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Atom transfer polymerisation of methyl methacrylate: use of chiral aryl/alkyl pyridylmethanimine ligands; with copper(I) bromide and as structurally characterised chiral copper(I) complexes

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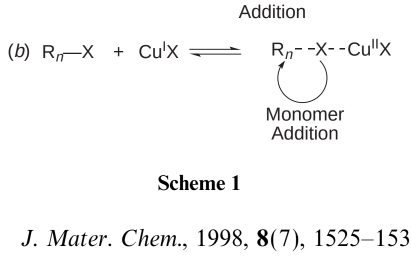
The use of *chiral* catalysts in the living radical polymerisation of methyl methacrylate *via* atom transfer polymerisation (ATP) has been investigated in an effort to control the stereochemistry of the polymer backbone. Two enantiomerically pure *chiral* catalysts have been prepared and used in the ATP of methyl methacrylate: the structurally characterised complex, bis[*N*-(1-phenylethyl)-2-pyridylmethanimine]copper(I) tetrafluoroborate, $[Cu(C_{14}H_{14}N_2)_2][BF_4]$, and the reaction product of copper(I) bromide with *N*-(1-cyclohexylethyl)-2-pyridylmethanimine, $[Cu(C_{14}H_{20}N_2)_2][Br]$. Both catalysts were found to be suitable for the ATP of methyl methacrylate in conjunction with either ethyl 2-bromo-2-methylpropanoate in xylene at 90 °C or 4-methoxybenzenesulfonyl chloride in diphenyl ether at 90 °C. The system yields polymer of relatively narrow polydispersity; however, the use of these chiral catalysts did not significantly affect the stereochemistry of the polymer backbone. This may be due to the chiral centre being too distant from the propagating site to exert any influence over the monomer addition step, or that the reaction proceeds *via* a completely free-radical mechanism. This is, however, the first time a discrete, structurally characterised copper complex has been used as an effective ATP catalyst. The bond lengths of the complexed ligand indicate the oxidation state of the copper to be +1 in the complex.

Controlled polymerisation of acrylic and methacrylic monomers is of continuing interest,[1] providing the potential for a wide range of novel materials from currently available monomers. This has been the objective of many research programs which have produced a number of different systems to achieve this aim, *viz. living/pseudo-living* polymerisation of methacrylates.[1] A major challenge is to avoid complications arising from side reaction with the ester group, or deprotonation of the polymer backbone in the case of poly(acrylics). These secondary reactions which destroy the living nature of the polymerisations have proven problematic as most developments have centred around anionic or anionic-type polymerisations. For example, group transfer polymerisation (GTP) has been perhaps the most widely studied system in recent years, and utilises silyl ketene acetals in conjunction with nucleophilic catalysts to control polymerisation, resulting in polymers with very narrow polydispersity indexes (PDI) in tetrahydrofuran at temperatures up to 80 °C.[2,3] GTP, as with most other systems which rely on anionic type propagation, is highly sensitive to protic impurities necessitating the use of rigorously dried and purified monomers and solvents. It is for this reason that we have been focusing on living free-radical polymerisation, which should be tolerant to many different impurities and functional monomers/solvents rendering the system more commercially viable. Although stable free radical mediated polymerisation using TEMPO and related nitroxide stable organic radicals is relatively successful for styrene and substituted styrene,[4,5] it is less so for acrylics and methacrylics. Also it is relatively easy to achieve living polymerisation of styrene by conventional anionic polymerisation, which is the basis for commercially available styrene-butadiene block copolymers. We are particularly interested in achieving controlled polymerisation of alkyl methacrylates and methacrylates containing functional groups in the ester side chain which can be used to synthesise polymers with a wide range of properties for differing applications. The use of transition metal mediated polymerisation is very attractive for this type of monomer.

Atom transfer polymerisation (ATP) has emerged as an effective, living, transition metal mediated polymerisation for a wide range of vinyl monomers; ATP has been derived from atom transfer chemistry developed for a range of organic transformations in more conventional organic synthesis,[6–8] in particular atom transfer cyclisation.[9] This was first demonstrated, almost simultaneously, by Sawamoto and Matyjaszewski. Sawamoto described the use of $RuCl_2(PPh_3)_3$ in conjunction with strong Lewis acids for the living polymerisation of methyl methacrylate.[10–12] In a related system, Matyjaszewski has been investigating the use of copper(I) halides with bipyridine and 4,4′-dialkyl substituted bipyridine ligands for the living polymerisation of styrene, methacrylates and acrylates.[13–17] Teyssie has used a well characterised Ni^{II} compound for the living polymerisation of alkyl methacrylates.[18] In all of these systems, polymerisation is thought to be mediated by a formal M_t^{n}/M_t^{n+1} redox couple and initiated by homolysis, or at least partial homolysis, of an alkyl halide [Scheme 1(*a*)]. Percec has extended the range of initiators to include sulfonyl halides which, due to the ease of homolysis of the sulfur–halogen bond, give a fast rate of initiation relative to propagation for virtually all monomers, and are so called '*universal initiators*' for ATP.[19–21]

We have been concentrating on a copper based ATP process[22–24] which uses Schiff bases of type **1** as electron accepting ligands on the metal.[25] These ligands stabilise formal Cu^I, relative to Cu^{II}, and promote effective ATP. Ligands based on



Scheme 1

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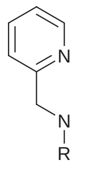
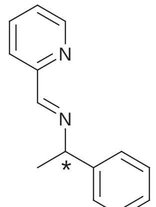


1 R = *n*-alkyl



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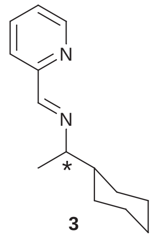

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the general structure **1** are extremely easy to synthesize by a simple condensation of pyridine-2-carbaldehyde with an appropriate primary amine, the reaction proceeding efficiently and quickly at ambient temperature and yielding the products as yellow oils which are readily purified by distillation. The wide variety of commercially available primary amines gives a large family of potential ligands and allows control over catalyst properties such as solubility in organic media and the Cu^I/Cu^{II} redox potential.

