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Preparation of Sodium-Capped Poly(lactic acid) Oligomers by Catalytic Initiation with a Sodium α-, β-, or γ-Hydroxyacids

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ABSTRACT: Lactic acid oligomers were prepared using sodium and potassium hydroxyacids as initiators for lactide polymerization leading to the formation of surface active molecules in a one-pot synthesis, requiring no additional catalysts or volatile organic solvents. The initiator systems that were investigated included sodium and potassium salts of lactate, mandelate, γ-hydroxybutyrate, α-hydroxybutanoate, α-hydroxyhexanoate, α-hydroxyoctanoate, α-hydroxyisovalerate, and 2,2-bis(hydroxymethyl)butyrate. Poly(lactic acid) oligomers were successfully isolated from polymerizations initiated by all species listed using the catalyst-free synthetic route employed. The molecular weights of the oligomeric species ranged from 800 to 2400 Da (measured against poly(styrene) standards), and polydispersities were all below 1.5. All isolated polymers showed surfactant activity with low CMC values and a high propensity for aggregation that increases as molecular weight increases. Additionally, producing an A−B−A type polymeric structure, where the B block is defined as a moiety containing a single functional group, was shown to give improved application performance compared with the equivalent A−B type structure.

Introduction

Poly(lactic acid) (PLA) has become a highly desirable commercial polymer because of its biodegradable and biorenewable nature. It has found a wide range of applications from biomedical sutures to biodegradable packaging for food. In the commercial processes, cornstarch is fermented to produce lactic acid, which can then be used to form PLA and lactide, the cyclic diester formally formed by dimerization of two lactate units with the loss of two water molecules. In practice, it is usually obtained from the depolymerization of short PLA chains.[1]

Lactide polymerization is the best method for producing high-molecular-weight polymers[2] and copolymers[3] of PLA with a predictable polydispersity. ROP of lactide was first investigated by Carrothers et al.[6] using alkaline salts as the catalysts at 150 °C. This resulted in a resin, with water possibly being involved in the initiation process; however, the process that has been most widely adopted on a commercial basis employs stannous octanoate (bis(2-ethylhexanoato)tin(II))[1,4] as the catalyst in the presence of an alcohol initiator. Over the last few decades, new catalysts and methodologies have been developed.[2,5] Living ring-opening polymerization (LROP) of lactide can be carried out by organometallic catalyst initiators containing an alkoxide functionality. The reaction proceeds through the binding of a lactide molecule, followed by nucleophilic attack by the alkoxide resulting in ring-opening. This produces a new metal alkoxide species bound through the oxygen moiety of the alkoxide group of the incorporated lactide that then undergoes the same reaction, leading to further ring-opening and thus propagating chain growth (Figure 1).

There are many specially designed catalyst systems developed in this way for producing long PLA chains (200 000 Da). Some have been developed with wider applications for stereoselective control of the different lactide stereoisomers during ring-opening polymerization.[5]

Alkali metal salts, such as lithium *tert*-butoxide, have been used in lactide polymerization, but they are prone to undesirable side reactions such as transesterification, chain scission, and multimodal polymer distributions. For example, Kricheldorf et al.[7] studied metal salts of lactates and mandelates as lactide ROP initiators. They found that the alkali metal salts were all good transesterification catalysts so that they did not produce long-chain PLA. An exception to this general observation was noted when zinc lactate was used. In a recent study by Miller et al.[8] a sodium complex [EDBPH]Na$(MeOH)_2(THF)_2$ (EDBPH = 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol)), which is nontoxic and an approved food additive, was found to be highly active in lactide polymerization with good conversions and polydispersities.

To date, there are few uses of PLA in the preparations of surfactant materials, and the physical chemistry of PLA within the surfactant industry has not been widely reported, although some work has been carried out using condensation polymerization methods in this area.[9] In this article, we report the ring-opening polymerization of lactide using alkali metal salts of hydroxyacids as initiators to make surface active molecules.

Experimental Section

Materials. L- and *rac*-lactide were purchased from Aldrich and dried by sublimation at 115−120 °C for 4 h prior to use. Sodium lactate was provided by PURAC chemicals, sodium γ-hydroxybutyric acid (GHB) was purchased from Aldrich and used without purification, and mandelic acid and

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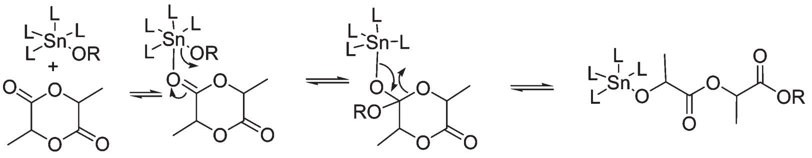


Figure 1. Simplified mechanism for living, metal-alkoxide-initiated polymerization of lactide to form PLA.

2,2-bis(hydroxymethyl)butyric acid (BHB) were purchased from Aldrich and converted to the sodium or potassium salt prior to use.

Preparation of Initiators. Sodium or potassium α-hydroxybutyrate, -hexanoate, and -octanoate were produced from their 2-chloro or 2-bromo precursors by refluxing in an aqueous sodium or potassium carbonate solution (ratio 2:1 carbonate/substrate) for 2 h before the water was removed and the product was extracted by washing with ethanol and diethyl ether.

