Available online at www.sciencedirect.com
SCIENCE DIRECT®
European Polymer Journal 40 (2004) 1095–1104
EUROPEAN POLYMER JOURNAL
www.elsevier.com/locate/europolj

Polymerization of methyl methacrylate in the presence of iron(II) complex with tetradentate nitrogen ligands under conditions of atom transfer radical polymerization

Khalid Ibrahim [a,*], Katariina Yliheikkilä [b], Adnan Abu-Surrah [c], Barbro Löfgren [a], Kristian Lappalainen [b], Markku Leskelä [b], Timo Repo [b], Jukka Seppälä [a]

[a] *Laboratory of Polymer Technology, Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FIN-02015 HUT, Finland*
[b] *Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki, P.O. Box 55, FIN-0004 Helsinki, Finland*
[c] *Department of Chemistry, Hashemite University, P.O. Box 150459, Zerqa 13115, Jordan*

Received 29 October 2003; received in revised form 18 December 2003; accepted 18 December 2003
Available online 29 January 2004

Abstract

Four tetradentate nitrogen ligands, viz. dichloro{[*N*,*N*′-diphenyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**1**), {[*N*,*N*′-dioctyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**2**), {[*N*,*N*′-dibenzyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**3**), and (1*R*,2*R*)-(−)-*N*,*N*′-di(quinoline-2-methyl) di-iminocyclohexane (**4**), were investigated as novel complexing ligands in iron-mediated atom transfer radical polymerization (ATRP) of methyl methacrylate where ethyl-2-bromoisobutyrate was the initiator in *o*-xylene at 90 °C. With ligands **1** and **2** the experimental molecular weights increased gradually with monomer conversion. High to moderate conversions (87%, 43%) were obtained in relatively short times (90 min for **1** and 30 min for **2**), which indicates an efficient catalyst system, but after these times a dramatic increase in viscosity of the polymerization medium led to loss of control. It is noteworthy that polymerization proceeded in a controlled manner with ligand **1**, which has two rather bulky substituents on the N-atom. Such bulky ligands did not work for a copper-based system, where they led to excessive terminations or other side reactions. When the bulkiness of the substituents was significantly increased, as in ligand **3**, a decrease in polymerization rate and loss of control occurred. Ligand **4** was less efficient than the other ligands, probably because the ethylene bridge was replaced by cyclohexane bridge.

Keywords: ATRP; Controlled free radical polymerization; Methyl methacrylate; Bulkiness; Deactivation; Chain transfer agent

1. Introduction

Controlled radical polymerization is one of the most rapidly developing areas of polymer science. Several new methods have been developed to obtain control over molecular weights, narrow molecular weight distributions, functionalities, architectures, and well-defined compositions [1–3]. One of these polymerization methods is atom transfer radical polymerization (ATRP), 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 [4].

ATRP utilizes a reversible halogen abstraction step, in which the metal at lower oxidation state (in the present case Fe^{2+}) reacts with an alkyl halide, generating

* Corresponding author. Tel.: +358-945-16177; fax: +358-945-22622.
E-mail address: kibrahim@cc.hut.fi (K. Ibrahim).

0014-3057/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2003.12.018

a radical and a metal complex at higher oxidation state (in the present case X–Fe^{3+}). The radical adds a monomer to generate the polymer chain. The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and a lower oxidation state metal [5].

The molecular weight of the polymer is controlled in ATRP, since both initiation and deactivation are fast; all the chains begin to grow at approximately the same time, and a low concentration of active species is maintained. ATRP has tolerance toward a wide variety of functional groups in the monomer and has been applied successfully for the preparation of well-defined polymers such as styrene, substituted styrenes [6], (meth)acrylate [7], and acrylonitrile [8]. As catalysts, ATRP systems use Cu [1,6–8], Ru [3,9], Rh [10], Ni [11], Pd [12], Co [13], and Fe [14,15] transition metals in conjunction with suitable ligands such as substituted and unsubstituted bipyridines, phosphorus-containing ligands, and multidentate amines [16].

Several reports describe the use of ATRP in iron-mediated polymerization of methyl methacrylate. Matyjaszewski and coworkers [17,18] report the use of iron halide complexes in both homogeneous and heterogeneous conditions for the living polymerization of methyl methacrylate. They used a variety of coordinating ligands, including halide anions, trialkylamines, and triphenylphosphine. The polymerization rate, as well as the molecular weight distribution ($M_w/M_n = 1.1$–1.5), were affected by the structure of the coordinating ligand and the monomer employed. Sawamoto's group [14] describe the synthesis of poly(methyl methacrylate) catalyzed by iron(II)bis(triphenylphosphine) dichloride [$FeCl_2(PPh_3)_2$]. In this case the polymers exhibited narrow molecular weight distributions throughout the polymerization ($M_w/M_n = 1.1$–1.3). Yan and Zhu [19] used low toxic organic acids such as isophthalic acid and acetic acid as novel ligands in iron-mediated ATRP. The resulting poly(methyl methacrylate) exhibited acceptable narrow molecular weight distributions ($M_w/M_n =$ 1.2–1.5). Although ATRP of methyl methacrylate polymers was achieved in the above-mentioned studies, high conversions were obtained only at rather long reaction times or else the molecular weight distributions (M_w/M_n) became broader at relatively low conversions. Earlier, we reported [20] the synthesis of *n*-butyl methacrylate by ATRP with the $FeCl_2 \cdot 4H_2O(PPh_3)_2$ catalytic system in bulk and in solution. A linear increase in the number average molecular weight versus monomer conversion was observed with quite narrow molecular weight distributions ($M_w/M_n < 1.3$).