ATP has already been demonstrated to give excellent control over molecular weight and polydispersity. In addition it would be desirable to be able to control the stereochemistry of the polymer backbone. The stereochemistry of the polymer can have significant effects on materials properties such as the glass transition temperature (T_g), as well as other mechanical properties. Previously we have suggested that ATP of MMA utilising a Cu^I catalyst with ligands based on **1** may not proceed *via* a free-radical mechanism, and we have postulated a concerted propagation mechanism as being a possibility where the halogen is not fully abstracted from the propagating polymer[24] [Scheme 1(*b*)]. Indeed, Teyssie has suggested, in his studies of the ATP of MMA using a Ni^{II} complex, that propagation may occur *via* a coordinate mechanism, whereby the halide from the initiator remains partially bonded to both the growing polymer chain and the metal centre.[18] If the catalyst is bound to the growing polymer chain, or even in the vicinity as a '*radical cage complex*' it may be possible to influence the stereochemistry of the polymer backbone by the use of chiral metal catalysts, produced from enantiomerically pure, chiral Schiff base ligands. It is noted that the stereochemistry of all poly(methyl methacrylate) produced *via* ATP to date (including Cu^I, Ru^{II} and Ni^{II} systems) has been reported to be consistent with free radical polymerisation, *i.e.* described by Bernoullian statistics with the persistence ratio close to unity.

The work outlined in this paper investigates the possibility of using the chiral Schiff bases **2** and **3** with Cu^I halides as ATP catalysts. Results for both the *R* and *S* enantiomers of **2** and **3**, as well as for a racemic mixture in the case of **2**, are reported. In all of the studies of copper(I) mediated ATP published to date, the active copper complex has been formed *in situ* by addition of excess ligand to a suspension of Cu^I halide in the reaction solution. We report the use of well defined, fully characterised copper(I) compounds (arising from **2**) which were isolated by recrystallisation, characterised and subsequently used as discrete compounds in the polymerisation reaction.

Experimental

General

Methyl methacrylate (Aldrich, 99%) was purified by passing through a column of activated basic alumina to remove inhibitor. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[26] Xylene (Fisons, 99.8%), ethyl 2-bromo-2-methylpropanoate (Aldrich, 98%), 1-phenylethylamine (Aldrich, 98%), 1-cyclohexylethylamine (Aldrich, 98%) and 4-methoxybenzenesulfonyl chloride (Avocado, 98%) were used as received.

(*R*)-,(*S*)- and (±)-*N*-(1-Phenylethyl)-2-pyridylmethanimine [(*R*)-2,(*S*)-2 and (±)-2]

A typical preparation was carried out as follows: (*R*)-1-phenylethylamine (2.5 g, 0.02 mol) was added dropwise to a stirred solution of pyridine-2-carbaldehyde (2.2 g, 0.02 mol) in Et_2O (*ca.* 20 ml). To the reaction mixture was added $MgSO_4$ (1–2 g). The reaction was stirred at room temperature for 4 h after which time the solvent was removed *in vacuo* yielding (*R*)-*N*-(1-phenylethyl)-2-pyridylmethanimine (3.8 g, 90%) as a clear, slightly yellow, oil, bp 107 °C at 0.5 mmHg; δ_H(250 MHz, 298 K, $CDCl_3$) 8.50 (d, 1H, Py-H), 8.36 (s, 1H, C*H*=N), 7.96 (d, 1H, Py-H), 7.57 (t, 1H, Py-H), 7.20 (m, 6H, Py-H/Ph-H), 4.51 [q, 1H, Ph(Me)C*H*], 1.50 (d, 3H, Me); δ_C(250 MHz, 298 K, $CDCl_3$) 159.6 (*C*H=N), 153.9, 148.4, 135.6, 127.7, 125.9 (Py), 143.5, 126.1, 123.2, 120.7 (Ph), 68.7 (*C*H_3), 23.8 [*C*H(Me)Ph]; ν_{max}(neat)/cm^{-1} 1646s, 1587s, 1567s (C=N); $[\alpha]_D$ −1.342[(*R*)-**2**], +1.321[(*S*)-**2**], 0.000 [(±)-**2**] (*c* 1, acetone).

(*R*)- and (*S*)-*N*-(1-Cyclohexylethyl-2-pyridylmethanimine [(*R*)-3 and (*S*)-3]

A typical preparation was carried out as follows: (*R*)-1-cyclohexylethylamine (6.5 g, 0.051 mol) was added dropwise to a stirred solution of pyridine-2-carbaldehyde (5.47 g, 0.051 mol) in Et_2O (*ca.* 30 ml). To the reaction mixture was added $MgSO_4$ (1–2 g). The reaction was stirred at room temperature for 4 h after which time the solvent was removed *in vacuo* yielding (*R*)-*N*-(1-cyclohexylethyl-2-pyridylmethanimine (9.4 g, 85%) as a clear, slightly yellow, oil, bp 96 °C at 0.5 mmHg; δ_H(250 MHz, 298 K, $CDCl_3$) 8.48 (d, 1H, Py-H), 8.17 (s, 1H, C*H*=N), 7.85 (d, 1H, Py-H), 7.54 (t, 1H, Py-H), 7.11 (m, 1H, Py-H), 2.97 [q, 1H, Cy(Me)C*H*], 1.65 (m, 4H, Cy-H), 1.36 (m, 1H, Cy-H), 1.09 [s, 3H, C(H)(Cy)CH_3], 1.07 (m, 4H, Cy-H), 0.81 (m, 4H, Cy-H); δ_C(250 MHz, 298 K, $CDCl_3$) 159.4 (*C*H=N), 154.7, 149.0, 136.1, 124.1, 121.0 (Py), 71.4 (*C*H_3), 43.4, 29.6, 26.0, 19.5 (Cy), 26.1 [*C*H(Me)Cy]; ν_{max}(neat)/cm^{-1} 1647s, 1588s, 1568s (C=N); $[\alpha]_D$ −2.003 [(*R*)-**3**], +2.022 [(*S*)-**3**] (*c* 1, acetone).