Sodium α-hydroxyisovalerate was produced by the direct oxidation of *rac*- or L-valine. This was carried out in water at 0 °C by slowly adding first sulfuric acid (1.5 equiv, 1 mol dm^{-3}) and then sodium nitrite (1.5 equiv). The mixture was stirred for 3 h at 0 °C before being allowed to warm to RT and was stirred for over 24 h. The product was extracted using ethyl acetate, dried over $MgSO_4$, and recovered on the rotary evaporator in ~70% yield. It was converted to the sodium or potassium salt, by dissolving in aqueous sodium or potassium hydroxide solution (1:1 ratio) and recovering by evaporation. The samples were first dried in an oven at 80 °C and then stored under vacuum over (but not in contact with) P_2O_5 for 24 h prior to use. All salts of α-, β-, or γ-hydroxyacids were stored in vacuo over P_2O_5 prior to use.

Preparation of Surface Active PLA Oligomers. Sodium salts of PLA polymers were prepared in a one-pot melt polymerization. Lactide (4.32 g, 30 mmol), after sublimation, was heated to melting (130 °C) in a round-bottomed flask completely immersed in an oil bath before the addition of initiator (2.5–5 mmol). The reactions were allowed to proceed for between 20 and 80 min depending on the initiator type and the ratio of initiator/lactide. The resulting polymer melt was then transferred to a cold ceramic mortar and ground into fine powder after cooling. The resulting polymer was analyzed by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, DSC, TGA, and GPC where appropriate.

NMR, MALDI-TOF MS, and GPC Analysis. All NMR spectra were carried out in $CDCl_3$ (without internal standard) on a Bruker Avance 300 or 500 spectrometer recording at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR.

Matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectra were recorded using an Applied Biosystems 4800 MALDI-TOF spectrometer with methanol as solvent.

Gel permeation chromatography (GPC)-based molecular weight analysis was carried out using a PL-GPC 120 system with THF as the eluent at 40 °C. The molecular weight was calibrated using poly(styrene) standards with toluene as the flow rate marker at a flow rate of 1 mL min^{-1}. The instrument was fitted with an RI detector for molecular weight analysis.

Thermal and Water Uptake Analysis of PLA Oligomers. Thermal gravimetric analysis (TGA) was conducted to determine the thermal stability characteristics of the materials and the extent of water uptake by the oligomers.

TGA was carried out using a Netzsch TG 209 instrument operating from 25 to 300 °C, where samples of up to 5 mg were analyzed using dry alumina crucibles in air.

Water uptake was carried out by wetting the polymer at high concentration (~50 mg cm^{-3}) before recovering the polymer by filtration and evaporation of water. The recovered polymer was dried in vacuum desiccators for 24 h over P_2O_5 before its degradation was analyzed using the same TGA program as that for thermal degradation. Any loss in mass between 50 and 100 °C was attributed to loss of water.

Differential scanning calorimetry (DSC) was also carried out to support the TGA data using a Netzsch DSC 204 instrument operating between −30 and 150 °C using sample amounts of up to 5 mg in aluminum pans.

Determination of Surface Tension of PLA polymers. Surface tension measurement was carried out on a Nima ST9000 manual tensiometer using the Wilhelmy plate method.[10] Surfactant concentrations of 1 mg cm^{-3} were typically used where the polymer was suitably water-soluble.

Critical Micelle Concentration. The critical micelle concentration (CMC) was ascertained using conductivity measurements with concentration variation from 0.001 to 0.1% and by plotting a graph of conductance versus concentration to obtain the CMCs.

Dynamic Light Scattering. Dynamic light scattering (DLS) was carried out to ascertain the hydrodynamic radius of polymer micelles and aggregates produced from these polymers via a Zetasizer Nano Series (Malvern Instruments) particle size analyzer. The scattering angle was fixed at 90°, and the measurements were recorded at a constant temperature of 20 °C. The polymer concentration was set at 1 mg cm^{-3}.

Turbidity Measurement. PLA (1 mg cm^{-3}) solutions in water were prepared and placed in a water bath at the desired temperature. The point of turbidity was taken to be the time taken until a marked point became obscured by the polymer suspension.

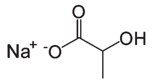
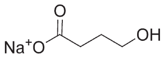
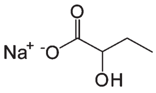
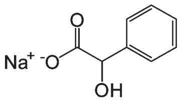
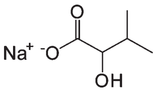
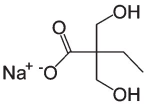
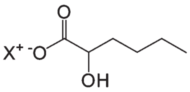
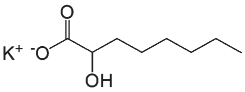
Emulsification Tests. *Water/Toluene*. A solution (10% w/w) of the polymer in toluene was prepared so that the overall concentration in the emulsions would be 2.5%. Because of the heat produced by the high shear Silverson mixer, all emulsification tests were carried out using an ice bath to reduce toluene evaporation, which would cause immediate splitting. The polymer solution (25 cm^3) was added to a beaker and sheared using the Silverson mixer at shear rates of <6000 rpm. To the solution, distilled water (75 cm^3) was slowly added via a syringe over a period of 10 min. The emulsion was then sheared for a further 20 min before being allowed to stand for 10 min. Any emulsification properties were then noted such as creaming, breaking, and so on. For the more stable emulsions, samples were taken for DLS to measure the emulsion sphere size.

