The Unexpected Behaviour of Epoxidised Macromonomers Derived from Catalytic Chain Transfer During Ring Opening Copolymerisation

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ADDITIONAL INFORMATION

Mechanistic Investigation into the Ring-Opening of e-MMA$_2$. According to the conditions used, ring-opening and polymerisation should occur via the activated monomer mechanism (AMM), in which the alcohol initiates the polymer chain resulting in a neutral chain end which cannot undergo backbiting reactions. This is clearly not the case in this situation. To probe the nature of the active mechanism, ^{1}H NMR was used to monitor the ring-opening reaction over time. To a 1:1 molar mixture of $BF_3{\cdot}OEt_2$ and BzOH, e-MMA$_2$ was added sequentially in equimolar batches. After each addition, ^{1}H NMR was used to confirm complete ring-opening (Figure 2) and SEC to confirm that propagation was not the major ring-opening mechanism (Figure S1). It should be noted, however, that an increase in the complexity and number of signals in the spectrum suggests the possibility of oligomerisation if not polymerisation. It was noticed that a signal at 3.4 ppm in the ^{1}H NMR (which was previously attributed to splitting of the methoxy protons) increased as more equivalents of e-MMA$_2$ were added (Figure 2(a)).

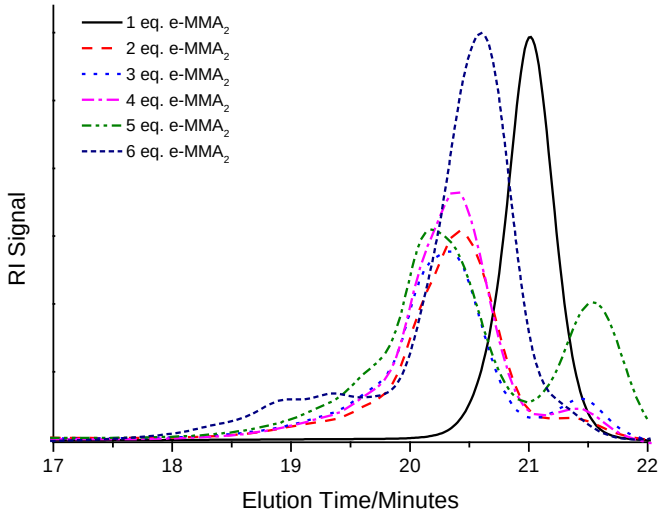
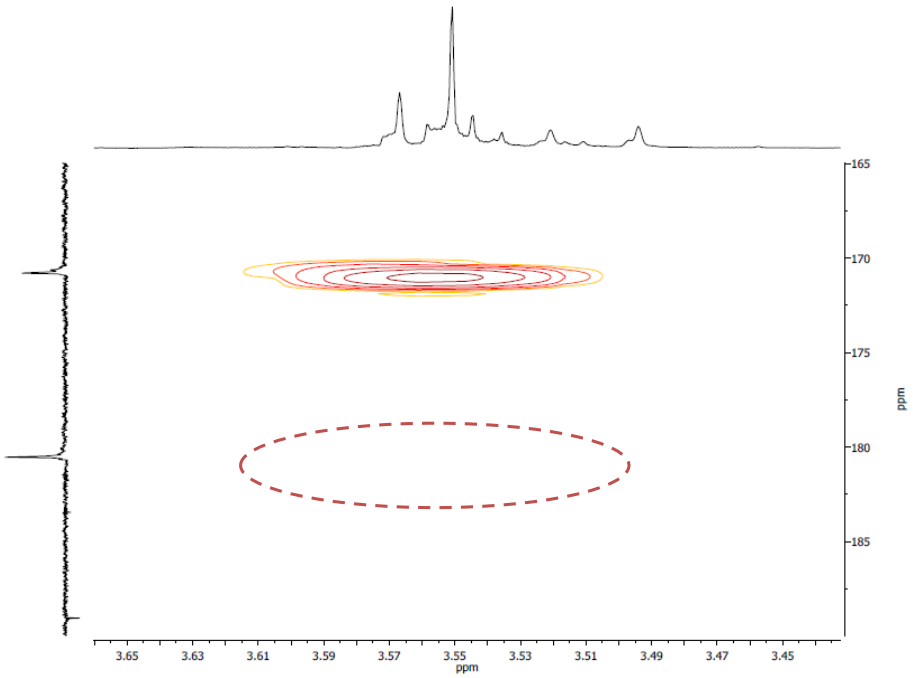


Figure S1. SEC chromatogram of multiple additions of e-MMA$_2$ (1-5, dashed) to benzyl alcohol in the presence of $BF_3.OEt_2$ compared to e-MMA$_2$ (solid).

