



Understanding the acceleration in the ring-opening of lactones delivered by microwave heating



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ARTICLE INFO

Article history:

Received 23 August 2013

Received in revised form 31 October 2013

Accepted 12 November 2013

Available online 16 November 2013

Keywords:

Ring opening

Cyclic lactones

Tin

Ester

Microwave

Acceleration

Polymerisation

ABSTRACT

This paper reports the first detailed study focussed upon identifying the influence that microwave heating (MWH) has upon the mechanistic steps involved in the tin catalysed ring-opening of lactones such as ϵ -caprolactone (CL). Direct comparison of conventional (CH) and microwave (MWH) heated kinetic studies showed that a key factor in the reduction of the polymerisation cycle time with MWH was the elimination of the induction period associated with in situ catalyst manufacture and initiation. NMR studies demonstrated that the most significant mechanistic change contributing to the observed induction time reduction/elimination was faster initiation (i.e., reaction of the initiator/catalyst complex with the first monomer unit). Consequently, analysis of the dielectric properties of the reaction components predicted that this MWH induced change was related to the selective volumetric heating of both the catalyst and the monomer. Furthermore, this indication of the greater significance of the initiation step in defining the length of the induction period suggests that this is the rate determining step of the process, whether conducted by CH or MWH. Increasing the catalyst concentration was demonstrated to produce significant reductions in reaction heat-up time and to induce a significant (up to 30 °C) overshoot in reaction mixture bulk temperature in with MWH only. Thus supporting the conclusion that selective heating of the organometallic species in the system contributes directly to differences in the reaction conditions and which need to be taken into account when drawing comparisons with CH systems. Consequently, both effects were concluded to be thermally generated from selective volumetric heating.

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1. Introduction

Ring-opening polymerisation (ROP) has been industrially applied for many years to produce a large range of polyesters of great social/economic importance.¹ However, recent studies have extended this basic technique to synthesise more complex, specifically designed polymeric structures by utilising novel catalysts to deliver significant mechanistic control. Consequently, facile ROP synthesis of architectural copolymers such as block/

graft structures,^{1–4} and/or introduction of terminal functionality via use of specific initiating moieties have been reported.⁴

Much of the recent interest in polyesters from cyclic monomers such as ϵ -caprolactone (CL) has been inspired by their biocompatibility and/or biodegradability. Poly(caprolactone) (PCL) is of particular interest because of its attractive mechanical properties and miscibility with a wide range of common solvents and polymers.¹ Consequently, achieving the efficient and rapid ROP of CL has been a significant target and also the subject of a recent detailed literature review.¹ Most of these studies focused on the control characteristics achieved by adopting particular catalytic mechanisms/species. However, there has been little commercial exploitation of these new catalyst systems, because most have yet to achieve the regulatory clearance required for industrial exploitation and/or are not commercially available.

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As a result, recent developments in processing techniques, including microwave heating (MWH), have also been investigated to determine if they could deliver improvements in PCL production. In microwave heated ROP (MROP), volumetric heating replaces the convection/conduction heating delivered by conventional heated ROP (CROP).^{5,6} However, the literature conclusions on the existence/root causes of any resultant MWH benefits have been inconsistent. Some MWH studies claimed benefits such as rate enhancements,^{5,6} whilst others highlighted negative effects such as rate/yield reductions.⁷ Consequently, the MROP of CL has been investigated with a variety of catalysts, microwave instruments, and solvents.^{7–20} Bulk MROP using a titanium⁸ and zinc powder catalyst at 2.45 GHz⁹ was claimed to deliver accelerated rates compared to conventional heating (CH), whether the energy was applied continuously^{8,9} or pulsed into the reaction mixture.¹⁰ Similarly accelerated reaction rates were also reported when using benzoic acid¹¹ and lanthanide halide catalysts at the same frequency.¹² MWH polymerisations involving organic solvents and ionic liquids have also been conducted.^{7,13} For example, higher monomer conversions were obtained by using zinc oxide as a catalyst and 1-butyl-3-methylimidazolium tetrafluoroborate as the ionic liquid solvent.¹³ Meanwhile, both rate acceleration and deceleration were reported with enzyme catalysed MROP using a lipase catalyst in either ether, benzene, or toluene, where the performance was concluded to be dependent on the solvent employed.⁷

Tin(II) octanoate ($\text{Sn}(\text{Oct})_2$) has been used as a catalyst for bulk MROP of CL when in the presence of an alcohol initiator,^{9,14–17,19,20} and increased rates have also been reported under non-isothermal conditions.^{9,14,15} Investigation of the heating characteristics of CL monomer and the polymerisation mixture at a frequency of 2.45 GHz concluded that the mass of CL present in a sample had a strong influence on the heating characteristics of the specific sample.¹⁵ Increasing the amount of monomer present induced an increase in the bulk temperature of the sample in experiments conducted at the same power levels. From a comparison of $\text{Sn}(\text{Oct})_2$ catalysed MROP conducted at 2.45 GHz and 'flash' CH (i.e., introduction into a hot salt bath) it was concluded that the rate observed in 'flash' CH was superior to that achieved by MWH at the powers applied to the sample in the microwave applicator used.¹⁶ Further comparison of the kinetics of MWH and 'flash' CH at various temperatures led to the conclusion that the 'flash' CH rate enhancement was a purely thermal effect as it obeyed Arrhenius's law. However, the increase in the MWH rate constants were claimed not to fit this law, suggesting the presence of a non-thermal microwave effect upon the polymerisation.¹⁷ It was also reported that this conclusion was supported by an observed abrupt change in k_p . A large scale MROP study at 2.45 GHz, where the reaction temperature was monitored by an IR sensor, reported an inter-dependency between the applied power and/or monomer mass with the reaction temperature. The higher the power and mass, the higher the temperature achieved.¹⁸ Meanwhile, $\text{Sn}(\text{Oct})_2$ catalysed ROP synthesis of CL macromonomers using methacrylic and acrylic acid initiators, where the temperature was assessed using a fibre optic thermocouple, demonstrated no significant rate acceleration when comparing MWH and CH.¹⁹ MROP of CL was also investigated using $\text{Sn}(\text{Oct})_2$ both with and without 1,4-butadienol initiator and a variable frequency reactor. These polymerisations were kept at a constant temperature, within the range 120–200 °C, by pulsing the power and it was concluded that microwave energy delivered an enhanced polymerisation rate with this system.²⁰

