A novel route to the preparation of aldehyde end-functionalised oligomers *via* catalytic chain transfer polymerisation

Thomas P. Davis,*[a] Michael D. Zammit,†[a] Johan P.A. Heuts[a] and Keith Moody[b]

[a] *School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Sydney, NSW 2052, Australia. E-mail: t.davis@unsw.edu.au*

[b] *Orica, Newsom St, Ascot Vale, VIC 3032, Australia*

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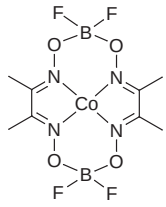
Catalytic chain transfer polymerisation of ethyl α-hydroxymethacrylate with cobaloxime boron fluoride is shown to be an effective route for the production of oligomers with an aldehyde end-functionality.

Catalytic chain transfer polymerisation has proven to be a very efficient technique for molecular weight control in free-radical polymerisation.[1] The catalytic nature of this process and the very high chain transfer constants associated with the used chain transfer agents (*i.e.* certain low spin Co^{II} complexes such as cobaloximes and porphyrins) require only parts per million quantities for a molecular weight reduction by orders of magnitude. Numerous experimental investigations have shown this process to be most efficient for monomers containing an α-methyl group, such as the methacrylate series of monomers.[1,2] Chain transfer constants (*i.e.* the ratio of the chain transfer and the propagation rate coefficients) for cobaloxime boron fluoride



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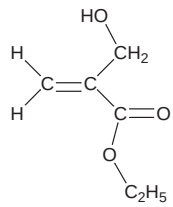

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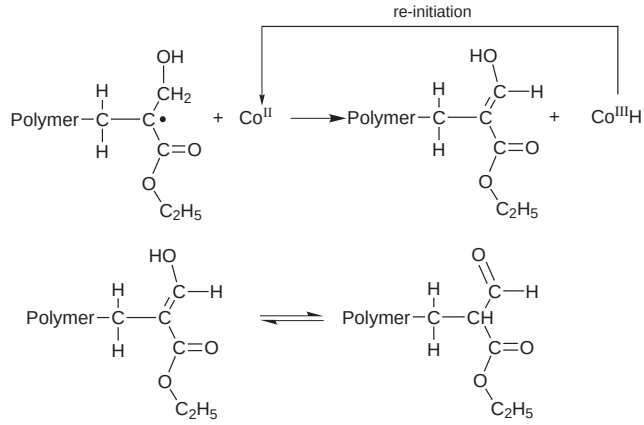
1 in methyl methacrylate polymerisation are typically of the order 10^4, whereas they are typically an order of magnitude smaller for styrene (*i.e.* a monomer without an α-methyl group).[2]

The use of catalytic chain transfer agents instead of conventional chain transfer agents such as mercaptans has a further advantage in that it introduces an end-functionality in the form of a terminal double bond, which can subsequently be modified. In the present investigations, our main aim is to introduce a different end-functionality without the need for a post-polymerisation modification. Our target is the acetoacetyl functionality, which has found interesting uses in the field of thermoset coatings chemistry.[3] This functionality can be used for a whole series of crosslinking reactions and Michael additions. Here, we show that this functionality can be introduced by the catalytic chain transfer polymerisation of ethyl α-hydroxymethacrylate **2**, a monomer which belongs to the methacrylate series (and hence should readily undergo the catalytic chain transfer reaction), and whose derived polymeric radical should give the acetoxyacetal functionality *via* a tautomeric rearrangement of the formed enol after the abstraction of a hydrogen atom of the α-hydroxymethyl group (see Scheme 1).

Ethyl α-hydroxymethacrylate **2** was prepared according to the method described by Villieras and Rambaud.[4]‡ It was found that the monomer readily undergoes free-radical polymerisation yielding polymers consisting of approximately 700 monomer units (at 60 °C, [AIBN] = 10^{-2} M) as determined by gel



Scheme 1

permeation chromatography using a poly(methyl methacrylate) calibration curve. In order to investigate the catalytic chain transfer behaviour of ethyl α-hydroxymethacrylate with COBF, we estimated its chain transfer constant [with respect to a poly(methyl methacrylate) calibration curve] using the conventional Mayo procedure.[5] In this procedure, the chain transfer constant is determined from the slope of a plot of the reciprocal degree of polymerisation (1/DP) *vs.* the ratio of [chain transfer agent] to [monomer]. In Fig. 1, such a plot is shown for the current system at 60 °C and a chain transfer constant of 700 is found.§ This value, which we expect to be higher once we can use the true Mark–Houwink constants in our molecular weight analysis, clearly indicates that the current monomer is suitable for catalytic chain transfer polymerisation.

