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An efficient iron-based catalyst bearing *N*-alkyl-2-pyridylmethanimine ligand for atom transfer radical polymerisation

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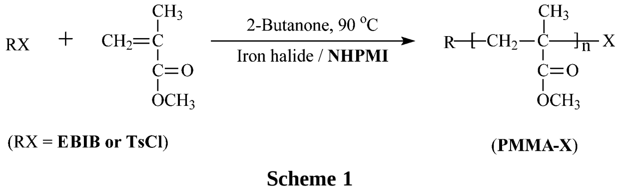
The combination of iron(II) bromide with one equivalent of *N*-(*n*-hexyl)-2-pyridylmethanimine is shown to be an efficient catalyst for the well-controlled atom transfer radical polymerisation of methyl methacrylate.

Atom transfer radical polymerisation (ATRP) is now well established as a highly versatile method for the synthesis of polymers with controlled structures.[1] So far, a number of different metal–ligand combinations have been used to catalyze ATRP, including systems based on Cu,[2] Ru,[3] Pd,[4] Rh,[5] Ni,[6] and Fe.[7] Of these, iron offers particular attractions because of its low cost, low toxicity, and biocompatibility.

Recently, iron-based catalysts based on imine ligands have drawn much attention in ATRP.[7h,k,l,n] Gibson *et al.* used FeCl$_2$ complexes bearing α-diimine ligands for the polymerisations of methyl methacrylate (MMA)[7l] and styrene.[7k] The α-diimine ligands containing alkylimino substituents induced well-controlled ATRP of both MMA and styrene, while those with arylimino substituents gave rise to chain transfer processes.[7k,l] *N*-Alkyl-2-pyridylmethanimines and their derivatives were also utilised in the iron-mediated ATRP systems.[7h,n] Matyjaszewski *et al.* described the use of a diiminopyridine–FeBr$_2$ complex for the ATRP of MMA, but the reaction was not controlled.[7h] Gibson *et al.* applied a series of preformed complexes of FeCl$_2$ with *N*-alkyl-2-pyridylmethanimines (and their derivatives) in the ATRP of both MMA and styrene.[7n] The ATRP of styrene was controlled, while the results from the ATRP of MMA were not satisfactory. The polymerisation of MMA using 2-(*N*-cyclododecylimino)-6-methylpyridine as the ligand provided the optimal results, but the polydispersity indices (PDIs) of the obtained polymers were still quite high (PDI = 1.49–1.64 depending on the initiators used). Besides, the reactions were rather slow (32 h for a full conversion). Therefore, the utilisation of *N*-alkyl-2-pyridylmethanimines in the iron-mediated ATRP of MMA has achieved little success up to now although they are very effective ligands for the copper-mediated ATRP of MMA,[8] styrene,[9] and butyl acrylate.[10] Here we report the well-controlled ATRP of MMA catalyzed by the *in situ* formed complex of FeBr$_2$ with one equivalent of *N*-(*n*-hexyl)-2-pyridylmethanimine (NHPMI)[8a] (Scheme 1) and the significant effect of the molar ratio of iron halide to NHPMI on the polymerisation.

The iron halide/NHPMI-catalyzed polymerisations of MMA were carried out in 2-butanone at 90 °C with a molar ratio of MMA to initiator of 150 and a volume ratio of 2-butanone to MMA of 2.† The homogeneous ATRP of MMA using FeBr$_2$/NHPMI as the catalyst and ethyl 2-bromoisobutyrate (EBIB) as the initiator was performed with [MMA]$_0$/[EBIB]$_0$/[FeBr$_2$]$_0$/[NHPMI]$_0$ = 150/1/1/2. The curved kinetic plot of ln([M]$_0$/[M]) *versus* reaction time (*t*) indicates the presence of radical termination during the reaction (Fig. 1a). The molecular weights of the obtained polymers determined by size exclusion chromatograph (*i.e.*, $M_{\mathrm{n,SEC}}$) firstly decrease and then remain almost constant with monomer conversions (C_{MMA}), and the PDIs of the polymers are high (around 1.5, Fig. 1b). It is known that addition of a certain amount of deactivator (metal salt in its higher oxidation state) to an ATRP system at the beginning of the reaction can reduce radical termination and thus lower PDIs of the polymers.[7f,8c,d] Therefore, 20% of FeCl$_3$ relative to FeBr$_2$ was added into the studied system. The addition of FeCl$_3$ has little influence on the polymerisation rate, but significantly improves the molecular weight control. The $M_{\mathrm{n,SEC}}$ of the polymers start to increase linearly with C_{MMA}, though they are higher than the theoretical values ($M_{\mathrm{n,th}}$). In addition, the PDIs of the polymers are also slightly lower (Fig. 1b).