Water/Squalane. For PLA-based emulsifiers, an overall concentration of 2.5 mg cm^{-3} was used, and water/squalane ratios of 1:1 and 3:1 were principally employed. First, the surfactant was dissolved as much as possible in water using sonication before the squalane was added. It was resonicated after the addition of squalane. The solutions were then shaken rigorously for 1 min and allowed to stand for 1 min initially. The time taken for the emulsion to break or become thixotropic was recorded.

Analysis of Emulsion Type. A drop of emulsion was placed onto anhydrous (blue) cobalt(II) chloride paper. Oil in water emulsions spread as a pink area on the paper, whereas water in oil emulsions give a pink area surrounded by a pronounced blue corona.

Tilt Angle Method. The tilt angle method is an observational method for detailing thixotropy/dilatancy. For the tilt angle method, the emulsion is prepared in a closed sample vial. The emulsion is agitated (usually by shaking) for a period and then allowed to rest for a set time. After the time has elapsed, the vial is tilted first to 90° and then to 180°. If the emulsion collapses at 90 or 180°, then the emulsion has not sufficiently thickened. The emulsion is agitated again, and the time increased, and this is repeated until thickening increases or splitting occurs.

Table 1. Summary of Oligo-LA Produced in a Melt Polymerization at 130 °C Initiated by Sodium or Potassium α-, *β*-, or *γ*-Hydroxcarboxylates

Initiator	Sample No	Lactide	Ratio M: I	Approx. M_n (^{1}H NMR)[a]	M_n (GPC)[b]	M_w (GPC)	PDI (GPC)	Tg (°C)	Surface Tension (mNm^{-1})	Hydrodynamic Radius (nm)
 Lactate	**1**	rac	6 : 1	1032	847	1211	1.39	35.3	43.55	96
	2	rac	12 : 1	1984	1560	2145	1.5	43.4	-	181
	3	L	6 : 1	1032	820	1149	1.4	26.1	49.77	121
	4	L	12 : 1	1984	1429	2282	1.46	44.9	48.4	158
 γ-Hydroxybutyrate	**5**	rac	6 : 1	1050	-	-	-	-	46.2	-
	6	L	12 : 1	2000	-	-	-	-	-	-
 α-hydroxybutyrate	**7**	L	6 : 1	1061	962	1347	1.4	42.3	47.33	249
	8	L	12 : 1	1800	-	-	-	31.8	49.5	-
 Mandelate	**9**	L	6 : 1	950	-	-	-	48.6	49.65	-
	10	L	12 : 1	-	1337	2226	1.43	-	-	237
	11	rac	12 : 1	1790				41.7	-	-
	12	L	12 : 1	1600				41.4	-	-
 α-hydroxyisovalerate	**13**	rac	6 : 1	1146	828	1175	1.42	33.8	46.1	165
	14	rac	12 : 1	1700	-	-	-	39.2	-	-
	15	L	12 : 1	1700	-	-	-	36.8	-	-
 2,2-bis-hydroxymethylbutyrate	**16**	rac	12 : 1	1320	2359	3398	1.44	40.6	47.75	251
	17	rac	12 : 1	1024				39.2	-	-
	18	L	12 : 1	1600				43.9	-	-
 2-hydroxyhexanoate	**19**[c]	L	12 : 1	1800	852	1169	1.37	38.2	47.5	288
	20[d]	rac	12 : 1	1700	-	-	-	35.5	44.45	-
	21[d]	L	12 : 1	1900	-	-	-	38.5	-	-
 2-hydroxyoctanoate	**22**	L	6 : 1	1200	1212	1804	1.49	-	-	362
	23	rac	12 : 1	1800	-	-	-	29.1	-	-
	24	L	12 : 1	1800	-	-	-	25.4	-	-

[a] Determined by integration relative to the lactate end group. [b] Determined by GPC. [c] X = potassium. [d] X = sodium.

Several things are noted during this, any separation (two emulsion phases), any stages of thickening, and any precipitation/sedimentation.

Results and Discussion

The results for the ring-opening polymerization of lactide to produce surface-active PLA are summarized in Table 1. To attempt to understand the mechanism of initiation, we carried out melt polymerization reactions initiated by sodium salts of simple carboxylic acids (ethanoate, stearate) or by sodium ethanoate dissolved in small amounts of ethanol. Simple sodium carboxylates yielded no polymer, whereas the presence of a small quantity of NaOAc/EtOH led to oligomer formation. These reactions suggest that the polymerizations initiated by hydroxy acids proceed mainly through an intramolecular tautomerization mechanism (Figure 2) by either a ring-type transition state for sodium 4-hydroxybutyrate (GHB) or by cation transfer such as that for the α-hydroxycarboxylates. The resulting alkoxide is then the active catalyst and initiator for lactide polymerization.

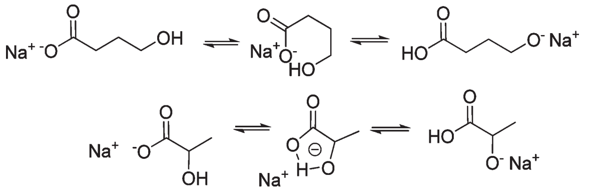


Figure 2. Intramolecular tautomerization mechanism required to produce the initiating alkoxide in GHB or lactate for lactide ring-opening polymerization.

