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The Importance of Ionic Conduction in Microwave Heated Polyesterifications

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Abstract

Significant increases in the reaction rate and final conversion of a model polyesterification are reported by the use of microwave heating. These increases have been demonstrated when both organometallic and inorganic acidic catalysts have been employed. Furthermore, the results achieved by application of microwave heating were shown to be influenced by the type of catalyst that was employed. Catalyst species whose mechanistic cycles involve an associative bond were found to exhibit better performance when electromagnetic heating was applied. These observations have been attributed to the fact that electromagnetic energy in the microwave region is non-ionising and thus will not promote the cleavage of formal bonds. However, it will have significant influence on the charge separation that will be achieved in systems which involve associative bonds *via* an energy transfer mechanism that involves ionic conduction. This increase in rate has been attributed to two thermal effects which are both related to the implementation of microwave heating. The first is attributed to the volumetric heating of the reaction medium, i.e. efficient heating of the diol reagent leading to improved energy transfer through the entire reaction medium. This in turn results in the reaction medium achieving the target temperature in a significantly shortened time compared to conventional

heating. The second is the successful application of selective heating, in this case greater efficiency by which the catalysts are heated by the electromagnetic energy as the energy couples directly into these molecular species rather than conduction/convection from the bulk reaction medium. This improved direct energy transfer leads to locally higher temperatures at these catalytic centres and so increased reaction rates, where catalysts that undergo ionic condition can interact with the non-ionising microwave energy to a greater extent than a catalyst whose cycles require the scission of a bond. Additionally, the influence of ionic conduction was also shown to lead to the rates of un-catalysed microwave heated polymerisations systems being comparable to conventionally heated samples which did contain a catalyst, thus is proposed to be a general mechanistic phenomenon and not solely focused on catalysis.

Introduction

Polyesters are a family of polymers that are applied in a broad range of applications and are typically divided into two distinct groups defined by the end application *i.e.* thermoplastics and thermosets. Thermoplastics are polymeric materials which are typically solvent soluble and pliable at elevated temperatures, allowing them to be readily and reproducibly mouldable at high temperatures.¹ Thermosets (commonly known as pre-polymers or pre-pregs) are materials that, once heated, undergo an irreversible chemical transformation to create a solvent insoluble, extended three-dimensional network.² These differing properties have led to polyesters being exploited in many aspects of everyday life including; fabrics for clothes/home furnishing,^{3,4} plastic bottle manufacture,^{5,6} coatings,^{7,8} and many more. There are a number of synthesis routes commonly employed in the industrial manufacture of polyesters, with melt polycondensation being the method considered in this publication. This method generally involves the reaction of an aliphatic or aromatic dicarboxylic acid and a diol at high temperatures (>200 °C),⁹ where elevated temperatures are implemented to influence both the

kinetics of reaction and mass transfer within the process. Consideration of the mass transfer is important because the reaction mechanism involves a dynamic equilibrium and so the condensate must be removed from the reaction medium. This is to minimise the reverse-reaction, resulting in reformation of the original reagents *via* reaction of the condensate molecule with the ester groups within the polyester chains. Mass transfer strategies commonly employed in industry include; addition of vacuum to the head space,^{10,11} addition of sparging (streaming inert gas through the reactants),^{2,12} azeotropic solvent evaporation^{13,14} and rapid agitation of the reaction medium.¹⁵

Furthermore, a catalyst is typically employed to increase reaction rates and help achieve high conversion levels. Currently, the most commonly applied catalysts are based around organotin compounds because they have proved to be robust and effective with a broad range of monomers and reaction conditions at low catalyst loadings and this flexibility has led them to be extensively used in both industry and academia.^{16–20} Therefore, this study was focussed upon investigating the relative efficiency of two industrially applied organotin catalysts, tin(II) 2-ethylhexanoate (tin octanoate, $\text{Sn}(\text{Oct})_2$) and dihydroxybutyl tinchloride (DHBTC), when the reactions were heated by conventional heating (CH) methods, i.e. *via* a heating mantle, and microwave heating (MWH). The performance of these organometallic catalysts were then compared to that of two non-metallic esterification catalyst, again using both heating methods, to define if the use of volumetric heating *via* the application of microwave energy would allow metal free catalysis to be more widely adopted industrially. The structures of the catalysts used in this study are shown below in Figure 1.

Figure 1. Molecular structures of catalysts investigated.

