Halogen exchange during atom transfer polymerisation of methyl methacrylate mediated by copper(I) *N*-alkyl-2-pyridylmethanimine complexes

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Highly efficient exchange between the halogen arising from the copper(I) halide and the alkyl halide originating from the initiator occurs during atom transfer polymerisation of methyl methacrylate mediated by copper(I) *N*-alkyl-2-pyridylmethanimine complexes.

Living/controlled polymerisations of vinyl monomers lead to the synthesis of polymers with well controlled architecture and predetermined molecular weight. Living/controlled *radical* polymerisation is of increasing importance due to the resilience of free-radical polymerisations to impurities and protic species invariably present in the monomer, solvent, *etc.* Transition metal mediated atom transfer polymerisation has been pioneered by Matyjaszewski, using Cu^IX (X = Cl, Br) in conjunction with 2,2-bipyridine[1] and substituted bipyridines,[2–5] and Sawamoto, using $[Ru(PPh_3)_3Cl_2]$.[6–8] Since then a number of different systems using transition metal complexes to polymerise styrenes, methacrylates and acrylates have been reported including $[Ni(PPh_3)_3X_2]$,[9] [Ni{*o*,*o*-$(Me_2NCH_2)_2C_6H_3$}Br],[10] $[Pd(OAc)_2(PPh_3)_4]$,[11] $[Rh(PPh_3)_3Cl]$,[12] and [Cu(*N*-alkyl-2-pyridylmethanimine)$_2$X].[13] More recently Teyssie has reported $FeCl_3$ mediated polymerisation in the presence of PPh_3 for the living/controlled polymerisation of methyl methacrylate (MMA) initiated with a conventional free-radical initiator, AIBN.[14]

It has been previously demonstrated that atom transfer polymerisation is an excellent one step method for the preparation of α-functional polymers.[15–17] The alkyl halide initiator can possess a wide variety of functionalities without causing loss of performance or control over the reaction. Although the existence of several different functionalities at the α-terminal end group has been demonstrated, no detailed study has been made on the nature of the ω-terminal end group. The assumption has been that the ω-terminal end group contains the halogen atom originating from the initiator molecule.

The aim of the work reported here was to investigate the possibility, and extent, of halogen exchange between polymer and catalyst in the polymerisation of methyl methacrylate mediated by [Cu(*N*-alkyl-2-pyridylmethanimine)$_2$X] complexes. During the course of this work two papers appeared referring to the possibility of halogen exchange in atom transfer polymerisation. Sawamoto reported observing the presence of both bromide and chloride ω-end groups in the ^1H NMR spectrum of PMMA from bromomalonate initiation catalysed with $Ru(PPh_3)_3Cl_2$.[18] Matyjaszewski *et al.* stated that exchange can occur between the halogen from the initiator and the halogen on the catalyst for BnBr and 2-bromopropionate with Cu^IX/4,4-di(nonan-5-yl)-2,2-bipyridine catalyst; however, no experimental details were provided.[19] In addition, Matyjaszewski reported similar exchange occurring during the polymerisation of MMA based on matrix-assisted laser desorption ionisation time of flight (MALDI-TOF) and electro-spray ionisation (ESI) mass spectrometry;[19] again, no spectra or experimental details were provided. We have found that this approach is fraught with difficulties due to the ease of fragmentation of these type of polymers within the mass spectrometer.[20]

Table 1 Reaction conditions and results for poly(methyl methacrylate) produced using atom transfer polymerisation with sulfonyl halide initiators and copper halide catalysts

Reaction[a]	Initiator[b]	Mediator	*t*/h	M_n[c]	PDI[d]	Halogen on ω-end group
A	TsBr	CuBr	3	4130	1.10	Br
B	TsCl	CuCl	48	2170	1.06	Cl
C	TsCl	CuBr	22	1900	1.08	Cl
D	TsBr	CuCl	11	4170	1.09	Cl

[a] See footnote ‡. [b] Synthesis of TsBr modified from the preparation of TsI by Truce *et al.* (ref. 22). [c] Number average molecular weight measured by SEC, using THF as eluent at 1 ml min^{-1} calibrated with narrow molecular weight distribution PMMA standards. [d] Polydispersity index from SEC.

In order to study the effects of halogen exchange, PMMA was synthesised using four different combinations of initiator and copper(I) halide (Table 1, reactions A–D). In each case the ligand used to complex copper(I) was *N*-pentyl-2-pyridylmethanimine and the polymerisation was carried out in xylene solution (35% w/w). The polymerisations were allowed to proceed until the number average molecular weight, M_n, reached approximately 2000–4000 g mol^{-1} (20–40% conversion), as monitored by size exclusion chromatography (SEC). Polymerisations were stopped, by cooling to room temperature, at low conversion in order to minimise termination by conventional radical-radical interactions. Low molecular weights were targeted to enable end group analysis by ^{13}C NMR spectroscopy. Fig. 1 shows the ^{13}C NMR spectra of the products from reactions A–D between δ 68 and 58, the –*C*–X region, to focus on the nature of the ω-end group. For reaction A the ω-terminal [–*C*(CH_3)(CO_2Me)Br] can be seen as three peaks between δ 58.9 and 58.3, Fig. 1(*a*), which correspond to *racemic*