(*R*,*R*)-, (*S*,*S*)- and (±)-Bis[*N*-(1-phenylethyl)-2-pyridylmethanimine)copper(I) tetrafluoroborate [$Cu(C_{14}H_{14}N_2)_2$][BF_4] [(*R*)-4, (*S*)-4 and (±)-4]

[$Cu(MeCN)_4$][BF_4] was prepared by the method of Kubas.[27] A typical preparation was carried out as follows: to [$Cu(MeCN)_4$][BF_4] (2.0 g, 6.47 mmol) in MeOH (35 ml) was added (*R*)-*N*-(1-phenylethyl-2-pyridylmethanimine, (*R*)-**2** (2.7 g, 12.94 mmol). The reaction immediately became a deep red–brown colour and was stirred for 4 h. After this time the solution was filtered and concentrated to *ca.* 20 ml and then allowed to cool slowly to −40 °C, whereupon red crystals of [$Cu(C_{14}H_{14}N_2)_2$][BF_4] formed in 70% yield (2.57 g), mp 96–99 °C; δ_H(250 MHz, 298 K, [$^2H_6$]acetone) 8.85 (s, 1H, C*H*=N), 7.96 (m, 1H, Py-H), 7.86 (m, 1H, Py-H), 7.42 (br, 1H, Py-H), 7.12, 6.99 (br, 5H, Ph-H), 4.91 [br, 1H, Ph(Me)C*H*], 1.55 (br, 3H, Me); δ_C(250 MHz, 298 K, [$^2H_6$]acetone) 161.04 (*C*H=N), 151.89, 149.98, 139.16, 125.94, 120.36 (Py), 142.98, 129.4, 127.1, 115.72 (Ph), 67.98 [*C*(CH_3)PhH], 38.47 [C*C*H_3(Ph)H]; ν_{max}(Nujol)/cm^{-1} 1612m, 1586s (C=N).

Crystal structure determinations

A suitable crystal of (*R*)-**4** was quickly glued to a quartz fiber, coated in dry Nujol and cooled in the cold nitrogen gas stream of the diffractometer. The structure was solved by direct methods. Anisotropic thermal parameters were used for all non-H atoms whilst hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters (U = 0.08 Å^3), riding on the supporting atom. The structure solutions were carried out using SHELXTL[28] version 5.0 software on a

Silicon Graphics Indy workstation, refinements were carried out using SHELXTL[29] software, minimising on the weighted *R* factor *wR*2.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/96.

Typical polymerisation procedures

Ethyl 2-bromo-2-methylpropanoate initiator in xylene solvent. Compound **4** (0.25 g, 4.65×10^{-4} mol)] [or Cu^{I}Br (0.066 g, 4.65×10^{-4} mol) and **3** (0.30 g, 1.40×10^{-3} mol)] was placed into a nitrogen filled flask and subjected to three vacuum/nitrogen fill cycles. An aliquot of MMA (5.0 ml 4.65×10^{-2} mol) together with xylene solvent (5.0 ml) was added to the flask, which was then placed into an oil bath at 90 °C with stirring. To this mixture was added **6** (0.09 g, 4.65×10^{-4} mol) to initiate polymerisation. Periodically, 1–2 ml samples were removed for conversion and molecular weight analysis.

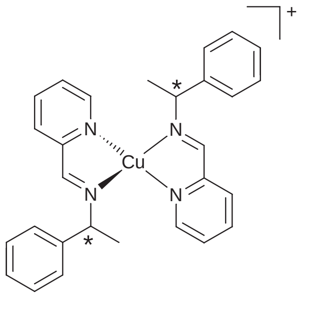
4-Methoxybenzenesulfonyl chloride initiator in Ph$_2$O solvent. The procedure detailed above was followed, except that Ph$_2$O (5.0 ml) was substituted for xylene and **7** (0.095 g, 4.65×10^{-4} mol) was used as the initiator.

Polymer analysis. Polymer conversion was determined by gravimetry for polymerisations performed in xylene and by ^{1}H NMR spectroscopy in the case of reactions performed in Ph$_2$O. At the end of the reaction the polymer was precipitated into light petroleum (bp 40–60 °C) and dried in a vacuum oven at 70 °C for 8 h, for stereochemical analysis by ^{13}C NMR spectroscopy. Molecular weight distributions were measured using size exclusion chromatography (SEC) on a system equipped with a guard column, one 30 cm mixed E column (Polymer Laboratories) and a differential refractive index detector, using tetrahydrofuran at 1 ml min^{-1} as the eluent. Poly(methyl methacrylate) standards in the range (6×10^4 to 200 g mol^{-1}) were used to calibrate the SEC analysis. Quantitative ^{13}C NMR spectra were obtained on a Bruker AM400, using a Bruker inverse gated acquisition routine, for the analysis of polymer microstructure.

Results and Discussion

Polymerisations

The polymerisation of MMA with the three forms of **4** [(*i.e.* (*R*)-**4**, (*S*)-**4** and (±)-**4**] and with **6** as initiator in xylene at 90 °C gave reproducible number average molecular masses, M_n, with PDI between 1.4 and 1.6 (Table 1). In each case the first order rate plot (Fig. 1) shows a linear slope, indicating the number of active species remains constant throughout the reaction and that the rate of polymerisation is independent of the stereochemistry of the catalyst. Each experiment exhibited an apparent induction period of approximately 35 min. These induction periods have been observed previously in similar systems and are ascribed to the time required to establish the equilibrium shown in Scheme 1. It should be noted that the apparent induction time may actually be S-shaped due to a slowly increasing rate of reaction during the time taken to establish the equilibrium. Although M_n increases with conversion with all three catalysts, as expected for a living polymerisation, the actual values are consistently higher than expected for 100% initiator efficiency (Fig. 2). In addition, the PDI is relatively broad (1.4–1.6 as compared to 1.2 for similar systems[23]). Together with the high M_n, this suggests inefficient initiation and/or side reactions such as termination in the polymerisation.