Sn(Oct)₂ was selected due to its wide use as a catalyst in esterification processes,^{16,17} and the significant number of previous studies involving its use in MWH reactions.^{21–24} DHBTC was selected as its primary use has also been in step-growth polyesterification systems,^{25,26} and because it exhibits a different state at room temperature (RT) than Sn(Oct)₂. The former catalyst is liquid at RT, the latter is a solid. This physical state difference can potentially create differences in the degree of interaction with incident microwave energy that a compound can achieve and this is typically highlighted by differences in the dielectric properties exhibited by the two materials.^{27,28} Typically, liquids are observed to heat more effectively when exposed to electromagnetic (EM) energy than solids, which is attributed to a greater degree of freedom as the dipoles/charged pairs in the structure have to align with the phase of the EM field. This has also been shown to result in differences in the solution state, which has been related to the level of solvation that a solid material achieves when introduced to a particular solvent/reaction mixture. The lower the level of solvation the lower the response to the incident EM energy.^{24,28} Therefore, it was hypothesised that these tin catalysts would potentially interact with the EM energy and thus contribute to the heating/reactivity of the medium differently, leading to differences in reactions rates and/or reaction mechanisms observed. However, this would only

be the case if the catalyst type significantly influences the rate or selectivity in the polyesterifications under microwave heated conditions.

To extend this study two inorganic, acid catalysts, phosphoric acid (PA) and pyrophosphoric acid (PPA), were selected because they are non-metal containing species and thus have potential environmental/sustainability advantages compared to the organometallic equivalents, e.g. reduced potential to result in discolouration *via* the presence of water and oxygen, reduced toxicity and ease of use in scale-up.²⁹ These specific acid catalysts were selected due to their prior successful use in polyesterifications.^{25,26,30} Additionally, in certain polymer syntheses it has been previously demonstrated by Adlington et al. that di/tri/oligomeric species have higher dielectric properties than their mono and polymeric counterparts.³¹ This phenomenon was explained by their proposal that these oligomeric structures are still small enough to have free dipole movement while exhibiting a greater viscosity, which means that there is greater molecular friction created from any increase in molecular movement induced by the EM field. Hence, the comparison of PA and its dimer PPA was conducted to investigate if this oligomeric effect may have increased EM energy influence over a catalyst activity due to its increased dielectric loss (ϵ''). In an applied MW field, the dielectric loss is a measure of a materials ability to dissipate adsorbed MW energy as heat and if this could then be exploited as an important factor in accelerating/differentiating polyesterifications *via* EM heating (see dielectric property definitions in experimental section).

Thermal versus Non-Thermal Microwave Effects: MWH has been of specific interest in recent years as it has offered an efficient way of heating chemical reactions. It has also been previously reported that by its implementation to organic reactions, higher yields and better control can be achieved when compared to CH equivalents.^{32–35} However, recently it has been shown that many of these reports may have been due to the inaccuracy in bulk temperature monitoring.³⁴ Moreover, in the specific area of microwave polymerisation, the view that the differences

observed between MWH and CH reactions are related to thermal effects has been supported by a number of prior publications by the authors.^{24,28,31} Therefore, in this study, as in these prior reports, stringent bulk temperature measurement was applied to make sure this phenomenon was negated.

Experimental

Materials: 1,6-hexanediol (99 %) (HD), adipic acid (AA) (≥ 99 %) tin(II) 2-ethylhexanoate (92.5 - 100 %) ($\text{Sn}(\text{Oct})_2$), crystalline phosphoric acid (≥ 99.999 %) and pyrophosphoric acid (≥ 90 %) were purchased from Sigma Aldrich. Dihydroxybutyl tinchloride was supplied by BNT chemicals GmbH. All chemicals were used as received without further purification.

Characterisation - ^1H NMR Analysis: ^1H (δ_{H}) NMR spectra were recorded at 25 °C using a Bruker DPX-300 spectrometer (300 MHz) or Bruker AV-400 (400 MHz) and chemical shifts were recorded in δ_{H} (ppm). Samples were prepared as solutions in CDCl_3 or MeOD, depending on conversion level to which chemical shifts were referenced (residual chloroform at 7.26 ppm, residual methanol at 3.31 ppm). Analysis of the spectra was conducted using MestReNova 10 software. The ^1H NMR (300 MHz or 400 MHz, CDCl_3 or MeOD, 25 °C) for an AA and HD derived polyester are as follows: AA. δ_{H} 1.60 (4H, CH_2), δ_{H} 2.32 (4H, CH_2), HD δ_{H} 1.42 (4H, CH_2), δ_{H} 1.56 (4H, CH_2), (monomer/end group) δ_{H} 3.56 (2H, $\text{HO}-\underline{\text{CH}_2}$), (oligo/polymer chain) δ_{H} 4.09 (2H, $\text{HO}-\underline{\text{CH}_2}$). To calculate the conversion from the NMR data the size of the integral exhibited by the oligo/polymer resonance at 4.09 ppm was compared to the resonance of the HD monomer at 3.56 ppm. This figure was then multiplied by 100 to give a percentage.

