

Copper mediated living radical polymerisation: interactions between monomer and catalyst †

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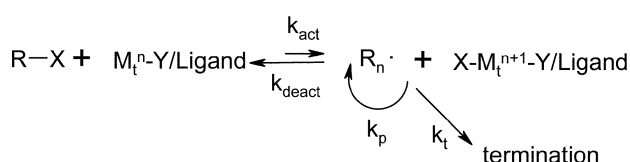
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The mechanism of copper(I) mediated living radical polymerisation (ATRP) of vinyl monomers has been widely assumed to be relatively simple. However, monomer reactivity ratios in ATRP can be significantly different from those in conventional radical polymerisation, and the exact nature of the catalyst is not well understood due to rapid exchange of ligand and monomer at the copper centre under the polymerisation conditions. This paper illustrates aspects of this catalyst system, which complicate the accepted mechanism of this new and important reaction.

Coordination of aminoethyl methacrylates and methoxy[poly(ethylene glycol)] methacrylate monomers is demonstrated by NMR with $r_{\text{MMA}} = 0.96(2)$, $0.98(1)$ and $0.97(1)$ for dimethylaminoethyl methacrylate (DMAEMA), (diethylamino)ethyl methacrylate (DEAEMA) and (*tert*-butylamino)ethyl methacrylate (TBAEMA) under free radical polymerisation and $0.74(3)$, $0.79(3)$ and $0.69(3)$ for transition-metal mediated polymerisation.

Introduction

Transition-metal mediated living radical polymerization, reported independently by Sawamoto¹ and Matyjaszewski² in 1995, has proven a remarkably efficient method of producing polymers with a wide range of functionalities and architectures.³ The polymerization, which is often referred to as atom transfer radical polymerization (ATRP), is believed to follow a free-radical mechanism, shown in Scheme 1, that contains as its key step the reversible abstraction of a (pseudo)halogen from the initiator or dormant polymer chain, creating a free radical which propagates *via* conventional free-radical addition to monomer. Monomer reactivity ratios, polymer stereochemistry (tacticity), and the insensitivity to many functional groups are in most cases similar to those observed in traditional free-radical polymerizations. Nevertheless, the presence of an additional step (activation/deactivation) and of an additional species (the metal complex) in the reaction may be expected to affect the mechanism and ultimately the properties of the resulting polymer.



Scheme 1 Mechanism of transition-metal mediated living radical polymerization.

The power of this technique is the ability to incorporate many different functional groups without affecting the living character of the reaction. These functional monomers often contain donor atoms such as N or O, and have the potential to coordinate to the catalyst. With catalysts based on ruthenium, rhodium, nickel, iron and molybdenum, π -bonding of the monomer may also be significant.⁴

Whilst there is little doubt that ATRP proceeds *via* a homolytic cleavage of a carbon–halogen bond, there is a subtle distinction between a carbon based *free radical* and a *radical* which exists in an environment different to the bulk media. This is an interesting distinction as *free radical* terminology is used to describe both free and complexed radicals. We prefer to think

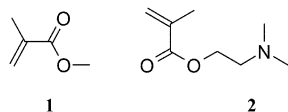
of a free radical as one which exists free from interactions which significantly modify its chemistry and this is distinct to a radical that exists in either a complexed or pseudo-complexed form. In the current context this is important as it has become common practice to apply kinetic data obtained from bulk homopolymerisations to ATRP. Under appropriate conditions, significant differences can be observed between free-radical and transition-metal mediated polymerizations. For example, there are dramatic increases in the rate of polymerization in the presence of oxyethylene groups,⁵ substituted phenols⁶ and in aqueous⁷ or ethylene carbonate⁸ solution. It is likely that these differences are due to interactions between these solvents or additives and the catalyst,⁹ which affect the rates of activation and deactivation (k_{act} and k_{deact} in Scheme 1). Where there is a possibility of interaction between monomer and the catalyst, it is natural to ask whether such interactions may not only affect the nature of the catalyst, but also that of the monomer and/or propagating radicals. Such an effect is strongly suggested by a recent paper describing the enantioselective transition-metal mediated polymerization of 2,4-pentanediy dimethacrylate in the presence of a chiral ligand.¹⁰