Therefore, largely independent of the catalyst/initiator system or reactor type utilised, the majority of authors claim to have observed ROP rate enhancements with CL by adopting MWH. However, these conclusions have often been drawn without conducting

direct CH comparisons or without applying the same temperature measurement methods to both methods. Rather, many conclusions are solely based on the analysis of the product polymer properties, such as molecular weight (Mwt). Furthermore, no formal kinetic study of MROP using an alcohol/ $\text{Sn}(\text{Oct})_2$ has been conducted. Therefore, although CROP of CL using $\text{Sn}(\text{Oct})_2$ /alcohol is widely accepted to be a controlled/pseudo living polymerisation, there has been no investigation into the control characteristics exhibited by MROP using this control system. In addition, very little information about the dielectric properties of either the monomer or polymerisation mixture has been reported to explain any MWH effects observed.

Thus, this paper reports an investigation of MROP of CL using $\text{Sn}(\text{Oct})_2$ /benzyl alcohol (BzOH) as the catalyst/initiator system, which is accompanied by; (a) direct measurement of the dielectric properties of both reagents and reaction mixtures across a broad temperature range, which includes the target reaction temperature, (b) comparative kinetic GPC and NMR studies and (c) direct measurement of the bulk reaction medium temperature in order to identify/explain the root causes of any empirically observed difference between MWH and CH reaction times. In addition, the controlled characteristics of the polymerisation at different target DPs and catalyst concentrations were assessed in order to demonstrate that MROP exhibited these traits.

2. Results and discussion

This study focused on bulk ROP of CL, using $\text{Sn}(\text{Oct})_2$ /BzOH as the catalyst/initiator system. This was because; (a) such 'solventless' reactions represent a more sustainable/lower VOC synthetic methodology,^{22,23} (b) this removed any influence of solvent behaviour on the different heating methods, (c) $\text{Sn}(\text{Oct})_2$ is widely used in industrial production because it has US Food & Drug Administration approval and (d) BzOH exhibits a unique ¹H NMR resonance, isolated from those of the main polymer chain useful in M_n determination.^{24,25}

The variation in dielectric properties with temperature for each MROP precursor was determined to aid in understanding/predicting the interaction between microwave energy and the materials within the reaction mixture. For this purpose, a comparison of the loss tangent ($\tan \delta$) was used. The value $\tan \delta$ is defined as the ratio of dielectric loss to dielectric constant and is a convenient way of representing the MWH capability of a particular material.²⁶

It was observed that the $\tan \delta$ values of both CL and BzOH declined as the temperature increased, whilst that of $\text{Sn}(\text{Oct})_2$ gradually rises over this temperature range. At 30 °C the values of $\tan \delta$ for both CL and BzOH are significantly higher than that of $\text{Sn}(\text{Oct})_2$. Therefore, at this temperature as a bulk material, $\text{Sn}(\text{Oct})_2$ is considered the least likely to contribute to the microwave heating of the ROP system by a significant margin. Meanwhile, at 150 °C, the chosen reaction temperature, the $\tan \delta$ values of the CL and $\text{Sn}(\text{Oct})_2$ are now almost identical (0.12 and 0.10, respectively) whilst that of BzOH is essentially zero (0.03). Therefore, this data would predict that at the chosen reaction temperature CL and $\text{Sn}(\text{Oct})_2$ should exhibit significant microwave heating profiles and so would be predicted to undergo selective heating compared to BzOH in an MROP at 150 °C (Fig. 1).

2.1. Temperature and power versus polymerisation time profile

In the MROPs conducted in this study, the microwave energy was introduced to the vessel continuously and the maximum power that could be delivered from the CEM reactor was 300 W. Therefore, the power/temperature profile required to achieve and maintain a temperature of 150 °C in the CL/BzOH mixture was

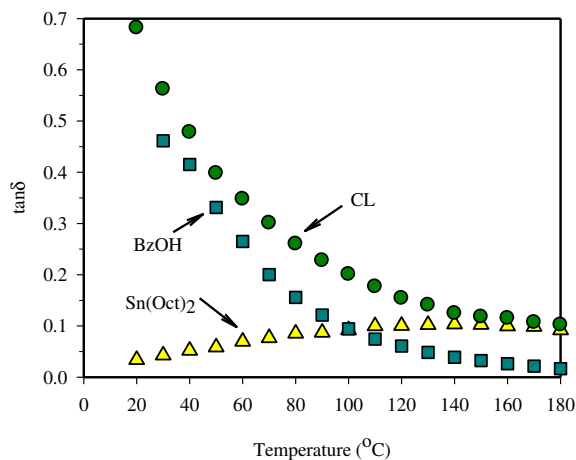


Fig. 1. Temperature dependence of $\tan \delta$ of CL (●), BzOH (■) & Sn(Oct)₂ (▲) (2.45 GHz).

recorded. A typical profile is shown in Fig. 2 (the periodic sharp decreases/increases in both temperature and power traces indicate the moment samples were taken).