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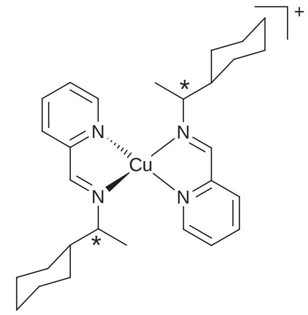

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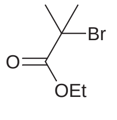

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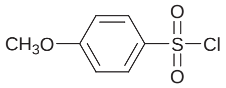

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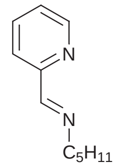

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We have previously observed that the substituents on the Schiff base ligand play an important role in determining the position of the equilibrium between dormant and active polymer chains, which is central to the reaction mechanism[30] (Scheme 1). The 1-phenylethyl substituent used in this case is more sterically demanding than an *n*-alkyl group and this may be the reason for the poor molecular weight control observed when the reaction is performed in xylene. The steric requirements of the ligands are clearly an important factor in the relative stabilities of Cu^{I} and Cu^{II}, as are electronic factors.

When the initiator is changed to 4-methoxybenzenesulfonyl chloride **7** with diphenyl ether as solvent, linear first order rate plots with an apparent induction period of approximately 30 min are obtained (Fig. 3). The rate of reaction is again independent of the catalyst stereochemistry. M_n increases with conversion and shows much better agreement with that expected for 100% initiator efficiency (Fig. 4) compared with the previous case. Thus, the initiator efficiency is higher with **7** than **6**. Also, the PDIs are much narrower in all cases (*ca.* 1.2) and PDI narrows as conversion increases (Table 2). Both of the results are consistent with Percec's[20] suggestion that the rate of initiation of MMA using **7** is fast relative to the rate of propagation which results in narrower PDIs.

The rate of reaction using **7** in diphenyl ether is slightly lower (*ca.* 30%) than that using **6** in xylene (Table 3). This difference in rate is most likely due to the effect of the solvent on the position of the equilibrium shown in Scheme 1, resulting in a different concentration of active species and hence a change in rate. Diphenyl ether may act as a weakly coordinating solvent which will naturally affect the nature and/or rate of formation of the active copper species. There may also be a small difference due to the different initiators used. A lower concentration of active species would result in a lower rate of termination due to normal radical–radical reactions and this, coupled with the faster rate of initiation[20] from **7**, results in better molecular weight control.

The polymerisation of MMA in xylene, mediated by copper(I) catalysts made *in situ* by mixing Cu^{I}Br and (*R*)-**3** or (*S*)-**3** [resulting in the catalyst (*R*)-**S** or (*S*)-**5**] and using **6** as the initiator again gave reproducible rates of polymerisation (Fig. 5). The rate of polymerisation is independent of the catalyst stereochemistry and the first order kinetic plot is linear with an apparent 30 min induction period (Fig. 5). M_n increases linearly with conversion (Fig. 6), but is slightly higher than the theoretical M_n, similar to the behaviour seen with **4**. The rate of polymerisation is slightly slower than with **4** (Table 3),

Table 1 Experimental results for the polymerisation of MMA using ATP with (*R*)-**4**, (*S*)-**4** and (±)-**4** and ethyl 2-bromo-2-methylpropanoate initiator **6** in xylene at 90 °C

	(*R*)-4			(*S*)-4			(±)-4		
t/min	conversion	M_n	PDI	conversion	M_n	PDI	conversion	M_n	PDI
60	0.051	3200	1.40	0.060	4030	1.42	0.056	2290	1.38
120	0.152	4030	1.41	0.179	4780	1.47	0.180	3250	1.38
180	0.242	4310	1.46	0.249	5010	1.65	0.250	4340	1.63
240	0.331	4510	1.52	0.333	5420	1.54	0.370	5320	1.51
300	0.408	5420	1.42	0.412	6200	1.46			
360	0.505	6430	1.48	0.503	6570	1.44			

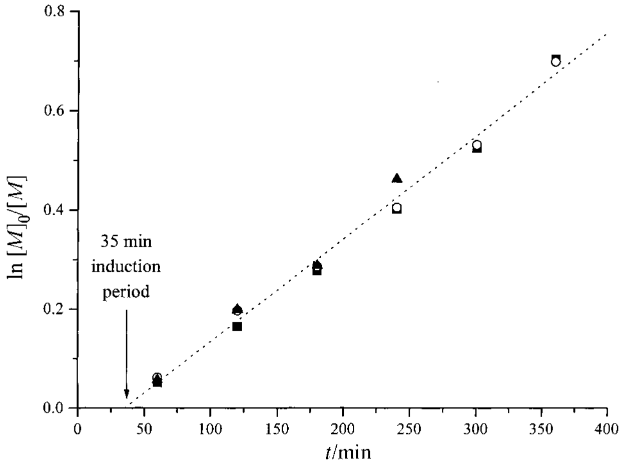

Fig. 1 First order rate plot for the polymerisation of MMA by ATP using (■) (*R*)-**4**, (○) (*S*)-**4** and (▲) (±)-**4** catalysts at 90 °C in xylene using **6** as an initiator