The M_n values for the polymers formed by these ring-opening reactions correspond well to those theoretically predicted by the lactide-to-initiator ratios employed (Table 1). In nearly all cases, the polymer has incorporated only one initiator, although there are some cases, for example, sample 16 in Table 1, where M_n obtained from an NMR measurement is considerably less than the value obtained by GPC. In this case, it is possible that two or three initiators are incorporated into some chains. This may arise because of condensation of the growing chain with a molecule of initiator. For sample 16, this could lead to further polymerization because of the extra hydroxo group. Simple condensation of two growing chains could also lead to the incorporation of two initiator groups (Figuire 3a). These condensation reactions would lead to the loss of water, which can hydrolyze chains with the loss of some surfactant properties. The MALDI-TOF MS for sodium-lactate-initiated polymers have confirmed in all cases that one initiator molecule has been incorporated into the oligomeric structure, although the peaks attributed to transesterification (see below) could also arise from condensation of two chains. Such condensed chains, however, would be expected to

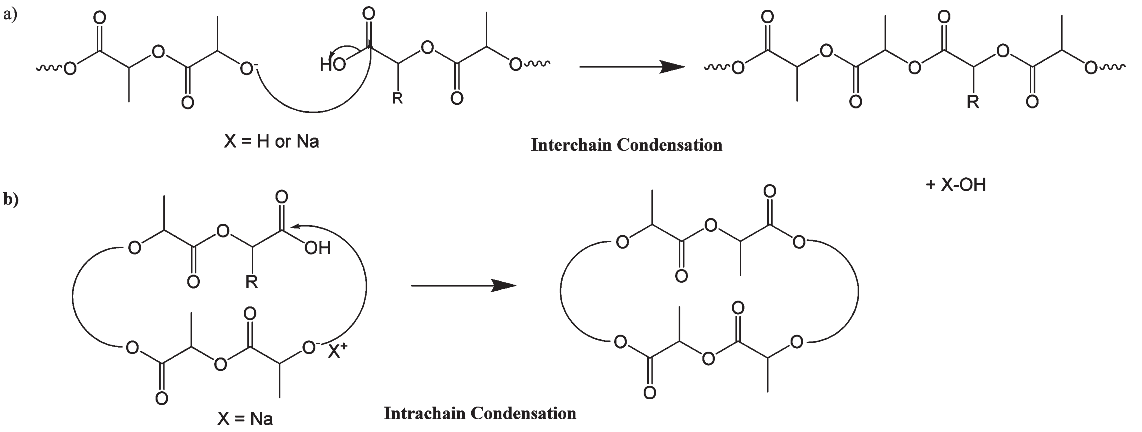


Figure 3. (a) Interchain condensation reaction resulting in an initiator molecule in the middle of the chain as well as at its terminus and (b) intrachain condensation resulting in ring formation and loss of surfactant end groups.

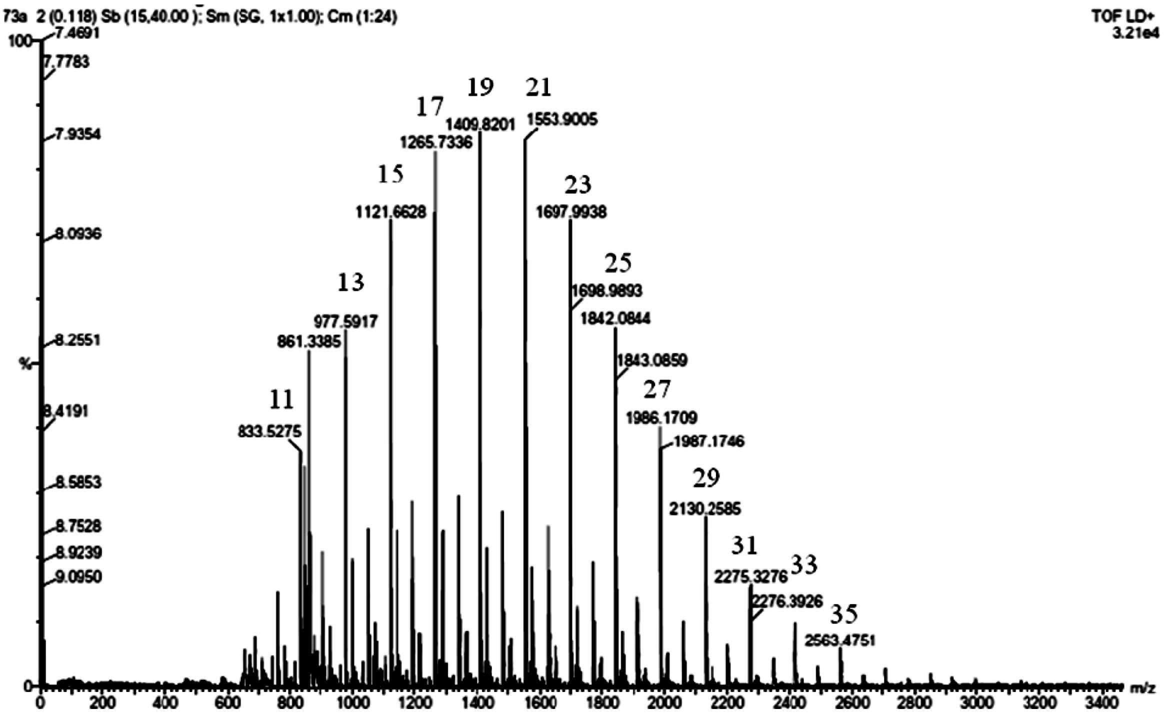


Figure 4. Product distribution observed for Na-lactate-initiated oligo-LA, showing odd numbers of repeat units increasing from 11 LA units to > 35 LA units.