Aliphatic amines are coming to play an important role in atom transfer radical polymerization owing to their low cost. In general, multidentate nitrogen ligands work well in copper-mediated ATRP by providing the desired reactivity [21].

In this paper we report the synthesis of the tetradentate nitrogen ligands dichloro{[*N*, *N*′-diphenyl-*N*, *N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**1**), {[*N*, *N*′-dioctyl-*N*, *N*′-di(quinoline-2-methyl)]-1,2- ethylene diamine} (**2**), {[*N*, *N*′-dibenzyl-*N*, *N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine} (**3**), and (1*R*,2*R*)-(−)-*N*, *N*′-di(quinoline-2-methyl) di-iminocyclohexane (**4**) and their use as complexing ligands in iron-mediated ATRP of methyl methacrylate (MMA)) initiated by ethyl 2-bromoisobutyrate ($(CH_3)_2CBrCO_2Et$). Ligands **1** and **2** were synthesized for the first time, while ligands **3** and **4**,which were synthesized earlier, were used here as ATRP ligands for the first time.

2. Experimental section

2.1. Materials

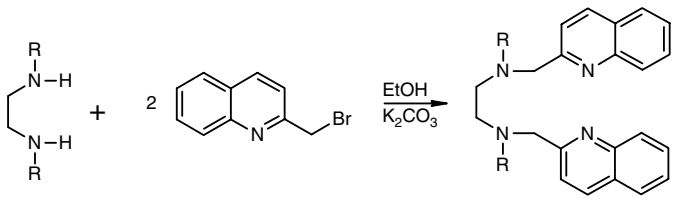
Methyl methacrylate (MMA) (Aldrich, 99%) was purified by passing it through a column of activated basic alumina to remove inhibitor. It was then stored under nitrogen at −15 °C. *n*-Butyl methacrylate (*n*-BMA) (*purum* grade from Fluka) was purified by washing with 5% sodium hydroxide aqueous solution, followed by washing with water. The organic portion was dried for 24 h under anhydrous sodium sulfate, filtered, and finally distilled under reduced pressure. It was stored under nitrogen at −15 °C. $FeCl_2$ was obtained from Aldrich and used without purification. Ethyl-2-bromoisobutyrate ($(CH_3)_2CBrCO_2Et$) (Aldrich, 98%) was dried under molecular sieves. The following reagents were purchased from Aldrich: quinaldine (95%), *N*-bromosuccinamide (99%), *N*, *N*-dibenzylethylene diamine (99%), quinaldine-2-aldehyde (97%), and diaminocyclohexane (98%). The starting materials for *N*, *N*-diphenylethylene diamine were purchased as follows: benzaldehyde (99%) from Fluka and ethylene diamine (98%) from J.C. Baker. All solvents were purchased as HPLC grade and dried with molecular sieves or distilled over Na under argon atmosphere.

2.2. Synthesis

Tetradentate ligands **1**–**4** were prepared as shown in Scheme 1 with good to moderate yields. The syntheses were performed under argon atmosphere using standard Schlenk techniques to eliminate traces of air or moisture. Analysis of the ligands gave satisfactory results. Water formed in the synthesis of the ligand **1** was removed with Dean–Stark apparatus.

2.2.1. [*N*, *N*′-Diphenyl-*N*, *N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine (1)

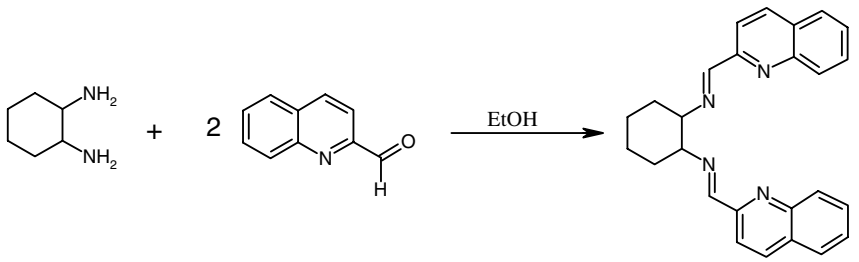
A mixture of *N*-bromosuccinamide (25 g, 140.8 mmol), quinaldine (18 g, 125.6 mmol), and α,α′-azobis-



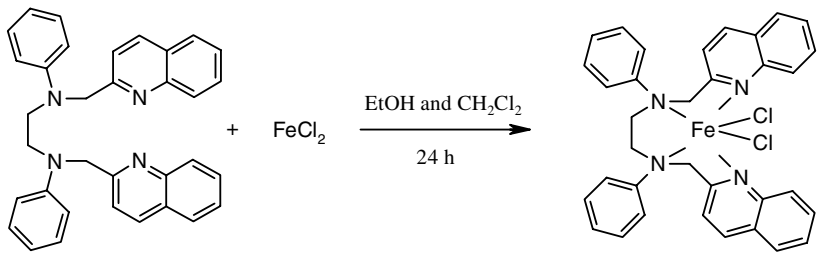
Ligand **1**: R = Ph

Ligand **2**: R = C_8H_{17}

Ligand **3**: R = CH_2Ph



Ligand 4



Complex **5**

Scheme 1. Synthesis routes for the tetradentate ligands **1**–**4** and complex **5**.

isobutyronitrile (AIBN) (0.6 g) in 400 ml of CCl_4 was heated under reflux for 5 h with continuous stirring. The resulting red solution was allowed to cool to room temperature and filtered. Removal of the solvent in vacuum left a red oil. Recrystallization from petroleum ether (300 ml) gave 2-bromomethylquinoline as brownish crystals (10.41 g, 46.88 mmol, 37%). The compound was stored at −50 °C.