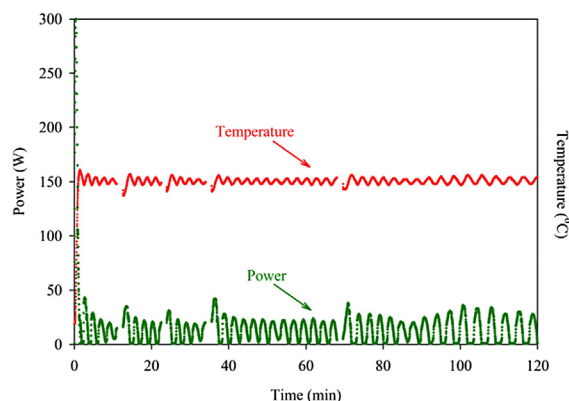


Fig. 2. Typical power and temperature against time profiles for a mixture with a CL/BzOH ratio of 87:1 using MWH at 150 °C.

This profile comparison shows that a short period of high (full 300 W) power was required to raise the reaction mixture to the desired reaction temperature (150 °C). After this, generally a very low power level of approximately 5–25 W was required to maintain this temperature over a 2 h period.

2.2. MROP control characteristics

MROP kinetics using Sn(Oct)₂/BzOH at 150 °C were studied for a target DP=87 polymer. Fig. 3 depicts the resultant semi-logarithmic plot of $\ln([M]_0/[M])$ versus time obtained from a 150 °C MWH experiment with a relative molar ratio CL/BzOH/Sn(Oct)₂ of 87:1:0.012, which demonstrated that a linear relationship was obtained.

A similar linear relationship was found in the plot of M_n versus conversion (Supplementary data Fig. S1). The conversion corrected M_n values of the final polymers were also found to be in close agreement with the calculated, theoretical M_n values (see Table 1), as expected from a controlled system (accepting a small error due to using poly(styrene) GPC standards). Thus it was concluded that this MROP does exhibit controlled characteristics.

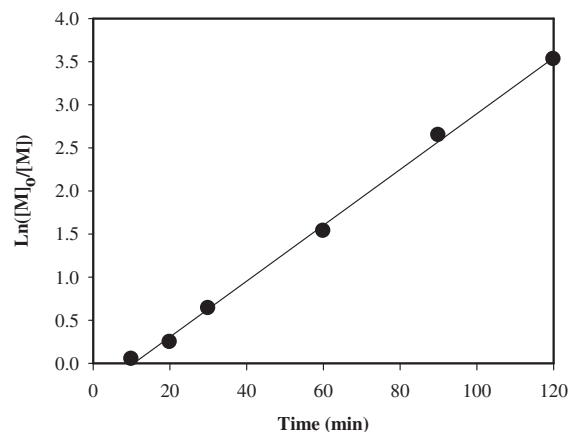


Fig. 3. Semi-logarithmic kinetic plot of $\ln([M]_0/[M])$ versus time. The CL/BzOH/Sn(Oct)₂ relative molar ratio was 87:1:0.012 conducted at 150 °C with MWH.

Table 1

Final polymer properties of CL MROP using set BzOH/Sn(Oct)₂ ratio to deliver different target DPs

[CL] : [BzOH] ratio	Time (min)	Conv (%)	DP	M_n^a theoretical (g/mol)	M_n^b conversion corrected (g/mol)	\bar{D}
20:1	60	96	19	2200	2100	1.35
50:1	90	98	52	5900	5700	1.64
87:1	120	98	86	9800	9600	1.77

^a End-group analysis by ¹H NMR.

^b GPC Mwts were corrected via Mark–Houwink–Sakurada relationship using $K=1.09 \times 10^{-3}$ dL/g and $\alpha=0.6021$.

These results indicated that MROP follows a first-order rate law and that little/no termination is evident until high conversion, again as would be expected for a controlled polymerisation. Furthermore, whilst the \bar{D} values (Fig. 4) fluctuated from 1.2–1.8, in practice the \bar{D} values are typically around 1.2–1.4 for the majority of the reaction indicating good control until monomer levels are depleted sufficiently to allow trans-esterification side reactions to become significant. Duda et al. reported that such side reactions normally cause an increase in \bar{D} in CH reactions. These include segmental exchange of macromolecules (inter-esterification) and macrocyclisation (intra-esterification).²⁷ The former is thought to be primarily responsible for broadening \bar{D} . The increase in MROP \bar{D}

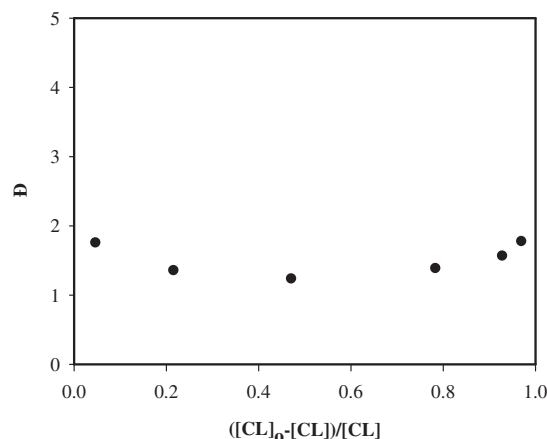


Fig. 4. Dependence of \bar{D} on the degree of conversion at 150 °C using MWH. \bar{D} determined by GPC using PS standard. The CL/BzOH/Sn(Oct)₂ molar ratio was 87:1:0.012.

indicated these side reactions also occurred in MWH polymerisations. However, polymers with low \bar{D} values (1.2–1.4) can be readily obtained if monomer conversion is restricted to below 80%.