Gel Permeation Chromatography Analysis (GPC): GPC analysis was performed using an Agilent 1260 Infinity series HPLC with an online degasser, isocratic pump, automated liquid sampler, thermostatted column oven and differential refractive index detector. The columns used consisted of 2×7.5 mm I.D. by 300 mm L - Agilent PLgel Mixed E, 3 μm particle size

Columns (Linear Separation range – up to 25 kg.mol⁻¹ relative to Polystyrene). With a 7.5 mm ID by 50 mm L – Agilent PLgel 3 µm column guard. The eluent used was THF (HPLC grade, ≥99.99 %, inhibitor free)). Preparation of sample involved dissolving the sample in THF (1 – 2 mg/mL) and then passing the sample through syringe filters (Whatman, 25 mm, 0.2 µm). Once dissolved, the analysis was conducted by flowing the sample through the columns at 1 mL/min at 40 °C. Data was analysed using Astra 6.1 software (Wyatt technology, USA).

Differential Scanning Calorimetry (DSC): DSC analysis was completed using a TA-Q2000 DSC (TA Instruments, USA), calibrated using sapphire and indium standards. The sample (1 – 4 mg) was prepared in Tzero platinum pans and processed from -90 to 80 °C through 2 heating and cooling cycles at a ramp rate of 20 °C/min under an N₂ atmosphere. The peak in the heat capacity during the second temperature ramp was used for T_m analysis which was conducted using Universal Analysis software provided by TA instruments.

General adipic acid, 1,6-hexanediol polyesterification synthesis: 1,6-hexanediol (15 g, 126 mmol), adipic acid (18.55 g, 126 mmol) and 1 % mol equivalent catalyst (1.26 mmol) were added to a vessel of specific geometry to fit into the microwave cavity. The mixture was heated to 185 °C over a 3 hour cycle period, with constant stirring *via* a magnetic flea at 300 rpm, with the start of the reaction (time = 0 secs) being defined as when the heating commenced. Aliquots (0.1 mL) were extracted at 15 minute intervals throughout the reaction cycle, the temperature of which was instantly quenched and the sample stored in a -20 °C freezer for analysis using the methods described above. Note: for the MWH reactions a maximum input power (P_{max}) of 200 W was used. Forward and reflected power were displayed on the Sairem Miniflow 200SS microwave reactor touchscreen digital front panel. The reflected power was minimised using the in-built stub tuner and sliding short throughout the reaction as the dielectric properties of the reaction mixture changed.

Reactor Geometries: All MWH reactions were conducted using a Sairem Miniflow 200SS (Maximum power 200 W, operating at 2.45 GHz). This apparatus contained a TE_{01n} single mode cavity and both a short circuit and stub tuner for impedance matching purposes. The purpose of the short circuit is to superimpose the incident and reflected waves onto the reaction media. This configuration allowed applied and reflected power levels to be carefully monitored so energy delivered to the samples could be optimised. Temperature was monitored using an optical fibre (OF) temperature sensor which was directly inserted into the reaction bulk *via* a septum and cylindrical microwave choke. The choke allows sampling of the reaction mixture whilst ensuring the microwave energy is contained within the cavity to levels below those required by Health and Safety regulations.^{36,37} Consequently, the 50 mL vessel used possessed an elongated neck to approx. 14 cm in total length. This vessel was also used for comparative CH reactions which involved the use of a Drysyn® heating mantle placed on an IKA Basic hotplate, to ensure direct comparison of the mass transfer characteristics could be made. The hotplates thermocouple was attached to the Drysyn® heating mantle to allow temperature control of the heating system. A K-type thermocouple was inserted into the CH reaction mix to ensure an accurate reaction temperature was evaluated for direct comparison with the MWH reactions in terms of heating rates and set reaction temperatures. The data presented is representative of the results observed from at least 3 repeats of the same reaction system within the specific reactor glassware described here. The same glassware was applied to both conventional and microwave reactions to ensure that the levels of mass transfer that could be achieved as a result of the vessel was identical.

Dielectric Property Definitions: The dielectric properties of a particular molecular entity can be expressed in a number of ways to best rationalise/predict how it will respond to an incident electromagnetic (EM) field.^{38,39} The real part of its complex permittivity (dielectric constant, ϵ') defines the extent to which it will store energy through polarisation.^{40,41} The imaginary part

of complex permittivity (dielectric loss factor, ϵ'') expresses its ability to dissipate this stored energy into heat.^{40,41} Lastly, a third parameter loss tangent ($\tan \delta = \epsilon'' / \epsilon'$) can then be defined, which indicates the potential for the material to heat under the influence of an applied electric field.

Results and Discussion

Tin catalysis in linear melt polycondensations: To assess the difference of catalyst efficiency between CH and MWH polycondensation reactions, a combination of monomers that would produce linear polymers were specifically selected. AA and HD (see Figure 2) were chosen because the reaction media/product materials would be manageable in terms of viscosity, processing temperature (185 °C) and would also be solvent soluble so amenable to analysis.

Figure 2. Schematic representation of adipic acid, hexanediol polyesterifications which were conducted at 185 °C for 3 hours.

