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1	Lactone-Layered Double Hydroxide Networks: Towards Self-Assembled
2	Bioscaffolds
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8	Abstract
9	This paper describes the conversion of a layered anionic initiator (carbonate-intercalated layered
10	double hydroxide, (LDH-carbonate)) into a self-assembled resin-embedded network during the in-

situ polymerisation of one or more lactone monomers using the LDH-carbonate as the sole 11 initiator. Uniquely in this paper, no long-chain acid intercalant is present in the LDH-carbonate to 12 act as an additional initiator species, and this is the first known report of a copolymerisation of 13 these lactones using LDH as an initiator. The formation of a network is in marked contrast to the 14 behaviour of most in-situ polymerisations using layered species, where the latter retains its layered 15 structure at the molecular level and is either intercalated or exfoliated to form a nanocomposite. 16 The molecular disintegration of the LDH sheets is unusual. Nine new insoluble materials 17 (scaffolds) are isolated from various L,D-lactide & ε-caprolactone (LC) and L,D-lactide & δ-18 valerolactone (LV) copolymer hybrids. The latter hybrids are polymerised using the LDH-19 carbonate as initiator at 150 °C for 24 h without using conventional metal catalysts. Each insoluble 20 phase is isolated from each primary hybrid product using dichloromethane (DCM) to selectively 21 22 dissolve the soluble polymer phase.

X-ray diffraction (XRD) is used to verify the morphology of the insoluble phases. This demonstrates that the molecular sheets of the LDH-carbonate are fully dismantled during the polymerization. Porous, network morphology is established for some of the insoluble phase structures using scanning electron microscopy (SEM). This indicates potential suitability of these self-assembled insoluble phase materials as bioscaffolds for artificial cell growth. Nuclear magnetic resonance spectrometry (NMR) was used to determine the ratio of ester to acidic carbonyls in the insoluble phase. Energy dispersive X-ray spectroscopy was also used to determine the ratio of magnesium to aluminium in the insoluble phases.

31 Keywords

32 poly(lactide), caprolactone, valerolactone, layered double hydroxide, tissue scaffold, network.

40 1.0 Introduction

Tissue engineering has evolved greatly since the mid-1980s into a multidisciplinary field targeting 41 the restoration, maintenance and improvement of tissue functions Fay et al. (2007), Langer & 42 Vacanti (1993), Chen et al. (2009), Vaz et al. (2005), Vunjak-Novakovic et al. (2010), 43 Operpenning et al. (1999), Schmidt & Leach (2003), Kuo et al. (2010). In particular, poly(lactic 44 45 acid) (PLA) is a popular polyester material that is used in tissue engineering because of its excellent biocompatibility and mechanical properties. Good adherence and differentiation properties have 46 been observed for osteoblasts cultured on PLA membranes. Santos et al. (2009), Liu et al. (2004). 47 48 Similar to PLA, poly(ε -caprolactone) (PCL) and poly(δ -valerolactone) (PVL) are often employed for use in bio-scaffold applications. Their advantage in this application is their relatively low 49 degradation rate (during hydrolysis in aqueous media). Therefore, they have been copolymerized 50 with a variety of polymers including collagen, poly(glycolic acid), poly(lactic acid) and 51 poly(ethylene oxide), Vroman & Tighzert (2009). 52

Layered double hydroxides (LDHs) comprise an unusual class of layered inorganic materials with
positively charged layers and weakly bound, usually exchangeable, charge-balancing anions
Manzi-Nshuti et al. (2009). LDHs have been studied and characterized by multiple researchers,
e.g., Perez-Amaro et al. (2009), Swanson et al. (2013), Kang et al. (2004).

Ring-opening polymerization (ROP) has been proposed as the main mechanism by which a monomer can be ring-opened at the cation of an LDH sheet, and can then propagate to form a polymer chain anchored on this LDH sheet, McCarthy et al. (2013). Generally, ROP may occur by either cationic, anionic or coordination-insertion routes Kricheldorf (2001). In addition to ROP at the LDH sheet, a combination of polycondensation of ring-opened monomers and ROP by free ions in the polymer bulk may also occur.

In this paper, the formation of various insoluble polymer-based Mg poly(lactone) networks have 63 been demonstrated by polymerizing different lactone monomer combinations using LDH-64 carbonate as an initiator for the first time; this is an approach, which avoids the use of any 65 potentially toxic conventional metal catalysts. There is also no long-chain acid intercalant present 66 in the LDH, as used previously (McCarthy et al. (2013)), which proves that the LDH itself is 67 68 sufficient to initiate polymerisation and network formation without the aid of a long chain intercalant. Some of the insoluble network phases are potentially suitable for use as bioscaffolds 69 for cell growth, based on their porous morphology. The main advantage of this system over 70 71 established scaffold fabrication technologies is the capacity to tailor the chemistry of the resin material using different monomer combinations and types of layered double hydroxide. The 72 scaffold is self-assembled at the molecular level and does not require specialised electrospinning 73 or other physical deposition technologies (e.g. chemical vapour deposition, photolithography, or 74 electron beam lithography, Prabhakaran (2012). This provides the potential to remove such 75 deposition steps from scaffold preparation, hence reducing cost. It also provides the potential to 76 modify the cations and intercalated species of the LDH-initiator to include beneficial active 77 ingredients for the cell growth process directly in the scaffold structure. 78