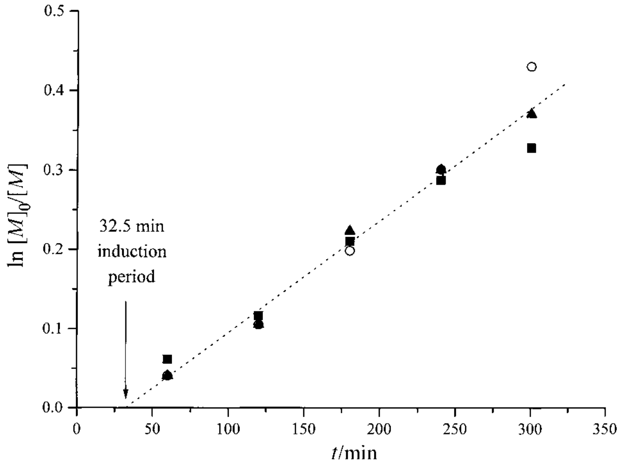

Fig. 3 First order rate plot for the polymerisation of MMA by ATP using (■) (*R*)-**4**, (○) (*S*)-**4** and (▲) (±)-**4** catalysts at 90 °C in diphenyl ether using **7** as initiator

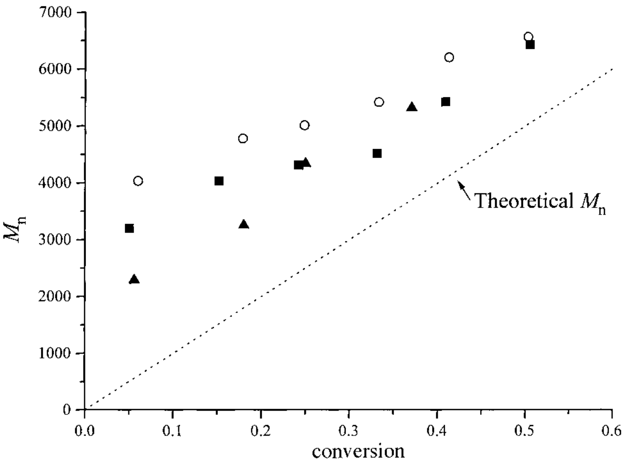

Fig. 2 Dependence of molecular weight on conversion for the polymerisation of MMA by ATP using (■) (*R*)-**4**, (○) (*S*)-**4** and (▲) (±)-**4** catalysts at 90 °C in xylene using **6** as initiator

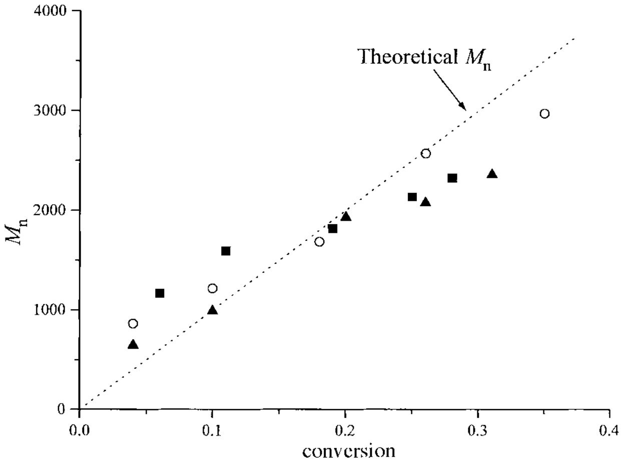

Fig. 4 Dependence of molecular weight on conversion for the polymerisation of MMA by ATP using (■) (*R*)-**4**, (○) (*S*)-**4** and (▲) (±)-**4** catalysts at 90 °C in diphenyl ether using **7** as an initiator

however the PDI is narrower (Table 4). When **7** is used as the initiator in diphenyl ether solvent a broadening of PDI is observed at longer reaction times which may to be due to termination reactions. The rate of reaction is significantly lower than in the other systems and may suggest that the equilibrium shown in Scheme 1 is not positioned for effective ATP. The first order rate plot shows that the rate of reaction is unaffected by the stereochemistry of the catalyst (Fig. 7). Again M_n increases with conversion as would be expected for a controlled polymerisation (Fig. 8). A difference in the polymerisations mediated by **4** and **5** is that the counter ion to the copper is BF_4^- and Br^-, respectively. This may influence the polymerisation reaction since the Br^- may coordinate to the copper complex, whereas the BF_4^- is non coordinating.

Polymer microstructure

The stereochemistry of polymers from all polymerisations was determined by analysis of ^{13}C NMR spectra (triad region, 44–46 ppm, corresponding to the backbone quaternary carbon), according to the assignment of Peat and Reynolds.[31,32] Table 8 shows the triad fraction, diad fraction and persistence ratio ρ [eqn. (1)] of PMMA prepared by ATP with (*R*)-**4**, (*S*)-**4**, (±)-**4**, (*R*)-**5**, (*S*)-**5** and a non-chiral ATP ligand, and for conventional free-radical polymerisation. The stereoregularity is similar in each case, indicating that the use of these chiral Schiff base ligands has no significant influence on the stereochemistry of monomer addition. The lack of stereochemical control can be explained in several ways: (i) the chiral centre on the ligand may be too far away from the monomer addition

Table 2 Experimental results for the polymerisation of MMA using ATP with (*R*)-**4**, (*S*)-**4** and (±)-**4** and 4-methoxybenzenesulfonyl chloride **7** as initiator in Ph_2O at 90 °C

	(*R*)-**4**			(*S*)-**4**			(±)-**4**		
t/min	conversion	M_n	PDI	conversion	M_n	PDI	conversion	M_n	PDI
60	0.06	1170	1.36	0.04	860	1.36	0.04	640	1.43
120	0.11	1590	1.30	0.10	1220	1.25	0.10	990	1.37
180	0.19	1820	1.27	0.18	1690	1.20	0.20	1930	1.27
240	0.25	2130	1.26	0.26	2570	1.21	0.26	2070	1.16
300	0.28	2320	1.21	0.35	2970	1.22	0.31	2360	1.17