In the copolymerization of two monomers, A and B, the reactivity ratio, r_A , is defined as the ratio $k_{\text{AA}}/k_{\text{AB}}$, where k_{AA} is the rate constant of the reaction between a growing polymer chain having A as its terminal unit and monomer A (homopropagation), and k_{AB} is the rate constant of the reaction between the same chain and monomer B (crosspropagation). The corresponding reactivity ratio for monomer B, r_B , is defined in the same way. There have been several reports on reactivity ratios in transition-metal mediated polymerizations,^{11–13} which have generally concluded that the reactivity ratios are very similar to those observed in conventional free radical polymerization. As the reactivity ratios are determined by the rate constants of homo- and cross-propagation, which in turn are determined by the propagation mechanism (radical, ionic, coordination, *etc.*), these results are evidence that the mechanism of propagation in ATRP is similar to that of conventional radical polymerization.

The reactivity ratios, r_{MMA} , of methyl methacrylate (MMA, **1**) with methacrylate-terminated poly(dimethyl siloxane)¹⁴ and with poly(lactic acid) methacrylate¹⁵ have recently been measured and were each found to be significantly higher in conventional free radical than in atom transfer radical polymerizations. Similar results have been recorded in the copolymerization of *n*-butyl acrylate with methacrylate-terminated poly(methyl methacrylate) macromonomer.¹⁶ The difference in

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reactivity ratios between the two types of polymerization was attributed to the large size of the macromonomer: in conventional free radical polymerization, rapid growth of the polymer chain depletes the local concentration of macromonomer, which diffuses to the active chain end more slowly than the small comonomer. In living polymerizations, the individual chain lifetimes are much longer: this allows the macromonomer to diffuse to the active site, maintaining equality between local and bulk concentrations.



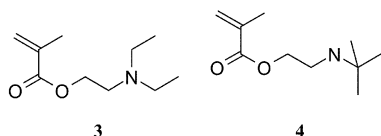
In addition to its high molecular weight, poly(lactic acid methacrylate) contains functional groups that are potentially able to coordinate to the catalyst. This in itself may be responsible for the altered reactivity ratio.

To test this hypothesis, we have copolymerized MMA with low mass comonomers such as dimethylaminoethyl methacrylate (DMAEMA, **2**), which can coordinate to the catalyst. The reactivity ratio, r_{MMA} , has been measured under both transition-metal mediated and conventional radical polymerization conditions. The use of low mass monomers ensures that both comonomers diffuse at the same rate, minimizing any local variations in monomer concentration. In a further set of experiments, a series of methoxy[poly(ethylene glycol)] methacrylate monomers containing different numbers of repeat units were copolymerized with MMA under transition-metal mediated conditions to investigate the effect of increasing molecular weight on monomer reactivity. Coordination of DMAEMA to the catalyst has been investigated by ^1H NMR.

Results and discussion

Aminoethyl methacrylate monomers

We have investigated the reactivities of a number of small monomers that would be expected to coordinate with the catalyst. The monomers chosen were DMAEMA, (diethylamino)ethyl methacrylate (DEAEMA, **3**) and (*tert*-butylamino)ethyl methacrylate (TBAEMA, **4**). These monomers give rise to hydrophilic polymers which are being investigated as new materials for a range of applications.



Monomers **2–4** were copolymerized with a large excess of MMA, and the relative rates of consumption of the comonomers throughout the polymerisation were monitored using ^1H NMR spectroscopy. Molecular weights of the resulting polymers were not measured, but polymerizations under similar conditions (100 : 1 [monomer] : [catalyst] ratio) give polymers with number-average degrees of polymerization, DP_n , very close to the theoretical value of $100/x$ (where x is conversion).

