SYNTHESIS AND CHARACTERISATION OF A WATER-SOLUBLE INITIATOR FOR ATOM TRANSFER RADICAL POLYMERISATION

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ABSTRACT
A water-soluble Atom transfer radical polymerisation (ATRP) initiator (1,2-dihydroxypropane-3-oxy-2-bromo-2-methyl propionyl) has been synthesised by a two step reaction which involved esterification of the starting material and hydrolysis of the intermediate product. ^{1}H NMR of both the intermediate and final products has confirmed the structure of the targeted products and also the reactions produce high yield and sufficient purity. This initiator will be very useful in the polymerisation of water-soluble monomers in order to produce polymers with controlled molecular weight and narrow polydispersity.

Keywords: Atom transfer, ATRP, Initiator, Polymerisation

INTRODUCTION

Free-radical polymerisation is the most important industrial process for producing various vinyl polymers. However, conventional free radical polymerisation techniques do not produce controlled molecular weights and molecular weight distributions due to large amount of chain transfer and termination reactions. In order to overcome these drawbacks, a new polymerisation technique known as Atom Transfer Radical Polymerisation (ATRP) was pioneered independently by (Matyjaszewski and Wang, 1995) and (Sawamoto *et al.*, 1995).

Since its inception, ATRP also known as transition metal mediated living radical polymerisation has proven to be robust for the design of polymers of complex architecture and precise molar mass. This type of polymerisation is inert to many functional groups present in monomers or solvents, tolerant to impurities present in solvents and monomers and also allows for the facile synthesis of many polymers of novel structure and topology (Haddleton *et al.,* 2000).

Mechanism of ATRP

The general mechanism for transition metal-mediated ATRP involves the generation of radicals (active species) through a reversible redox process catalysed by a transition metal complex (M_t^n-Y/Ligand, where M_t is a transition metal having an oxidation number n, Y may be another ligand or a counter ion) which undergoes a one electron oxidation with concomitant abstraction of a halogen atom (X) from an initiator (dormant species; R-X). This process occurs with a rate constant of activation (k_{act}) and deactivation (k_{deact}). Polymer chains grow by the addition of intermediate radicals to monomers in a similar manner to a conventional radical polymerisation, with the rate constant of propagation (k_p). Termination reaction (k_t) may also occur in ATRP but it's very negligible. This process generates oxidised metal complexes (M_t^{n+1}) as persistent radicals to reduce the concentration of growing radicals thereby minimising termination reactions. The control of molar mass and of polydispersity in controlled radical polymerisation is achieved by converting the chain propagating radicals into a "dormant form" in equilibrium with the active form. This ensures a very low concentration of the active species and reduces termination reaction (Matyjaszewski and Xia, 2001).
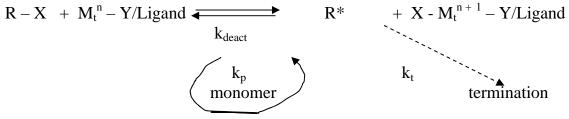
$$R - X \; + \; M_t^n - Y/Ligand \; \xrightleftharpoons{k_{deact}} \; R^* \qquad + \; X - M_t^{n+1} - Y/Ligand$$

$$\underset{monomer}{k_p} \qquad\qquad \underset{termination}{k_t}$$

Figure 1: Mechanism of transition metal-mediated ATRP

ATRP Initiators

Like other polymerisation systems, ATRP is a multicomponent system which includes monomer, initiator, catalyst, solvent and temperature. Each of these components plays a significant role in ATRP hence careful choice of a suitable component is very essential for a successful ATRP.

Alkyl halides (RX) or their derivatives are mostly used as ATRP initiators and their main role is to determine the number of initiated chains. The polymerization rates in ATRP are first order with respect to the concentration of RX and the halide group (X) must rapidly and selectively migrate between the growing chain and the transition metal complex.

Bromine and chlorine are the halogens that afford the best molecular weight control while iodine and fluorine do not work very well in ATRP due to very low C-I and very fast C-F bond dissociation energies respectively (Patten and Matyjaszewski, 1998).

The choice of an ATRP initiator is a very important factor in a successful ATRP and also depends on the type of the polymer to be synthesised e.g. homopolymer, block copolymers or multi arm star polymers. Many researchers have demonstrated easier methods of preparation of ATRP initiators mostly by esterification of hydroxy-functional compounds with 2-bromo-2-methylpropionyl bromide or its derivatives (Angot *et al.,* 1998), (Vidts and Du-Prez, 2006), (Jankova *et al.,* 1998).

