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# Novel Polymers from Atom Transfer Polymerisation Mediated by Copper(I) Schiff Base Complexes

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SUMMARY: The use of copper(I) Schiff base complex catalysed atom transfer polymerisation of methacrylates is described. The use of a range of functional and multi-functional initiators enables the synthesis of a range of functional and star polymers to be prepared under undemanding synthetic conditions. End capping with silyl enol ethers allows for ω-functional polymers. The combination of novel initiators, functional monomers and end capping allows an unprecedented array of macromolecular structures to be produced with limited need for protecting group chemistry.

## Introduction

Transition metal mediated living polymerisation has emerged as an efficacious method for the living polymerization of vinyl monomers since its inception by Sawamoto using Ru(II) catalysts 1) 2) and Matyjaszewski with Cu(I) bpy complexes 3). This chemistry allows the synthesis of a wide range of novel polymers under relatively undemanding conditions. The process is inert to most functional groups and impurities present in monomers, reagents and solvents 4). Indeed one of the only conditions that seems to destroy the catalyst is low pH, especially where may become protonated thus changing the nature of the catalyst 5). An impressive range of new polymers has been reported, for example, Fukuda and co-workers 6) have synthesised glycopolymers by metal mediated living polymerisation. As an example of the ability to prepare macromolecules with controlled architecture the synthesis of block

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copolymers by transition metal mediated living polymerisation has emerged by two synthetic routes;

1. Synthesis of a well defined A block by living radical polymerisation that is isolated and subsequently used as a macroinitiator for the reinitiation of a second monomer.
2. Synthesis of a macroinitiator by introduction of initiating groups onto polymers by chemical modification of a pre-formed polymer e.g. from condensation or ring-opening polymerisation.

We have been using of a range of Schiff base ligands used in conjunction with Cu(I)Br and an appropriate initiator as a versatile and extremely effective living polymerisation system for acrylics and other vinyl monomers 7). In this paper we illustrate some of the recent developments that we have been working on and we report a range of polymers that have been synthesised for diverse applications. The examples chosen serve to illustrate the diversity of this chemistry.

## Experimental

***General Information***. For general procedures see previous publications 7) 8). All reactions were carried out using standard Schlenk techniques under a nitrogen atmosphere. Methyl methacrylate and styrene were purified by passing down an activated basic alumina column so as to remove inhibitor, water and other protic impurities. For detailed procedures the reader is directed to both our previous publications in the area and future detailed papers in each area 7) 8).

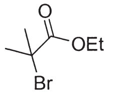
***Typical synthesis of a macroinitiator***. Synthesis of Kraton L-1203 Macroinitiator. Kraton L-1203 168.15 g (0.04 mol) was dissolved in anhydrous tetrahydrofuran 600 mL. Triethylamine 8.4 mL (0.06 mol) was added to the mixture followed by the addition with stirring of 2-bromo-2-methyl propionyl bromide 7.4 mL (0.06 mol). The reaction was allowed to stir overnight at room temperature. The viscous product was dissolved in $CHCl_3$ 500 mL and the solution was sequentially washed with saturated $NaHCO_3$ solution and water. The $CHCl_3$ layer was dried with $MgSO_4$ filtered and the solvent was removed to leaving a clear colorless viscous liquid. Yield = 165.9 g

***Typical polymerisation with a macroinitiator: Polymerisation of MMA with 1 as initiator; [MMA]/[I]/[Cu]/[L] = 100/1/1/2 in 66% toluene solution***. Initiator **1**, (0.268 g, 0.5 mmol) Cu(I)Br (0.072 g, 0.5 mmol) were dissolved in deoxygenated toluene (10.6 mL) in a Schlenk tube prior to the addition of *N*-propyl-2-pyridinalmethanime (0.180 g, 1.15 mmol). The solution was further deoxygenated via three freeze pump thaw cycles and the solution heated to 90 $^{o}$C. Deoxygenated inhibitor free MMA (10.6 mL) was subsequently added (t = 0). Samples were removed periodically for analysis, via syringe. Polymerisation of other monomers with **1** as initiator was carried out under similar conditions.

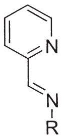
***General instrumentation***. GPC was carried out using a Polymer Laboratories (PL) guard column (50 × 7.5 mm), and two Mixed-C columns (300 × 7.5 mm). THF was used as the eluent at a flow rate of 1 mL/min, and data were collected at 1 point/s from a DRI detector. The system was calibrated with log molecular weight expressed as a third order polynomial of elution volume based on Polymer Laboratories PMMA and PSTY standards and pure samples of MMA dimer and trimer. The SEC data are presented as 'PMMA equivalent' or 'PSTY equivalent' molecular weights. Elemental analysis was performed using a CE440 Elemental Analyser, Leeman Labs Inc. Infrared analysis were carried out with a Bruker Vector 22 FTIR spectrometer equipped with a Golden Gate Single Reflection Diamond ATR accessory, P/N 10500 series, Graseby Specac. NMR spectra were recorded on Bruker AC250 and AC400 spectrometers.

