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Highly crystalline as-polymerized poly(L-lactide)

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Summary

Two new lactone polymerization catalysts, tin(II)-bis(2,4-pentanedionato-O,O') ($Sn(Acac)_2$) and zinc-bis(2,2-dimethyl-3,5-heptanedionato-O,O') ($Zn(DMH)_2$), together with tin(II)-2-ethylhexanoate ($Sn(Oct)_2$), were used to study the effect of the catalyst in the L-lactide polymerization on the nascent polymer structure. Using $Zn(DMH)_2$ an ultra high crystalline polymer was obtained with a ΔH_m of 100 $J.g^{-1}$. Independent of the catalyst and the crystallinity the structure of the crystalline polymer was a pure α-structure as revealed by WAXS-measurements. SAXS-measurements showed a long period for both the $Sn(Oct)_2$ and the $Zn(DMH)_2$ polymer of about 33 nm., the latter revealing a more complex highly regular structure with up to fourth-order reflections. SEM micrographs showed a fibrillar like structure for the $Zn(DMH)_2$ polymer.

Introduction

The physical and mechanical properties and the texture of as-polymerized (nascent) polylactones have not extensively been described. Investigations concerning for instance organic-metal lactone polymerization catalysts and lactone polymerization conditions have been mainly restricted to the activity of the catalyst and the monomer sequence in the lactone copolymer products (1,2).

The properties of the as-polymerized poly(L-lactide), such as its high mechanical strength and its rate of hydrolytic degradation, have been shown to be more advantageous in its use as biodegradable osteosynthetic devices comparred to compression moulded poly(L-lactide) devices (3,4).

Because chain scission, due to hydrolysis, first takes place in the amorphous regions, the crystallinity of a poly(L-lactide) implant will increase in time (4). The structure of the nascent material after prolonged degradation will consist of extended lamellar folded chain crystals with little or no coherence (5). At this point fragments of the implant may elicit a mild vascular foreign body response (6).

It is apparent that not only the physical and mechanical properties but also the biomedical behavior is largely determined by the structure and crystallinity of the as-polymerized polymer structure.

In this communication we will present some results of the polymerization of L-lactide with two new lactone polymerization catalysts, namely tin(II)-bis(2,4-pentanedionato-O,O'), in short $Sn(Acac)_2$, and zinc-bis(2,2-dimethyl-3,5-heptanedionato-O,O'), in short $Zn(DMH)_2$, in comparison with tin(II)-2-ethylhexanoate, in short $Sn(Oct)_2$.

We will discus the effect of the catalyst on the structure of the obtained nascent polymers.

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Experimental

L-lactide (C.C.A., Gorinchem, The Netherlands) was recrystallized from toluene (Merck, distilled from sodium) under a nitrogen atmosphere.

2,2-Dimethyl-3,5-heptanedione (HDMH) was prepared according to the procedure of Kopecky et al. (7), using ethylpropionate and 3,3-dimethylbutanone as starting materials (yield 60%, bp. 114-116 °C, 50 mm Hg).

Zinc-bis(2,2-dimethyl-3,5-heptanedionato-O,O'), in short $Zn(DMH)_2$ was synthesized by the method of Finn et al. (8), using toluene, zincoxide and HDMH. The product was recrystallized from pentane (yield 70%).

Tin(II)-bis(2,4-pentanedionato-O,O'), in short $Sn(Acac)_2$, was prepared according to the method of Wakeshima et al. (9), using p-xylene as a solvent (yield 80%, bp. 85-92 °C, 0.05 mbar.).

Tin(II)-2-ethylhexanoate (Sigma Chem. Comp., St. Louis, USA), in short $Sn(Oct)_2$, was used as received.

Polymerizations were carried out in vacuum (10^{-3} mbar.) sealed, silanized glass ampoules at 110 °C for 100 hours.

DSC measurements were performed by means of a calibrated Perkin Elmer DSC-7 operated at a scanspeed of 10 °C $min.^{-1}$ using samples of approximately 10-15 mg.

An ISI-DS 130 scanning microscope operated at 10 KV was used to study the fracture surfaces of PLLA samples.

Dynamic mechanical thermal analysis, using a Rheometrics RSA II, was performed at 1 Hz and at a heating rate of 1 °C $min.^{-1}$ over a temperature range of -150 to +200 °C in the dual cantilever mode at 0.05 % strain. Samples (50x6x1 mm.) were machined out of as-polymerized PLLA .