MATERIALS AND METHODS
2,2-dimethyl-1,3-dioxolane-4-methanol (97%, Acros), anhydrous tetrahydrofuran (Acros), Triethylamine (99.7%, Acros), 2-bromo-2-methylpropionyl bromide (98%, Acros), methoxybenzene (Acros). All other reagents and solvents were obtained at the highest purity available and used without further purification. All glassware was washed thoroughly, rinsed several times with de-ionised water and oven-dried overnight at 160°C prior to use.

Synthesis of Water-Soluble Atrp Initiator
The synthesis of the ATRP initiator (1,2-dihydroxypropane-3-oxy-(2-bromo-2-methylpropio-nyl) was carried out in two steps as follows;

(i) Synthesis of 2,2-dimethyl-1,3-dioxolane-4-methoxy-(2-bromo-2-methyl propionyl)
Triethylamine was dried over KOH pellets and glassware were dried overnight prior to use. 2,2-dimethyl-1,3-dioxolane-4-methanol (0.04 mol, 5.29 g), triethylamine (0.08 mol, 8.10 g) and anhydrous tertahydofuran (50 ml) were charged in to a 100 ml round-bottom flask equipped with a magnetic stirrer and cooled to 0°C with an ice bath.

2-bromo-2-methylpropionylbromide (0.044 mol, 5.44 ml) was added drop wise via a syringe. The mixture was subsequently stirred for 45 minutes while being brought to ambient temperature. The reaction mixture was poured in to an excess of cold water and then extracted with 50 ml of diethyl ether. The organic layer was separated, washed with a saturated solution of sodium carbonate, acidified water (pH 4.5) and a second aliquot of sodium carbonate. The organic layer

was dried over anhydrous sodium sulphate, filtered and the solvent removed under vacuum.

2,2-dimethyl-1,3-dioxolane-4-methoxy-(2-bromo-2-methylpropionyl) was finally isolated as a slightly yellowish oil. The product yield was 86%.

0.1g of the oil was dissolved in equal amount of deuterated chloroform (CDCl$_3$) and the ^{1}H NMR was obtained using a JEOL DELTA-GX-270 MHz NMR spectrometer. The spectrum is presented in Figure 3.

(ii) Synthesis of 1,2-dihydroxypropane-3-oxy-(2-bromo-2-methylpropionyl) (water-soluble ATRP initiator).
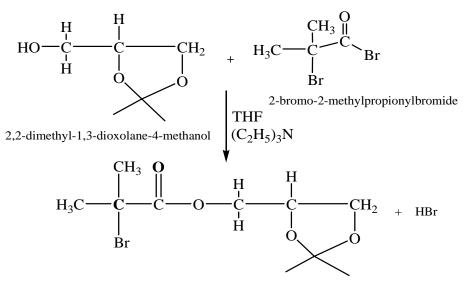A mixture of 5 g of 2,2-dimethyl-1,3-dioxolane-4-methoxy-(2-bromo-2-methyl propionyl), 15 ml of glacial acetic acid, 40 ml of water and 5 drops (catalytic amount) of methoxybenzene were stirred for 30 minutes at 80°C in a 250 ml round-bottom flask. The solution was cooled to room temperature prior to the addition of 50 ml of diethyl ether in a 1 litre separating funnel.

The crude product was obtained from the combined organic layers following the removal of solvent under vacuum. The crude product (yellowish oil) crystallises overnight on standing at ambient temperature and yields a yellowish solid that weighed 3.54 g. The product was further recrystallised from 90 ml of toluene and crystals were obtained. The percentage yield was 70%. 0.1 g of the product was dissolved equal amount of deuterated chloroform (CDCl$_3$) and the ^{1}H NMR was obtained using JEOL DELTA-GX-270 MHz NMR spectrophotometer. The spectrum is presented in Figure 5.

RESULTS AND DISCUSSION
The Synthesis of the ATRP initiator involved 2 steps. In the first step, high purity reagents and anhydrous solvents were used. This is necessary in order to avoid any unwanted side reactions normally caused by the presence of impurities e.g. water in the reaction medium.

Similarly, the acidic by-product (HBr) produced in step 1 was neutralised with saturated solution of sodium carbonate until there was no effervescence, an indication of the complete neutralisation of the HBr by-product. The high percentage yield (86%) obtained indicated the effectiveness of this method. The chemical equation involved in the formation of intermediate product (2,2-dimethyl-1,3-dioxolane-4-methoxy-(2-bromo-2-methyl propio- nyl) is as follows;

Figure 2: Reaction scheme for the synthesis of intermediate for ATRP initiator.