79 **2.0 Materials and Methods**

ε-caprolactone (97%) and δ-valerolactone (technical grade) were both obtained from Aldrich. εcaprolactone, which is liquid at room temperature, and δ-valerolactone were stored at 4 °C before
use. L,D-lactide (99%) was obtained from Alfa Aesar. All the three materials mentioned above
were used as monomers in the polymerization process. The initiator, synthetic layered double
hydroxide carbonate, was obtained from Aldrich. LDH-carbonate has a layered structure with a
high anionic exchange capacity that allows it to host and release various anionic compounds. Its

chemical formula is Mg₆Al₂(CO₃).(OH)₁₆.4H₂O. Since L,D-lactide and LDH-carbonate are both
sensitive to moisture, it is essential to avoid their re-adsorption of water. Thus, when they were not
being used immediately, they were both stored over a desiccant. L,D-lactide was sublimed
immediately prior to reaction to remove moisture.

90 **2.1 Sample Preparation**

A schematic of the specimen preparation process is given in Figure 1. This comprised the polymerisation of a mixture of monomer(s) plus LDH followed by dissolution of the product in methylene chloride followed by centrifugation of the solution to result in an insoluble residue which was dried to result in two separate phases of the polymer, soluble (SOL) and insoluble (INSOL).

96 2.1.1 Reaction Set 1: Mixture of L,D-lactide and LDH-Carbonate

97 A mixture of L,D-lactide and LDH-carbonate was prepared in the ratio of 95:5 by mass. 5 g of the 98 mixture was put into a 100 ml glass bottle, followed by intense mixing using a mechanical mixer 99 (Vortex Genie obtained from VWR International). Since L,D-lactide sublimes at 125 °C, an 100 aluminium foil was used to seal the vial and retain the subliming monomer at the reaction 101 temperature (150 °C). The product of this reaction was labelled PLDLA-HYB (HYB = hybrid), 102 while its soluble and insoluble phases were labelled PLDLA-SOL and PLDLA-INSOL, 103 respectively.

2.1.2 Reaction Set 2: Mixtures of L,D-lactide & ε-Caprolactone (LC) and L,D-lactide & δValerolactone (LV) with LDH-Carbonate.

The LDH-carbonate initiator comprised 5% by mass of each overall reaction mixture, while the
monomer mixtures, L,D-lactide & ε-caprolactone (hereafter referred to as LC) and L,D-lactide &
δ-valerolactone (hereafter referred to as LV) were mixed in the ratios of 1:2, 1:1, and 2:1,

respectively, by mass. The resulting products were LC1:2-HYB, LC1:1-HYB, LC2:1-HYB,
LV1:2-HYB, LV1:1-HYB, and LV2:1-HYB.

111 **2.1.3** Hybrid polymerization process

All the initial hybrid polymer products with different initial monomer ratios were synthesised at 113 150 °C for 24 h in a Heraeus Incubator oven. The 100 ml reaction vials were fully sealed by 114 aluminium foil wrap at the top of each vial to prevent escape of monomer vapour at temperatures 115 greater than 125 °C. A minimal headspace was allowed to ensure that the L,D-lactide vapour 116 remained trapped in intimate contact with the reaction bulk.

117 Separation of each initial hybrid product into soluble (SOL) and insoluble (SOL) fractions by methylene chloride solvent extraction and centrifugation. Each initial hybrid product consisted of 118 a soluble polymer, an insoluble polymer-salt complex phase and any residual monomers. 119 120 Therefore, methylene chloride (dichloromethane (DCM)) (obtained from Fisher Chemicals) was used as a solvent to dissolve the soluble polymer phase so that the insoluble phase could be 121 isolated. The extraction procedure was as follows: Once each reaction sample was cooled to room 122 temperature, 60 ml DCM was added to the sample in a vial and the solution was mixed with a 123 magnetic stirrer for 12 h (the concentration of the solution was about 0.083 g/ml). Once the hybrid 124 125 was fully dissolved in the solvent, the solution was equally separated into four 15 ml centrifuge tubes that were placed in a centrifuge. The centrifuge (Sigma 4-16 centrifuge) was operated at a 126 speed of 800 rpm or 10375 RCF (Relative Centrifuge Force), for 10 min. When the centrifugation 127 128 was finished, the upper supernatant was gently poured off or removed by syringe, and the insoluble residue was allowed to dry fully at room temperature for 24 h. Then, the centrifuge tubes were 129 placed in an oven at 50 °C for an hour to ensure complete removal of the methylene chloride 130 (boiling point: 39 °C). 131

132 **2.1.4 Characterisation Methods**

The samples used for characterization studies were desiccated and finely powdered. 133 Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer/Seiko machine under a 134 nitrogen atmosphere avoiding further oxidations. Isothermal thermogravimetry was performed by 135 heating the well-mixed primary product after polymerization at 150 °C for 6 h with an initial 136 137 heating rate of 20 K/min. Note that these isothermal TG measurements were unable to remove the δ -valerolactone and ε -caprolactone monomers, which both have higher boiling points (ε -138 caprolactone: 253 °C; δ-valerolactone: 260 °C). Therefore, at 150 °C, only the amount of residual 139 140 L,D-lactide in each of the products could be calculated. Determination of ε -caprolactone and δ valerolactone was subsequently made by conducting isothermal measurements on hybrid reaction 141 products at 260 °C for 6 h. However, at 260 °C some decomposition of the respective polymers 142 can also occur, which means that the residual ε -caprolactone and δ -valerolactone are likely 143 overestimated. Then, initial primary product samples from the same batch were also heated by 144 145 temperature-ramp to 600 °C at a heating rate of 10 K/min. An Al pan was used to hold samples. The typical sample masses for both procedures were 19 mg and 16 mg, respectively. The mass 146 loss was measured in a N₂ atmosphere, with N₂ flowing at 100 ml/min to minimize the extent of 147 148 any oxidation. The temperature, time and mass loss for each specimen were.