Reactivity ratios are usually determined using instantaneous forms of the copolymer composition equation, in which the comonomer concentrations are assumed to remain constant. This requires polymerizations to be stopped at low conversions. In living polymerizations, however, the polymer is dominated by oligomeric species at low conversions. These species show significant chain length dependence of the rate constants of propagation,¹⁷ so reactivity ratios obtained at low conversion are not comparable to those obtained from conventional radi-

cal polymerizations, in which high molecular weight polymer is produced from the start of the reaction.

By using an integrated form of the copolymer composition equation, it is possible to obtain results at conversions of 0.1–0.95 ($M_n \approx 1000$ –9500). Within this molecular weight range, the rate coefficients of propagation and hence the reactivity ratios are expected to be approximately constant and equal to their long-chain limits.

The use of a large excess of MMA allows the reactivity ratio of MMA (r_{MMA}) to be evaluated using a simplified form of the copolymer composition equation, which can be readily integrated. The resulting, integrated equation is shown below (eqn. (1)):

$$[\text{M}_1]/[\text{M}_1]_0 = ([\text{M}_2]/[\text{M}_2]_0)^{r_1} \quad (1)$$

in which M_1 is the monomer in excess (MMA in these experiments). This expression is equivalent to the more common, linear expression given in eqn. (2).¹⁸

$$\ln\{[\text{M}_1]_0/[\text{M}_1]\} = r_1 \times \ln\{[\text{M}_2]_0/[\text{M}_2]\} \quad (2)$$

While eqn. (2) is a convenient form in which to graph results, the transformation of experimental results ($[\text{M}]/[\text{M}]_0$) into logarithmic expressions produces severe distortions in the experimental error structure, with the effect that data points are effectively given greater weight as the conversion increases.

In this work, experimental data was fitted directly to eqn. (1) using non-linear least-squares fitting. Fig. 1 shows a typical set of experimental results. This procedure allows a more accurate estimation of both the reactivity ratio and its associated error than conventional linear least-squares fitting of eqn. (2). Fig. 2 gives a graphical representation of the results, including 95% confidence intervals (obtained from the non-linear fitting procedure). The reactivity ratios, r_{MMA} , are given in Table 1.

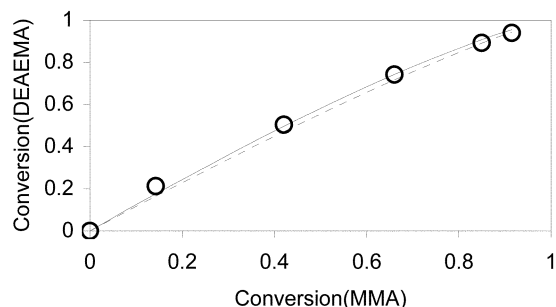


Fig. 1 Representative experimental results, showing best fit to eqn. (1) (—). Results of conventional linear fitting to eqn. (2) are shown for comparison (---).

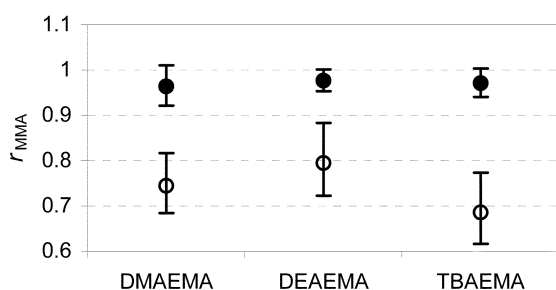


Fig. 2 Reactivities of coordinating monomers (r_{MMA}) in free radical (●) and transition-metal mediated polymerizations (○), showing 95% confidence intervals.