have higher molecular masses than the individual chains from which they are formed, especially if the arise late in the oligomerisation process. Transesterification reactions (including ring-closing esterification), which arise from attack by the alkoxide chain end upon the backbone of a second chain, can affect the polymer surfactant properties by leading to (a) the formation of free NaPLA chains with molecular weights much lower than that theoretically predicted and (b) chains that are no longer surface active (i.e., they have lost the ionic headgroup by intrachain ring closing, Figure 3b) that dominate the overall surfactant properties. Evidence of transesterification is provided by the growth of intermediate peaks (separation 72 amu) in the MALDI-TOF MS. Such peaks are observed in these reactions after prolonged reaction times. A small extent of transesterification is evident in the polymer analyzed in Figure 4.

Observation of the methine C peaks at ~69 ppm in the ^{13}C NMR spectra showed that the oligomers produced have the expected tacticity for L-PLA (isotactic); however, for *rac*-lactide, the shorter chains result in a different statistical distribution for the tacticity with somewhere between three and five peaks normally observed. By comparison with the works of Munson[11] and Coates,[12] this is not unexpected given that these polymer chains are shorter. Therefore, both the statistical probabilities and the number of possible tetrad sequences along a single polymer chain are reduced.

Sodium lactate proved to be an efficient initiator for lactide oligomerization, where it is proposed that the alkoxide is the actual initiator, and the resultant oligomers exhibited good surfactant properties, confirming that one end group of the oligomer is a carboxylate. We have investigated the initiation of ROP using other sodium salts of hydroxy carboxylic acids. The results, which are collected in Table 1, show that all hydroxyacids tested are active initiators and that the molecular weight of the oligomers produced depends upon the lactide/initiator ratio rather than the structure of the initiator.

Sodium BHB contains two hydroxyl groups, and when it was used as the initiator, the PLA structure was further altered. The resulting polymer exhibits an A−B−A type structure as opposed to the A−B type produced by the other initiators. NMR spectroscopy confirms that initiation takes place from both

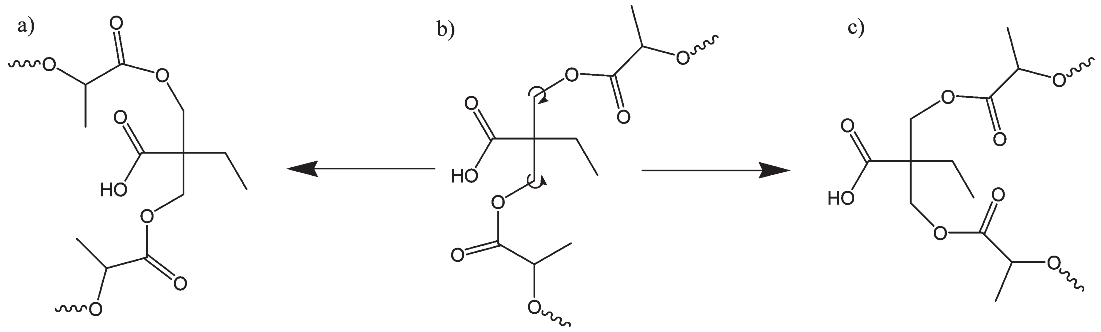


Figure 5. Different methods for BHB-initiated polymer to orientate to maximize or minimize hydrophilic/hydrophobic interactions.

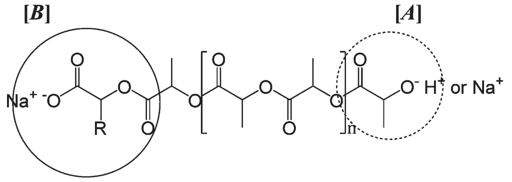


Figure 6. Surfactant structure of PLA-based surfactants indicating sites of hydrophilicity. Each chain bears only one negative charge.

hydroxide groups to give the polymers shown in Figure 5, although the level of growth occurring away from each hydroxyl site is not necessarily equal. This inequality may perhaps arise because of the possible ways BHB can orient itself in solution. If we consider free rotation around the CH_2O bonds (originally in the initiator), then the polymer can orient itself in several different ways. It could orient itself to maximize hydrophobic interactions by covering the polar head (Figure 5a), or it can orient itself away from the polar head (Figure 5c) or any random position in between (Figure 5b). The structure shown in Figure 5c may lead to vesicle formation.

Surfactant Properties. PLA-based surfactants produced in this study show very different types of surfactant behavior in terms of surface tension, aggregation, foaming, and turbidity. In terms of surface tension, it is not possible to be certain whether the anion is the carboxylate or the alkoxide from the data available (Figure 6). However, the pKs of the conjugate acids suggest that the alkoxide [A] will be protonated and the carboxylate ion [B] will be the polar end group. The size of the R group has some effect on the surface tension of the solution and has an effect in terms of aggregation, where bulky initiators like sodium mandelate or potassium hydroxyoctanoate (surface tension could not be determined due to aggregation) tend to have higher surface tensions and aggregate much more readily, as seen in the DLS data (Table 1). Furthermore, it was discovered that over time (24 h) the micelles continue to grow and aggregate. Repeat measurements conducted 24 h after the initial surface tension assessment on samples 1 and 3 in Table 1, which are initiated from sodium lactate, showed that the micelles had doubled in size from 96 to 184 nm and tripled from 121 to 384 nm respectively over 24 h in water. The rapid aggregation of these micelles occurs because of the very low CMCs recorded for the PLA surfactants ($\sim 5 \times 10^{-9}$ mol cm^{-3} as measured using conductivity) relative to those of standard surfactants (typically 8×10^{-6} mol cm^{-3} for sodium dodecyl sulfate).