Through the choice of monomers and processing conditions, this model system was designed to deliver linear, flexible thermoplastic polyesters that should have good solubility in standard organic solvents. This is important because, the direct comparison of the molecular weights achieved when CH or MWH were applied was a key methods by which mechanism /efficiency differences may be assessed. This study is of specific interest to the coatings industry as knowledge generated in these model studies is expected to be directly applicable to a wide range of condensation polymers and related monomers.

Therefore, a set of reactions were conducted using both tin catalysts defined in Figure 1 and these were compared to a reaction without catalyst, and the conversion versus time plots for these reactions are described in Figure 3.

Figure 3. Plot of conversion vs. time for adipic acid, hexanediol polyesterifications both in the presence and absence of tin catalysts at 185 °C using both CH and MWH heating methods with no mass transfer applied.

Figure 3 shows that there was a significant difference in both the reaction rate and final conversion between the non-catalysed and tin catalysed reactions. The tin catalysed reactions exhibited significantly faster rates after 60 mins of the reaction cycle and achieved higher final conversions than the non-catalysed reactions with both heating methods. Comparing the two heating methods data suggested that by implementing MWH there was a significant increase in reaction rate in all cases and also in the final conversion of both the uncatalysed and $\text{Sn}(\text{Oct})_2$ experiments. These reactions demonstrated that, in CH based polyesterifications, it is vital to use a catalyst if target conversion of monomer to polymer is to be achieved in a commercially viable time scale. However, in the MWH reaction in which no catalyst was applied, it was

possible to achieve reaction rates that are similar to CH tin catalysed reactions. Both MWH tin catalysed reactions reached 85% conversion in < 20 minutes, approximately a third of the time it took the best CH experiment to reach this level. This increase in reaction rate was attributed to two key thermal effects introduced by the application of MWH. The first was attributed to the increased efficiency of heat transfer throughout the entire reaction medium because the energy is directly interacting with molecular species evenly distributed in the media. Resulting in the set reaction temperature being achieved in a much shorter time than with CH. This observation was supported by comparing the heating profiles of the CH and MWH reactions, an example of which is shown in Figure 4.

Figure 4. Comparison of CH and MWH heating profiles for an adipic acid, hexanediol polycondensation conducted at 185 °C using tin octanoate with circles depicting when the internal temperature achieved the desired reaction temperature.

Figure 4 showed that for the MWH reactions a bulk temperature of 185 °C was achieved in ~10 minutes compared to ~95 minutes for conventional heating. This difference was proposed to be one of the factors that explained why there was such a large rate increase between the CH and MWH results as processing at a higher temperature will lead to a higher reaction kinetics

and improved mass transfer, therefore pushing the dynamic equilibrium toward condensate evaporation and polymer formation. This difference in the heat transfer characteristics was attributed to thermal effects namely successfully achieving volumetric heating in the MWH polymerisation ensuring that the entire bulk is being heated much more uniformly than in the CH case and demonstrating the potential that the selective heating of key species may allow more effective heating of the bulk. The heat transfer from the walls of the vessel in the CH case was also demonstrated to become very inefficient at higher temperature resulting in a prolonged period to get from ~ 150 to 185°C and difficulty in controlling the bulk temperature.

Unfortunately, attempts to match the conventional and microwave heating profiles at this laboratory scale proved impossible to achieve on the small scale due to practical difficulties incurred both when attempting to slow the microwave reactions down or speed the conventional chemistry up at this scale. Therefore, to investigate the this heat up phenomena further, a larger scale reactor was designed and constructed to make the control of the system more straight forward. An investigation of the practical effects of changing the reaction heat up profiles for a typical polyesterification has been included in this prior manuscript.⁴²

To investigate this observation further the dielectric properties of the reagents were evaluated to gauge their likely influence on the reaction medium when undergoing EM heating at 2.45 GHz and this data is shown in Figure 5 and Table S1, ESI.

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Figure 5. Plot of the variation in $\tan\delta$ with temperature for the tin catalysts from RT to > 200°C at 2.45 GHz with the reaction temperature indicated by the dotted vertical line.

The $\tan\delta$ values of hexanediol was observed to be significantly larger those of all other reagents in the RT to reaction temperature region. Therefore, it was concluded that the hexanediol species would be the main component that would interact with the incident EM energy and therefore produce the rapid heat-up behaviour noted in the MWH experiments.

The second observation when assessing the difference in reaction rates between CH and MWH for the two tin catalysts was a swap in catalyst efficiency between the heating methods. This was best demonstrated by assessing the conversion of the polymers for each catalyst at 15 minutes into the reaction cycle, as shown in Table 1.

Table 1. Initial conversion percentages for tin catalysts in AA, HD polyesterification

Entry	Catalyst	Heating Method	^a Conversion % after 15 minutes of reaction	Conversion difference between heating methods (%)
1	Sn(Oct) ₂	CH	21	71
2		MWH	92	
3	DHBTC	CH	39	40
4		MWH	79	

^a Conversion calculated using ¹H NMR.