^{1}H-^{13}C gHMBC was used to identify the peak at 3.4 ppm observed in the ^{1}H NMR. Strikingly, it seems that only one of the methoxy groups of e-MMA$_2$ is coupled to a carbonyl (Figure S2a). This indicates that a methoxy group has been eliminated. Ring-opening of e-MMA$_2$ with an alcohol (in this case BzOH), results in a species that contains a hydroxyl group. In a normal cationic ring-opening mechanism, this hydroxyl group opens the next monomer and propagation continues. However, it is thought that the alcohol end group may also back-bite onto the ester functionality, forming a ring and liberating methanol (Scheme S1). The epoxide ring can be opened on both sides (1,2 and 2,1) which results in a 5 or 6 membered ring (**2** and **3**) respectively. However, the signals characteristic to a six-membered ring (doublet around 5.4 ppm) are not present, implying that only 5-memebered rings are formed. The instability of the 6-membered ring compared to the 5-membered ring is supported by

literature on cyclic esters.[45, 46] The methanol liberated upon cyclisation of e-MMA_2 into **2** plays a further role as it can also act as an initiator, ring-opening e-MMA_2. The ring-opened epoxide can then also back-bite to form a 5-memebered ring, again liberating methanol. This hypothesis is supported by the ^{1}H-^{13}C gHMBC results, which shows cross-peaks at 2.9/3.3 (^{1}H) and 60 (^{13}C) ppm and 3.0 (^{1}H) and 75 (^{13}C) ppm corresponding to methanol initiated e-MMA_2 (Figure S2b).

(a)



(b)

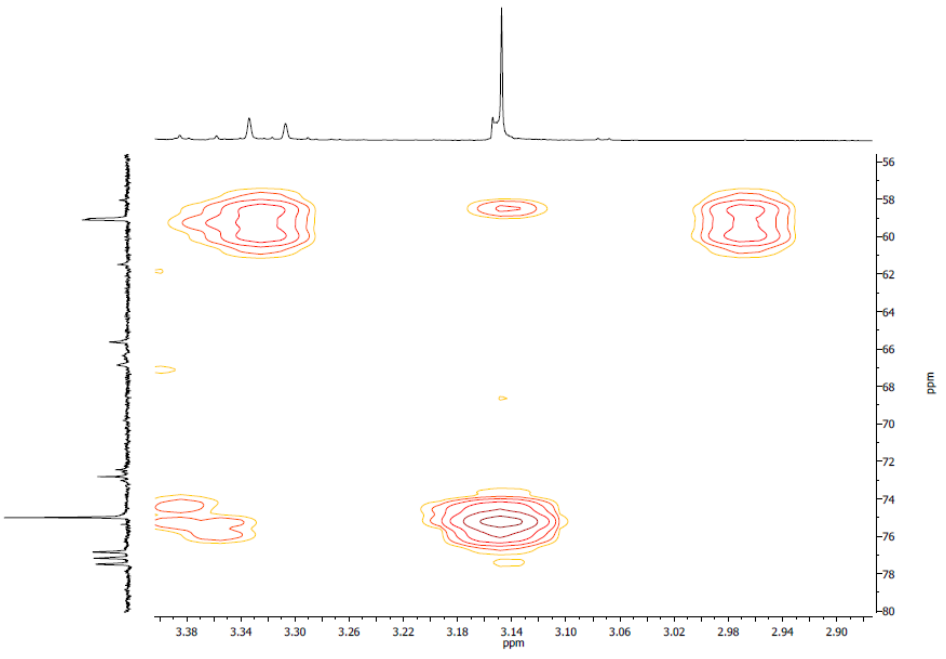


Figure S2. Partial ^{1}H-^{13}C gHMBC NMR spectra of entry 10, Table 1.

Scheme S1. Cyclic back-biting of e-MMA_2 to **2**.