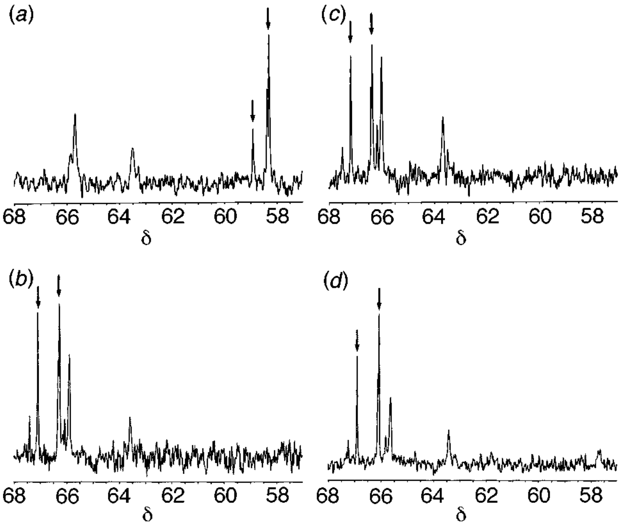
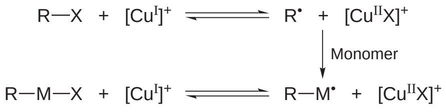


Fig. 1 ^{13}C NMR spectra of PMMA made by ATP, initiated with (*a*) TsBr and CuBr, (*b*) TsCl and CuCl, (*c*) TsCl and CuBr, and (*d*) TsBr and CuCl. Marked peaks are from halogenated ω-end groups.

(syndiotactic) and *meso* (isotactic) terminal units respectively. The position of the halogenated carbon atom was verified by comparison with a spectrum of a model compound, methyl-2-bromoisobutyrate, $[(CH_3)_2C(CO_2Me)Br]$, δ 55.4. The product from reaction B shows a similar set of peaks due to $[–C(CH_3)(CO_2Me)Cl]$ shifted downfield, between δ 67.1 and 66.3 [Fig. 1(*b*)], as expected for a chlorinated carbon relative to a brominated one. On examining the spectrum from the product of reaction C [Fig. 1(*c*)] it can be seen that the polymer has exclusively chlorinated ω-end groups with peaks between δ 67.2 and 66.4, *i.e.* the product is the same as that from reaction B. There are no peaks observed in the region δ 58.0 to 60.0 corresponding to a bromine ω-end group functionality. Thus, no observable halogen exchange occurs between the bromide originating from copper(I) bromide and the propagating polymer end capping group, a chlorine atom originating from the initiator. This result is what might be expected for the generally accepted mechanism for atom transfer polymerisation (Scheme 1), *viz.* the halogen atom that originated on the initiator is transferred between transition metal complex and polymer chain end throughout the reaction and is present as the ω-end group of product. For reaction D, three peaks between δ 66.9 and 66.1 are observed corresponding to $[–C(CH_3)(CO_2Me)Cl]$ with no peaks upfield due to brominated ω-end groups [Fig. 1(*d*)]. This result is surprising because the polymer exclusively has chlorinated ω-end groups even though a sulfonyl bromide initiator was employed, so complete halogen exchange has occurred.



Scheme 1

Our results show that polymerisation of MMA by atom transfer polymerisation mediated by a Cu(*N*-alkyl-2-pyridylmethanimine)$_2$X complex in xylene at 90 °C in the presence of both bromine and chlorine atoms results in solely chloro ω-functional polymer. This can be attributed to the greater strength of the C–Cl bond compared with the C–Br one, *i.e.* the formation of a C–Cl bond is energetically favourable and its homolysis is less facile. This result differs from that of Sawamoto, who found a mixture of Cl and Br in the ω-end group when polymerising MMA initiated with a bromomalonate compound and $Ru(PPh_3)_3Cl_2/Al(OPr^i)_3$ in toluene at 80 °C,[18] and Matyjaszewski, who claimed to have observed a mixture of Cl and Br ω-end groups.[19] Therefore, the tendency for exchange to occur must be effected by the transition metal complex and/or reaction conditions.

The observation of halogen exchange shows that the mechanism of atom transfer polymerisation is more complicated than first thought.[13,19] It is likely that, in reactions where both Cl and Br species are present, the Cu^{II} species contains both in similar states regardless of their origin (initiator or catalyst) and exchange could then occur as the propagating polymer centre abstracts one or other halogen in the deactivation step. Alternatively, exchange may occur by nucleophilic attack of the halide counter-anion from the catalyst at the alkyl halide group of initiator or deactivated polymer. The reaction may also involve bimetallic species with bridging halide or oxygen containing ligands.[3,21] It is not yet known whether exchange occurs at the first reaction step or whether several halogen transfer cycles are involved.

The occurrence of halogen exchange results in competitive rates of polymerisation which complicates the polymerisation kinetics. This may result in a broadening of the molecular weight distribution of the product and also effect the evolution of number average molecular mass with conversion when the reaction is carried out to high conversion. To avoid these effects, therefore, it is advisable to match the halides between the copper(I) salt and the initiator. This is currently under further investigation in our laboratory. It is also noted that this is the first instance of sulfonyl bromides being used as effective initiators for atom transfer polymerisation.

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Notes and References

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‡ In a typical polymerisation, CuX (0.93 mmol) and TsX (0.93 mmol) ([Cu]:[initiator] = 1:1) were placed in a predried Schlenk flask which was evacuated and then flushed with dry nitrogen three times. Methyl methacrylate (10 ml, 93 mmol) was added and the suspension stirred while adding *N*-pentyl-2-pyridylmethanimine (1.87 mmol, [ligand]:[Cu] = 2:1) which instantaneously formed a deep brown solution. Xylene (20 ml) was added and the flask was heated in a thermostatted oil bath at 90 °C. The polymer was isolated by passing the cooled reaction solution down a column of activated basic aluminium oxide to remove catalyst and precipitating into hexane. ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer with a minimum of 4000 scans.

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