## Results and Discussion

Polymerisation is achieved by using α-activated bromo initiators, **1**, in conjunction with copper(I) Schiff base, **2**, ligands. Ligands of type **2** are synthesized from the condensation of pyridine 2-carbaldehyde with primary amines in quantitative yield 7). The abundance of available primary amines lead to the availability of a range of catalysts with varying solubility and redox potential.



**1**



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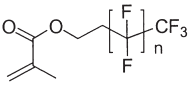


**3**

***Polymerisation of functional monomers.***

Many different monomers, including both hydrophobic and hydrophilic monomers may be polymerised with bromo initiators in conjunction with copper(I) based catalysts. For example, hydrophobic fluorine containing monomers, **3**, may be statistically co-polymerized with MMA to give polymers with narrow PDi, controlled Mn in a living polymerisation, Fig. 1. Blends of these statistical co-polymers with MMA form coatings with fluorine rich surfaces as seen by contact angle measurements with water; 4% **3** 104.5$^0$ (adv.), 74.7$^0$ (rec.); 7.4 % **3** 104.5$^0$ (adv), 74.7$^0$ (rec.); PMMA 72.8$^0$ (adv.), 59.2$^0$ (rec.).

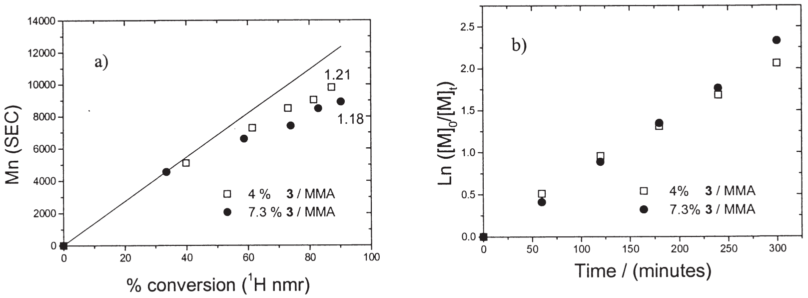
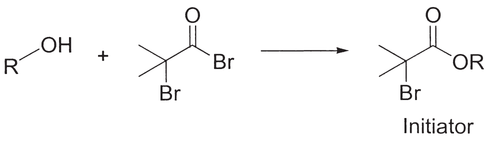
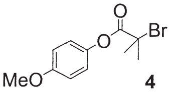


Fig. 1: Statistical copolymers of **3** and MMA with **1** as initiator and Cu(I)Br/n-propyl **1** catalyst a) Evolution of Mn with conversion and b) first order kinetic plots

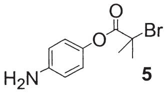
***Use of functional initiators to α-functional polymers***



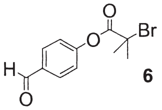
Functional initiators may be easily prepared by the condensation of both aromatic and aliphatic alcohols with 2-bromo isobutyrate, as above. For example, a range of phenols with methoxy, **4**, primary amino, **5**, and aldehyde, **6**, functional initiators are effective initiators for the living polymerisation of MMA leading to polymers with corresponding α-functionality,



**4**



**5**



**6**

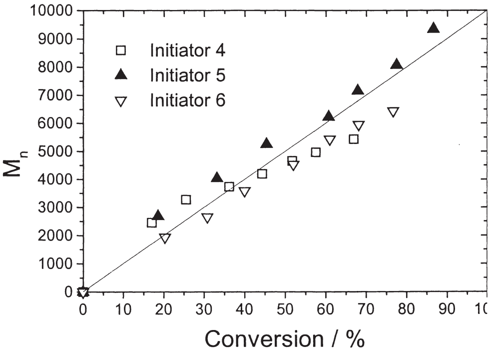


Fig. 2: Evolution of Mn with conversion for the polymerisation of MMA with phenolic ester functional initiators, **4-6**, under standard polymerisation conditions.

Fig 2. This approach can be utilised to prepare a wide-range of α-functional narrow molecular mass distribution polymers of varying composition.

## Star polymers based on simple sugars.

An extension of the above approach is the preparation of multi-functional initiators from polyols. This has been previously exploited by both Gnanou [9)] and Sawamoto [10)] for the synthesis of star polymers from calixarenes. We have been using this approach with simple sugars and have previously reported the use of glucose to produce 5-arm star polymers. This is illustrated by the use of sucrose that forms an octa-functional initiator on reaction with eight equivalents of 2-bromo isobutyrate.