Scanning electron microscopy (SEM) was performed using a Philips XL30 FEGSEM. Prior to the
SEM imaging, the samples were sputter-coated with Pt using a sputter-coater (Gatan Inc.) for 3
min. Typical SEM parameters were: Beam energy: 8 keV, rotation angle: 50°, rotation rate: 30
rpm.

153 The X-ray Diffraction (XRD) spectra were obtained on a Bruker D8-Advance spectrometer using 154 K α radiation ($\lambda = 0.154$ nm) over a 2 θ range of 2-70 ° with a scan rate of 0.50 °/min. The 155 uncertainty of the measurement was ± 0.01 °. Prior to the test, the samples were ground to powder. 156 FTIR was used to obtain the FTIR absorption spectra using a Nicolet 5700 FTIR spectrometer. For 157 each sample, 32 scans were employed over a wavenumber range 400 cm⁻¹–4000 cm⁻¹.

¹³C Nuclear Magnetic Resonance (NMR) spectra of the extracted scaffold residues were obtained using a Bruker Advance III 400 MHz spectrometer. The settings used were 1.36 seconds acquisition time, 32768 points counted and 24038 Hz sweep width. 7200 Hz was selected as the spin rate for the tests of all the insoluble scaffold solid powders so that a higher resolution of peaks could be obtained within the shorter acquisition time. Adamantane was used as the standard reference for tuning purposes.

EDX (Energy dispersive X-ray) analysis of scaffold samples was performed with a Philip XL30 FEGSEM scanning electron microscope equipped with an Rontec (now Bruker) energy dispersive spectroscopy (EDS) analytical system (with a silicon drift diode detector). 0.05 g material samples were pressed mechanically into a circular disc with 10 mm as the diameter. To quantify the chemical content of areas with different area space (around 46000 μ m²) on the homogeneous sample surface, distinctly different topographical areas (N \geq 3) were chosen from the sample and examined at 10 kV using Quantax 400 (from Bruker) software.

172 3.0 Results and Discussion

173 **3.1 Specimen Appearance**

Photographs of a selection of the specimens are presented in Figure 2. Fig 2(a) shows PLDLA-HYB as produced, while Figure 2(b) shows a selection of the insoluble phase materials isolated from various hybrids as labelled. The latter specimens, especially PLDLA-INSOL, were fine fibrous materials that could be pressed into cohesive mats.

3.2 Thermogravimetric analysis (TGA)

179 Isothermal and ramp TGA were used to measure the residual solid mass yields (to derive polymer

180 mass yields by calculation) of the various single- and multi-lactone/LDH polymer hybrid products,

respectively. The polymer mass yields determined are shown in Figures 3 and 4.

3.2.1 Isothermal Thermogravimetric Analysis: Homopolymers.

In the polymer mass yield data, (Figure 3), the PLA and PCL homopolymer hybrids achieved 183 above 87% polymer yield by mass but the PVL-HYB achieved a yield of only 48.5%. As δ-184 valerolactone does not vaporise at 150 °C, it cannot have accounted for the mass loss in this TG 185 test. Thus, the monomer or its short chain PVL polymer derivatives may have decomposed into 186 smaller straight chain products, which may have vaporised at 150 °C. The isothermal TG of 187 188 PLDLA-HYB, polymerized under the same conditions, shows a high polymer yield of 87.3% by mass, which is slightly lower than the value of 88% by mass reported in the literature for stearate-189 190 intercalated LDH by McCarthy et al. (2013).

3.2.2 Isothermal Analysis: Copolymer Products.

Figure 4 shows isothermal TG data for samples that were synthesised from binary mixtures of either L,D-lactide and ε -caprolactone (LC hybrids) or L,D-lactide and δ -valerolactone (LV hybrids) with various monomer combination ratios. The polymer mass yields of some of these

copolymerization products were slightly higher than those of the single monomer-derived products 195 (Fig. 3). Thus, ε -caprolactone may have polymerised more easily on initiation sites of the LDH in 196 the presence of L,D-lactide as an enabling co-monomer. Since both the ε -caprolactone and δ -197 valerolactone molecules are larger than the L,D-lactide molecule, they may not diffuse into the 198 LDH galleries as well as L,D-lactide. Hence, during the copolymerization, the LDH sheets may 199 200 have been firstly partly expanded or dismantled by the L,D-lactide propagation, and then the other two monomers were better able to diffuse into the LDH structure and access the internal sheet 201 reaction sites. For example, when δ -valerolactone was copolymerised with L,D-lactide in three 202 203 ratios using LDH, (LV series) the isothermal polymer mass yields were significantly increased from 48.5% by mass (PVL) to above 84% by mass. The polymer mass yields (which are adjusted 204 to account for the original 5% by mass LDH-carbonate in the original reaction mixtures) and 205 insoluble fractions for the various hybrid products are shown in Table 1. 206