Table 2. Initial Foam Height and Foam Stability after 1 min in Surfactant Tests of Oligolactides Made Using Different Hydroxycarboxylic Acid Initiators and Different Chirality Lactide

sample	lactide	initiator	M_n (LA units)	surfactant quotient	initial foam volume (cm^3)	foam stability (cm^3)
11	*rac*	NaMan	25	4	4	2
12	L	NaLMan	22	4	7	4
14	*rac*	NaHiVA	26	4.5	3	1
15	L	NaHiVA	24 to 25	5	5	1
17	*rac*	NaBHB	5 to 6 per arm	5	23	12
18	L	NaBHB	11 per arm	5	8	4
20	*rac*	KHHxA	22 to 23	5	5	2
21	L	KHHxA	26 to 27	5	6	2
23	*rac*	KHOctA	24	3	1	0
24	L	KHOctA		4.5	4	2

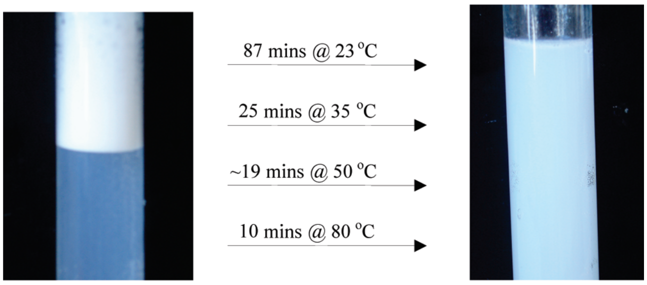


Figure 7. Solution of **3** (1 mg cm^{-3}) becoming turbid at a given time and temperature.

The PLA-based surfactants produced in this study were observed to be relatively low-foaming surfactants. Furthermore, the foam heights and stabilities could be related to the surfactant shape and the size of the R group (Table 2). Sodium-BHB-initiated surfactants showed the greatest foam height and stability, and this can be rationalized by the architecture of the molecule. The BHB-initiated surfactants were consistently observed throughout the different surfactant tests to produce differentiated results as a result of the A−B−A from those obtained with the other single hydroxyl initiators.

The turbidity behavior of the PLA sodium salts was also studied by the method detailed in the Experimental Section. They were found to exhibit behavior similar to poly(oxyethylenated) surfactants, where a cloud point can be defined as the time that a solution goes from clear to opaque at a particular temperature. With the PLA oligomers, as the temperature increases, so does the rate at which turbidity develops (Figure 7).

Emulsification of PLA Sodium Salts. The emulsification behavior of these sodium PLA salts surfactants was assessed using the emulsification tests described in the Experimental Section. Specifically, water/oil ratios of 3:1 for water/toluene and 1:1 for water/squalane were employed. The emulsions that are made of water and toluene were all deemed unstable except in the case where sodium-mandelate-initiated PLA (entry 10 in Table 1, to be discussed in a separate paper) was used as the emulsifier. In this instance, the emulsion exhibited shear thickening qualities, forming a thick paste during shearing, and the emulsion did not break for several weeks afterward (Figure 8). All other tested emulsions broke after a few minutes. Table 3 presents the results of studies on various surfactants using a high shear mixing.

Water/squalane mixtures were analyzed using the shaking method described in the Experimental Section because of the lower solubility of the polymers in squalane. The results obtained using squalane and this analytical method showed that these oligomers exhibited some of the same non-Newtonian behavior that was observed with water/toluene mixtures. In this instance, thixotropic (shear thinning) emulsions were formed. Once the emulsion had formed, it thickened as it settled. Using rigorous shake and the tilt angle method,[14] we measured the time to reach thixotropy and recorded it for several samples. (See Table 4.) Breaking was taken as the time taken for water separation to occur and be detected by visual inspection. However, clearly, this does not indicate a loss of all emulsification. In sample 2, even though water separated quickly, the emulsion reformed on shaking, and even after separation, the W/O upper layer remained viscous and gel-like. In the other samples, water separation occurred after several days or weeks, except in the case of NaBHB, where the oligomer has the A−B−A structure, for which the emulsion did not break. It is proposed that the stability of this emulsion arises because of the molecular architecture, which gives this molecule the ability to rearrange so as to optimize the arrangement of the hydrophobic and hydrophilic parts at the interface such that it stabilizes a larger area of the vesicle surface. This molecular organization thus increases the level of emulsion stabilization achieved per mole of oligomer added.


After 1 day After 1 month

Figure 8. Photographs of a water/toluene emulsion made using PLA initiated by sodium mandelate taken after 1 day and 1 month, where it shows no splitting.

The more stable emulsions tend to form water in oil (W/O) macro-emulsions. However, in the cases where breaking occurs, we observe mixed emulsions where a W/O emulsion phase sits above an O/W phase, and the emulsions easily recombine on shaking. The formation of the two phases may be related to the polydispersity of the polymers. The broader range of PLA backbone lengths leads to a greater range in solubility behavior for the oligomers. The more water-soluble polymers (shorter PLA chains) remain in the O/W phase, whereas the more hydrophobic species (longer PLA chains) remain in the W/O phase.