2.3. Control over Mwt

The effect of changing BzOH concentration to obtain differing target Mwts was also investigated when using MWH at 150 °C. In these experiments, the Sn(Oct)₂ concentration was held constant (CL/Sn(Oct)₂ ratio fixed at 1:1.37 × 10⁻⁴) and the ability to synthesise via MROP target DPs of 20, 50 and 87 were investigated. The data in Table 1 showed that target DPs could be achieved at high monomer conversion, i.e., between 96 and 99% conversion, by simply changing the [CL]₀/[BzOH]₀ molar ratio, again supporting the conclusion that the MROPs are exhibiting controlled polymerisation properties. Decreasing [BzOH] (increasing target DP) was also observed to result in higher \bar{D} values. Therefore, it was concluded that for shorter chains, the segmental exchange reactions between the polymers were reduced. This was attributed to a lower viscosity in the lower Mwt bulk polymerisation reducing any monomer diffusion problems.

2.4. Direct comparison between CROP and MROP

A series of kinetic studies were conducted using both CH and MWH employing Sn(Oct)₂/BzOH and targeted to achieve DPs of 87 and 20 at 150 °C. An open-vessel reactor system with mechanical stirring was employed to ensure that both types of polymerisation were performed under identical conditions of temperature and pressure. This also minimised any potential for high-pressure thermal effects on the polymerisation when using MWH, such as bulk-superheating caused by the high-pressure build up in a sealed vessel, which have been reported in previous literature studies.²⁸ The CH and MWH data from these experiments are directly compared in Fig. 5. MWH was observed to deliver a significant reduction in the overall polymerisation cycle time. For DP=87, after only 2 h the MROP reached 97% conversion, meanwhile the CROP achieved only 92% after 5 h. Similarly for DP=20, after 1 h MROP conversion was 98%, whilst 2 h was required to reach the same conversion with CROP (see Supplementary data Fig. S2). Upon detailed analysis of this data it was observed that there were a number of factors that contributed these faster cycles. However, if conducted at the same temperature, whilst retaining efficient stirring and to a similar level of conversion (within the region of

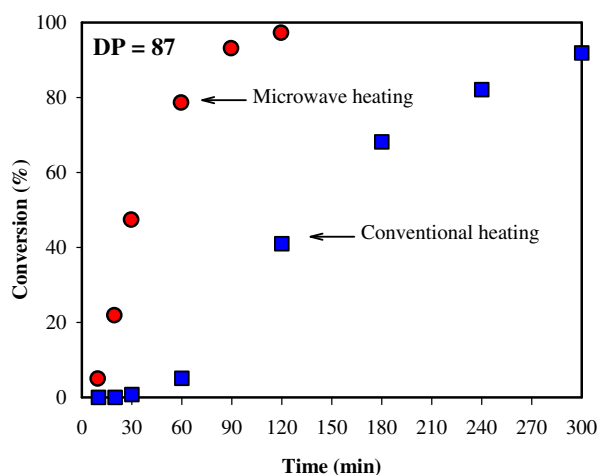


Fig. 5. Comparison of polymerisation kinetics using CH (■) and MWH (●) at 150 °C for DP 87. [CL]/[Sn(Oct)₂]=1:1.37 × 10⁻⁴.

90–97%), then no significant difference in \bar{D} was observed with the final products.

2.4.1. Rapid heat-up. It was observed that with CH it took ~10 min for the reaction mixture to reach 150 °C, whilst using MWH this temperature was reached after only 1–2 min. This difference was attributed to microwaves heating the medium via more efficient volumetric heating, where the energy is introduced instantaneously through the entire bulk. Thus eliminating the reliance on/dominance of conduction/convection processes found in CH methods.²⁹ An additional contribution to shortening of this heat-up time from selective heating is discussed below.

2.4.2. Induction period. Fig. 5 and Supplementary data Fig. S2 confirm the presence of a variable length induction period (typically >30 min) within CH reactions for both target DPs. These periods of ‘inactivity’ are followed by a linear relationship between conversion and time during the propagation stage. However, in the MWH reaction this induction time has been severely reduced or even eliminated. Part of this induction time reduction was attributed to the differential heat-up times exhibited by the different heating methods discussed above.³⁰ However, after taking this into account, a >20 min difference in the on-set of initiation and propagation between the two methods still required explanation. This additional reduction was attributed to localised/selective MWH heating of individual components effecting the polymerisation mechanism.³⁰ The induction period has been linked to the need to form the ‘true’ catalytic species from the initiator and Sn(Oct)₂ pre-catalyst via the process shown in Fig. 6.²³

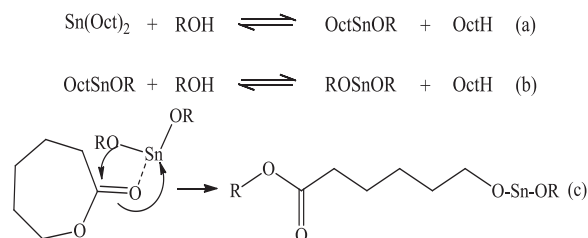


Fig. 6. Mechanism of formation of (a) monoalkoxide, (b) dialkoxide, (c) the first species of ring-opening process (‘1 mer’).