Table 3 Comparison of the slopes from first order rate plots of different systems

	$k_p[R^\cdot]/s^{-1}$	
catalyst	**6**	**7**
(*R*)-**4**, (*S*)-**4**, (±)-**4**	3.46×10^{-5}	2.35×10^{-5}
(*R*)-**5**, (*S*)-**5**	2.37×10^{-5}	0.52×10^{-5}

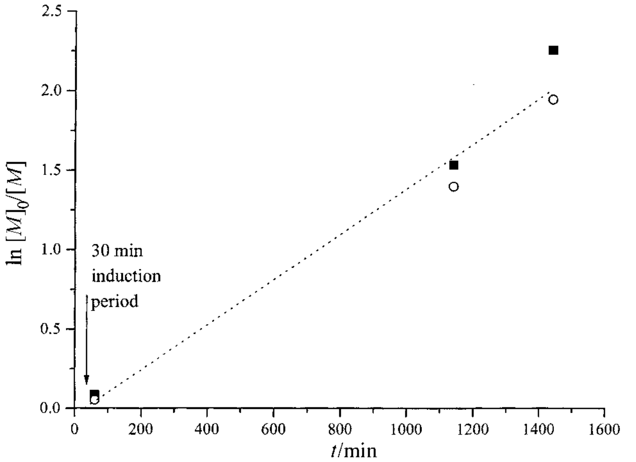

Fig. 5 First order rate plot for the polymerisation of MMA by ATP using (■) (*R*)-**5** and (○) (*S*)-**5** catalysts at 90 °C in xylene using **6** as an initiator

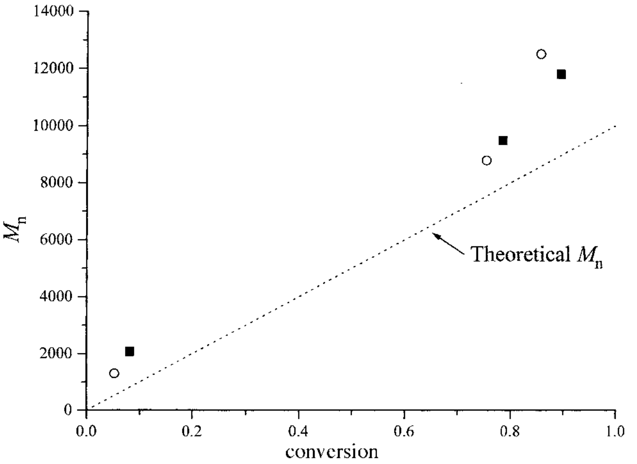

Fig. 6 Dependence of molecular weight on conversion for the polymerisation of MMA by ATP using (■) (*R*)-**5** and (○) (*S*)-**5** catalysts at 90 °C in xylene using **6** as initiator

site to play a role; (ii) the catalyst may not be rigid enough to exert significant stereocontrol on the growing polymer chain since the chirality is in a very flexible ligand (also the complexed ligand is in dynamic equilibrium with the ligand in solution[30]); (iii) the ATP reaction may be purely free-radical and so the catalyst would play no part in the monomer addition step. We anticipate that a more strongly complexed and rigid chiral Schiff base ligand may be able to provide some degree of stereocontrol in ATP and this is currently under study in our laboratory.

Table 4 Experimental results for the polymerisation of MMA using ATP with (*R*)-**5** and (*S*)-**5** and ethyl 2-bromo-2-methylpropanoate initiator **6** in xylene at 90 °C

	(*R*)-**5**			(*S*)-**5**		
t/min	conversion	M_n	PDI	conversion	M_n	PDI
60	0.081	2070	1.15	0.052	1300	1.13
1140	0.784	9480	1.42	0.753	8780	1.44
1440	0.895	11800	1.31	0.857	12500	1.37

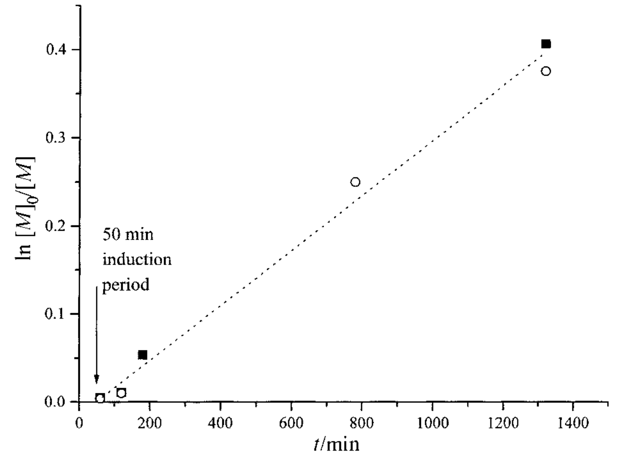

Fig. 7 First order rate plot for the polymerisation of MMA by ATP using (■) (*R*)-**5** and (○) (*S*)-**5** catalysts at 90 °C in diphenyl ether using **7** as initiator

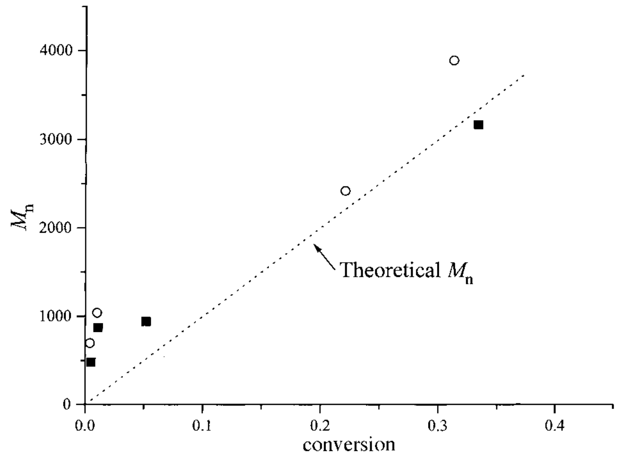

Fig. 8 Dependence of molecular weight on conversion for the polymerisation of MMA by ATP using (■) (*R*)-**5** and (○) (*S*)-**5** catalysts at 90 °C in diphenyl ether using **7** as an initiator

$$\rho = 2(m)(r)/(mr) \quad (1)$$

Table 5 Experimental results for the polymerisation of MMA using ATP with (*R*)-**5** and (*S*)-**5** and 4-methoxybenzenesulfonyl chloride **7** as initiator in Ph_2O at 90 °C