Scheme 1

We further investigated the effect of the molar ratio of iron halide to NHPMI on the EBIB-initiated ATRP of MMA. The ATRP with ([FeBr$_2$]$_0$ + [FeCl$_3$]$_0$)/[NHPMI]$_0$ = 1 proved to be much better controlled than that with ([FeBr$_2$]$_0$ + [FeCl$_3$]$_0$)/[NHPMI]$_0$ = $\frac{1}{2}$ (Fig. 1). The kinetic plot of ln([M]$_0$/[M]) *versus t* in the former case is linear with a pseudo-first-order rate constant (k_{app}) of 7.0 × 10^{-5} s^{-1}. The $M_{\mathrm{n,SEC}}$ increase linearly with C_{MMA}, and the PDIs of the polymers remain rather low up to high C_{MMA} (1.26 at a C_{MMA} of 84%).

The FeBr$_2$/NHPMI-catalyzed ATRP of MMA was also carried out in dried 2-butanone using *p*-toluenesulfonyl chloride (TsCl) as the initiator. The reaction with [MMA]$_0$/[TsCl]$_0$/[FeBr$_2$]$_0$/[NHPMI]$_0$ = 150/1/1/2 shows a curved kinetic plot of ln([M]$_0$/[M]) *versus t* (Fig. 2a), revealing the occurrence of radical termination.

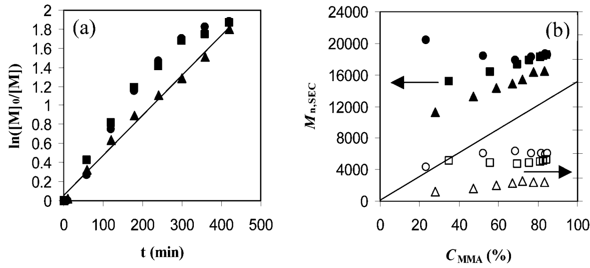


Fig. 1 (a) Kinetic plot of ln([M]$_0$/[M]) *versus t* and (b) dependence of $M_{\mathrm{n,SEC}}$ and PDIs of the polymers on C_{MMA} for the ATRP of MMA at 90 °C. [MMA]$_0$/[EBIB]$_0$/[FeBr$_2$]$_0$/[FeCl$_3$]$_0$/[NHPMI]$_0$ = 150/1/1/0/2 (●), 150/1/1/0.2/2.4 (■), and 150/1/1/0.2/1.2 (▲). MMA/2-butanone = $\frac{1}{2}$ v/v. The line in Fig. 1b (or Fig. 2b) refers to $M_{\mathrm{n,th}}$.

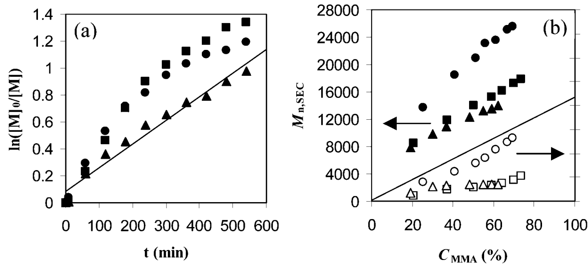


Fig. 2 (a) Kinetic plot of ln([M]$_0$/[M]) *versus t* and (b) dependence of $M_{\mathrm{n,SEC}}$ and PDIs of the polymers on C_{MMA} for the ATRP of MMA at 90 °C. [MMA]$_0$/[TsCl]$_0$/[FeBr$_2$]$_0$/[NHPMI]$_0$ = 150/1/1/2 (●), 150/1/1/1 (■), and 150/1/0.5/0.5 (▲). MMA/2-butanone = $\frac{1}{2}$ v/v.