A solution of *N*,*N*′-diphenylethylene diamine (3.1 g, 14.6 mmol) in ethanol (50 ml) and K_2CO_3 was added to a solution of 2-bromoquinaldine (7.1 g, 32 mmol) in ethanol (50 ml) under continuous stirring. The reaction mixture was heated at reflux temperature. The stirring was continued for two days at room temperature. Water (200 ml) was added to the reaction mixture to dissolve K_2CO_3 and the white precipitate that formed was filtered off and washed with water (3×10 ml), ethanol (3×10 ml), and petroleum ether (2×10 ml). Toluene (100 ml) was added to remove water from the product and the mixture was heated in a Dean–Stark apparatus for 5 h. Toluene was evaporated and the light brown product (4.43 g, 8.97 mmol, 58%) was dried in vacuum.

Anal. Calc. for $C_{34}H_{30}N_4$ (494.629): C 82.56; H 6.11; N 11.33. Found: C 82.07; H 6.25; N 11.01%; MS: 494 (25%, M^+), 247 (100%, $M^+-C_{17}H_{15}N_2$), 142 (98%, $M^+-C_{24}H_{22}N_3$).

^{1}H NMR chemical shifts δ (ppm): $\delta = 3.77$ (s, 4H, CH_2 bridge), $\delta = 4.78$ (s, 4H, CH_2), $\delta = 6.57$–8.00 (22H, aromatic); ^{13}C NMR chemical shifts δ (ppm): 48.90; 58.00; 112.63; 117.32; 119.27; 126.40; 127.56; 127.87; 129.00; 129.70; 129.87; 137.12; 148.08; 160.29.

2.2.2. [N,N′-Dioctyl-N,N′-di(quinoline-2-methyl)]-1,2-ethylene diamine (2)

Octylamine (19.0 g, 147.0 mmol) was placed in the reaction vessel and dibromoethane (5.4 g, 28.7 mmol)

was added slowly through a septum. The reaction mixture was refluxed at 135 °C for 24 h with continuous stirring. Octylamine boils at 177 °C and excess of octylamine was removed in vacuum. NaOH (4 g, 100 mmol) was dissolved in water (50 ml) and added to the reaction mixture in an ice bath. A white precipitate, N,N'-dioctylethylenediamine, was filtered off and washed with hexane (2×15 ml).

Yield 3.4 g, 12.0 mmol, 42%. MS: 284 (5%, M^+), 156 (40%, $M^+-NHC_8H_{17}$), 142 (85%, $M^+-CH_2NHC_8H_{17}$), ^{1}H NMR chemical shifts δ (ppm) = 0.88 (t, 6H, CH_3), 1.27–1.48 (m, 24H, CH_2), 1.72 (s, 2H, NH), 2.55 (t, 4H, CH_2N), 2.71 (s, 4H, CH_2 bridge); ^{13}C NMR chemical shifts δ (ppm) = 14.26, 22.83, 27.56, 29.46, 29.72, 30.34, 32.02, 49.72, 50.24.

A solution of N,N'-dioctylethylene diamine (1.3 g, 4.6 mmol) in ethanol (20 ml) and K_2CO_3 (2.1 g, 15 mmol) was added to a solution of 2-bromoquinaldine (3.1 g, 14.0 mmol) and ethanol (20 ml) under stirring. The reaction mixture was heated at reflux temperature and the stirring was continued at room temperature for three days. The solvent was evaporated. Water (50 ml) was added and extracted with pentane (3×40 ml). The organic layers were combined and the solvent was evaporated leaving a yellow oil. The oil was purified by column chromatography. The column was treated with triethylamine and a gradient run was carried out with hexane and ether (1:1) as starting eluents and ether as final eluent.

Yield 0.90 g, 1.6 mmol, 35%. ^{1}H NMR chemical shifts δ (ppm) = 0.85 (t, 6H, CH_3), 0.82–1.44 (m, 24H, CH_2), 2.49 (t, 4H, CH_2 bridge), 2.71 (s, 4H, CH_2N), 3.90 (s, 4H, CH_2), 7.44–8.04 (m, 12H, aromatic); ^{13}C NMR chemical shifts δ (ppm) = 14.23, 22.77, 27.34, 27.52, 29.41, 29.61, 31.96, 52.64, 55.28, 61.94, 121.23, 126.06, 127.50, 127.66, 129.07, 129.35, 136.20, 147.64, 161.53 n_D^{20} 1.5534.

2.2.3. [*N,N'-Dibenzyl-N,N'-di(quinoline-2-methyl)*]-*1,2-ethylene diamine* (**3**) [22]

Benzaldehyde (22.3 g; 0.21 mol) and 1,2-ethylene diamine (6.0 g; 0.1 mol) were refluxed at 120 °C for 1/2 h. The mixture was cooled to room temperature and 30 ml of EtOH was added. The mixture was kept at −20 °C overnight and the solids were filtered off and washed with EtOH (10.0 g, 0.042 mol, 42%). Small portions of a suspension of $LiAlH_4$ (1.3 g; 0.034 mol) in Et_2O were added to the product and refluxed for 1 h. The mixture was cooled to room temperature and water was slowly added. The solids were filtered off and washed with Et_2O. Water phase was extracted with Et_2O (2×10 ml) and the combined organic layers were dried over Na_2SO_4. The drying agent was filtered off and the solvent was evaporated in vacuum, leaving the product (N,N'-dibenzyl-ethylene diamine) as yellow oil (7.22 g, 0.030 mol, 88%).

^{1}H NMR chemical shifts δ (ppm): $\delta = 1.47$ (s, 2H, NH), $\delta = 2.71$ (s, 4H, CH_2 bridge), $\delta = 3.73$ (s, 4H, CH_2 benzyl), $\delta = 7.21$–7.29 (m, 10H, aromatic); ^{13}C NMR chemical shifts δ (ppm): 48.77, 53.88, 126.80, 128.04, 128.30, 140.54.