When implementing CH, $\text{Sn}(\text{Oct})_2$ was shown to have achieved a lower conversion after 15 mins when compared to DHBTC, reaching a conversion of 21 % (Table 1, Entry 1) compared to 39 % (Table 1, Entry 3) respectively. By comparison, with MWH, $\text{Sn}(\text{Oct})_2$ catalysed conversion at 15 minutes was 92 % (Table 1, Entry 2) compared to 79 % (Table 1, Entry 4) with DHBTC. Overall, this differential increase between the heating methods (71% for $\text{Sn}(\text{Oct})_2$ compared to 40% for DHBTC) indicated a different efficiency of interaction with the incident EM energy for the two catalysts.

Consequently, the molecular weights and melting transitions of the final polyester materials, *i.e.* the product isolated after 180 minutes of reaction time, were investigated and these data are detailed in Table 2.

Table 2. Molecular weight and melting transition of polyesters formed using different catalysts and heating methods.

Entry	Catalyst	Heating Method	^a Final Conv. (%)	^b M_n^{GPC} (g.mol ⁻¹)	^b $\bar{D}^{\text{GPC}}$	^c T_m (°C)
1	None	CH	77	1,000	1.83	39.33
2		MWH	85	1,660	2.33	43.47
3	DHBTC	CH	96	4,580	2.36	54.58
4		MWH	93	2,460	2.59	51.96
5	Tin	CH	89	1,580	2.07	46.88
6	Octanoate	MWH	94	3,900	2.33	53.60

^a Conversion calculated using ¹H NMR. ^b Calculated using a GPC with THF solvent and PS standards. ^c Deduced using a DSC.

This data demonstrated that the differences between the CH and MWH reactions at 15 mins of reaction are maintained throughout the entire cycle, as the final conversions, molecular weights and melting transitions were higher in the non-catalysed (Table 2, Entries 1 & 2) and $\text{Sn}(\text{Oct})_2$ (Table 2, entries 5 & 6) reactions when MWH is used. Directly comparing the two tin

catalysts showed that with the CH system (Table 2, Entry 3 for DHBTC and Entry 5 for Sn(Oct)₂) the DHBTC catalyst gave higher molecular weights and melting transitions than Sn(Oct)₂. Whereas, when using MWH, the reverse is the case (Table 2, Entry 4 for DHBTC and Entry 6 for Sn(Oct)₂). In the CH system (Table 2, Entry 3 for DHBTC and Entry 5 for Sn(Oct)₂) the DHBTC catalysts out performs Sn(Oct)₂. This is confirmed by the DHBTC polymer exhibiting a M_n^{GPC} that was 3,000 g.mol⁻¹ higher than the equivalent Sn(Oct)₂ polymer, an increased conversion of 7 % and a T_m that is ~8 °C higher. By comparison, the MWH (Table 2 entry 4 for DHBTC and entry 6 for Sn(Oct)₂) shows that the Sn(Oct)₂ final polyester had the superior properties; i.e. M_n^{GPC} increase of ~1,500 g.mol⁻¹, conversion by 1 % and T_m by ~2 °C.

In both cases, the expected trends for such a condensation were observed, namely: (a) to achieve significant molecular weight (i.e. > 2,000 g.mol⁻¹) it was necessary to reach a conversion by ¹H-NMR in excess of 90% and (b) increasing the conversion level above this threshold was also accompanied with an increase in the polydispersity ($\bar{D}$), suggesting that driving to very high conversion there result in the onset of some side reaction and/or branching. These support the conclusion that there has been no basic mechanistic difference introduced by using MWH rather than the differences noted are thermal in nature

Again, the dielectric properties of the catalysts were compared to see if they indicated a difference in their response to the EM energy. As the catalysts exhibit different physical states at RT (Sn(Oct)₂, liquid and DHBTC solid) a significant difference in dielectric properties (specifically in regards to $\tan\delta$, see definition in experimental section) was observed in the region from RT to reaction temperature. This data is shown in Figure 5 to allow comparison with the data from the relevant monomers. The $\tan\delta$ values for Sn(Oct)₂ were observed to be significantly higher than those of the DHBTC in the region below the target reaction temperature, which was attributed to its liquid physical form. Thus it was proposed that whilst the reaction was heating up to reaction temperature, the EM energy will be coupled into the

$\text{Sn}(\text{Oct})_2$ catalyst more efficiently compared to the solid DHBTC catalyst. The interaction of the latter will therefore be determined by its level of solvation by the monomers. Furthermore, in a previous study of ring opening polymerisation (ROP) with $\text{Sn}(\text{Oct})_2$ the authors had demonstrated that MWH increased the rate at which the true catalytic species was formed compared to when CH was applied.^{43,44} This could also contribute to an increased rate in this process, where the proposed mechanisms for these interactions are detailed in Figure S1, ESI.