The rapid formation of the first active monoalkoxide (Fig. 6,a) is followed by a second equilibrium to form the actual catalyst, which is a tin dialkoxide (Fig. 6,b). This initiator will then ring-open the monomer via the coordination–insertion (C+I) process to form the first chain component of the polymerisation (the ‘1 mer’), which will subsequently continue to ring-open the remaining monomer during propagation until the monomer is exhausted.²³ Literature evidence for this induction period explanation was provided by the studying diols as initiators, they were found to slow the initiation process because they act as a bidentate ligand exhibiting a strong interaction between diol and Sn(Oct)₂.²³ Additionally, in the specific case of the BzOH/Sn(Oct)₂ initiator system, strong complex formation has been reported between Sn(Oct)₂ and BzOH even at ambient temperature by means of ¹H, ¹³C and ¹¹⁹Sn NMR.^{24,25,31} Therefore, the induction period observed in the practical data can be rationalised as being a consequence of either the slow formation of the equilibrium to generate the ‘true’ catalyst and/or strong complexation of the BzOH, which leads to a slow rate for the initial C+I process, both of which will contribute to a slow initiation process. Furthermore, the fact that the polymerisation demonstrates predictable characteristics after induction period, suggests that the C+I reaction does not commence until the ‘true’ initiator formation has been fully completed, defining that one of these initial stages is the rate determining step (RDS).

The severe reduction/elimination of the induction period in the MROP would suggest that either or both of the 'in situ' 'true' catalyst or the '1 mer' formation is/are significantly shorter when MWH is applied compared to CH. To test this hypothesis, the kinetics of BzOH consumption was followed using ^1H NMR by taking samples every 10 min to a point where the induction was completed, i.e., first 30 min for a target DP=20 at 150 °C. In practice this meant only one MWH sample could be taken as after this point the induction period had been completed (see Fig. 7).

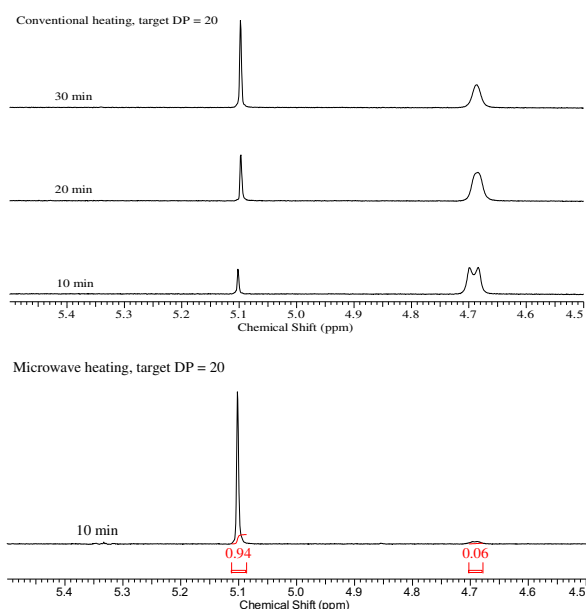


Fig. 7. ^1H NMR for a DP=20 using CH (top) (10, 20 and 30 min) and MWH (bottom) (10 min) in CDCl_3 .

This analysis followed the depletion of methylene proton next to the hydroxyl group of free benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, $\delta=4.69$ ppm) and the growth of benzyl ester end-group of the polymer chain ($\text{C}_6\text{H}_5\text{CH}_2\text{OCO}-$, at 5.11 ppm) as the catalyst formation and/or initiation process proceeds. A target DP=20 was chosen to maximise the signal from these methylene protons, because it requires the largest initiator/catalyst loading and produces the lowest Mwt synthesised in this study, thus produces the greatest level of chain end moieties.

GPC analysis of this polymerisation demonstrated that no conversion to polymer was observed within the first 30 min. However, the NMR data showed that during this induction time, conversion of free BzOH into benzyl ester end group was observed (Fig. 7 top—14% after 10 min increasing to 48% at 30 min). This indicated that conversion to the '1 mer' did occur during this section of the reaction cycle. Meanwhile, with MWH approximately 100% BzOH conversion was noted after only 10 min (Fig. 7 bottom). Thus faster formation of '1 mer' was demonstrated with MWH. This increased rate has been attributed to the selective heating of the organometallic species and monomer in the system at 150 °C, as predicted by the dielectric properties. This results in either a faster local rate of reaction and/or the precursors overcoming the dilution factor in the mixture as a result of the selective heating they undergo.

To provide further spectroscopic evidence to support these conclusions concerning faster organometallic reactions, a series of specific experiments were conducted to follow the progress of $\text{Sn}(\text{Oct})_2/\text{BzOH}$ reactions via both ^1H and ^{13}C NMR (see Supplementary data, Fig. S3), when using both CH and MWH.

Firstly, ^1H and ^{13}C NMR analysis of the direct reaction of BzOH and $\text{Sn}(\text{Oct})_2$ in a 2:1 ratio at 150 °C was investigated and compared between two heating methods. The expected products were identified by cross-referencing to the literature and were quantified by comparison of the proton NMR integrals.^{24,25,31} This study determined that the conversions to the tin dialkoxide achieved via the two heating methods were not significantly different. Inspection of the literature proposed mechanism would predict this result, because this process, i.e., Fig. 6 steps (a) and (b), is suggested to be in a dynamic equilibrium. Thus, it would appear that the MWH is promoting the reverse reaction as significantly as the forward reaction, as would be expected from a purely thermal process. Consequently, a similar kinetic experiment was conducted but in the presence of 1 mol of CL monomer at 150 °C (reagent ratio CL/BzOH/ $\text{Sn}(\text{Oct})_2=2:2:1$) using both heating methods and the progress of the reaction was again followed by ^1H NMR (see Supplementary data, Fig. S4). The ratio of the relative integrals in the ^1H NMR of the combined complexation peaks to the free BzOH indicated 33% conversion to the '1 mer' after only 1 min MWH case, whilst example CH example required 20 min to achieve a similar conversion level (35%). However, there was more than one resonance in the 5.00 ppm region of the ^1H NMR spectrum upon complexation of the CL monomer to the 'true' Sn catalyst. This has been attributed to the presence of the monomer resulting in the formation of additional complexes/transition states, e.g., not all of the tin catalyst species will successfully coordinate to just a single CL monomer. At this point, these individual complexes have not been definitively linked to a specific resonance with the NMR and represents a task that is currently under further study.