Ligand **3** was synthesized analogously to ligand **1**, but water formed in the reaction did not cause problems in this synthesis and refluxing with toluene was not required. A solution of N,N'-dibenzyl-ethylene diamine (2.0 g, 8.3 mmol) in ethanol (50 ml) and K_2CO_3 (4 g) was added to an ice-cooled solution of 2-bromoquinaldine (4.1 g, 18.3 mmol) in ethanol (60 ml) under stirring. The reaction mixture was heated at reflux temperature and stirring was continued at room temperature for two days. Water (75 ml) was added to the reaction mixture to remove K_2CO_3. The resulting white precipitate (3.81 g, 7.29 mmol, 89%, m.p. 168 °C) was filtered off and washed with water (3×20 ml), ethanol (3×20 ml), and petroleum ether (3×20 ml) and dried in vacuum.

Anal. Calc. for $C_{36}H_{34}N_4$: C 82.41; H 6.92; N 10.68. Found: C 82.67; H 6.82; N 10.91%. ^{1}H NMR chemical shifts δ (ppm): $\delta = 2.75$ (s, 4H, CH_2 benzyl), $\delta = 3.60$ (s, 4H, CH_2 quinaldine), $\delta = 3.87$ (s, 4H, CH_2 bridge), $\delta = 7.20$–8.05 (22H, aromatic); ^{13}C NMR chemical shifts δ (ppm): 52.20, 59.40, 61.63, 121.13, 126.18, 127.12, 127.73, 128.38, 129.07, 129.13, 129.46, 136.36, 139.36, 139.38, 147.67, 161.21.

2.2.4. (*1R,2R*)-*(−)-N,N'-Di(quinoline-2-methyl) di-iminocyclohexane* (*4*)

The crystal structure of the ligand was determined earlier and the synthesis was done according to a published method [23]. To a solution of quinaldine-2-aldehyde (0.88 g, 5.60 mmol) in ethanol (30 ml) was added a solution of diaminocyclohexane (0.29 g, 2.54 mmol) in ethanol (15 ml). Stirring was continued overnight and the pale yellow precipitate was filtered off and washed with hexane (2×10 ml). Recrystallization was done from a mixture of CH_2Cl_2 and Et_2O.

Yield 0.64 g, 1.63 mmol, 64%, m.p. 183 °C. MS: 392 (30%, M^+), 128 (28%, $M^+-C_{17}H_{17}N_3$). ^{1}H NMR chemical shifts δ (ppm): $\delta = 1.57$–1.90 (8H, cyclohexane), $\delta = 3.65$ (t, 2H, cyclohexane), $\delta = 7.44$–8.07 (12H, aromatic), $\delta = 8.52$ (s, 2H, CH); ^{13}C NMR chemical shifts δ (ppm): 24.58, 32.93, 74.06, 118.76, 127.33, 127.82, 128.91, 129.67, 129.74, 136.55, 147.90, 155.16, 162.07.

2.2.5. *Dichloro{[N,N'-diphenyl-N,N'-di(quinoline-2-methyl)]-1,2-ethylene diamine}iron(II)* (*5*)

Solid iron(II)chloride (0.164 g, 1.29 mmol) was directly added to a stirred solution of **1** (0.8 g, 1.617 mmol) in EtOH (40 ml) and CH_2Cl_2 (25 ml). Stirring was continued for 24 h, after which solvent was evaporated and 20 ml of THF was added. Part of the THF was evaporated and 20 ml of Et_2O was added. The brownish

yellow product that formed (0.754 g, 1.21 mmol, 94%) was filtered off and washed with Et_2O (2×5 ml) and dried in vacuum. Anal. Calc. for $C_{34}H_{30}N_4FeCl_2$: C 65.72; H 4.87; N 9.02. Found: C 65.70; H 4.93; N 8.77%.

2.3. Polymerization

Polymerization of methyl methacrylate 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 monomer, ligand, 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 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 alumina to remove the catalyst, and the polymer was precipitated with an excess amount of methanol. The dried product was characterized by ^{1}H NMR and GPC techniques and the conversion was determined by gravimetry.

2.4. Characterization

The percentage conversion of the MMA monomer was determined by weighing the dried polymer. The molecular weights were determined by room temperature SEC (Waters System Interface Model, Waters 510 HPLC Pumps, Waters Differential Refractometer, Waters 700 Satellite Wisp, and four linear PL gel columns: 104, 105, 103, and 100 nm connected in series). Chloroform was used as solvent and eluent. The samples were filtered through a 0.5 μm Millex SR filter. Injected volume was 200 μl and the flow rate was 1 ml min^{-1}. Nearly monodisperse polystyrene standards in the range 2×10^6–150 g/mol were used for primary calibration.

The ^{1}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 ($CDCl_3$).

The ^{1}H NMR spectra of the ligands were recorded using a Varian Gemini 200 spectrometer at 200 MHz. For ^{13}C NMR spectra of the ligand, a Varian Gemini 200 spectrometer operated at 50.286 MHz was used. Mass spectra were recorded with a JEOLJMS-SX102 EI$^+$ instrument using a direct inlet system and electron impact ionization 70 eV. Elemental analyses were performed at the Department of Pharmacy, University of Helsinki, with an EA 1110 CHNS-O CE instrument.

3. Results and discussion

The polymerizations described in the following were examined for fulfilling the well-known ATRP requirements.

3.1. Polymerizations with ligand 1/$FeCl_2$

Polymerization of MMA was first carried out with the synthesized complex **5** (Scheme 1) and then with the complex formed in situ. As the two routes gave the same results, all subsequent polymerizations were carried out with complexes formed in situ.