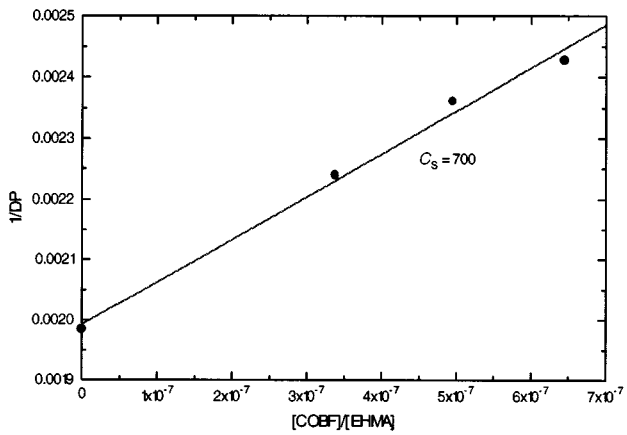


Fig. 1 Mayo plot for the determination of the chain transfer constant (C_S) for COBF in a free-radical polymerisation of ethyl α-hydroxymethacrylate at 60 °C.

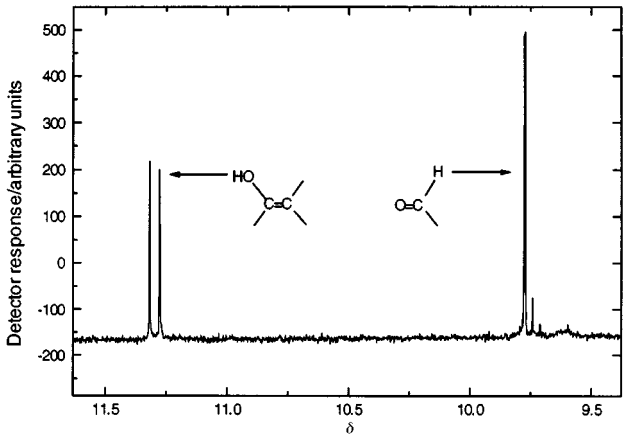


Fig. 2 Expansion of the 300 MHz ^{1}H NMR spectrum of poly(ethyl α-hydroxymethacrylate) in the region between δ 9.5 and 11.5, clearly indicating the presence of aldehyde (δ 9.77) and enol (δ 11.29) endgroups.

The homopolymers obtained *via* catalytic chain transfer polymerisation were analysed using 300 MHz ^{1}H NMR spectroscopy (Bruker ACF 300), and the most interesting region of the obtained NMR spectrum is shown in Fig. 2. The signals that are shown in this figure do not appear in the spectrum of the monomer and can be attributed to the formyl proton (δ9.77) and to enolic hydroxyl protons (δ 11.29). Both signals are characteristic for diketonic systems displaying a keto–enol tautomeric equilibrium.[6] Although further and more detailed NMR studies are required for a more detailed assignment of the signals (*e.g.* whether intramolecular hydrogen bonding occurs),[7] the current results are sufficient proof that the aldehyde end-functionality is indeed formed in significant quantities.

In summary, we have clearly shown that ethyl α-hydroxymethacrylate readily undergoes an effective catalytic chain transfer polymerisation with COBF, and that using this procedure the very useful aldehyde end-functionality is introduced.

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Notes and references

† Present address: Dulux Australia, McNaughton Rd, Clayton, VIC 3168, Australia

‡ *Monomer synthesis*. The synthesis route of Villieras and Rambaud was followed exactly, with the only difference that the addition step of the potassium carbonate solution was carried out at 0 °C instead of room termperature. Yield: 75%. δ_H($CDCl_3$, 298 K, 300 MHz) 5.8 and 6.2 (=CH_2), 1.28 (–CH_3), 2.63 (–OH), 4.23 (–CH_2–); ν_{max}(NaCl)/cm^{-1} 1630 (C=C), 1710 (C=O).

§ *Chain transfer constant measurements*. The monomer was purged with high purity nitrogen gas for 1 h prior to use. Two stock solutions were prepared: (i) an initiator stock solution, and (ii) a catalyst stock solution. (i) The initiator solution was prepared by dissolution of approximately 220 mg of AIBN in 45 ml of monomer. (ii) The catalyst stock solution was prepared by dissolution of approximately 3 mg of catalyst into 10 ml of solution (i) and a subsequent 10-fold dilution with solution (i). Four reaction mixtures were then prepared, each containing 4.0 ml of initiator solution and 0, 0.2, 0.3 and 0.4 ml of catalyst stock solution, respectively. At all stages of these preparations, care was taken to exclude oxygen from the reaction mixtures. The reaction ampoules, specially modified for use with standard Schlenck equipment, were further deoxygenated by two freeze-pump-thaw cycles and subsequently placed in a waterbath (thermostatted at 60 °C) for 15 min. Finally the obtained polymer was isolated and molecular weight analysis performed with gel permeation chromatography.

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