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Table 1 Redox potentials ($E_{\frac{1}{2}}$) and peak separation ($\triangle E_p$) for complexes

Complex	$[FeBr_2]_0$/ $[NHPMI]_0$	$E_{\frac{1}{2}}$/mV	$\triangle E_p$/mV
1	1 : 1	1130	120
2	1 : 2	1100	180

The $M_{n,SEC}$ of the polymers increase linearly with C_{MMA}, but are much higher than $M_{n,th}$ (Fig. 2b). The PDIs of the polymers increase with C_{MMA} and reach 1.63 at a C_{MMA} of 70%. Addition of iron(III) halide into the system makes the controllability of the reaction even worse. The use of $[FeBr_2]_0/[NHPMI]_0 = 1$ in the studied system again improves the controllability of the reaction. The initiation efficiency ($f = M_{n,th}/M_{n,SEC}$) increases and the PDIs of the obtained polymers decrease significantly (1.31 at a C_{MMA} of 74%). However, the PDIs of the polymers increase with C_{MMA}, suggesting the existence of radical termination. The concentrations of $FeBr_2$ and NHPMI were, therefore, reduced to the half amounts in order to minimize radical termination.[8d] As expected, the polymerisation rate decreases with the decrease of $FeBr_2$ and NHPMI concentrations, and radical termination is minimized, which is demonstrated by the linear kinetic plot ($k_{app} = 3.0 \times 10^{-5}$ s^{-1}, Fig. 2a). The PDIs of the polymers are rather low and remain almost constant throughout the reaction (typically *ca.* 1.24, Fig. 2b).

In order to obtain a better understanding of the differing catalytic behavior of the complexes formed by different molar ratios of $FeBr_2$ to NHPMI, the redox potentials and reversibility of the iron complexes were analysed by cyclic voltammetry (CV).‡ Both complexes were found to have a reversible Fe(II)/Fe(III) redox couple around 1100 mV, and $\triangle E_p$(complex) is 120 and 180 mV for complex **1** and **2**, respectively (Table 1, $\triangle E_p = 280$ mV for ferrocene). This large $\triangle E_p$ difference appears to correlate well with the catalytic activity of the complexes.[7k,n] Besides, the larger steric hindrance of complex **2** to the halogen transfer in ATRP than complex **1** might also be partly responsible for their differing catalytic behavior.

In summary, we have demonstrated that the *in situ* formed complex of $FeBr_2$ with one equivalent of NHPMI is an efficient catalyst for the ATRP of MMA, where fast polymerisation, linear increase of $M_{n,SEC}$ with C_{MMA} and low PDIs of the polymers were obtained. Fine tuning of the complex sterics and electronics as well as further optimisation of reaction conditions would be expected to yield even more active and well-controlled polymerisation systems. Current studies are focused on examining these features and applying this catalytic system in the ATRP of other monomers. For this purpose, automated parallel robot systems will also be used.

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Notes and references

† *Typical polymerisation procedure.* $FeBr_2$ (0.2052 g, 0.951 mmol), $FeCl_3$ (0.0324 g, 0.200 mmol) and NHPMI (0.2209 g, 1.161 mmol) were added to a mixture of MMA (14.2308 g, 142.137 mmol) and 2-butanone (24.2481 g) in a three-neck round-bottom flask (100 mL). The reaction mixture was bubbled with argon for 40 min, and then the flask was immersed into a thermostated oil bath at 90 °C and magnetically stirred for 1 h under argon. The initiator EBIB (0.1905 g, 0.977 mmol) was added slowly (in 2 min) into the system to start the reaction. At timed intervals, an aliquot (1.0 mL) was taken with a degassed syringe and diluted with tetrahydrofuran (THF), then precipitated from a rapidly stirred acidified (5%) methanol solution. Monomer conversions were determined by the gas chromatograph (GC) measurements. Molecular weights and PDIs of the polymers were determined with a Waters size exclusion chromatograph (SEC) equipped with a Waters model 510 pump and a model 410 differential refractometer (40 °C). THF was used as the eluent at a flow rate of 1.0 mL min^{-1}. A set of two linear columns (Mixed-C, Polymer Laboratories, 30 cm, 40 °C) was used. The calibration curve was prepared with polystyrene (PS) standards, and molecular weights were recalculated using the universal calibration principle and Mark–Houwink parameters (PS: $K = 1.14 \times 10^{-4}$ dL g^{-1}, $\alpha = 0.716$; PMMA: $K = 0.944 \times 10^{-4}$ dL g^{-1}, $\alpha = 0.719$).