For $\text{Sn}(\text{Oct})_2$, there are two proposed mechanisms. (1) *Carboxyl coordination of pre-catalyst (Scheme (ai), Figure S1)*: This involves coordination of the ester to the pre-catalyst Sn centre to create a strong dipole, and therefore electrophile, at the carboxyl group. This allows insertion of the hydroxyl group at the carboxyl's carbon and the displacement of a molecule of water. This scheme suggests that the Sn centre is only coordinated to the carboxyl/ester and does not become involved in the growing chain by creating a formal bond. Rather the bond between the Sn centre and the polyester is only an associative bond involving an electrostatic charge/a lone pair interaction. (2) *Coordination and Insertion of pre-catalyst (Scheme (aii), Figure S1)*: Unlike scheme (ai), in this mechanism there is a formal covalent bond formed with the Sn centre and the growing ester chain which is preceded by intramolecular H-bonding to help catalyse the reaction.^{43,44} This is similar to the proposed mechanism for DHBTC (Scheme (b), Figure S1) which is based on a Lewis acid mechanism.^{16,45} In the proposed DHBTC reaction scheme, the Sn catalyst species is inserted into the carboxyl/ester chain and forms a covalent tin-alkoxide bond. This can then form intermolecular H-bonds with the alcohol and catalyse ester formation.

Therefore, whilst the initial similarity in the reaction rate observed from the two catalysts in the 0 – 80% conversion region is attributed to the rapid heat up resulting from the dominance of the hexanediol dielectric properties in heating the medium. It was proposed that the greater efficiency of the $\text{Sn}(\text{Oct})_2$ catalysed reactions above 80% conversion was related to the more

efficient direct selective heating of this species *via* application of MWH than was achieved with DHBTC. This is therefore also a thermal effect, as the catalyst $\text{Sn}(\text{Oct})_2$ achieves a higher local temperature than the DHBTC systems so exhibits faster kinetics. In this case, this difference was not thought to be a physical form difference, as the increased $\tan\delta$ values indicated that DHBTC should be fully solvated / in liquid physical form at this temperature. Rather, it was proposed that the fact that $\text{Sn}(\text{Oct})_2$ favours the carboxyl coordination polyesterification mechanism due to the lack of formal bond scission in the mechanism whilst the proposed DHBTC mechanism does require the scission of formal chemical bonds. This explanation is supported by the fact that microwave energy is non-ionising, *i.e.* it is not sufficient to break chemical bonds,^{46,47} rather, it will just increase their energetic state. Therefore, when the catalyst contains an associatively bonded “ester adduct” within the catalytic transition state, the MWH promotes the catalysis cycle at the heart of the reaction to a higher degree than a formally bonded catalytic cycle via the ionic conduction mechanism of energy transfer. This latter observation would also potentially explain the acceleration of the pre-catalyst to true catalyst stage in the $\text{Sn}(\text{Oct})_2$ mechanism reported in the MWH acceleration of lactide polymerisation which will also involve ionic conduction of the associatively bonds in the pre-cursor.²⁵

At this point it was unclear whether $\text{Sn}(\text{Oct})_2$ follows this mechanism in both heating methods, increasing reaction rate by the directed selective heating throughout the reaction media or whether the CH favours the coordinative insertion method.

Acidic catalysis of linear polycondensation reactions: To build on the mechanistic pathways conclusions drawn from the tin catalyst study, an investigation of the influence that MWH would have on the mechanism of two different acidic catalysts, phosphoric acid (PA) and pyrophosphoric acid (PPA) (See Figure 1), was conducted. The data from these experiments,

see Figure 6, demonstrated that implementing MWH also increased the rate of these acid catalysed reactions when compared to the CH equivalents.

Figure 6. Plot of conversion % vs. time for AA, HD polycondensation at 185 °C using different heating methods, acid catalysts and tin catalysts for comparison with MWH.

Again, as with the tin catalysts, this was partially explained by the increased efficiency of the heat transfer in MWH and therefore quicker thermal heat-up times being observed. Interestingly, whilst there is an observable difference in the rates of the PA and PPA catalysed CH reactions in the region up to ~70% conversion, those of the MWH are almost identical through the entire cycle. This was attributed to two factors related to the MWH selective heating throughout the reaction media, increasing the energy transfer into the acidic species and increasing their local molecular temperature leading to; (a) increasing the acid ionisation in both catalysts such that they exhibit similar acidity and/or (b) PPA being readily hydrolysed by the condensate of the reaction (i.e. H₂O) into PA and so harmonising the reaction rates.^{48,49} Table 3 contains a comparison of the initial conversion rate for the acid and tin catalysts

Table 3. Initial conversion percentages for tin and acid catalysts in AA, HD polyesterification.