3.1.1. Effects of catalyst/initiator molar ratio, using hydrated iron(II) chloride catalyst, and using Cu(I) chloride catalyst on polymerization of MMA with ligand 1

Before studying ATRP of methyl methacrylate (MMA) with ligand **1**/$FeCl_2$, we examined first the effect of the catalyst to the initiator molar ratio. This is important since the major disadvantage of ATRP is the large amount of catalyst usually required to achieve polymerization control [24]. Additional cost and metal residues in the final polymer may then be limitations for industrial applications. In Table 1, the first three entries show that polymerization results were clearly best when the molar ratio of catalyst to initiator was 1. 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.

To study the effect of water traces on the rate of polymerization (entry 4), a hydrated iron(II) chloride was used instead of an anhydrous one. The rate of the polymerization increased (monomer conversion reached 90%), but the molecular weight distribution became broader than that of the polymerization system without water. This probably occurred because the halogen transfer equilibrium shifted, more or less, from dormant to active species in the presence of water [19].

For comparison, the last entry of Table 1 describes the effect of replacing iron(II) chloride with copper(I) chloride. The result of this was a low conversion polymer with molecular weight distributions and molecular weights much higher than the theoretical ones. Similar results have been reported by Zhu and Yan [25]. Our results are also in agreement with Matyjaszewski and coworkers [26], who suggest that steric hindrance around N-atoms should be minimized and show that ligands with two bulky substituents on N-atoms in aliphatic amines are not efficient in copper-based ATRP. We believe that the greater electron donor strength of the ligand plays an important role in the efficiency of ATRP catalysts. In the case of iron(II), the high Lewis basicity of the ligand (**1**) may lower the redox potential

Table 1
Characteristics of the MMA polymerization[a]

Entry	Catalyst	[Cat]/[ln]	Conversion (%)	M_w/M_n	M_n, exp
1	1 + $FeCl_2$	1	87.5	1.35	26000
2	1 + $FeCl_2$	0.5	48	1.55	20700
3	1 + $FeCl_2$	0.25	29	1.58	21000
4	1 + $FeCl_2 \cdot 4H_2O$	1	90	1.62	36000
5	1 + CuCl	1	64	2.24	450500

[a] Conditions: $T = 90$ °C, [monomer]:[initiator] = 200:1, [catalyst]:[ligand] = 1:1, time = 90 min, solvent, *o*-xylene, 33%, v/v.

of the iron(II) complexes facilitating halide abstraction from the dormant polymer chain. This would shift the equilibrium toward the growing polymer radicals and increase the rate of polymerization [27].

3.1.2. Controlled polymerization of MMA

MMA was polymerized at rather high concentration (6.28 M) in *o*-xylene at 90 °C (without any additives, i.e., deactivator as $FeCl_3$).

In order to obtain information about the solution polymerization mechanism, we determined the ATRP kinetics for MMA using ethyl 2-bromoisobutyrate ($(CH_3)_2CBrCO_2Et$) as initiator. The dramatic increase in viscosity of the polymerization medium forced us to stop the reaction after 90 min, however.

Fig. 1 shows a semi-logarithmic plot of the homogeneous ATRP of MMA in 33% (v/v) *o*-xylene. The polymerization was initiated with ethyl 2-bromoisobutyrate and run at 90 °C. The plot of $\ln([M]_0/[M]_t)$ versus time is linear (apparent rate constant $k_p^{app} = 3.87 \times 10^{-4}$ s^{-1}), suggesting a constant number of propagating species throughout the reaction. It is worth mentioning that, when the reaction was continued for 120 min, loss of control was seen in the broad molecular weight distribution ($M_w/M_n = 1.7$) and very high experimental molecular weights. The loss of control may be attributed to the dramatic increase of viscosity and final vitrification of the polymerization medium at high conversion, which can be expected to change the rate of exchange between the active and dormant species and accordingly broadening the molecular weight distribution [25].

Fig. 2 presents a kinetic plot of conversion versus time, showing that monomer conversion increases with time, and that the reaction rate is relatively fast (87.5% conversion in 90 min) indicating an effective catalyst system.

The apparent linear increase in the number average molecular weight, M_n, exp (M_n(GPC) versus monomer conversion (as required for living polymerization) is demonstrated in Fig. 3. As can be seen, M_n(GPC) values are consistently higher than the theoretical ones, M_n, theo (M_n, theo = $(\Delta[M]/[R-X]_0)(M_w)_0$), where $\Delta[M]$, $[R-X]_0$, and $(M_w)_0$ present the concentration of consumed monomer, the initial concentration of the initiator, and the molecular weight of monomer, respectively). One reason for this deviation may be slow initiation relative to propagation owing to the dramatic increase in viscosity of the polymerization medium with conversion. Another reason could be that M_n(GPC) values were obtained using GPC calibrated with linear polystyrene standards and the deviation is thus due to differences in the hydrodynamic volume between MMA and linear polystyrene molecules. The latter seems to be less significant, as M_n(NMR) of PMMA obtained from the peak intensity ratio of that at $\delta = 3.58$ to that at $\delta = 4.09$ at the α-end (Fig. 5) was 18,000 g/mol, while the M_n(GPC) was 22,000 g/mol at the same conversion (53%). It is noted that as both M_n(NMR) and M_n(GPC)

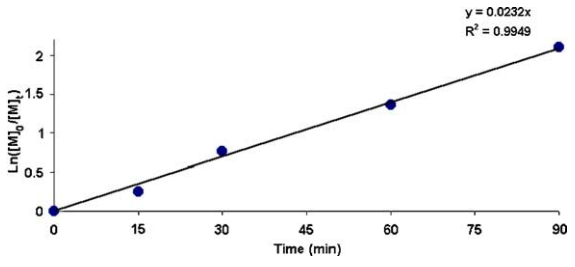


Fig. 1. First order kinetic plot of $\ln([M]_0/[M]_t)$ versus time in solution polymerization of MMA with $(CH_3)_2CBrCO_2C_2H_5$ as the initiator and **1** as the ligand in (33%, v/v) *o*-xylene at 90 °C. [Monomer]:[initiator]:[catalyst:]:[ligand] = 200:1:1:1.