Similarly, ^{1}H NMR of this intermediate product confirms the structure as shown in Figure 3
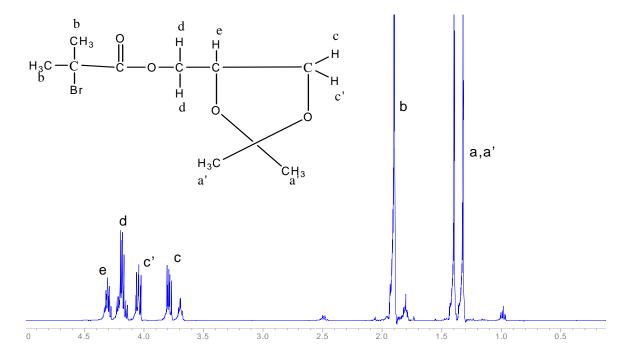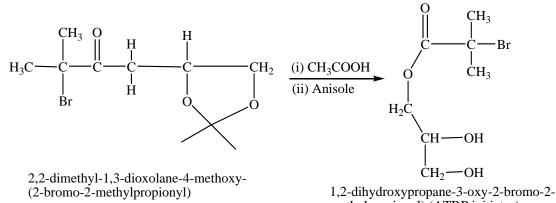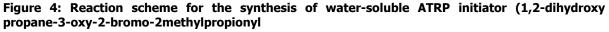

Figure 3: ^{1}H NMR of 2,2'-dimethyl-1,3-dioxolane-4-methoxy-(2-bromo-2-methylpropionyl) in Deuterated dimethyl sulfoxide (DMSO-d6), δ ppm: 1.31 and 1.38 [s, 3H, OC(CH$_3$)$_2$O], 1.93 [s, 6H, C(CH$_3$)$_2$Br], 3.76 (dd, 1H, CHCHO), 4.07 (dd, 1H, CHOCH$_3$), 4.18- 4.22 (dd, 2H, CH$_2$OCO), 4.31 (m, 1H, CHCH$_2$O).

In the 2nd step, the product above was hydrolysed in acidic medium using methoxybenzene (anisole) as catalyst to produce the water soluble ATRP initiator (1,2-dihydroxypropane-3-oxy-2-bromo-2methylpropionyl) as follows;

2,2-dimethyl-1,3-dioxolane-4-methoxy-
(2-bromo-2-methylpropionyl)

1,2-dihydroxypropane-3-oxy-2-bromo-2-
methylpropionyl) (ATRP initiator)

Figure 4: Reaction scheme for the synthesis of water-soluble ATRP initiator (1,2-dihydroxy propane-3-oxy-2-bromo-2methylpropionyl
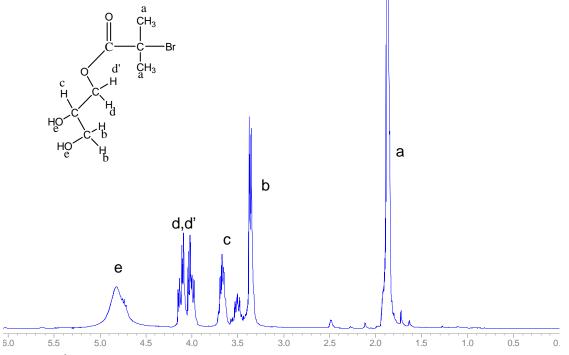

Figure 5: ^{1}H NMR of 1,2-dihydroxypropane-3-oxy-2-bromo-2methylpropionyl in Deuterated dimethyl sulfoxide (DMSO-d6), δ ppm: 1.93 [s, 6H, C(CH₃)₂Br], 3.42 (d, 2H, CH₂OH), 3.72 (m, 1H, CHOH), 4.04 (dd, 1H, CH_d'OC), 4.17 (dd, 1H, CH_dOC), 4.70- 4.90 (s, 1H, (OH)₂).

Similarly, ^{1}H NMR of the final product corresponds to the structure of the water-soluble ATRP initiator as shown in Figure 5. Further solubility test on this product confirm that it has an excellent solubility in water, hence it can be used as initiator in ATRP.

CONCLUSION
A water soluble ATRP initiator (1,2-dihydroxypropane-3-oxy-2-bromo-2-methylpropionyl) has been synthesised by a two step reaction. ^{1}H NMR of both the intermediate and final products has confirmed the structure of the targeted products. In view of the current need of conducting polymerisation in water due to the fact that water is non-toxic, relatively cheaper and environmentally friendly, this initiator will be very useful in the polymerisation of water-soluble monomers in order to produce polymers with well-defined molecular weight and narrow polydispersity.

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