The key observation here is that the polymerisation of either ε -caprolactone or δ -valerolactone alone produces dramatically different results to that of l,d lactide polymerisation: For PCL-HYB, a relatively high polymer mass yield is produced, but the insoluble mass fraction is far lower (7.2% by mass), than those for either PLDLA-HYB or any of the copolymer products. For PVL-HYB, the insoluble fraction is similarly low (6.2% by mass), indicating that L,D-lactide is a key promoter of insoluble material formation and may even be essential to enable the formation of network phases to mass fractions of the order of 25 to 30% by mass.

214 **3.3 Scanning Electron Microscopy**

A range of SEM images (Figs. 5-8) were taken to show the microstructure of the materials at
various magnifications. Materials shown are LDH-carbonate, (Fig 5a), the initial hybrid products,
(Figs. 4b and 5) and the scaffolds that were extracted from various polymer products: i.e., PLDLA-

HYB (L,D-Lactide alone), the LC hybrids (L,D-lactide & ε-caprolactone) and the LV hybrids
(L,D-lactide & δ-valerolactone), respectively, (Figs 7 & 8). In some insoluble phases of the above,
the porous structure and morphology beneficial for use as a bioscaffold are clearly visible (e.g.,
PLDLA-INSOL, LC-INSOL 1:1, and LV-INSOL 1:2, Figure 7), while the insoluble phases of
other products show no clear network formation (e.g., LC INSOL 1:1, LV INSOL 2:1, Fig. 8).

223 The porous structures of the network-forming insoluble phases are substantially heterogeneous in size and shape. For PLDLA-INSOL (Figure 7), a visible fibre-like structure can be seen extending 224 225 in a three-dimensional network, and the thickness of each pore wall is approximately 30-60 nm. 226 The highly hierarchical and heterogeneous structure of the material is also clearly visible. Two types of structure dominate: a) long fibrous strands of material (Fig. 7b), and b) shorter more 227 228 crosslinked strands of materials forming three-dimensional networks with oblong pores of length approximating 500 nm (Fig. 7c). However, no visible network can be seen in either PCL-INSOL 229 or PVL-INSOL (Fig. 6), and their morphologies show significant similarities to that of pristine 230 231 LDH-carbonate, (Fig. 5a), which suggests that neither ε -caprolactone nor δ -valerolactone in isolation will form significant insoluble phase material with LDH-carbonate. (This conclusion is 232 confirmed by the corresponding similarity of their respective X-ray diffraction spectra to that of 233 234 LDH-carbonate, (Fig. 10e, below) where reflections due to the Mg-O and Al-O bonds at LDH sheet level remain substantially unaltered relative to the pristine LDH-carbonate, indicating little 235 236 participation of the LDH-carbonate sheets as initiating sites). The PCL- and PVL-INSOL SEMs (Fig. 6) show relatively homogeneous structures consisting of microspheres, and PCL-INSOL is 237 characterised by much smaller grain structure than PVL-INSOL. However, in both of the latter, 238 there is an absence of the distinctive network morphology evident for PLDLA-INSOL in Fig. 7c. 239 Thus, it is clear that the L,D-lactide monomer is a key component for production of network 240

241 morphology characteristic of many bioscaffold materials and that neither PCL-INSOL or PVL242 INSOL could be deployed as scaffolds for many tissue types.

243 3.4 X-ray Diffraction

X-ray powder diffraction spectra for magnesium l,d-lactate hydrate, the nine insoluble fractions, 244 and pristine LDH-carbonate are shown below in Figs. 9, 10A and 10B. The LDH-carbonate 245 spectrum (Fig. 9(e)) is characterised by a first-order peak at 0.76 nm, which represents the 246 interlayer d-spacing of the LDH-carbonate initiator. The second peak at 0.38 nm is associated with 247 248 a non-basal reflection, which represents the distance between the two cations in the sheet (i.e., Mg^{2+} and Al^{3+}), Klawitter et al. (1976). The peaks in the region 35–45° represent the harmonic 249 signals of the first-order peak. In the region $2\theta = 50-70^\circ$, there are two visibly defined peaks at 250 251 0.152 and 0.149 nm. These are attributed to the bond distances of Mg-O and Al-O in the molecule structure, respectively Cochechi et al. (2010). In the PLDLA-INSOL spectra, a strong peak is 252 253 found at around 0.92 nm and multiple other peaks occur in the range 0.46–0.41 nm. The most intense of these peaks correspond closely to those of the magnesium L,D-lactate reference 254 spectrum. (i.e., those at 0.92 and 0.51 nm, respectively, which both correspond to peaks in the 255 256 PLDLA-INSOL residue spectrum).

The spectra of PCL-INSOL and PVL-INSOL (Fig. 9c and 8d) show almost the same pattern as the spectrum of LDH-carbonate except for two peaks located at 0.4 nm and 0.31 nm. Moreover, none of the characteristic peaks of Mg l,d-lactate are observed in the two insoluble spectra.