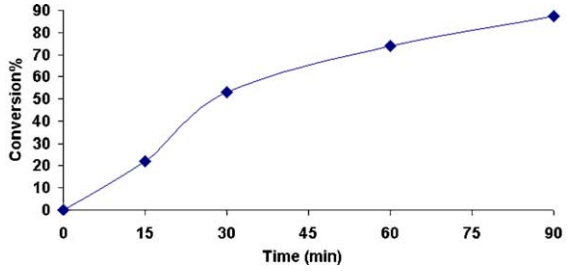


Fig. 2. Solution polymerization of MMA with $(CH_3)_2CBrCO_2C_2H_5$ as the initiator and **1** as the ligand in (33%, v/v) *o*-xylene at 90 °C. [Monomer]:[initiator]:[catalyst:]:[ligand] = 200:1:1:1.

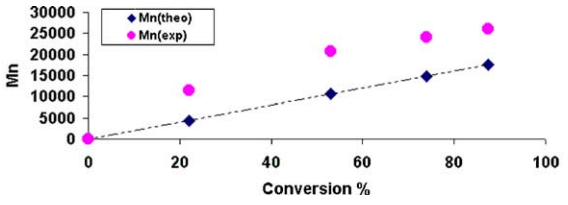


Fig. 3. Dependence of molecular weight on monomer conversion in (33%, v/v) solution polymerization of MMA at 90 °C in *o*-xylene. Conditions as in Fig. 1.

are quite close to each other, but far from M_n,theo (11,000 g/mol), we prefer to use M_n(GPC).

Fig. 4 shows the GPC curves of poly(methyl methacrylate), PMMA, to comprise single and symmetric peaks. A narrowing of molecular weight distribution with conversion, as exhibited in this figure, suggests formation of a controlled PMMA and, at the end of the reaction, molecular weight distributions are unimodal and acceptable narrow ($M_w/M_n = 1.35$).

3.1.3. End-group analysis

Both α- and ω-end groups of the PMMA prepared with ethyl-2-bromoisobutyrate were characterized by ^{1}H NMR spectroscopy (Fig. 5). The spectrum shows signals characteristic of the methylene protons (4.09 ppm) of the ethyl ester group at the α-end, along with the large absorptions of the main-chain PMMA units (3.58 ppm for the ester methyl). In addition, the small signal (3.82 ppm) near the main-chain unit can be attributed to the ester methyl protons adjacent to the bromine atom at the ω-end. These results are in agreement with ones reported by Sawamoto's Research Group [28].

3.1.4. Living polymerization of n-BMA

To test whether our ligand was suitable for broader use, we conducted living radical polymerization of *n*-BMA with the same initiating system and reaction conditions as used for the synthesis of MMA, but the monomer to initiator ratio was higher (degree of polymerization = 300). The reaction medium was less viscous than that of MMA at the same reaction time. The experimental molecular weights of the resulting polymers were in good agreement with the theoretical ones (conversion = 80%, M_n,theo = 34,000 g/mol, M_n(GPC) = 36,000 g/mol), and the molecular weight distributions were rather broad ($M_w/M_n = 1.6$ at 90 min). One possible explanation for the broad molecular weight distribution is that the concentration of iron(III) halide was decreased due to the low solubility of the complex.

3.2. Polymerization with ligand 2/$FeCl_2$

The effect of increasing steric crowding around the catalyst was investigated by introducing a long chain alkyl group (C_8H_{17}) to the N-atoms in the ligand. This should increase the solubility of the catalyst in the nonpolar solvent *o*-xylene (i.e., this ligand is oily and viscous, not solid like the other three ligands). The result was an increase in the rate of polymerization (Fig. 6, Table 2) and a broadening of molecular weight distribution(M_w/M_n). The evolution of M_n(GPC) with conversion was similar to that presented in Fig. 3. This behavior of higher M_n(GPC) and a broadening of molecular weight distribution (M_w/M_n) is attributed to the dramatic increase in the viscosity of the reaction medium with time. Table 2, entry 1, shows good ATRP results after 10 min reaction time ($M_w/M_n = 1.27$), but after 40 min (entry 4) the resulting polymer was rigid and control was lost (broader M_w/M_n, very high M_n(GPC)). Similar behavior was observed in the polymerization of MMA initiated by 2-bromopropionitrile and catalyzed by diiminopyridine/$FeBr_2$ ($M_w/M_n = 1.21$ for 5% conversion to 1.68 for 42% conversion, M_n(GPC)

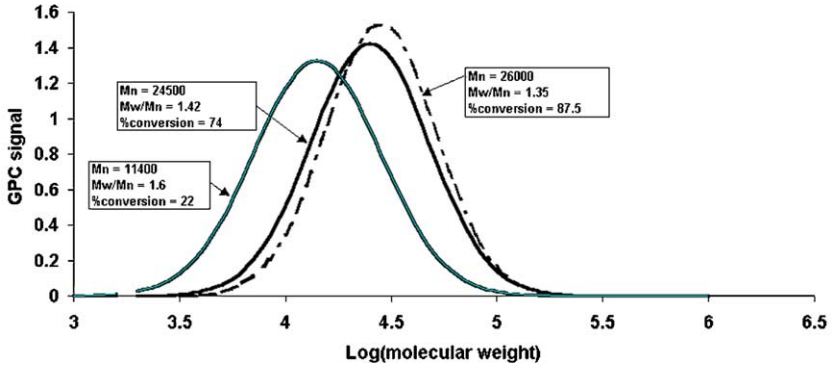


Fig. 4. Evolution of molecular weight with time and decreasing of polydispersites with conversion for the polymerization of MMA using the same conditions as Fig. 1.