However, this data clearly shows that by adding 1 mol of CL, the formation of the initiated '1 mer' is significantly faster using MWH than in the CH systems. This increase in the differentiation between heating method was explained by using the information gained from the dielectric property assessment, which showed that the $\tan \delta$ of both the CL and tin precursor were very similar at 150 °C and are much greater than that of the BzOH initiator. Thus, as both of these materials exhibit good potential to selectively transfer absorb energy into volumetric heating, the rate of the MWH reaction will be increased because both species are being influenced by the incident microwave energy. Furthermore, the fact that the observed rate difference produced via the selective heating in the MWH process has significantly increased compared to the CH system simply by adding a mole of monomer, indicates that the overall process of catalyst equilibrium formation occurs more quickly than the reaction of the dialkoxide with the first mole of monomer when selectively heated. This suggests that this latter initial C+I step is the true RDS related within the initiation mechanism.

This conclusion also explains the earlier observation that no polymerisation is observed until all the tin catalyst has been prepared. This indicates that the tin complex equilibrium is quickly established and is thus 'waiting' to take part in the initiation process. The reaction with the first CL moiety leads to a shift in the tin equilibrium encouraging the fast generation of more tin dialkoxide to restore the equilibrium. Furthermore, it can also be concluded that any step in the reaction cascade that required the C+I of monomer will also be slower than the catalysts equilibrium process and so this will also apply to the propagation stages. As a result of these differential rates, the polymer chains are all initiated in a short period of time before chain growth can become established and so controlled polymerisation behaviour is observed. Therefore, it can be concluded that the elimination of induction period has been attributed to both; (a) faster system heat-up and (b) the result localised/selective heating of the Sn species and the CL in the reaction mixture, which results in a significant increase in the rate the first C+I of the monomer to form the first species (1mer), i.e., C+I of

monomer at the tin active chain end is the true RDS for the polymerisation process.

2.4.3. Influence of catalyst concentration. To further elucidate the effects of the various components upon this induction period reduction, experiments were conducted to investigate the reaction mixtures heating characteristics when the quantities of initiator and pre-catalyst added to a bulk of monomer were systematically and individually varied. These experiments showed no significant bulk heating behaviour difference between the heating profiles when the concentration of BzOH was varied in the absence of Sn precursor. Rather, the times taken for these mixtures to reach the target temperature were the same and no significant temperature overshoot was observed, within experimental error. This data was supported by the power profile assessment discussed earlier (Fig. 2). However, the equivalent catalyst concentration study conducted in the absence of BzOH showed very different results when using MWH compared to CH. The heat profiles and a typical power profile observed from experiments involving solutions containing Sn(Oct)₂:CL ratios of 0:87, 0.012:87 and 0.024:1 are shown in Fig. 8.

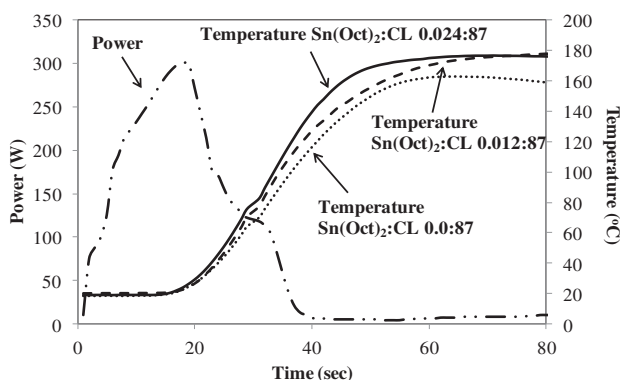


Fig. 8. MWH heating profiles and typical power profile for solutions with Sn(Oct)₂/CL ratios of 0:87, 0.012:87 and 0.024:87.

The set points were controlled by the internal IR sensor, as had the previous polymerisations, but in all cases the actual bulk reaction mixture temperature was measured using an optical fibre introduced into the bulk. In the MWH experiments, over the induction period it was observed that the samples that contained no catalyst reached the set point temperature in 0.7 min and demonstrated an average 10 °C temperature overshoot relative to the target set point of 150 °C. This 10 °C higher average temperature supports the conclusion that part of the reduced induction period is due to higher reaction temperatures because the CH experiments showed no more than a short lived 1–2 °C overshoot before stabilising at the target temperature. Furthermore, increasing the quantity of catalyst was found to both reduce the time taken for the system to reach the set point temperature and increase the size of the overshoot to ~30 °C. Meanwhile, the comparative CH experiment heat-up times were all observed to be identical to one another, with no shortening of the induction time or significant increase in the temperature overshoot noted. These observations were attributed to the fact that the catalyst is MWH selectively heating to such a significant degree that it is capable of effecting the overall bulk temperature of the system. This superheating of the catalyst consequently results in far higher/more efficient both manufacture of the ‘true’ catalyst and subsequent initiation of the polymer allowing the system to transit through the induction period very quickly. This also results in the subsequent propagation

reactions progressing at higher temperatures in the MWH system compared to the CH system and so results in an increase in propagation rate as a result. In fact, such inconsistencies in the actual system temperature of MWH and CH have been the subject of a number of recent reports.^{29,32}

Therefore, to ensure that this effect of catalyst concentration also effected the overall time required to conduct an MWH and CH polymerisation was investigated using a target DP=87 polymer and a reaction temperature of 150 °C. In these experiments three catalyst concentration levels, Sn(Oct)₂/CL/BzOH=0.012:87:1, 0.024:87:1, 0.5:87:1, were examined. The induction time, final reaction time and final polymer conversion achieved for these polymerisations are summarised in Table 2.