This evidence indicates that the LDH-carbonate sheets remain essentially intact for PCL-INSOL and PVL-INSOL, so that it is assumed that only a few monomers have attached to the internal LDH-carbonate sheet initiation sites within the interlayer. This finding is in accordance with the data found in TGA measurements (Table 1), which show very low insoluble mass fractions for
both PCL-INSOL and PVL-INSOL. By contrast, the PLDLA-INSOL shows a completely different
XRD spectrum to that of LDH-carbonate (Fig. 9b), demonstrating that LDH-carbonate has been
fully reacted and dismantled during the polymerization of L,D lactide alone. Moreover, the
PLDLA scaffold synthesised in this paper is morphologically similar to magnesium-lactate (one
strong identical peak at 0.92 nm), and is similar in structure to the magnesium-lactate reported by
McCarthy et al. (2014) [16] for L,D lactide polymerised with LDH-stearate.

270 The spectra of the other six copolymer-based scaffold residues, Figs. 10A and 10B, are 271 considerably different compared with that of the LDH-carbonate, demonstrating that new species have been generated by the reaction in each case. However, it is clear that the Mg-O peaks in these 272 273 copolymer spectra at 0.15 nm are substantially less intense compared with the equivalent peak in the LDH-carbonate spectrum, indicating that Mg is the dominant active cation consumed by 274 275 polymerisation and salt formation. Consistent with this, a compound similar, but not identical to, 276 magnesium lactate can be observed in the spectra of the insoluble species. However, it is clear that another salt most likely co-exists with the magnesium lactate. From literature crystallinity studies, 277 278 evidence for the existence of magnesium/aluminium carbonate, and magnesium/aluminium oxides 279 here can be excluded, Gunawan and Xu (2008), Cava et al. (2007). Therefore, the co-existent salts 280 are most probably magnesium caprolactate and magnesium valerolactate, as there are no other 281 feasible ester species. Insoluble species with magnesium lactate feature a higher degree of network 282 formation, and porous, open, three dimensional networks tend to dominate over other 283 morphologies (e.g. spherules), when Mg-lactate is present in the necessary concentration.

285 **3.5 Fourier Transform Infrared Spectroscopy**

The FTIR spectra of L,D-lactide, LDH-carbonate and various insoluble phases synthesised by 286 287 different monomer combinations are shown in Fig. 11 and Fig. 12. The FTIR spectrum for L,D-288 lactide (Fig. 11(a)) depicts its characteristic absorption bands at 1752, 1249, 928, 648, and 476 cm⁻ ¹. Specifically, 1752 cm⁻¹ represents the two carbonyl groups in the ring structure, while the peaks 289 in the range 1249-928 cm⁻¹ are attributed to -CH₃ and -CH groups, and the remaining peaks from 290 648 cm⁻¹ downwards represent water molecules. In the FTIR spectrum of LDH-carbonate, the peak 291 at 3412 cm⁻¹ represents the –OH group, while the CO_3^{2-} group is assigned to the peak at 1361 cm⁻¹ 292 ¹. The remaining peaks, which have wavenumbers lower than 770 cm⁻¹, are assigned to the water 293 molecules in the LDH-carbonate interlayers in the pristine hydrotalcite (LDH). 294

The features observed in the PLDLA-INSOL spectrum include the main peaks at 1585 cm⁻¹ (C=O), 295 1469 cm⁻¹ (bending -CH₃) and 1121 cm⁻¹ (stretch C-O) rather than the 1752 cm⁻¹ (ring carbonyls) 296 and 1249 cm⁻¹ (-CH₃ and -CH groups) from the monomer or 1361 cm⁻¹ (CO₃²⁻ group) from the 297 LDH-carbonate, Al-Itry et al. (2012), Heraldy et al. (2016), which indicates a clear distinction 298 between the insoluble phase and both of the latter species. This confirms that a substantial chemical 299 reaction has taken place between L,D-lactide and LDH-carbonate. However, the spectrum of 300 PLDLA-INSOL still shows broad peaks around 3338 and 553 cm⁻¹, which are attributed to 301 hydroxyl groups coming from the initiator layer surface or interlayer water molecules in the 302 system, Hussein et al. (2012). 303

The FTIR spectra of the co-monomer scaffolds, are quite similar to the PLDLA-INSOL spectrum. In particular, bimodal peaks around 1600 cm⁻¹ are seen in spectra for LC 1:2 (Fig.11(c)) and LV

1:1 (Fig. 12(d)). It is notable that the dominant peak for LC 2:1 (Fig. 11(e)) is 1637 cm⁻¹ with a

307 'shoulder' peak at 1593 cm⁻¹, whereas the latter peak is dominant for both LC 1:2-INSOL and LC

1:1-INSOL. The peak at 1637 cm⁻¹ can be attributed to bicarbonate ions, Arihara et al. (2001),
which could have been formed by the reaction of carbonate anions, water and atmospheric carbon
dioxide absorbed into the initiator inner layer space. Examining the copolymer scaffold FTIR
spectra, the peaks at 1585, 1121, and 553 cm⁻¹ are not as intense as those in the PLDLA-INSOL
spectrum; therefore, it is possible that PLDLA-INSOL has the most pronounced crystallinity of all
the scaffolds (See He et al. (2000) for a discussion of the application of FTIR to studying
crystallinity of a lactone polymer).