‡ CV analyses were performed in 2-butanone at room temperature, under nitrogen, using a Ag counter electrode, Pt working electrode, and a Ag/AgCl reference electrode with $[^nBu_4N][PF_6]$ (0.1 M) as an electrolyte (sweep rate: 200 mV s^{-1}). The ferrocene(II)/(III) couple ($E_{\frac{1}{2}} = 450$ mV and $\triangle E_p = 280$ mV) was used as a benchmarked redox couple. The solutions of $FeBr_2$ and NHPMI in dried 2-butanone were bubbled with argon for 40 min and then magnetically stirred at 90 °C for 1 h under argon. The obtained complex solutions were used for the CV measurements.

1 (*a*) K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921; (*b*) M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 2001, **101**, 3689.
2 (*a*) J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614; (*b*) J. S. Wang and K. Matyjaszewski, *Macromolecules*, 1995, **28**, 7901; (*c*) V. Percec and B. Barboiu, *Macromolecules*, 1995, **28**, 7970.
3 M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1995, **28**, 1721.
4 P. Lecomte, I. Drapier, P. Dubois, P. Teyssié and R. Jérôme, *Macromolecules*, 1997, **30**, 7631.
5 G. Moineau, C. Granel, P. Dubois, R. Jérôme and P. Teyssié, *Macromolecules*, 1998, **31**, 542.
6 (*a*) C. Granel, P. Dubois, R. Jérôme and P. Teyssié, *Macromolecules*, 1996, **29**, 8576; (*b*) H. Uegaki, K. Kotani, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1997, **30**, 2249.
7 (*a*) T. Ando, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1997, **30**, 4507; (*b*) K. Matyjaszewski, M. Wei, J. Xia and N. E. McDermott, *Macromolecules*, 1997, **30**, 8161; (*c*) H. Takahashi, T. Ando, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1999, **32**, 3820; (*d*) Y. Kotani, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1999, **32**, 6877; (*e*) M. Teodrescu, S. G. Gaynor and K. Matyjaszewski, *Macromolecules*, 2000, **33**, 2335; (*f*) J. Louis and R. H. Grubbs, *Chem. Commun.*, 2000, 1479; (*g*) Y. Kotani, M. Kamigaito and M. Sawamoto, *Macromolecules*, 2000, **33**, 3543; (*h*) B. Göbelt and K. Matyjaszewski, *Macromol. Chem. Phys.*, 2000, **201**, 1619; (*i*) M. Wakioka, K. Y. Beak, T. Ando, M. Kamigaito and M. Sawamoto, *Macromolecules*, 2002, **35**, 330; (*j*) C. Detrembleur, P. Teyssié and R. Jérôme, *Macromolecules*, 2002, **35**, 1611; (*k*) V. C. Gibson, R. K. O'Reilly, W. Reed, D. F. Wass, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2002, 1850; (*l*) V. C. Gibson, R. K. O'Reilly, D. F. Wass, A. J. P. White and D. J. Williams, *Macromolecules*, 2003, **36**, 2591; (*m*) R. K. O'Reilly, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2003, **125**, 8450; (*n*) V. C. Gibson, R. K. O'Reilly, D. F. Wass, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2003, 2824.
8 (*a*) D. M. Haddleton, C. B. Jasieczek, M. J. Hannon and A. J. Shooter, *Macromolecules*, 1997, **30**, 2190; (*b*) D. M. Haddleton, M. C. Crossman, B. H. Dana, D. J. Duncalf, A. M. Heming, D. Kukulj and A. J. Shooter, *Macromolecules*, 1999, **32**, 2110; (*c*) H. Zhang, B. Klumperman, W. Ming, H. Fischer and R. van der Linde, *Macromolecules*, 2001, **34**, 6169; (*d*) H. Zhang, B. Klumperman and R. van der Linde, *Macromolecules*, 2002, **35**, 2261.
9 (*a*) A. J. Amass, C. A. Wyres, E. Colclough and I. Marcia Hohn, *Polymer*, 2000, **41**, 1697; (*b*) S. Perrier, D. Berthier, I. Willoughby, D. BattCoutrot and D. M. Haddleton, *Macromolecules*, 2002, **35**, 2941.
10 H. Zhang and R. van der Linde, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 3549.