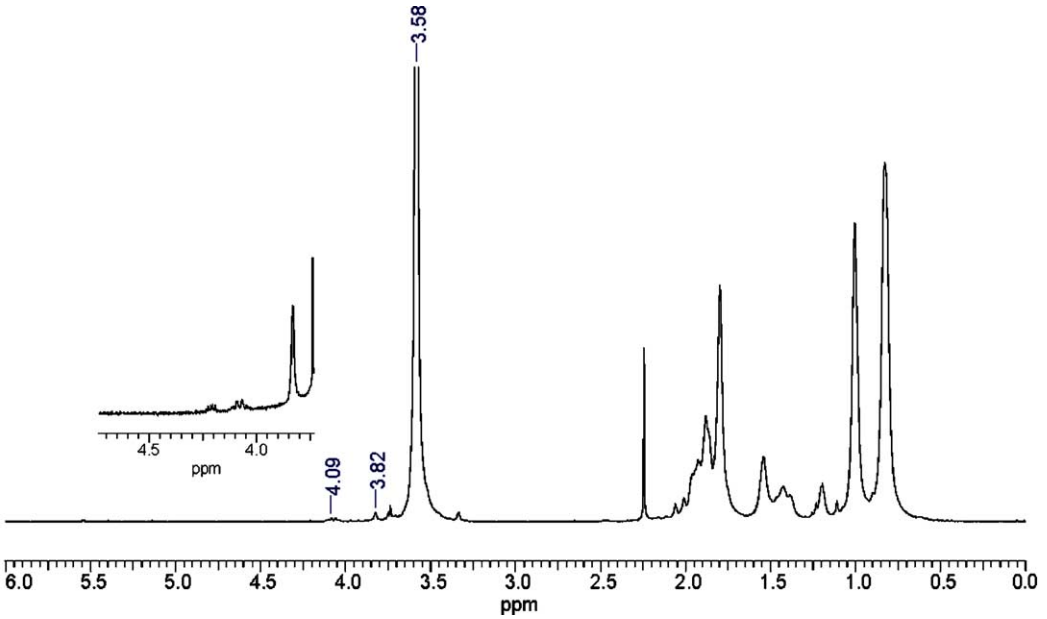


Fig. 5. Representative 300 ^{1}H NMR spectrum of PMMA.

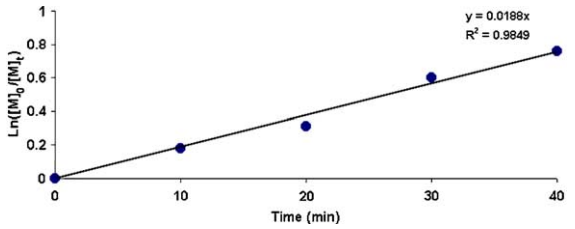


Fig. 6. First order kinetic plot of $(\ln[M]_0/[M]_t)$ versus time in solution polymerization of MMA with $(CH_3)_2CBrCO_2C_2H_5$ as the initiator and **2** as the ligand in (33%, v/v) *o*-xylene at 90 °C. [Monomer]:[initiator]:[catalyst:]:[ligand] = 200:1:1:1.

was higher than M_n, theo) [29]. A possible explanation for this behavior is that chain transfer reactions occurred during the polymerization. It is clear that the substituents on the ligands play an important role in determining the position of the equilibrium between dormant and active polymer chains.

3.3. Polymerizations with ligand 3/$FeCl_2$ and ligand 4/$FeCl_2$

To further study the effect of steric hindrance of the ligands on ATRP, we introduced ligand **3** which is bulkier than ligands **1** and **2**. And to study the effect of replacing the ethylene bridge between the nitrogens with a cyclohexane bridge, we introduced ligand **4**.

Table 3 summarizes the results of the polymerization experiments. As shown by the first three entries in the table, as steric hindrance around the nitrogen increases, the control of ATRP becomes worse, and the polymers exhibit higher molecular weights, broader molecular weight distributions, and lower rates of reaction in relative to ligands **1** and **2**. The semi-logarithmic plot of $\ln([M]_0/[M]_t)$ versus time (Fig. 7) shows a slight deviation from linearity, indicating a decrease in the concentration of growing radicals during the polymerization, evidently due to termination reactions. A possible explanation for this behavior may be chain transfer with the formed iron(III) halide after initiation. That is,

Table 2
Results of the ATRP polymerization of MMA using ligand **2**[a]

Entry	Time (min)	Conversion (%)	M_w/M_n	M_n, exp	M_n, theo
1	10	16	1.27	15000	3200
2	20	27	1.36	23000	5400
3	30	43	1.55	27000	8600
4	40	53	2.4	61500	10600

[a] Conditions: $T = 90$ °C, solvent, *o*-xylene (33%, v/v), [monomer]:[initiator]:[catalyst]:[ligand] = 200:1:1:1.

Table 3
Results of the ATRP polymerization of MMA using ligands **3** and **4**[a]

Entry	Ligand	Time (h)	Conversion (%)	M_w/M_n	M_n(exp)
1	**3**	1	8	1.78	550000
2	**3**	2	21	1.92	555000
3	**3**	3	53	1.78	500000
4	**4**	4	No polymers		
5	**4**	7	Traces		

[a] Conditions: $T = 90$ °C, solvent, *o*-xylene (33%, v/v), [monomer]:[initiator]:[catalyst]:[ligand] = 200:1:1:1.