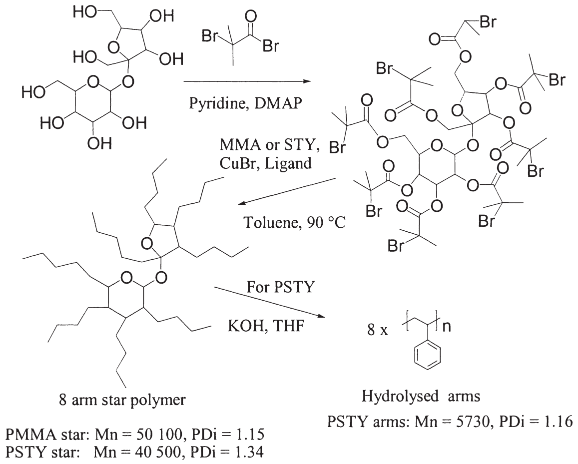


Fig. 3: Synthesis of octafunctional initiator and eight arm star polymers based on a sucrose initiator.

## Block copolymers from macroinitiators

An important aspect of any living polymerisation technique is the ability to prepare block copolymers. The transformation of alcohols into initiators can be exploited here, as

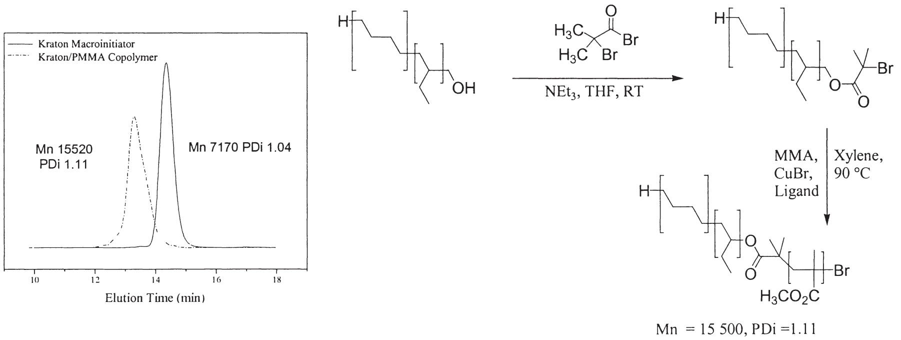
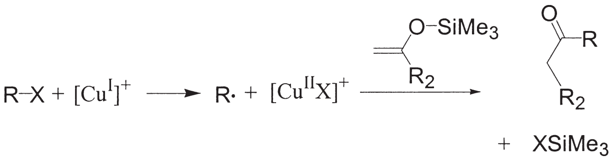


Fig. 4: Poly(ethylene/butylene-b-MMA) copolymer by polymerisation with macro-initiator form Kraton L-1201 under standard polymerisation conditions.

previously been demonstrated by Kops [11] and Matyjaszewski [12]. An example of this is the synthesis of a macro-initiator from α-hydroxyl functional poly(ethylene-butylene), a commercial product available from Shell (Kraton L-1201) 13), Fig. 4. This approach avoids complications arising from termination of the A block, found in all cases where sequential addition of monomers is employed. An added advantage of this approach is that initiator efficiency is always very high as termination by radical-radical reactions is not as prevalent with such high mass initiators as is found for small molecule initiators.

### ω-Functional polymers from end-capping reactions

The terminal group of a polymer from atom transfer polymerisation is usually a tertiary bromide. This has been previously been transformed into more useful functionality via an azide group. An alternative approach is to use an end-capping reagent in the polymerisation that essentially uses a non polymerisable monomer, previously described by Sawamoto. We have been using this chemistry to end-cap a propagating polymer with protected functional trimethyl silyl enol ether, which is subsequently transformed into a hydroxyl on deprotection, Fig. 5. The hydroxyl group can be subsequently transformed into a macromonomer by condensation with, for example, methacryloyl chloride.



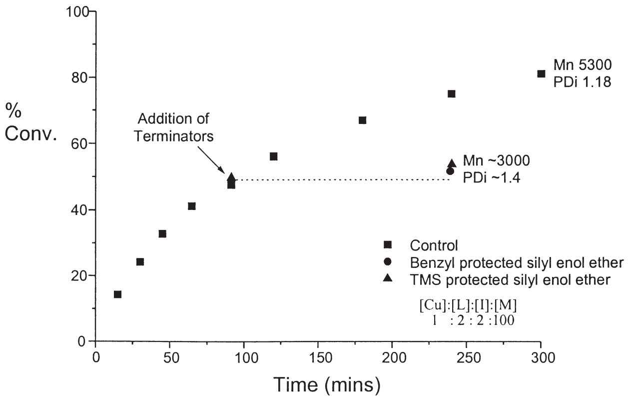


Fig. 5:End capping of PMMA with silyl enol ether to yield hydroxyl functional polymer

## General Discussion

Transition metal mediated living polymerisation is an extremely versatile method to produce a wide range of polymers under relatively undemanding conditions. The use of protecting group chemistry can usually be avoided. This presentation has given an overview of some of the chemistry being developed to produce both $\alpha$ and $\omega$ functional polymers, star polymers, functional polymers and block co-polymers using copper(I) Schiff base catalysed chemistry. Full details of all of this chemistry will be the subject of future publications.

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