	(*R*)-**5**			(*S*)-**5**		
t/min	conversion	M_n	PDI	conversion	M_n	PDI
60	0.005	484	1.29	0.004	698	1.16
120	0.011	875	1.24	0.01	1040	1.23
180	0.052	943	1.23	—	—	—
780	—	—	—	0.221	2420	1.41
1320	0.334	3170	1.53	0.313	3890	1.66

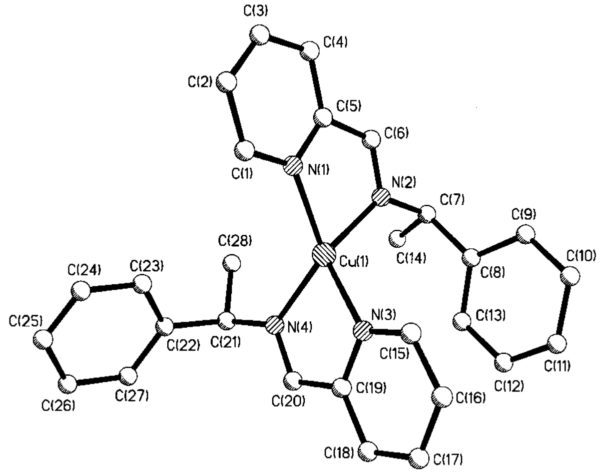

Fig. 9 Crystal structure of the ATP catalyst (*R*)-**4** used in polymerisation studies. The BF_4^- counter ion is omitted for clarity.

Table 7 Summarised crystallographic data for (*R*)-**4**

Crystal parameters	
Formula	$C_{56}H_{56}Cu_2B_2F_8N_8$
M	1141.79
Crystal system	Tetragonal
Space group	*P*4(3)
a/Å	16.9382(4)
b/Å	16.9382(4)
c/Å	19.5734(5)
α(°)	90
β(°)	90
γ(°)	90
reflections	8192
U/Å^3	5615.7(2)
Z	4
dimensions /mm	0.4 × 0.4 × 0.3
D_c/g cm^{-3}	1.350
μ(Mo-Kα/mm^{-1}	0.828
T/K	180
Data collection[a]	
Data collected *h*	−17 to 21
k	−22 to 22
l	−26 to 20
total reflections	34133
independent reflections	12021
observed reflections [$F_o \geq 4\sigma(F_o)$]	6965
θ range (°)	1.20 to 28.58
F(000)	2352
Refinement	
R[b]	0.0680
*wR*2[c]	0.1999
S	0.914
Δ/e Å^{-3} (max, min)[d]	1.062, −0.340
T(max, min)[e]	1.000, 0.7479
Flack parameter	0.03(2)
weighting scheme *a,b*[f]	0.087, 12.428

[a] Data collected on a Siemens 3 circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). [b] $R = \Sigma|F_o - F_c|\Sigma F_o$ [for $F_o \geq 4\sigma(F_o)$]. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ for all data. [d] Peaks of unassigned residual electron density. [e] By SADABS. [f] $w^{-1} = \sigma^2(F_o^2) + aP + bP$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$, where $\max(F_o^2,0)$ indicates that the larger of F_o^2 or 0 is taken, *a* and *b* are values set by the program.

Crystal structure discussion

Diazobutadiene (DAB) ligands have been shown to stabilise low formal oxidation states of the transition metals.[33] The pyridylmethanimine ligands **2** and **3** used in this work have similar electronic characteristics to DAB type ligands, with bipyridine based ligands also thought to be similar. In general, it has been assumed in ATP that the added catalyst contains copper with a formal oxidation number of +1 since it is produced from the complexation of Cu^I and neutral ligands; however, this may be an oversimplification. Recent studies of complexes of ytterbium and *tert*-butyldiazabutadiene (Bu^tDAB) have shown that when zero valent Yb^0 is ligated by three Bu^tDAB ligands, although the overall complex is neutral, the formal oxidation state of the Yb metal centre is +3, with each Bu^tDAB ligand having a formal charge of −1, $Yb^{III}(Bu^tDAB^-)_3$.[34] This difference in the behaviour of DAB ligands, on the one hand stabilising low oxidation states and on the other causing one electron oxidation of the metal by the ligand, prompted us to investigate the actual oxidation state of copper complexes used in this work by examination of the structure of the complex using X-ray crystallography.

The crystal structure of (*R*)-**4** was determined and it was

Table 6 Comparison of fractions of diads and persistence ratio of poly(MMA) prepared under different conditions

		stereochemistry[b]					
initiator[a]	catalyst	*mm*	*mr*	*rr*	*m*	*r*	ρ
6	(*R*)-**4**	0.0315	0.362	0.607	0.212	0.788	0.925
6	(*S*)-**4**	0.0349	0.367	0.598	0.219	0.781	0.930
6	(±)-**4**	0.0357	0.374	0.590	0.223	0.777	0.926
7	(*R*)-**4**	0.0256	0.378	0.597	0.214	0.786	0.892
7	(*S*)-**4**	0.0322	0.372	0.596	0.218	0.782	0.917
7	(±)-**4**	0.0337	0.367	0.600	0.217	0.783	0.927
6	(*R*)-**5**	0.0440	0.385	0.572	0.236	0.764	0.939
6	(*S*)-**5**	0.0354	0.373	0.592	0.222	0.778	0.926
7	(*R*)-**5**	0.0269	0.381	0.593	0.217	0.783	0.893
7	(*S*)-**5**	0.0310	0.407	0.562	0.235	0.766	0.882
6	**8**[c]	2.77	34.8	62.4	0.202	0.798	0.925
AIBN[d]	—	4.82	36.5	58.7	0.231	0.769	0.973