Table 2

MWH and CH polymerisations for a DP=87 at 150 °C with [BzOH]/[Sn(Oct)₂] molar ratios of 1:0.012, 1:0.024, 1:0.5

Heating method	[CL]/[BzOH]/[Sn(Oct) ₂] ratio	Induction time (min)	Reaction time (min)	Conv (%)
MWH	87:1:0.012	3	120	98
MWH	87:1:0.024	1	20	97
MWH	87:1:0.5	0	2	99
CH	87:1:0.012	30	300	92
CH	87:1:0.5	12	22	99

At the ratio BzOH/Sn(Oct)₂=1:0.012, 97% conversion was achieved within 120 min using MWH. Surprisingly, when the catalyst concentration was only doubled to 1:0.024, the reaction time to reach 97% conversion was reduced to 20 min. Similarly, when the catalyst concentration was increased 40 times to 1:0.5, the polymerisation was completed (99% conversion) within only 2 min, demonstrating a dramatic effect of catalyst concentration of polymerisation time. However, in the case of the CH experiments, whilst similar significant reductions in reaction time are observed, as would be expected from the literature, significant inductions times still remain. Therefore, these polymerisations have shown that the observed effects of adding the organometallic precursor to a polymerisation mixture does result in the reduction and/or elimination of the induction period and that this can be attributed to the selective heating of the organometallic species present, which in turn leads to extremely rapid reaction heat-up and higher reaction temperatures in the MWH reactions relative to the comparative CH polymerisations. Thus, the overall temperature effects on the propagation rate are the subject of on-going studies.

3. Conclusions

The investigation on the ROP of CL using BzOH/Sn(Oct)₂ and MWH has shown that the polymerisation exhibits controlled/pseudo living characteristics similar to when conducted via CH methods. Comparison of MWH and CH polymerisations demonstrated a significant reduction in the total reaction cycle time with MWH. This reduction in the polymerisation time was noted to rely upon a significant reduction/elimination of the induction period, which is related to the formation of the ‘true’ catalytic species and its involvement in the initiation of the polymer chain. This effect was initially attributed to the selective volumetric heating the tin species and the CL monomer, based on an assessment of the reagents dielectric. This assessment showed that the tan δ of both these species were essentially identical at the set reaction temperature and exhibited values at/or above 0.1 indicating that they should contribute significantly to system heating within an MWH experiment. Meanwhile, the BzOH initiator was shown to be essentially transparent at the reaction temperature.

This conclusion was confirmed by NMR kinetic studies conducted on both (a) the complex formation during a polymerisation and (b) specific organometallic reactions conducted to focus on catalyst formation and initiation alone. These both demonstrated a faster depletion of free BzOH to form the initiated species occurred in the MWH reactions. This study also suggested that the true RDS of the polymerisation process is the coordination and insertion of the first CL monomer, as the rate of formation of the dialkoxide is little changed between the two heating methods because it is an equilibrium process. This in turn would significantly contribute to the controlled nature of the ROP mechanism.

A subsequent systematic study of the effects of varying catalyst and initiator concentration demonstrated significant differences between the CH and MWH results when the tin precursor levels were varied. Increasing the tin precursor concentration was found to both reduce the system heat-up period and deliver a significant temperature overshoot above the target set reaction temperature, which contributes to a higher actual MWH reaction time. This confirmed the pivotal role that the small quantities of organometallic species have on the overall reaction temperature and highlighting that these species must be significantly superheated if these catalytic concentrations result in a 30 °C increase in the bulk temperature. Consequently, these observations confirmed that these reaction time reductions are attributed to thermal effects only and that there is no specific microwave effect present.

4. Experimental

4.1. Materials

All chemicals were used as received without purification. ϵ -Caprolactone (99%) was purchased from Acros, Karl-Fisher titration determined its water content to be 67 ppm. Tin 2-ethylhexanoate (96%) was purchased from Advocado. Anhydrous benzyl alcohol (99%) was purchased from Sigma–Aldrich. Toluene was distilled then stored over molecular sieves.

4.2. Characterisation

4.2.1. Determination of monomer conversion by NMR. ^1H NMR spectra on kinetic/non-precipitated samples were recorded in CDCl_3 using a Bruker DPX-300 spectrometer (300 MHz). For purified polymers, a Bruker DPX-400 spectrometer (400 MHz) was used. Number-average Mwt (M_n) was determined by end-group analysis using ^1H NMR analysis by comparing the integral of methylene proton resonance adjacent to the carbonyl group (Ha, 4.1 ppm), to that of methylene proton (Hx, 5.1 ppm) belonging to the benzyl ester end group. The monomer conversion was determined by comparing the integral of the proton resonance of the methylene moiety adjacent to oxygen of the carbonyl group for both the monomer ($-\text{CH}_2\text{OCO}-$, $\delta=4.24$ ppm) and polymer ($-\text{CH}_2\text{OCO}-$, $\delta=4.07$ ppm).

4.2.2. Determination of tin reaction kinetics by ^1H and ^{13}C : ^{13}C NMR. Using the spectrometer detailed above, the spectra frequency was chosen at 100.613 MHz with standard Zg pulse sequence at 90°. Relaxation time was 2 s with number of scan of 64. ^{13}C NMR: The spectra frequency was chosen at 400 MHz with standard Zg pulse sequence at 90°. Relaxation time was 1 s with number of scans of 128.