End-group Analysis. The end groups observed when THF is polymerised in the presence of e-MMA_2 are shown in Figure S3. We believe that the methoxy end groups originate as a result of chain scission. The scission of chains via the *in-situ* formation of BF_4^- H^+, cleaves the ether bonds, which can then react further with methanol (produced as a result of the formation of the cyclic structure, **2**) resulting in methoxy-based end groups. As chain scission can occur at any point in the chain and multiple times within the same chain, polymers with two methoxy end groups can also be formed. Similarly, pTHF end-capped with two **2** groups is thought to be a result of chain scission, giving rise to chains ends which are capable of ring-opening e-MMA_2.

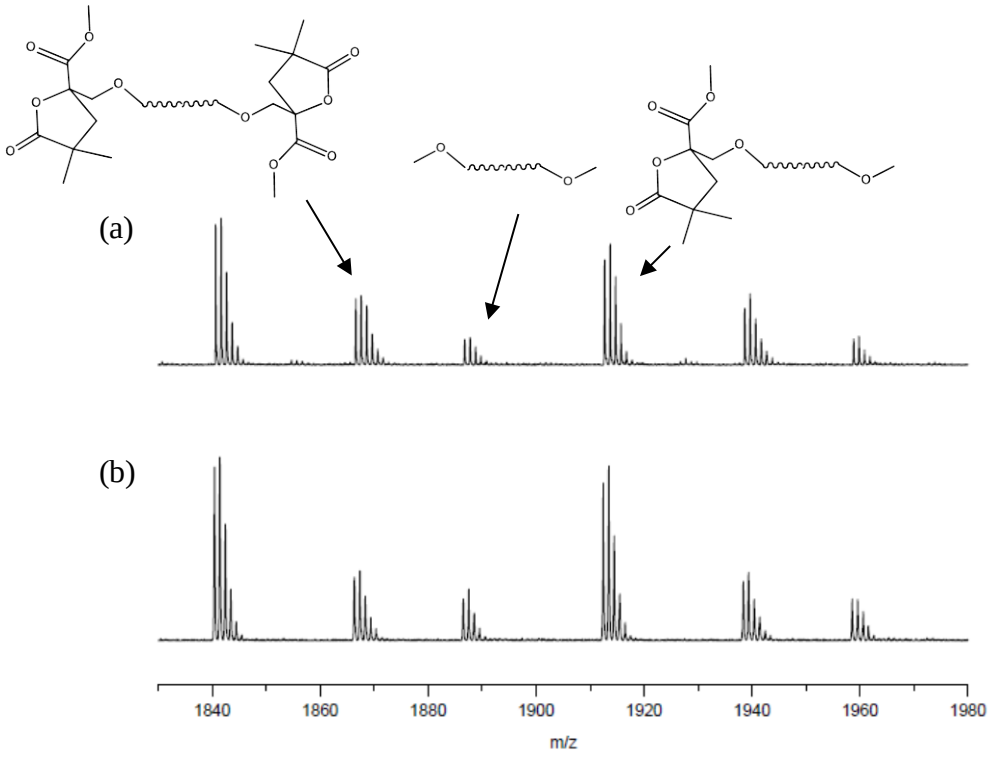


Figure S3. MALDI-ToF-MS of entry 3 (Table 2), quenched with (a) ethanol and (b) methanol.

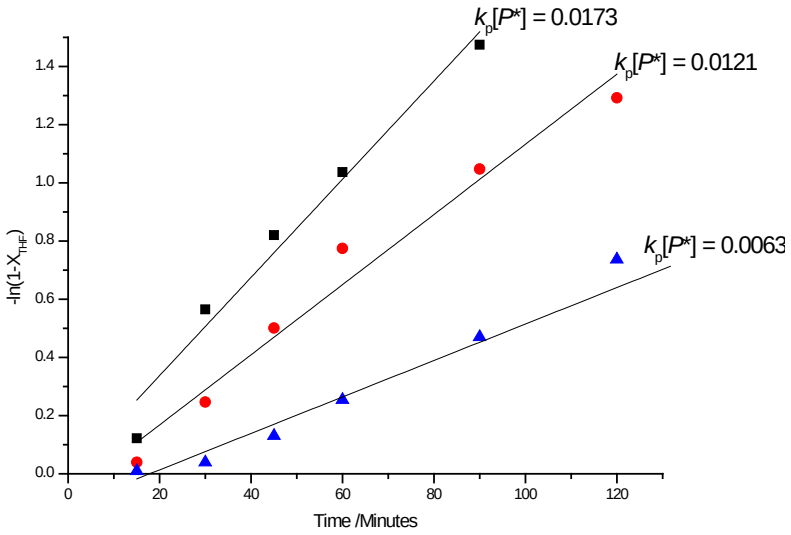


Figure S4. Semilogarithmic kinetic plots for the three copolymerisations between THF and e-MMA$_2$. Ratio of e-MMA$_2$:THF = 10:100 (■), 4:100 (●) and 1:100 (▲).