Small angle X-ray scattering (SAXS) was carried out using a Kratky camera with an entrance slit of 40 μm. equipped with a proportional counter and an electronic scanner. Ni-filtered CuK_α-radiation was used.

Wide angle X-ray scattering (WAXS) was carried out with CuK_α-radiation using a Statton camera with pinhole collimation.

An Ubbelohde viscometer (type Oa) was used for the determination of the intrinsic viscosity of the polymer in chloroform at 25 °C. The viscosity average molecularweight was estimated using the formula:

$$[\eta] = 5.45.10^{-4} M_v^{0.73}$$

Results and discussion

Compounds containing metal-oxygen bonds are among the most active lactone polymerization catalysts (10). A potential class of catalysts are metal-1,3-diketonates (see fig. 1) in which the oxygen atom of both carbonyl groups in the 1,3-keto-enol ligand are generally coordinated to the metal.

In table 1 and 2 a comparison is made between the polymerization conditions and products of $Sn(Oct)_2$, the preferred lactone polymerization catalyst in recent literature, and the two new catalysts. The monomer conversion of all samples was over 99%, as measured by 300 MHz ^1H NMR. Although the molecular weight, obtained by using $Zn(DMH)_2$, appears to be a little lower there is no linear relationship between the M_v and the monomer to catalyst ratio, suggesting the two compounds function purely as catalysts and not as initiators, as already has been shown for $Sn(Oct)_2$ (11).

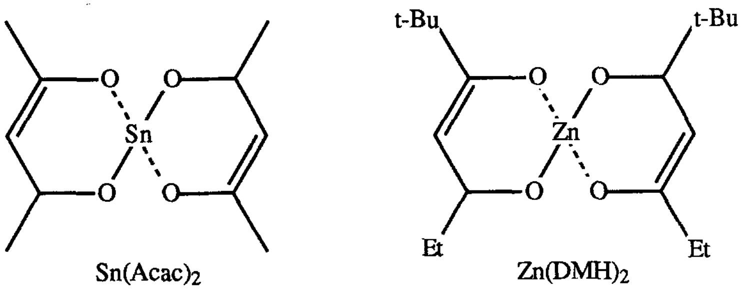


Figure 1: Two metal-1,3-diketonates, tin(II)-bis(2,4-pentanedionato-O,O') ($Sn(Acac)_2$) and zinc-bis(2,2-dimethyl-3,5-heptanedionato-O,O') ($Zn(DMH)_2$) suitable as lactone polymerization catalysts.

Table 1: Polymerization conditions and products of the different catalysts.The polymerization temperature was 110 °C.

sample	catalyst	mon./cat. ratio	polym. time (hours)	mol. weight (M_v*10^{-5})
1	$Sn(Oct)_2$	15,000	100	9
2	$Sn(Acac)_2$	11,000	120	10
2-a	$Sn(Acac)_2$	2,000	100	9
3	$Zn(DMH)_2$	13,500	120	7
3-a	$Zn(DMH)_2$	9,000	140	7
3-b	$Zn(DMH)_2$	1,000	190	8

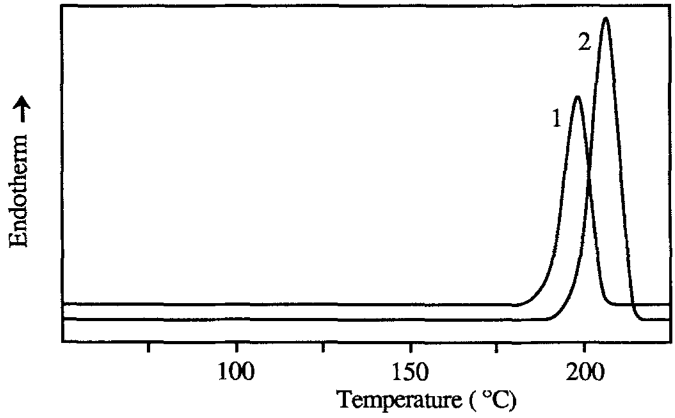


Figure 2: DSC thermograms of PLLA obtained with $Sn(Oct)_2$ (1) and $Zn(DMH)_2$ (2).

Table 2 : Thermal properties of PLLA samples obtained by using different catalysts.