Thermal Properties of PLA Sodium Salts. The glass-transition temperatures for these sodium PLA oligomers are lower than the literature quoted values for PLA polymers because the chain lengths of the oligomers are below the entanglement length for PLA. Another major difference is that they have no discernible melting point, even when heated to 200 °C; instead they thermally decompose over 180 °C (as shown by TGA in the upper trace in Figure 9).

Lower temperature degradation may be dictated by (a) the thermal properties of the initiator species, (b) the thermal activity of the bond type that links the initiator to the polymer chain, and (c) the presence of cyclic species as terminal species on the polymer chain. All of these can act as centers for increased levels of chain instability. Such instability has been observed in other polymers; for example, with PMMA, the presence of halide species from an ATRP initiator, terminal carbon−carbon double bonds from catalytic chain transfer, and lactone chain ends all contribute to increased thermal instability.[15] Alternatively, this may relate to the fact that the oligomers exhibit very low levels of crystallinity and are essentially amorphous materials because of their low molecular weights.

Unlike the case of PMMA, PLA is also hydrolytically unstable. This is a property often exploited in applications of PLA such as dissolvable surgical sutures or packaging that degrades faster when buried in wetter environments. Therefore, the decrease in thermal stability of these materials may be related to increased levels of hydrolytic decomposition. The hydrolytic decomposition has been proposed to be a chain-end-inspired process. Therefore, the low molecular weight of the materials produced in this study results in a very high number of chain ends being present in the sample, increasing the potential effect of any water present.

Table 3. Emulsification Tests using Silverson High Shear Mixer

sample no. (Table 1)	no. of LA units from Mn (GPC)	emulsion description	hydrodynamic radius (nm)	
			after 1 h	after 24 h
4	∼22	emulsion split into two emulsion layers, O/W and W/O, signs of shear thickening	715	479
2	∼19	no separation after 10 min, full separation after 18 h.	669	559
10	19 to 20	shear thickening emulsion, v. stable, consistency of wallpaper paste.	398	

Table 4. Results of Emulsification Testing Using Water/Squalane 1:1 Emulsions

sample	M_n (LA units)	time to thixotropy (min)	time to breaking (approximately)	water separation after 20 min. (mm)	Is thixotropy retained?
2	26	2	10 min	14	yes
13	14	2	2 days	0	yes
16	8 per arm	2		0	yes
19	24	< 1	1 week	0	yes
22	16	6	2 days	0	yes

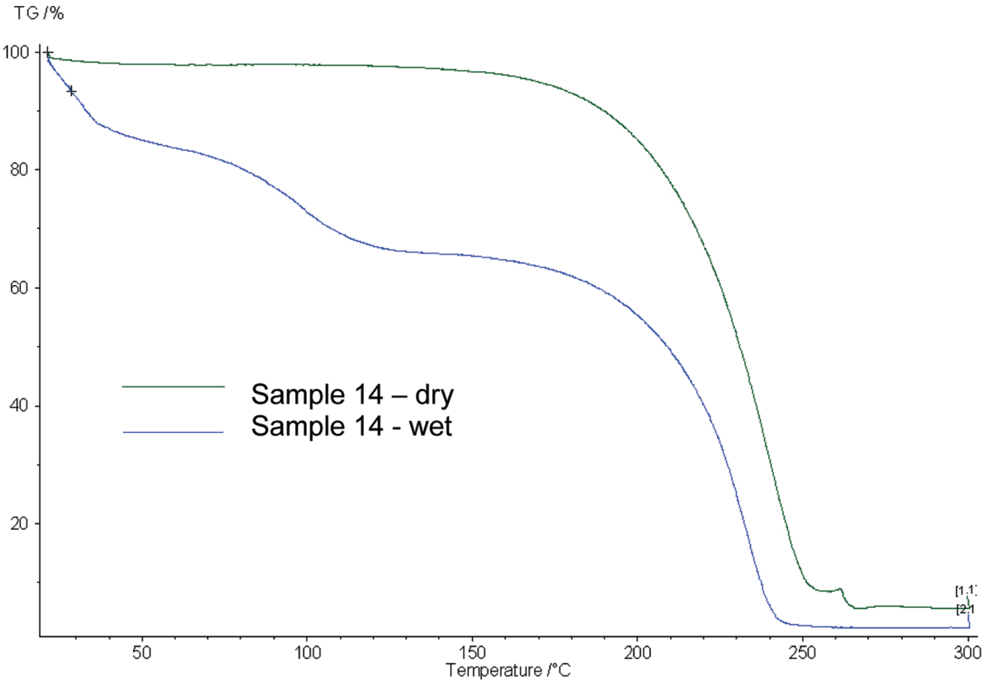


Figure 9. Thermal degradation of wet and dry polymer **14**, initiated using potassium 2-hydroxyisovlerate.