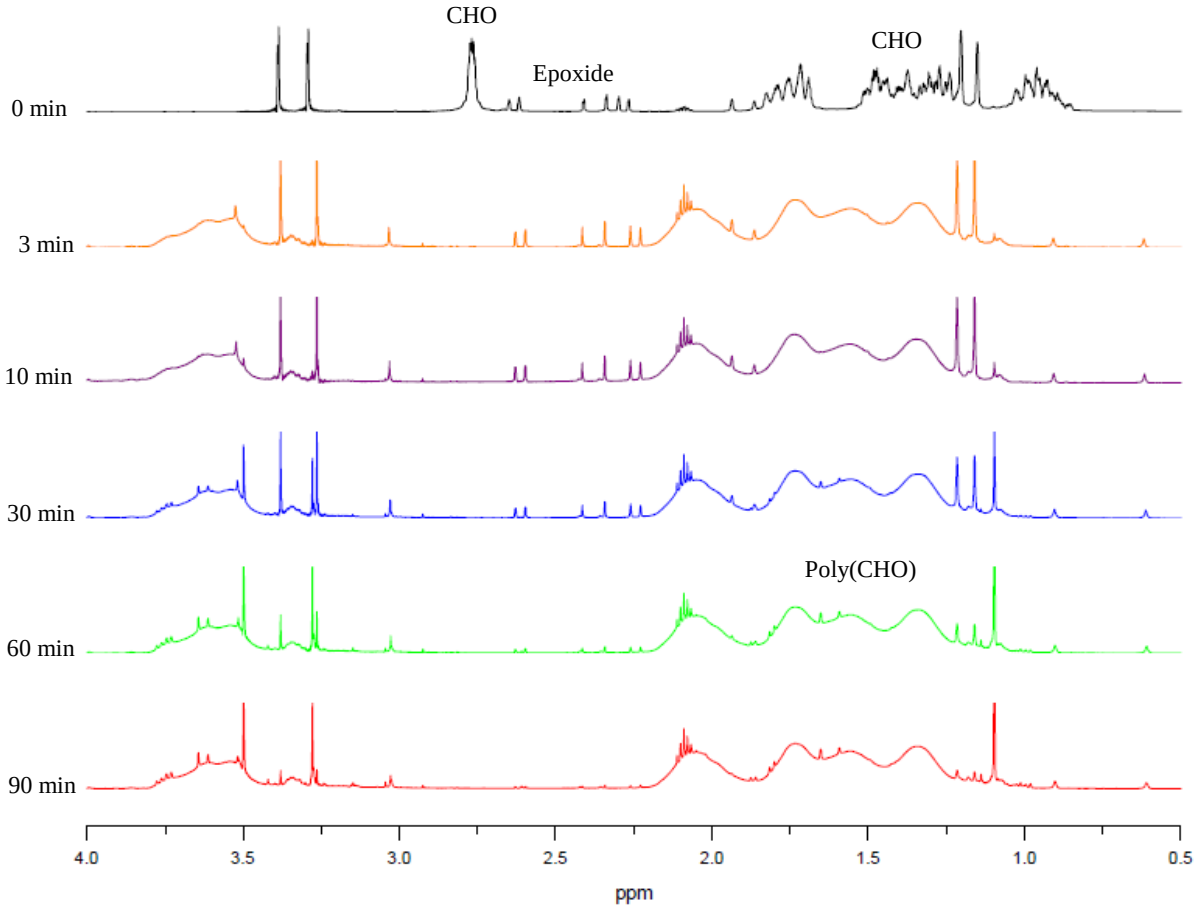


Figure S5. ^{1}H NMR (200 MHz, toluene-d_8) spectra of cyclohexene oxide (CHO) polymerised in the presence of e-MMA$_2$.