There is a clear difference between the free-radical and transition-metal mediated copolymerizations, similar to that observed previously in copolymerizations with macromonomers.^{14–16} In this case the difference cannot be explained by

Table 1 Reactivities of coordinating monomers (r_{MMA}) in free radical and transition-metal mediated copolymerizations

Coordinating monomer	Free radical ^a	Transition-metal mediated ^a
DMAEMA	0.96(2)	0.74(3)
DEAEMA	0.98(1)	0.79(3)
TBAEMA	0.97(1)	0.69(3)

^a Figures in parentheses are standard errors in the final digit.

differences in hydrodynamic radius between the comonomers, as these are minimal. The increased incorporation of the aminoethyl methacrylate (AEMA) monomers into the transition-metal mediated copolymers could potentially be explained by AEMA-terminated polymers having an increased rate constant of activation, k_{act} , compared to MMA-terminated polymers. Simulations have shown that differences in the rates of activation and deactivation for polymers with different terminal groups can lead to small apparent differences in reactivity ratios.¹⁹ It is by no means clear, however, that this would be sufficient to produce the large deviations observed here, even if k_{act} of AEMA monomers were several orders of magnitude greater than that of MMA, as deviations from free-radical behavior according to this model appear to be small except when both monomer reactivity ratios are substantially greater than 1 (e.g. examples 1C, 3B, 3C and 2D in reference 19). Such a large k_{act} would make controlled polymerization of AEMAs by transition-metal mediated polymerization virtually impossible due to the high radical concentrations and termination rates that would ensue. Nevertheless, there are many reports of successful controlled polymerizations of these monomers.^{20–23}

Hence it appears that the two explanations previously advanced to support differences in reactivities between ATRP and free radical copolymerizations are untenable in this case. Many reactivity ratios show solvent effects,²⁴ but the addition of catalytic amounts of copper complex is unlikely to have a significant effect on the solvent polarity. Such solvent effects are most often seen when charge-transfer structures play a significant role in stabilizing the transition state of the cross-propagation reaction as in styrene-MMA or styrene-acrylonitrile, but this is unlikely to be the case for MMA-DMAEMA where the two double bonds are very similar.

The most probable explanation for the change in r_{MMA} is coordination between the monomer, or propagating radical, and the copper catalyst. Coordination may affect the monomer reactivity by altering the electronic structure of the double bond, or simply through a mass effect (the mass of the monomer-copper complex will be much greater than that of the monomer alone, and this should cause an increase in the pre-exponential factor of the rate constant).²⁵ It is well known that the presence of Lewis acids may affect reactivity ratios, particularly in the case of styrene-MMA polymerizations;^{17,26} it is possible that a similar effect is observed in this case, with copper acting as the Lewis acid.

Trends in reactivities within the monomers appear to support this explanation, as the secondary amine, TBAEMA, shows the greatest deviation from free-radical reactivity ratios, while the most sterically hindered tertiary amine, DEAEMA, shows the least, suggesting that the extent of deviation is correlated with decreasing congestion around the nitrogen.

NMR studies of DMAEMA-copper interactions

¹H NMR spectra of mixtures of aminoethyl methacrylates and copper(I) bromide in d_8 -toluene at 90 °C show clear shifts in the absorptions of protons in close proximity to the nitrogen atom as well as the downfield vinylic proton (*cis* to the ester moiety), even in the presence of equimolar amounts of pyridyl methanimine ligand (Fig. 3). No change was observed in the