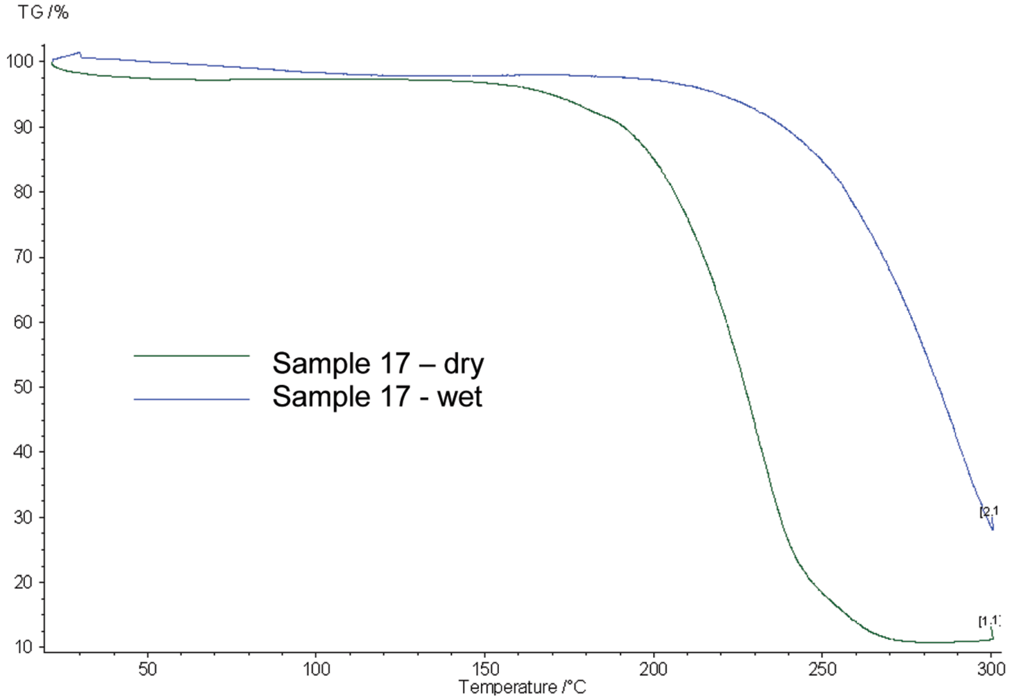


Figure 10. Thermal degradation of wet and dry polymer **17**, initiated using NaBHB.

Table 5. Data Concerning the Thermal Degradation of Various Sodium/Potassium PLA Polymers[a]

sample no.	degradation temperature (°C)						loss in mass of wetted polymer (%)		
	dry polymer		wetted polymer				water	polymer	overall
			water		polymer				
	onset	end	onset	end	onset	end			
14	214	259	49.9	135	214	240.9	34	62.4	96.4
20	210	265	90.7	108.6	231.3	254.2	21.5	70.39	91.9
15	221	272	91.7	151.6	237.8		16.15	95.39	100
17	207	280			256		0	69.7	69.7*
18	215	278			229.1	259.5	0	93.6	93.6
13	~148	~234	~110	~150	~170	~250	9.3	88.7	98

[a] Decomposition was still occurring at the end of the temperature ramp (300 °C).

This effect is discussed in more detail in an related publication by the same authors, where it has been demonstrated that the level of hydrolytic instability can be controlled by the choice of the type of terminal group that is built into the polymeric structure.[16]

To analyze whether retained water in the polymer is the reason behind the reduced thermal stability of these oligomers, a water uptake study was carried out using TGA. The results of this study are shown graphically in Figure 9 and in Table 5, which shows degradation data for PLA polymers that had been exposed to water and tested while still wet or after they had been dried. It was concluded from this data that even after drying, the polymers that had been exposed to water still retained some water. These results suggest that water is able to hydrogen bond to the polyester, possibly forming hydrogen bonding bridges between polyester chains. However in the decomposition studies, it was noted that wetting these materials did not affect the onset of decomposition and in some cases (including the A−B−A copolymer) actually thermally stabilized the oligomer, leading to an increase in the temperature of the onset of degradation. (See Figure 10.) This result was surprising because it had been thought that the presence of water in the polymer should facilitate hydrolysis and increase the rate of thermal decomposition because this forms the basis of many accelerated hydrolysis tests.[17] It is possible either that water is evolved from the polymer prior to full decomposition or that it has a stabilizing effect due to the particular molecular structure of the oligomer, as in the case where NaBHB was used as the initiator. The increase in stability when using the NaBHB initiators may again be a consequence of the A−B−A type structure,[18] which may lead to the formation of more stable micelles or vesicles with strong intra- and interchain interactions that would lead to the increased stability.

Conclusions

This study has demonstrated that it is possible to form surface-active PLA molecules in a one-pot procedure that does not require the addition of toxic or expensive catalysts by using salts of hydroxycarboxylic acids as initiators. MALDI-TOF analysis has been used to define the polymer end groups. This evidence coupled to the surface-active nature of the oligomers suggests that initiation proceeds via intramolecular rearrangement of the sodium of potassium salt of hydroxyl acid to produce an alkoxide that actually is the initiating species. Additionally, it was possible to reduce levels/rates of transesterification during the oligomerization by working at lower temperatures for shorter reaction times. In general the resultant oligomers have low CMCs and demonstrate a high propensity toward aggregation because of strong interactions between polymer chains in solution. The MALDI-TOF analysis also demonstrated that the use of BHB as an initiator resulted in the successful synthesis of an A−B−A copolymer structure. All oligomers were found to exhibit some level of interfacial/surfactant properties, as indicated by foaming studies and their ability to form relatively stable emulsions. By further analysis of the application-based interfacial test data, it was shown that the A−B−A structure resulting from the use of BHB as a initiator exhibited better surfactant properties when compared with the A−B structures that are produced by using the other initiators investigated.

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