The main conclusion from these results is a) the complete dissimilarity of spectra for insoluble

species to that of the LDH initiator, b) the close similarity (but not identity) of spectra for all

317 copolymer species to that of PLDLA-INSOL, which indicates that poly(lactide) is the dominant

318 species in the insoluble phases, and that the ε -caprolactone and δ -valerolactone monomers play a

negligible role in the formation of the insoluble phases.

320 **3.6** Solid ¹³C nuclear magnetic resonance spectroscopy

Figure 13 depicts the solid-state ¹³C NMR spectra of the LC insoluble residues. It also features the spectra of magnesium lactate hydrate, Fig. 13(2), and the original LDH-carbonate initiator, Fig. 13(1). Generally, three main peak-types can be observed in the spectra shown below, which represent the methylene (19–33 ppm), methine (68 ppm), and carboxyl (170–183 ppm) groups, respectively.

In Fig. 13(1) (and Fig. 14(1)), the NMR spectrum for the LDH-carbonate initiator is shown. Clearly, the majority of its characteristic peaks cannot be observed in the spectra of any of the insoluble moieties. However, the LDH spectrum has one peak (169.5 ppm) very close to a peak of the PLDLA-INSOL spectrum (168.4 ppm) which could be attributed to the carbonyl bond of the carbonate groups in both species. Nevertheless, the lack of all the other intrinsic LDH peaks in the
INSOL spectra, clearly demonstrates that the characteristic layered structure of the LDH has been
dismantled to beneath detectable limits during the polymerizations.

333 In Figs. 13(2), (and Fig. 14(2)), the reference spectrum for magnesium lactate is shown, while in Fig 12(3), the spectrum indicates the presence of PLDLA in the insoluble PLDLA-INSOL phase, 334 335 which has characteristic signals at 16.7, 69.0, and 169.4 ppm, respectively, Saito et al. (2006). In the figure, the methine resonance can be seen at 68.2 ppm, and two ester-carbonyl signals can also 336 be observed at 180.9 and 183.6 ppm (Fig. 13(2)) while ester peaks at 180.9 and 182.9 ppm also 337 show the presence of a magnesium polylactone ester in addition to polymer moieties (e.g., an acid 338 carbonyl at 177 ppm). In the LC series (Fig. 13(4)-(6)), the signals 24.2, 28.0, and 32.5 ppm 339 indicate the incorporation of ε -caprolactone moieties in the copolymer. Likewise, in the LV series 340 (especially Fig. 14(6)), the signals 27.7 ppm and 32.5 ppm are characteristic of δ -valerolactone 341 shifts. Magnesium lactate or other polylactone ester moieties are detectable in the scaffold spectra 342 343 for the LC and LV copolymer series at 180 and 183 ppm, respectively (Figs 13(4-6) and Fig 14(4-6)). The inorganic fraction of ester carbonyls in each insoluble species was determined by 344 calculating the peak integrals of the carbonyl groups of the polymer (acid carbonyls) and ester 345 346 moieties (ester carbonyls), respectively, as shown in Table 2.

This data indicates that no clear relationship exists between the initial monomer ratio and ultimate ester carbonyl yield in the insoluble phase. This would suggest that the ester carbonyl yield is driven by another factor, namely the number of Mg cations available to form ester moieties, which is primarily driven by the ratio of available LDH to monomer(s) in the reaction mixture.

Table 2 also shows the relevant calculated fraction of Mg in the original reaction mixtures, as wellas the corresponding fractions of ester carbonyl functions measured by NMR on an INSOL and

HYB basis, respectively. It is clear that there would be insufficient Mg or Al to account for all of 353 the ester moieties detected in the insoluble phases, if one assumed the formation of Mg or Al mono-354 lactate salts only (e.g., bonding of Mg with two single lactic acid monomers). Thus, in the absence 355 of non-metal ester-forming moieties, it is clear that only Mg or Al polylactone ester chains could 356 have formed (e.g., a Mg cation bonding to two polylactone chains to form a Mg polylactone ester). 357 358 Furthermore, based on Xray diffraction (XRD) evidence presented above, and previously, [1], Al polylactone ester moieties are not detectable in INSOL to any significant degree, so that only Mg 359 polylactone ester moieties are considered in this discussion. (Specifically, it was shown by 360 McCarthy et al. [16] that a Mg:Al element ratio of 11:1 existed in the INSOL phase). 361

Overall, these NMR spectra demonstrate the formation of salt moieties in the insoluble phases, the concurrent disassembly of LDH-carbonate initiator, and the ratio of ester to acidic carbonyl groups in these phases, which can be used to calculate the proportion of ester species in each insoluble phase. They fundamentally show the initiating activity of the LDH and its consumption to form a chemically different insoluble species during the polymerisation process.