Entry	Catalyst	Heating Method	^a Conv. % after 15 minutes of reaction	Conv. difference between heating methods (%)
1	Sn(Oct) ₂	CH	21	71
2		MWH	92	
3	DHBTC	CH	39	40
4		MWH	79	
5	PA	CH	39	18
6		MWH	57	
7	PPA	CH	34	25
8		MWH	59	

^a Conversion calculated using ¹H NMR

The differences in initial conversion rate between the acid and tin catalysts, highlighted that the rate increases on applying MWH were not as great, *i.e.* a conversion difference between heating methods of 18 % for PA (Table 3, Entry 5/6) and 25 % for PPA (Table 3, Entry 7/8). Additionally, the MWH and CH reactions using the PPA catalyst were also observed to have produced final products with very similar conversions, molecular weights and $\bar{D}$'s. Meanwhile, the PA results exhibited greater variation particularly in the larger $\bar{D}$'s observed, see Table 4.

Table 4. Molecular weight and melting transitions of polyesters formed using different catalysts and heating methods.

Entry	Catalyst	Heating Method	^a Final Conv. (%)	^b M_n^{GPC} (g.mol ⁻¹)	^b $\bar{D}^{GPC}$	^c T_m (°C)
1	DHBTC	CH	96	4,580	2.36	54.6
2		MWH	93	2,460	2.59	48.0
3	Sn(Oct) ₂	CH	89	1,580	2.07	46.9
4		MWH	94	3,900	2.33	53.6
5	PA	CH	94	2,750	2.47	54.1
6		MWH	94	3,130	2.60	54.9
7	PPA	CH	93	3,370	2.13	55.7
8		MWH	93	3,210	2.19	54.9

^a Conversion calculated using ¹H NMR. ^b Calculated using a GPC with THF solvent and PS standards. ^c Deduced using a DSC.

Comparing the M_n^{GPC} data that is related to a similar conversion level of ~93% in Table 4 (Entries 2, 4, 5, 6, 7 & 8) lead to a number of conclusions. The data suggested that implementing a non-organometallic catalyst can be beneficial to the polyesterification process because with both methods, a high conversion is achieved (94 and 93 % for PA and PPA respectively) after the 180 min cycle time.

Comparing the M_n^{GPC} values of the MWH experiments suggested that the acid catalyst have more similarity with the $\text{Sn}(\text{Oct})_2$ catalysed samples as they have achieved a chain build to $>3,000 \text{ gmol}^{-1}$. Therefore, as the polycondensation process for the acid catalysts is proposed to be a Fisher esterification (see Figure S2 in the ESI document) that involves ionic conduction as a heating method in the dissociation of the proton. This similarity in these results was thought to be significant as they predict that by implementing MWH the $\text{Sn}(\text{Oct})_2$ mechanism should also involve ionic conduction *via* the associated bonds involved. Meanwhile, the MWH polymerisation with DHBTC has not reached such high a chain build because of the need at all stages to create formal bonds within the mechanism. Thus it was hypothesised that DHBTC will have less interaction with the EM energy *via* dipole rotation due to the dipole movement being constricted by forming these new transient complexes. This reduction in catalyst efficiency will in turn lead to a longer reaction times, making these polymerisations will be more prone to glycol losses at a given temperature through distillation, oxidation or ether formation. Additionally, the observation that the use of dimeric acid catalyst resulted in relatively low $\bar{D}$'s being achieved suggested that the similarity in the reaction rates of the acid catalysts is less likely to be due to the conversion from PPA to PA, rather it is more likely due to the increase in acidity of the two catalysts upon applying MWH. This also supports the conclusion that using oligomeric materials does have an influence of MWH reactions as was

proposed from the study of methacrylate oligomers.³¹ To investigate these observations, the dielectric properties of the acid catalysts were measured and compared.

The acidic catalysts were shown to exhibit much higher $\tan\delta$ values from RT to reaction temperature than the tin catalysts. The $\tan\delta$ data presented in Figure 7 was, by necessity, recorded at 910 MHz, not 2.45 GHz, because the dielectric response of PPA was too high for the cavity perturbation equipment to record at the higher frequency. The limitations of the cavity perturbation equipment/technique used in this study has been discussed in the literature and 910 MHz was chosen as the analysis frequency because it is included in the other Industrial, Scientific and Medical (ISM) frequency bands allocated for microwave processing.⁵⁰

Figure 7. Dielectric properties of catalysts and monomers from RT to high temperature recorded at 910 MHz with indication of reaction temperature via dotted line.