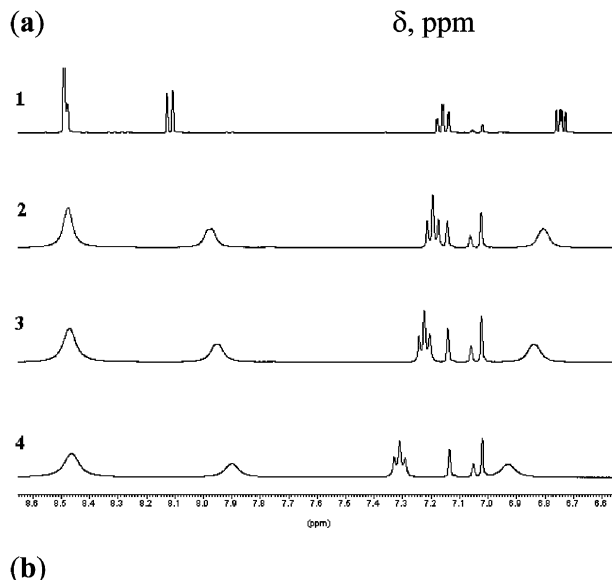
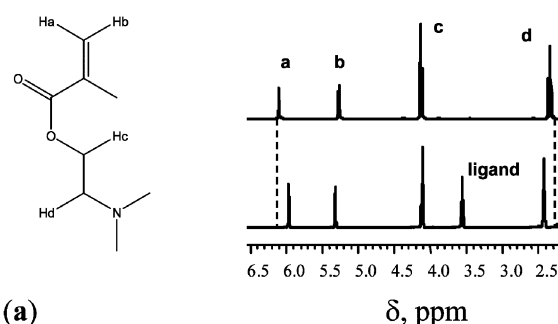
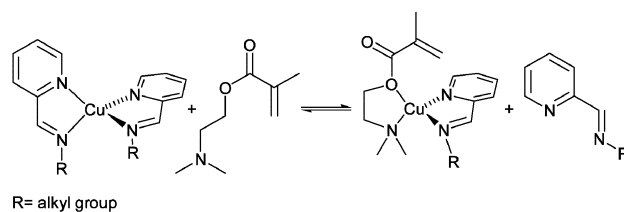


Fig. 3 (a) Partial ¹H NMR spectra (d_8 -toluene, 90 °C) of DMAEMA (top) and a 2/2/1 mixture of *N*-propyl 2-pyridylmethanimine, DMAEMA and CuBr (bottom). (b) Changing chemical shifts in the aromatic region of pyridylmethanimine ligand as the concentration of DMAEMA is increased. (d_8 -toluene, 25 °C): 1. free ligand; 2. ligand/CuBr 2 : 1; 3. ligand/CuBr/DMAEMA 2 : 1 : 2; 4. ligand/CuBr/DMAEMA 2 : 1 : 10.

position of the IR absorptions of the carbonyl groups of the aminomethyl methacrylates in the presence of copper(I) bromide.

This is indicative of chelation to copper through the amine and ester groups of the aminoethyl methacrylate, as shown in Scheme 2.



Scheme 2 Proposed equilibrium involving DMAEMA/*N*-propyl 2-pyridylmethanimine/copper(I) complexes.

The structure shown is not definitive, and we are unable to explain why the vinylic proton *cis* to the ester group is shifted upfield, indicating increased shielding, rather than downfield as might be expected from deshielding due to the copper. However, as this shift is only observed in the presence of copper (and not in mixtures of ligand and DMAEMA) it is logical to attribute it to interactions between the proton and either the copper itself or other ligands.

It is interesting to note that in the spectrum shown in Fig. 3 there are no traces of free ligand or free monomer. Addition of a larger excess of monomer resulted in a shift of the pyridine ¹H NMR signals, but again, no free ligand was observed. This could be consistent with a dynamic equilibrium involving

several copper(I) derivatives bearing the pyridine imine ligand and/or the DMAEMA monomer (Scheme 2). This process seems to be faster than the NMR timescale, therefore the signals observed probably represent an average value of the frequencies relative to each compound involved in such equilibrium.

We also observed a dependence of the ^1H NMR signals on the temperature and a plot of the chemical shift *versus* the temperature is reported in Fig. 4 for the vinylic proton H_a in *cis* position with respect to the ester function.

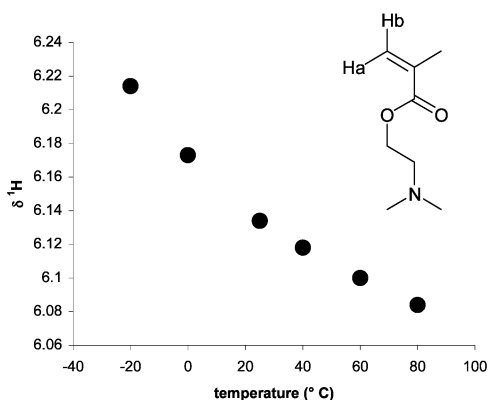
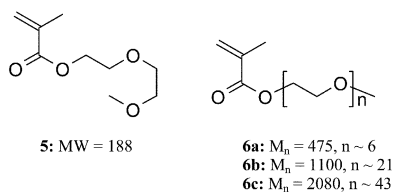


Fig. 4 δ -values of the *cis* vinylic proton (H_a) as a function of the temperature. Conditions: ligand/CuBr/DMAEMA: 2/1/4 in d_8 -toluene.