367 3.7 EDAX (Energy-dispersive X-ray spectroscopy): Elemental Analysis of Reaction Species 368 and Products

To complement the NMR analysis in Table 2, elemental analysis of the LDH-carbonate and the insoluble phases was conducted to determine the magnesium and aluminium content in the two polymer phases and to establish whether there was a fixed ratio of cations to ester groups in the insoluble phases which would indicate the mechanism of insoluble phase ester formation. The EDAX spectra are given in Figure 15, while Table 3 gives the corresponding elemental mass fractions as calculated from these spectra by taking the ratios of the areas under the relevant

element peaks. One advantage of this measurement is its ability to confirm the local mass ratios of 375 Mg to Al in each of the INSOL products and compare them with the original available fractions in 376 the LDH-carbonate initiator. Doing this, it can be seen that an initial ratio of Mg:Al = 1.98 is 377 measured in the LDH-carbonate initiator. This contrasts dramatically with almost complete 378 selectivity of the pure poly(L,d-lactide) system for Mg in the PLDLA-INSOL insoluble phase 379 380 (Mg/Al = 20.2). However, this trend is not observed for any of the copolymer INSOL phases, which all show Mg/Al ratios of the same order as that in the LDH-carbonate initiator (Mg/Al ~ 2). This 381 would imply significantly different polylactone ester formation mechanisms as Mg and Al vary in 382 valence, i.e., Mg^{2+} cations can form bidentate polylactone esters, whereas Al^{3+} cations can form 383 tridentate esters. Clearly, the different molecular structures of these poly(lactone) ester networks 384 could have an effect on the ultimate morphology of the insoluble phase network at the microscale, 385 and may indeed account for the different morphologies of the different copolymer insoluble phase 386 networks compared with that of PLDLA-INSOL. 387

388 Conclusions

In the current work, melt copolymerizations of various lactone monomer combinations of L,D-389 lactide, caprolactone and valerolactone have been performed for the first time using LDH-390 carbonate as an initiator. This process results in the formation of a novel embedded network in 391 each two-phase polymer product, and the layered double hydroxide initiator undergoes near 392 complete disintegration at the molecular level instead of intercalation or exfoliation. The 393 mechanisms of the synthesis are believed to be predominantly anionic ring-opening 394 polymerization and co-ordination-insertion polymerization (at the edges and faces of the LDH-395 396 carbonate sheets). Two phases, soluble and insoluble, were derived from all primary polymer products (hybrids) using dichloromethane (DCM, CH₂Cl₂) as extraction solvent. Some of these 397

398 CH₂Cl₂-insoluble phases, which have three-dimensional porous morphology at the microscopic
399 scale, can possibly be used as potential bio-scaffolds for cell growth.

The polymer mass yields of the nine hybrid products and their insoluble mass fractions have been established by TGA and gravimetric analysis, while the microstructures and morphologies of the pristine reactants, the initial hybrid polymer products, and the extracted scaffold residues have been established using Xray diffraction (XRD) and scanning electron microscopy (SEM). In general, the pores of all scaffolds produced are heterogeneously distributed (both spatially, and in terms of pore size), and the morphologies are strongly dependent on the type and relative content of monomers in the hybrid polymer-ionomer systems.

X-ray diffraction data demonstrated that LDH-carbonate sheets were almost fully dismantled
during the 24 h of polymerization in all the compositions except for the neat PCL- and PVLHybrids. (PCL-HYB, PVL-HYB), where there was no network formation. This suggests that L,Dlactide is a beneficial reaction component for maximisation of overall polymer yield and maximal
yield of insoluble scaffold material in these reaction mixtures.

This work confirms that carbonate-intercalated LDH-carbonate, the most common commercial 412 synthetic layered double hydroxide, is a viable initiator for the polymerisation of various lactone 413 homo- and copolymers to high polymer yields. It shows that a long chain acid intercalant species 414 is not essential to the polymerisation process. It is also possible to generate various embedded, 415 416 organically-insoluble networks with different morphologies that can be customised using different comonomer types and combinations. Moreover, if required, the structure of the layered double 417 hydroxide used can be altered by chemical design to vary the cation and anion content in the 418 scaffold according to the specific requirements of a bio-scaffold application, for example. This is 419 something not possible with current physical deposition techniques, which also currently comprise 420

- 421 additional fabrication cost. It is expected that these materials can be used in a variety of scaffold
- 422 applications and work continues to validate their performance.
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- 515
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- 517
- 518

FIGURES



520

519

- 521 Figure 1. Process schematic for polymerization of various products and their extraction with
- 522 methylene chloride to form scaffolds.





Figure 2. Photographs of selected specimens produced: a) PLDLA-HYB resin specimen
(semi-transparent) b) selection of insoluble phase materials after extraction of soluble
phases: i) PLDLA-INSOL, ii) LV-1:1-INSOL, iii) LC-1:1-INSOL



- 529 Figure 3. Polymer mass yields of initial homopolymer hybrids determined by heating at 150
- 530 °C isothermally for 6 h (n = 3). Error bars = standard deviation.



- 533 Figure 4. Polymer mass yields of hybrid products synthesised by different monomer
- combinations determined by heating at 150 °C isothermally for 6 h. (n = 3) Error bars =
- 535 standard deviation.



536

- 537 Figure 5. SEMs of (a) LDH-carbonate and (b) PLDLA-HYB at magnifications of 10,000 and
- 538 **1,000, respectively.**



540 Figure 6. SEMs of (a) PCL-INSOL and (b) PVL-INSOL at magnification of 5,000.



544 Figure 7. SEMs of good network formers: PLDLA-INSOL at magnification of a) 5,000, b)

545 12,500 and c) 40,000, (d1, d2) LC INSOL 1:2, and (e1, e2) LV INSOL 1:2.