Therefore, when implementing MWH, this data predicted that these catalysts would more significantly contribute to the heat-up process than the tin catalysts. But as they are present in low, catalytic concentrations, it was not thought to be the major factor that resulted in the harmonisation of the reaction rates. Especially as the PPA $\tan\delta$ is approximately twice that of

PA and hexanediol. Rather the Fischer esterification mechanism (see Figure S2 in ESI) proposes that the acidic protons from the catalysts interact with the monomeric acid moiety to catalyse the esterification.⁵¹ The high dielectric properties of the PA and PPA species, as shown in Figure 7 are because of the free H^+ ions that have high charge to weight ratios and therefore have are highly susceptible to EM energy. This suggests that they are very susceptible to undergoing an ionic conduction heating mechanism and so will exhibit increased acidity and be a more active catalyst for the targeted transformation.^{52,53} However, because the fisher esterification mechanism does partially proceed by the creation of formal bonds and does not involve associative bonds, the rate increased between CH and MWH is smaller when compared to that of the $Sn(Oct)_2$ catalysed reactions and is more in line with the DHBTC catalysed reactions.

Conclusions

This study has clearly shown that, by implementing a MWH strategy in the melt polycondensation of adipic acid and hexanediol to synthesise linear polyesters, an increased reaction rate can be achieved when compared to typical CH methods. This was attributed to the increased energy transfer efficiency of MWH, when compared to conductive/convective/radiative heating mechanisms that are involved in CH. This was attributed to two thermal effect;; (a) decreased heat-up times *via* volumetric heating of a specific reagent (hexanediol) and (b) promotion of energy transfer via ionic conductivity into selected associative bonds which involve the catalytic species (selective heating). Both of these are thermally based processes and allowed higher temperatures to be achieved in shorter time frames and so faster initial (up to 80% conversion) reaction rates and (b) also contributed to faster catalyst turnover in systems that involve charge/lone pair centred bonding interactions once the system was above 80% conversion. This latter observation also potentially explains

the acceleration of the pre-catalyst to true catalyst stage in the $\text{Sn}(\text{Oct})_2$ mechanism which will also involves ionic conduction.

The importance of ionic conduction as a heating mechanism for microwave based polyesterifications was proposed from observing (a) differential increases in reaction rate between CH and MWH and (b) a reaction rate efficiency switch being between the two tin catalysts investigated. The increase in reaction rate for the MWH compared to the CH reaction was observed to be significantly larger for the $\text{Sn}(\text{Oct})_2$ catalysed system when above 80% conversion. This rate increase was attributed to the difference in mechanistic pathways by which the polycondensations proceeded with the different tin centred species. $\text{Sn}(\text{Oct})_2$ was theorised to proceed *via* a mechanism that involved associative bonds i.e. charge/lone pair interactions only, from the tin centre to the polyester chain. This mechanism was theorised to be effected by the EM energy to a higher degree than the Lewis acid mechanism, which involved the insertion of the tin into the growing polymer chain *via* formal covalent interactions, as described for DHBTC. This difference was then related to the fact that microwave energy is non-ionising, so will not contribute to any bond scission process of formal chemical bond and increased restriction of dipole movement within the catalyst as a result of forming transition state complexes and supports the conclusion that these are thermal based effects.

These findings were supported by assessment of the product polymer characteristics. Unlike in the CH system case, the increase in MWt exhibited by the $\text{Sn}(\text{Oct})_2$ MWH product was significantly higher than the 1 % difference in final conversions would predict. This indicated a greater EM interaction can be achieved by the catalyst in the $\text{Sn}(\text{Oct})_2$ system, due to its preference for the associative mechanism. This leads to a higher catalyst local temperature, greater catalytic activity and shorter process cycle times. This, in turn, limits glycol losses and/or degradation, such that a higher molecular weight is achieved.

By implementing MWH with acidic catalysts, increased reaction rates were demonstrated compared to CH reactions and also the rates exhibited by the polymerisations with both catalysts became identical. As in the tin catalysed reactions, this was attributed to the efficient heat transfer and promotion of ionic conduction via selective heating when implementing MWH (thermally based effects). However, when comparing the increase in conversion efficiency from CH to MWH it was shown to be less than when compared to the tin catalysts, even though the dielectric properties of the catalyst were significantly higher than for the tin species. This was partly attributed to the mechanistic pathway being a Fischer esterification. This meant that ionic conduction resulted in the increase of the charge based dissociation and thus increased acidity of the catalyst, which resulted in the harmonisation of the MWH reaction rates. However, as some formal bond breaking is involved in the reaction mechanism, these processes are not increased significantly in rate by the application of MWH as the energy is non-ionising.

This acidic mechanism trait is similar for the Lewis acid mechanism described when implementing the DHBTC catalyst, which is attributed to its lower reaction rate increase compared to $\text{Sn}(\text{Oct})_2$. This was confirmed by minimal differences in the molecular weight and melting transitions between the CH and MWH reactions for these acidic catalysts. However, there was some benefit of implementing PPA, the dimeric acid, as a catalyst. This was the reduction in $\bar{M}_n$ for both CH and MWH when compared to the monomeric catalyst. It was also suggested that by implementing a dimeric acid catalysts high conversion and $\bar{M}_n$'s can be achieved in these polyesterifications with comparatively low $\bar{M}_n$'s. This supports work suggested previously that oligomeric species are beneficial, especially in MWH applications.

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