These studies show that there is an interaction between copper and DMAEMA under reaction conditions that changes the chemical environment of the double bond. It is this interaction, rather than diffusion phenomena or differences in activation or deactivation rates, that is primarily responsible for the altered reactivity ratios observed for the aminoethyl methacrylate monomers in the preceding section.

Methoxy[poly(ethylene glycol)] methacrylate monomers

The study was extended to a series of methoxy[poly(ethylene glycol)] methacrylates (**5**, **6**) in order to investigate the effect of increasing molecular weight on reactivity. If diffusion of macromonomer to the growing chain is an important factor in determining the amount of macromonomer incorporation, as has been proposed previously,^{14–16} it would be expected that r_{MMA} will increase with molecular weight in free radical polymerization, but stay approximately constant for the transition-metal mediated polymerizations.



At each molecular weight, similar results were seen as for the amino methacrylates, with higher levels of incorporation into the copolymer (lower r_{MMA}) in transition-metal mediated polymerizations than in free radical polymerizations (Fig. 5, Table 2).

As the molecular weight of the macromonomer increases, there is a general trend towards lower r_{MMA} within both the transition-metal mediated and free radical copolymerizations. This trend is not compatible with a diffusion control explanation, which predicts for conventional free radical polymerizations that as the macromonomer chain length increases, less of it will be incorporated into the copolymer, resulting in a higher

Table 2 Reactivities of methoxy[poly(ethylene glycol) methacrylate monomers (r_{MMA}) in free radical and transition-metal mediated copolymerizations

Macromonomer	Free radical ^a	Transition-metal mediated ^a
5	0.98(1)	0.85(3)
6a	0.95(3)	0.60(5)
6b	0.93(2)	0.76(4)
6c	0.95(3)	0.76(3)

^a Figures in parentheses are standard errors in the final digit.

Table 3 Selected bond lengths [\AA] and angles [$^\circ$]

Cu1–N08A	2.0254(19)	Cu1–N01A	2.0348(17)
Cu1–N08	2.0255(19)	Cu1–N01	2.0348(17)
C07A–N08A	1.270(3)	C07–N08	1.270(3)
N08A–Cu1–N08	124.25(12)	N08A–Cu1–N01	124.44(7)
N08A–Cu1–N01A	81.97(7)	N08–Cu1–N01	81.97(7)
N08–Cu1–N01A	124.44(7)	N01A–Cu1–N01	125.83(10)

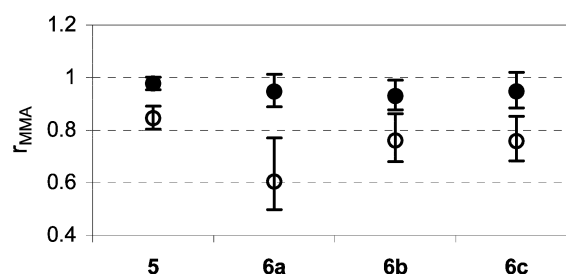


Fig. 5 Reactivities of methoxy[poly(ethylene glycol)] methacrylates as a function of number average molecular weight in free radical (●) and transition-metal mediated polymerizations (○). Error bars show 95% confidence intervals.

apparent r_{MMA} . In transition-metal mediated polymerizations, increasing the macromonomer molecular weight should have no effect. The slight increase in monomer reactivity (decreased r_{MMA}) with increasing chain length is in line with the known increase in propagation rate constants for alkyl methacrylates as the size of the ester group increases.²⁷

The more pronounced decrease in the transition-metal mediated polymerization results may reflect the macromonomers' increased ability to coordinate to copper as the number of potential ligating groups is increased. This should be counterbalanced by the increased likelihood that the copper will be coordinated to donor atoms that are too far away from the monomer double bond to influence its reactivity as chain length increases. The value of r_{MMA} decreases sharply from $M_n = 188$ (**5**) to $M_n = 475$ (**6a**) before increasing to what appears to be a stable value (**6b** and **c**) at longer chain lengths. This suggests that **6a**, containing on average 6 oxyethylene repeat units, is close to the optimum length for complexing the copper catalyst in such a way that it remains sufficiently close to the monomer double bond to affect its reactivity.