4.2.3. Determination of Mwt by GPC. In a typical procedure, a polymer solution of 7 mg/mL PCL in HPLC THF was prepared, and filtered through a 0.2 μm sieve to a GPC vial. The samples were then applied into a GPC, calibrated using narrow poly(styrene) standards ranging from 580 to 377,400 g/mol, for a typical time of 24.5 min. In

the assessment of control over Mwt, all samples were precipitated in MeOH prior to GPC analysis. All GPC equipment and standards were supplied by Polymer Laboratories (Varian) and the data analysed using the Cirrus software package.

4.3. Synthetic procedures

All polymerisations were conducted in the bulk. Bulk temperature was determined via an optical fibre probe inserted directly into the reaction.

4.3.1. ROP using microwave heating. The typical protocol for PCL synthesis using MWH for a target DP=87 was as follows. CL (25 g, 219 mmol) was weighed into a 100 mL round bottom flask. $\text{Sn}(\text{Oct})_2$ catalyst solution in toluene (0.5 mL of a 2.49×10^{-2} g/mL solution) and anhydrous benzyl alcohol (0.26 mL, 2.51 mmol) were then added via syringe. The flask was then placed in the cavity of a CEM reactor and fitted with a glass stir rod and PTFE paddle through a PTFE bearing through the reactor's choke (a tube of certain size to prevent leakage of microwaves). The content was stirred until homogeneous by an external mechanical stirrer. Following this, a pre-set programme was loaded into CEM controller, which contained the required temperature, power and time parameters and, which could be started/paused from the reactor control panel. For kinetic studies, the mechanical stirrer and the reactor programme were paused and aliquots extracted from the polymerising melt by pipette. The samples were then rapidly cooled and retained for GPC and NMR analysis.

4.3.2. ROP using conventional heating. The typical protocol was similar to that of MROP. The flask contents were stirred until homogeneous by an external mechanical stirrer and the flask was then immersed in a preheated oil bath (150 °C) for the appropriate reaction time with vigorous stirring. For kinetic studies, the mechanical stirrer was paused at set times through the reaction and aliquots extracted from the polymerising melt by pipette, rapidly cooled and retained for GPC/NMR analysis.

4.3.3. Control of Mwt with microwave heating. In the experiments to investigate control of DP, the molar ratio of $\text{CL}/\text{Sn}(\text{Oct})_2$ was kept constant at $1:1.40 \times 10^{-4}$ with CL (25 g, 219 mmol) and $\text{Sn}(\text{Oct})_2$ in toluene solution (0.5 mL of a 2.49×10^{-2} g/mL solution). The concentration of anhydrous benzyl alcohol was altered to achieve the target DP, (i.e., 87=0.26 mL, 2.51 mmol, 50=0.45 mL, 4.38 mmol and 20=1.13 mL, 10.95 mmol).

4.3.4. Catalyst concentration study with microwave heating. In experiments, which investigated the effect of catalyst concentration upon MROP reactions, the CL/BzOH molar ratio was kept constant at 87:1. For a target DP=87. They included CL (25 g, 219 mmol), anhydrous benzyl alcohol (0.26 mL, 2.51 mmol) and $\text{Sn}(\text{Oct})_2$ at the following concentration levels; (a) $\text{BzOH}/\text{Sn}(\text{Oct})_2=1:0.012$ with 0.5 mL of a 2.49×10^{-2} g/mL $\text{Sn}(\text{Oct})_2$ /toluene solution, (b) $\text{BzOH}/\text{Sn}(\text{Oct})_2=1:0.024$ with 0.5 mL of a 4.98×10^{-2} g/mL $\text{Sn}(\text{Oct})_2$ /toluene solution and (c) $\text{BzOH}/\text{Sn}(\text{Oct})_2=1:0.5$ by weighing $\text{Sn}(\text{Oct})_2$ (0.51 g, 1.26 mmol).

4.3.5. Measurement of dielectric properties. Cavity perturbation and coaxial probe techniques were used to measure the dielectric properties of the polymerisation component as described in previous publications.²¹ The perturbation techniques determine the dielectric properties by monitoring the change in the quality factor and shift in the resonant frequency in a cavity when a sample is introduced. The dependence of dielectric properties on the temperatures was assessed by using a conventional furnace as the heat source placed above a copper resonant cavity of specific

dimensions designed to resonate at certain frequencies. The sample was heated in the furnace until it has equilibrated at the target temperature for a specific measurement, at which point it was introduced into the cavity and the dielectric property measurement made in less than 2 s to avoid cooling. The experimental system consisted of a cylindrical copper cavity (diameter 570 mm height 50 mm) resonating in TM_{0n0} connected to a Hewlett Packard 875c vector network analyser. In the case of the open-ended coaxial probe technique the dielectric properties are calculated by measuring the phase and amplitude of the reflected signal when the probe was immersed into a sample. This technique requires a larger quantity of sample than the cavity perturbation method and is suitable for high loss materials.²¹ Hence, it was used to measure the dielectric properties of CL only. Similar to perturbation technique; the dependence of dielectric properties on the temperatures was carried out by using an external heater, in this case an electric isomantel. The coaxial probe consisted of an Agilent 8753 ES VNA (100–5000 MHz), and a coaxial probe was used to measure 500 mL of CL.²¹

Acknowledgements

The authors would like to thank the DICE initiative (EP/D501229/1) (D.J.I.) and Croda Ltd (N.T.N.) for funding.

Supplementary data

Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.tet.2013.11.031>.

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