[a] **6**, reaction in xylene; **7**, reaction in diphenyl ether; AIBN = 2,2′-azoisobutyronitrile, reaction in toluene. [b] *mm* = isotactic triads, *mr* = atactic triads, *rr* = syndiotactic triads, *m* = meso diads, *r* = racemic diads. [c] ATP with nonchiral catalyst, Cu^IBr and *N*-*n*-pentyl-2-pyridylmethanimine ligand **8**. The ratio of MMA : Cu^IBr : *N*-*n*-pentyl-2-pyridylmethanimine: ethyl 2-bromo-2-methylpropanoate was 100 : 1 : 2 : 1, reaction temperature = 90 °C. [d] Conventional free-radical polymerisation: 25% w/w MMA in xylene, [AIBN] = 0.027 mol l^{-1}, 90 °C, precipitated from MeOH, M_n = 14600, PDI = 1.74.

Table 8 Comparison of average bond length and angle data for $[Cu^{I}(L)_2]^+$ complexes

ligand	counter ion	bond length/Å				angle (°)		
		$C-N_{acyclic}$	$C-N_{cyclic}$	C—C	Cu—N	N—Cu—N	dihedral	reference
N-(1-phenylethyl)-2-pyridylmethanimine (*R*)-**4**[a,b]	BF_4^-	1.282	1.341	1.457	2.040	81.8	90.3	this work
		1.273	1.370	1.456	2.030	82.3	94.9	
N-*tert*-butyl-2-pyridylmethanimine	BF_4^-	1.270(4)	1.349(4)	1.467(5)	2.035	81.89(10)	81.9	37
		1.263(4)	1.352(4)					
		1.470(4)	2.035	81.84(10)				
tert-butyldiazabutadiene	Br^-	1.268(7)	1.290(7)[c]	1.453(8)	2.025(4)	82.2(2)	89.5	37
2,2′-bipyridine	ClO_4^-	1.325(14)	1.385(15)	1.440(15)	2.021(11)	81.5(4)	75.2	35
4,4′,6,6′-tetramethyl-2,2′-bipyridine[b]	Cl^-	1.347	1.360	1.488	2.040	81.35	68	36
1,10-phenanthroline[b]	$CuBr_2^-$	1.366	1.352	1.428	2.039	82.2	76.8	38
2,9-dimethyl-1,10-phenanthroline[b]	NO_3^-	1.360	1.361	1.450	2.063	83.4	85.7	39
$Yb^{III}(Bu^tDAB^-)_3$[c,d]	—	1.61(6)	1.51(6)	1.39(3)				34

[a] There are two molecules in the asymmetric unit. [b] Lengths are averaged (no estimated standard deviations for averaged data). [c] Second acyclic bond. [d] The Yb complex is included as an example of a DAB ligand with a formal −1 charge.

found that the asymmetric unit contains two similar molecules, one of which is shown in Fig. 9. The important characteristics are summarised in Table 7. The coordinating nitrogen atoms surround the metal centre in a distorted tetrahedral arrangement with the intra-ligand dihedral angles, between the mean planes defined by the central copper atom and each pair of bidentate nitrogen atoms, measured at 90.3 and 94.9°. The Cu—N distances range from 2.009(5)–2.050(6) Å, with an average distance of 2.040 Å. The C=N and C—C bond lengths for (*R*)-**4** are consistent with those found in similar neutral free ligands. These bond lengths indicate that the ligands are neutral and the tetrahedral structure of the complex indicates that the formal charge of the copper centre is +1. Additional material to that shown in Table 7, comprising the atomic coordinates, thermal parameters and all bond lengths and angles, is available from the Cambridge Crystallographic Data Centre.

Table 8 compares bond length and angle data for compound (*R*)-**4** and for a selection of related complexes. It can be seen that, for (*R*)-**4**, the Cu—N bond distances and the N—Cu—N bond angles are comparable with similar compounds. Interestingly, the $Cu-N^1N^2/Cu-N^3N^4$ dihedral angles determined for (*R*)-**4** are considerably larger than those seen for the related bipyridine,[35,36] *N*-*tert*-butyl-2-pyridylmethanimine[37] and phenanthroline[38,39] complexes, whilst comparing well with that determined for the similar *tert*-butyldiazabutadiene (Bu^tDAB) complex.[37] Presumably, steric factors are important due to the large 1-phenylethylamine group and packing forces, such as ring stacking, may also play a part. The C—N and C—C bond distances are very similar to those in the free ligand (1.283 and 1.496 Å for Bu^tDAB[40]) and normal $C(sp)^2-N(sp)^2$ (1.27 Å) and $C(sp)^2-C(sp)^2$ (1.48 Å) bond lengths. In contrast, the imine C—N and C—C bond lengths of Bu^tDAB^- in the ytterbium complex are significantly longer and shorter, respectively, since it is a −1 ligand.

Conclusions

This paper has shown that atom transfer polymerisation of methyl methacrylate can be effectively performed using well defined copper(I) complexes. It was found that the enantiomerically pure chiral ligands used had no effect on the stereochemistry of the resulting polymers; however, it may be possible *via* the use of more strongly complexed and rigid chiral Schiff base ligands. The use of a ligand with a methyl group β to the imine nitrogen significantly broadens PDI and reduces control over M_n when the reaction is performed in a nonpolar solvent, such as xylene, compared to Schiff base ligands with *n*-alkyl substituents. The control over M_n and PDI, however, can be improved if the reaction is performed in a more polar/weakly coordinating solvent such as diphenyl ether.

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