X-Ray analysis of the iminopyridine copper(I) catalyst

Although we have previously been able to determine the structure of some copper catalysts, the best catalysts have always proved difficult to crystallise, forming oils instead.^{28,29} However, we have recently been successful in the use of the ethyl substituted iminopyridine. Single crystals of an iminopyridine CuBr complex, suitable for X-ray diffraction study, have been grown by slow diffusion of hexane in a solution of *N*-ethyl 2-pyridylmethanimine and CuBr (molar ratio 2 : 1) in MMA, under a dinitrogen atmosphere. The structure consists of a mononuclear molecule containing one copper atom and two ligand units, in which the Cu(I) ion lies at the centre of a distorted

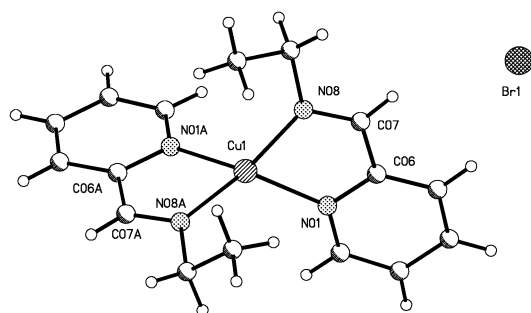


Fig. 6 Crystal structure of $[L_2Cu]Br$, with $L = N$ -ethyl 2-pyridylmethanimine.

tetrahedron, with a bromine atom as the counter-ion (Fig. 6). A large distortion from a regular polyhedron was observed, as can be noted from the values of the bond angles reported in Table 3. In fact, the angles originated by the chelating dinitrogen ligand $N01-Cu-N08$ are much smaller than the regular tetrahedral angle, while all the other $N-Cu-N$ angles are larger. This behaviour is typical for $Cu(I)$ complexes bearing chelating dinitrogen ligands.^{29,30}

It may be noted that the $Cu-N_{imine}$ and $Cu-N_{pyridine}$ separations are almost identical, and the formal double bond character of the imino linkages $C07-N08$ has been retained (1.270 Å).

Conclusions

We have shown that for a series of aminoethyl methacrylate monomers and a series of poly(ethylene glycol) macromonomers of different weights, the monomer reactivities in transition-metal mediated copolymerizations towards methyl methacrylate differ significantly from those observed in conventional free radical polymerizations. This is attributed to complex formation between monomer and catalyst, which alters the reactivity of the monomer. It is likely that monomer reactivities in transition-metal mediated polymerizations will differ significantly from those measured in free radical polymerizations for a wide range of functionalized monomers with the potential to undergo similar monomer-catalyst interactions. The rates of propagation of such monomers may also differ from those measured under conventional conditions; thus propagation rate constants obtained using the pulsed laser polymerization technique should be applied with caution to transition-metal mediated polymerizations. The potential of the catalyst to alter propagation rates and selectivities (compared to free radical polymerizations in the absence of Lewis acids) should be taken into account when designing polymerizations incorporating functionalized monomers.

Experimental

Materials

Methyl methacrylate and aminomethacrylate monomers (99%, inhibited with monomethyl ether hydroquinone) were obtained from Aldrich and passed over a column of activated basic alumina before use. Methoxy[poly(ethylene glycol)] methacrylate monomers (Aldrich) were used as received. Copper(I) bromide (Aldrich, 98%) was purified by a modification of the method of Keller and Wycoff.³¹ N -Alkyl 2-pyridylmethanimine was synthesized according to the method of Haddleton *et al.*³² Azobis(isobutyronitrile) (ACROS Chimica, 98%) was recrystallized from methanol. All other chemicals were purchased from Aldrich or ACROS Chimica and used as received.

