V, respectively, and 3 at 0.45 and 0.72 V, respectively. This indicates that the central iron atom for 3 is harder to oxidize. This difference in electron density on the iron atoms could be the reason for the higher activity of complex 3 (45% conversion).

The increased donicity of these ligands may also stabilize the iron(III) species [25] and therefore enhance



**Fig. 4** Solution polymerization of MMA with complex 3 as the catalyst. ([Monomer]:[Initiator]:[Catalyst] = 200:1:0.1)

**Fig. 5** First order kinetic plot of  $\ln([M]_0/[M]_t)$  versus time in the solution polymerization of MMA at 90°C using complex **3** as the catalyst. ([Monomer]:[Initiator]:[Catalyst] = 200:1:0.1)



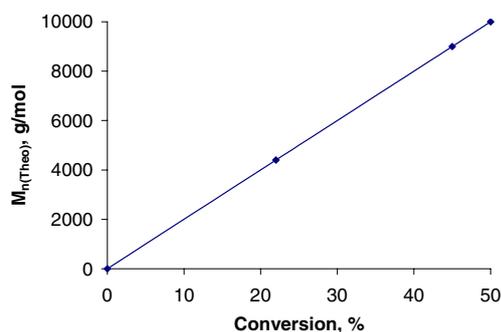
the rapid exchange of halides between dormant and active polymer chain ends.

Table 1 also shows the glass transition temperatures ( $T_g$ ) of the polymers ranged from 108 to 114°C for PMMA (entries 1–3) and 60°C for PtBA (entry 4). The value of  $T_g$  for PMMA synthesized in this study is in good agreement compared to 115°C for PMMA synthesized by traditional free-radical polymerization, whereas it is rather high for PtBA (49°C) [26, 27]. In addition, these  $T_g$  values are higher than those for the polymers produced via coordination polymerization ( $T_g \approx 127^\circ\text{C}$  for PMMA and between 35 to 62°C for PtBA) [14, 15].

Figure 3 shows GPC chromatograms of both PMMA (complex **2** and complex **3** in Fig. 1) and PtBA (complex **3**) which are single and symmetric peaks. Also it shows that there was almost complete initiation by the ethyl 2-bromo isobutyrate initiator, in particular for complex **3**.

### Kinetic study of PMM using complex **3**

To get a close idea about the kinetic of ATRP polymerization of MMA in the presence of complex **3** as the catalyst, further experiments were conducted. The polymerizations were homogeneous and darkly colored which indicated good solubility of the iron(II) complex in the polymeriza-



**Fig. 6** Dependence of molecular weights on monomer conversion in solution polymerization of MMA at 90°C using complex **3** as the catalyst. ([Monomer]:[Initiator]:[Catalyst] = 200:1:0.1)

tion medium. The kinetics of the solution polymerization of MMA at 90°C initiated by ethyl 2-bromo isobutyrate are presented in Figs. 4 and 5.

Figure 4 shows the increasing of monomer conversion with time as a basic requirement for living systems. The straight semi logarithmic 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 (Fig. 5).

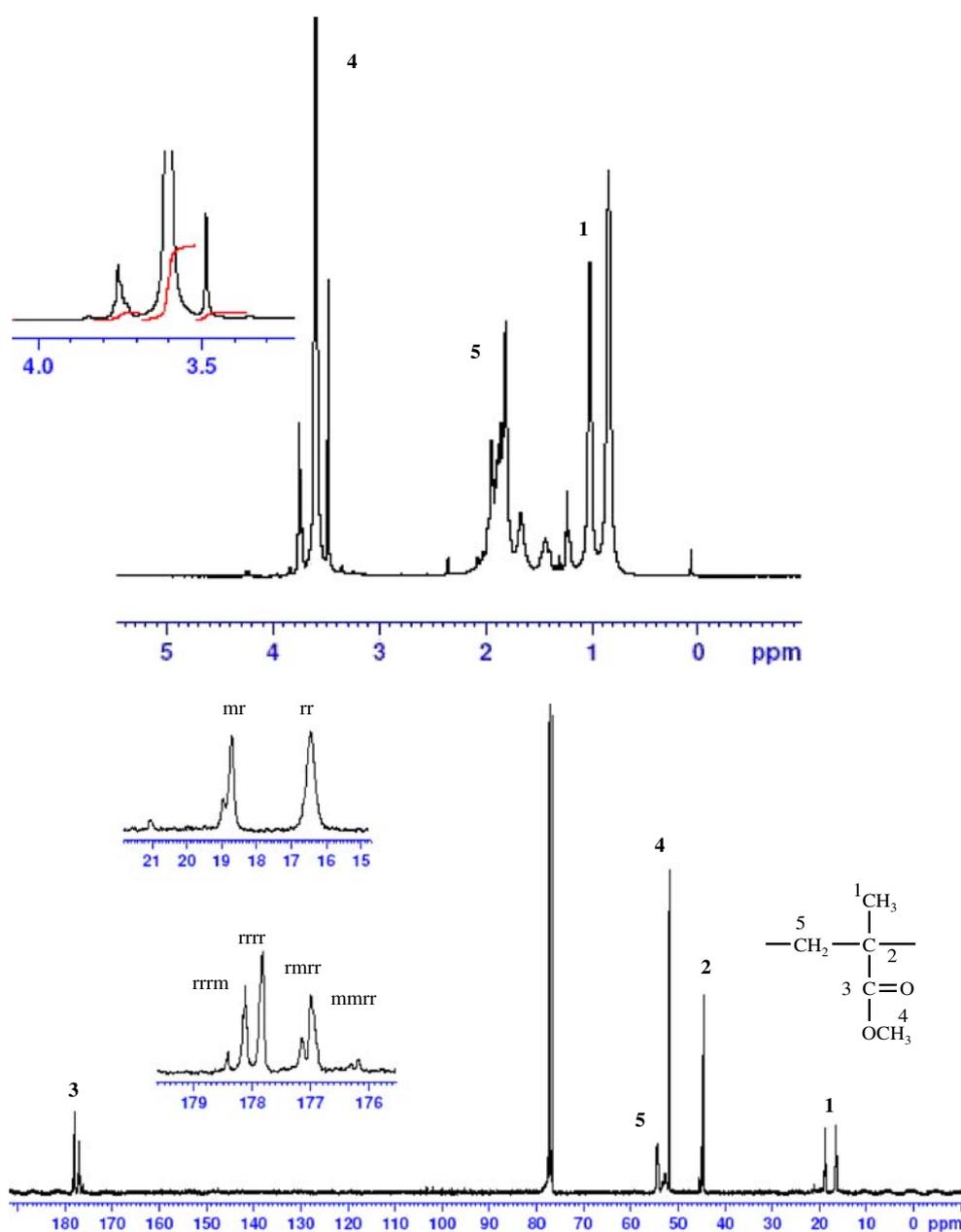
Figure 6 presents the linear evolution of number-average molecular weight,  $M_n(\text{Theo})$  versus monomer conversion indicating controlled/‘living’ process with a negligible amount of transfer reactions.