548 Figure 8. SEMs of non-network formers: a) LC INSOL 1:1 and b) LV INSOL 2:1.







551 (b) PLDLA-INSOL, (c) PCL-INSOL, (d) PVL-INSOL and (e) pristine LDH-carbonate.



Figure 10A. XRD spectra for scaffold residue synthesised using l,d-lactide and ε caprolactone monomers at different ratios.





Figure 10B. XRD spectra for scaffold residue synthesised using l,d-lactide and δvalerolactone monomers at different ratios.



560 Figure 11. Fourier transform infrared spectra of (a) L,D-Lactide monomer, (b) PLDLA-

561 INSOL and LC-INSOL series polymerised with L:C mass ratios of (c) 1:2, (d) 1:1, (e) 2:1

562 and (f) LDH-carbonate initiator.



565 Figure 12. Fourier transform infrared spectra of (a) LD-Lactide monomer, (b) PLDLA-

566 INSOL, the LV-INSOL series synthesised with L:V mass ratios of (c) 1:2, (d) 1:1, (e) 2:1

567 and (f) LDH-carbonate.



568

569 Figure 13. Solid State ¹³C NMR of various species in the reaction systems: (1) LDH, (2)

570 magnesium l-lactate hydrate, (3) PLDLA-INSOL, (4) LC 2:1 INSOL, (5) LC 1:1 INSOL, (6)

571 LC 1:2 INSOL, in the range 250-0 ppm.



572

573 Figure 14. Solid State ¹³C NMR of various species in the reaction systems: (1) LDH, (2)

574 magnesium l-lactate hydrate, (3) PLDLA-INSOL, (3) LV 2:1 INSOL, (4) LV 1:1 INSOL, (5)

575 LV 1:2 INSOL, (6) LV 2:1 INSOL in the range 250-0 ppm, respectively.





577 Figure 15. EDAX Spectra of the various insoluble phases and LDH-carbonate.

TABLES

580

581 Table 1. Overall polymer mass yields obtained from TGA and insoluble residue mass yields

582 in the polymer hybrids with various monomer combinations. (n = number or runs).

Name	Polymer Mass Yield	Mean Value at	Difference	Insoluble Mass Fraction	
	150°C, 6 h	260°C (ramp-	(on mean	(Standard Deviation)	
	(isothermal)	TG)	basis)		
	(n = 3)	(n = 2)			
	% by mass			% by mass	
PLDLA-HYB	87.3 (±4.3)	83.1	-4.2%	21.9 (±7.1)	
PCL-HYB	87.4 (±1.9)	85.6	-1.8%	7.2 (±0.3)	
PVL-HYB	48.5 (±2.3)	46.3	-2.2%	6.2 (±0.3)	
L:C 1:2-HYB	91.7 (±1.5)	90.9	-0.8%	23.1 (±4.6)	
L:C 1:1-HYB	90.8 (±3.1)	90.1	-0.7%	23.3 (±5.4)	
L:C 2:1-HYB	88.1 (±5.3)	86.4	-1.7%	23.2 (±6.0)	
L:V 1:2-HYB	87.1 (±3.1)	86.0	-1.1%	21.0 (±4.1)	
L:V 1:1-HYB	86.7 (±2.0)	86.3	-0.4%	22.5 (±4.7)	
L:V 2:1-HYB	87.8 (±0.2)	85.3	-2.5%	22.8 (±5.4)	

583

Table 2. Ester carbonyl mole fraction in the insoluble phases (INSOL) extracted from
different homopolymer and copolymer primary products (HYB).

	Original Mg	Ester carbonyl	Ester carbonyl	Mean number of	
Name	ion mole	mole fraction	mole fraction	poly(lactone) ester	
	hasis) (%)	(%)	(HYB Basis) (%)	units per Mg cation	
	Sub15) (/ 0)	(,,,)			
PLDLA-INSOL	0.30	22.4	4.9	8	
L:C 1:2-INSOL	0.27	15.4	3.6	7	
L:C 1:1-INSOL	0.27	15.4	3.6	7	
L:C 2:1-INSOL	0.29	38.0	8.8	15	
L:V 1:2-INSOL	0.24	28.7	6.0	13	
L:V 1:1-INSOL	0.25	43.1	9.7	19	
L:V 2:1-INSOL	0.27	31.0	7.1	13	

589 Table 3. EDAX Results for various insoluble phases and LDH-carbonate (% by mass).

590				
591	Specimen	Mg	Al	Mg/Al
592				mass ratio
593	LDH-			
594	Carbonate	17.20	7.83	1.98
595				
596	PLDLA-INSOL	18.21	0.9	20.2
597	L:C 1:2-INSOL	18.82	10.3	1.83
598	L·C 1·1-INSOL	16.05	7 12	2 25
599		10.05	/.12	2.23
600	L:C 2:1-INSOL	12.65	6.31	2.00
601	L:V 1:2-INSOL	19.89	10.25	1.94
602				
603	L:V 1:1-INSOL	17.87	10.40	1.72
604	L:V 2:1-INSOL	11.89	3.22	3.69

605

606 Table of Contents Graphic (for Table of Contents use only)