Analysis

NMR spectra were obtained on a Bruker DPX400 spectrometer using d_8 -toluene as solvent, 16 scans, RD = 1s, LB =

Table 4 Summary of crystallographic data

Chemical formula	$C_{16}H_{20}BrCuN_4$
Formula weight	411.81
Crystal system	Orthorhombic
Space group	$Fddd$
μ/mm^{-1}	3.519
$a/\text{Å}$	12.6388(19)
$b/\text{Å}$	22.178(6)
$c/\text{Å}$	25.069(6)
$V/\text{Å}^3$	7027(3)
T/K	180(2)
Z	16
Final $R1, wR2 [I > 2\sigma(I)]$	0.0288, 0.0660

–0.20 Hz. Infrared absorption spectra were recorded on a Bruker VECTOR-22 FTIR spectrometer using a Golden Gate diamond attenuated total reflection cell.

Copolymerizations

Mixtures of MMA (96.5 mol%) and aminoethyl methacrylate monomers **2** (3.5 mol%, 5.4 wt%), **3** (3.5 mol%, 6.3 wt%), and **4** (3.5 mol%, 6.3 wt%) were copolymerized by both conventional free radical polymerization with AIBN initiation and by copper(I) bromide mediated living radical polymerization using N -propyl 2-pyridylmethanimine as ligand (total monomer : ligand : copper = 100 : 2 : 1 molar ratio). All copolymerizations were carried out in solution in toluene or d_8 -toluene (1 : 1 toluene : monomer by volume) at 90 °C under nitrogen after freeze-pump-thaw degassing. For the transition-metal mediated polymerizations, samples were taken regularly and conversion was determined by 1H NMR spectroscopy (d_8 -toluene, 400 MHz). Free radical polymerizations were carried out in sealed NMR tubes within the NMR spectrometer (400 MHz) using d_8 -toluene as solvent, and scanned at regular intervals. A similar procedure was followed for copolymerizations of MMA (96.5 mol%) with monomers **5** (3.5 mol%, 6.4 wt%), **6a** (3.5 mol%, 14.7 wt%), **6b** (3.5 mol%, 28.5 wt%) and **6c** (3.5 mol%, 43.0 wt%). Conversions for each monomer were calculated from the NMR spectra by comparing the combined areas of the methylene peaks (2H) with the area of the combined monomer and polymer methoxy (MMA and methoxy[poly(ethylene glycol)] methacrylates, 3H) or $-CH_2O-$ (aminoethyl methacrylates, 2H) peaks. Reactivity ratios were calculated from these results using a modified version of the Jaacks method¹⁸ incorporating nonlinear least-squares fitting. Standard errors in the reactivity ratios were calculated using the inverted normal equations matrix and estimated variance of an observation of unit weight, equal to the sum of squared residuals divided by $m - 1$, where m is the number of observations.³³ The 95% confidence intervals shown in Fig. 2 and 5 were estimated from the standard errors of the reactivity ratios using a t -distribution with $m - 1$ degrees of freedom, and typically encompass 2.2–2.8 standard errors on either side of the point estimate.

Crystal structure determination

Crystallographic data for the complex $[Cu(C_8H_{10}N_2)_2]Br$ are summarised in Table 4. The molecular structure is shown in Fig. 6. Suitable crystals were quickly glued to quartz fibres, 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, riding on the supporting atom. The structure solution was carried out using SHELXTL³⁴ version 5.0 software on a Silicon Graphics Indy workstation, refinements were carried out using SHELXTL 96³⁵ software, minimising on the weighted R factor $wR2$.

CCDC reference number 208056.

See <http://www.rsc.org/suppdata/dt/b3/b303888b/> for crystallographic data in CIF or other electronic format.

Acknowledgements

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