### PtBA and PMMA tacticity

Various stereospecific polymerizations using Ziegler-Natta [28], metallocene [29], anionic [30, 31] or radical polymerization [32] have been reported earlier. Highly isotactic poly(*t*BA) has been synthesized using a chiral zirconocene ([*m*] diad 83%) [29] or with *n*-BuLi in the presence of LiOH ([*m*] diad 85%) [33]. The highest syndiotactic diad value reported is [*r*] = 63% for poly(*t*-BA) prepared by radical polymerization at low temperature [34] and a triad syndiotacticity [*rr*] of about 40% has been reported for anionic polymerization with diphenylmethyl lithium as an initiator [35].

Stereospecific living radical polymerizations of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were achieved with a combination of ruthenium-catalyzed living radical and solvent-mediated stereospecific radical polymerizations. Polar solvents for stereospecific radical polymerization seem more compatible with the late transition-metal catalysts for living radical polymerizations than the Lewis acids, which may cause deactivation of the metal catalyst or decomposition of the carbon-halogen terminus. A bulky fluoroalcohol, such as  $(\text{CF}_3)_2\text{CHOH}$ , which is effective for syndiospecific radical polymerization

**Fig. 7**  $^1\text{H-NMR}$  (Top) and  $^{13}\text{C-NMR}$  (Bottom) of Poly(MMA)



of MMA at a low temperature, was thus employed for the ATRP of MMA with ethyl 2-bromoisobutyrate/CuBr/Me<sub>6</sub>TREN at  $-20$  and  $-78^\circ\text{C}$  [36]. Highly syndiotactic poly(MMA)s with narrow MWDs were obtained (*rr*) 75%, *M<sub>w</sub>/M<sub>n</sub>*) 1.17 at  $-20$  although the *M<sub>n</sub>* values were higher than the calculated values. The addition of CuBr<sub>2</sub> improved the molecular weight control especially during the early stage of the polymerization [37].

According to poly(*t*BA) NMR spectroscopy, poly(*t*BA) materials prepared in the present study using the complex **3** is syndio-rich atactic with [*rr*] diads being 50%. This result is relatively higher than that reported by us using MAO activated bis(imino)pyridine)iron(II) dichloride complexes,

syndiorich atactic poly(*t*-BA) with [*r*] up to around 37% were isolated at room temperature [14, 15].

Figure 7 shows the  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  of Poly (MMA). Syndiotacticity of the poly(MMA) was determined with reference to the reported triad and pentad assignments [38].

Both  $\alpha$ - and  $\omega$ -end groups of the PMMA prepared with ethyl-2-bromoisobutyrate were characterized by  $^1\text{H}$  NMR spectroscopy (Fig. 7). The spectrum shows signals characteristic of the methylene protons (4.22 ppm) of the ethyl ester group at the  $\alpha$ -end, along with the large absorptions of the main-chain PMMA units (3.60 ppm for the ester methyl). In addition, the small signal (3.84 ppm) near the main-chain unit

can be attributed to the ester methyl protons adjacent to the bromine atom at the  $\omega$ -end. These results are in agreement with ones reported by Sawamoto's Research Group [39]. Signals of  $^{13}\text{C}$ -NMR of the poly(MMA) materials prepared by the complexes 1–3 (entries 1–3, Table 1) at  $\delta$  178.1, 177.8, and 176.9 ppm are assigned to rrrm, rrrr, and mmrr, respectively. The ratio of these signals, 32:42:26, corresponds to a syndio-rich atactic polymer [40]. Similar results have been reported with metallocene catalysts [41] and bis(imino)pyridineiron(II)/MAO catalysts systems [14]. It is believed that the type of the tridentate nitrogen ligand could be the main reason for achieving these tacticity values.

## Conclusion

Methyl methacrylate and *tert*-butyl acrylate were successfully polymerized by atom transfer radical technique using pentacoordinated iron(II) complexes with 2,6-bis[(imino)ethyl]pyridine-Schiff base ligands. These complexes proved to be active not only in the polymerization of MMA and *t*BA after activation with MAO but also as ATRP catalyst with minimum amount of catalyst concentration. In addition, polymerization with these catalysts via ATRP afforded polymers with very low molecular weight distribution ( $M_w/M_n$ ) and syndio-rich atactic poly(*t*BA) and poly(MMA) with relatively higher [rr] diads than those produced by the MAO activated bis[(imino)pyridineiron(II)-based catalyst systems.

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