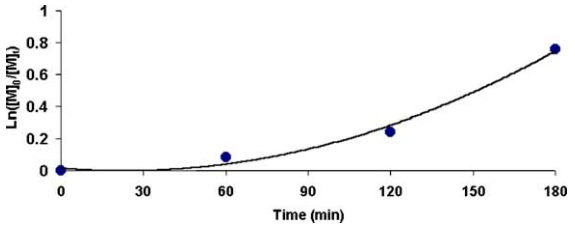


Fig. 7. Kinetic plot of $(\ln[M]_0/[M]_t)$ versus time in solution polymerization of MMA with $(CH_3)_2CBrCO_2C_2H_5$ as the initiator and **3** as the ligand in (33%, v/v) *o*-xylene at 90 °C. [Monomer]:[initiator]:[catalyst:]:[ligand] = 200:1:1:1.

one could have fast initiation, followed by slow deactivation and slow reactivation.

Essentially, once the radical is formed, the iron(III) halide just acts as a conventional chain transfer agent. The last two entries in the table, show that ligand **4** is not at all efficient as an ATRP ligand in comparison with the other ligands. This result agrees well with the results obtained by Xia et al. [26] in their investigations of the effect of linkage length between the two coordination nitrogens in copper-mediated ATRP. Our results indicate that ethylene linkage between the two nitrogens is optimal.

4. Conclusions

This study has shown that atom transfer radical polymerization of methyl methacrylate with activated ethyl-2-bromoisobutyrate ($(CH_3)_2CBrCO_2Et$) as alkyl halide can be efficiently performed using well-defined iron(II) complexes bearing tetradentate nitrogen ligands The solubility of the catalyst can be modified by changing the alkyl substituent on the ligand. The rate of polymerization is reduced when steric hindrance is increased on the ligand, as was seen not only in a decrease in the rate but also an associated increase in the polydispersity of the molecular weight distribution. Thus the steric effects of the ligands determine the catalyst selectivity and the solubility in the reaction mixture (ligands **1**, **2**, and **3**). The ligands with significant steric crowding (ligands **2** and **3**) exhibited low reactivity toward halogen abstraction because it is difficult for them to form the sterically more demanding Fe(III) species. Thus, the reactivity of our ligands in atom transfer radical polymerization was in the order **1** > **2** > **3**. The catalytic system where the ligand contained a cyclic bridge between nitrogens (ligand **4**) was not active in iron-mediated ATRP.

Acknowledgements

The authors wish to thank the Academy of Finland for financial support (decision number 73685). We also would like to thank Mr. Tapio Saarinen for his contribution regarding NMR spectrum.

References

[1] Wang J-S, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[2] Patten TE, Xia J, Abernathy T, Matyjaszewski K. Science 1996;272:866.
[3] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721.
[4] Shipp D, Wang J-L, Matyjaszewski K. Macromolecules 1998;31:8005.
[5] Davis K, Matyjaszewski K. Macromolecules 2000;33:4039.
[6] Qiu J, Matyjaszewski K. Macromolecules 1997;30:5643.
[7] Grimoud T, Matyjaszewski K. Macromolecules 1997;30:2216.
[8] Matyjaszewski K, Jo SM, Paik H-J, Gaynor SG. Macromolecules 1997;30:6398.
[9] De Clerg B, Verpoort F. Macromolecules 2002;35:8943.
[10] Percec V, Barboiu B, Neumann A, Ronda JC, Zhao M. Macromolecules 1996;29:3665.
[11] Granel C, Dubois P, Jerome R, Teyssie P. Macromolecules 1996;29:8576.
[12] Lecomte P, Drapier I, Dubois P, Teyssie P, Jerome R. Macromolecules 1997;30:7631.
[13] Normen J, Moratti S, Slark A, Irvine D, Jackson A. Macromolecules 2002;35:8954.
[14] Ando T, Kamigaito M, Sawamoto M. Macromolecules 1997;30:4507.
[15] Gibson V, O'Reilly R, Wass D, White A, Williams D. Chem Commun 2002:1850.

[16] Matyjaszewski K, Xia J. J Chem Rev 2001;101:2921, and references therein.
[17] Teodorescu M, Gaynor SG, Matyjaszewski K. Macromolecules 2000;33:2335.
[18] Matyjaszewski K, Wei M, Xia J, McDermott NE. Macromolecules 1997;30:8161.
[19] Yan D, Zhu Sh. Polym Prepr 2002;43(2):30.
[20] Ibrahim K, Löfgren B, Seppälä J. Eur Poly J 2003;39:939.
[21] Xia J, Zhang X, Matyjaszewski K. Polym Mater Sci Eng 1999;80:543.
[22] Rieger B, Abu-Surrah AS, Fawzi R, Steiman M. J Organomet Chem 1995;497:73.
[23] Abu-surrah AS, Laine TV, Repo T, Fawzi R, Steiman M, Rieger B. Acta Crystallogr C 1997;53:1458.
[24] Moineau G, Minet M, Dubois P, Teyssie P, Senninger T, Jerome R. Macromolecules 1999;32:27.
[25] Zhu S, Yan D. J Polym Sci: Part A: Polym Chem 2000;38:4308.
[26] Xia J, Zhang X, Matyjaszewski K. Polym Mater Sci Eng 1999;80:453.
[27] Louie J, Grubbs RH. Chem Commun 2000:1479.
[28] Uegaki H, Kotani Y, Kamigaito M, Sawamoto M. Macromolecules 1997;30:2249.
[29] Göbelt B, Matyjaszewski K. Macromol Chem Phys 2000;201:1619.