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

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ABSTRACT

This paper reports the first detailed study focussed upon identifying the influence that microwave heating (MWH) has upon the mechanic 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.

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 titanium[8] and zinc powder catalyst at 2.45 GHz[9] 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 acid[11] 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 ($Sn(Oct)_2$) 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 $Sn(Oct)_2$ 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, $Sn(Oct)_2$ 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 $Sn(Oct)_2$ 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/$Sn(Oct)_2$ has been conducted. Therefore, although CROP of CL using $Sn(Oct)_2$/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 $Sn(Oct)_2$/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 $Sn(Oct)_2$/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) $Sn(Oct)_2$ 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 $Sn(Oct)_2$ 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 $Sn(Oct)_2$. Therefore, at this temperature as a bulk material, $Sn(Oct)_2$ 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 $Sn(Oct)_2$ 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 $Sn(Oct)_2$ 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