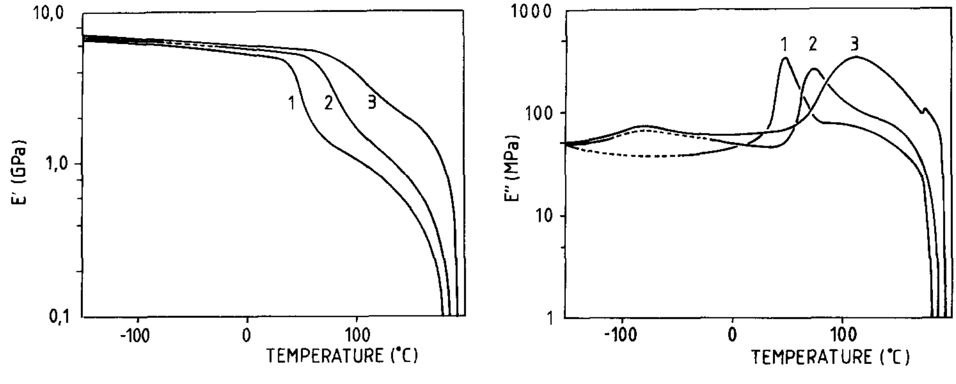
sample	catalyst	T_g (DMTA) (°C)	T_m (DSC) (°C)	ΔH_m ($J.g^{-1}$)
1	$Sn(Oct)_2$	54	194	72
2	$Sn(Acac)_2$	83	200	90
3	$Zn(DMH)_2$	121	207	100

DSC measurements reveal an increase in crystallinity and T_m at constant peak width, as is shown in table 2 and figure 2, for the poly(L-lactide) samples synthesized by different catalysts.

The most amazing fact is the high heat of fusion of the $Sn(Acac)_2$ and the $Zn(DMH)_2$ polymers. When taking 81 $J.g^{-1}$ as the ΔH_m for 100% crystalline material, as determined by extrapolating the ΔH_m to infinite crystal thickness for solution grown single crystals (12), the crystallinity of our polymer would be over the unrealistic value of 100%.

In figures 3 and 4 the dynamic mechanical spectra (the dynamic modulus, E', and the loss modulus, E") of the polymers 1, 2 and 3 are shown.

With regard to the main α-relaxation in the E" spectrum, which is related to the T_g, the least crystalline polymer, 1, exhibits a relatively narrow peak which becomes extremely broad (≈125 °C) for the most crystalline polymer, 3. At the same time the position of the peak moves up to a higher temperature. Although this behavior is typical for semicrystalline polymers the extent of temperature shift and peak broadening in this case is unique. In the E" curve of sample 3 a low temperature β-relaxation at -79 °C can also be seen, which is probably related to the polymer methyl group. The steepness and intensity of the E' drop above T_g shows a great reduction with increasing crystallinity. At 170 °C this reduction is about one decade. WAXS measurements of samples 1 and 3 show, besides intensity differences and narrowing of the reflections, identical patterns, indicating a pure α-structure for both samples (15). SAXS measurements of these samples (fig. 5) show that both polymers have a long period of 33 nm. In the high crystalline



Figures 3 and 4 : The dynamic modulus, E', and the loss modulus, E", vs.the temperature. PLLA samples in which $Sn(Oct)_2$ (curve 1), $Sn(Acac)_2$ (curve 2) and $Zn(DMH)_2$ (curve 3) were used as catalysts.

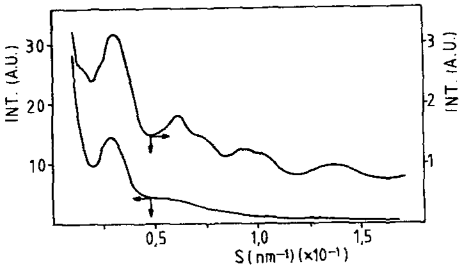


Figure 5 : SAXS intensity curves of high crystalline PLLA obtained with Zn(DMH)$_2$ (upper curve) and normal PLLA obtained with Sn(Oct) (lower curve).

sample up to a fourth-order reflections can be seen. A high number of SAXS reflections is well known for polymer single crystal mats but are an exceptional feature in the case of nascent material (16). The high number of reflections in combination with their low intensity suggests a highly crystalline highly regular structure. The shoulders at the SAXS reflections of sample 3 might indicate a polymer substructure as for instance is known from nascent polypropylene (13).

As can be seen in figure 7 scanning electron micrographs show a fibrillar structure at the fracture surface of the Zn(DMH)$_2$ polymer in contrast to the relative smooth surface of the Sn(Oct)$_2$ polymer in figure 6. The size of the fibrils is about 60 nm. which could be related to a very weak reflection in the SAXS curve.

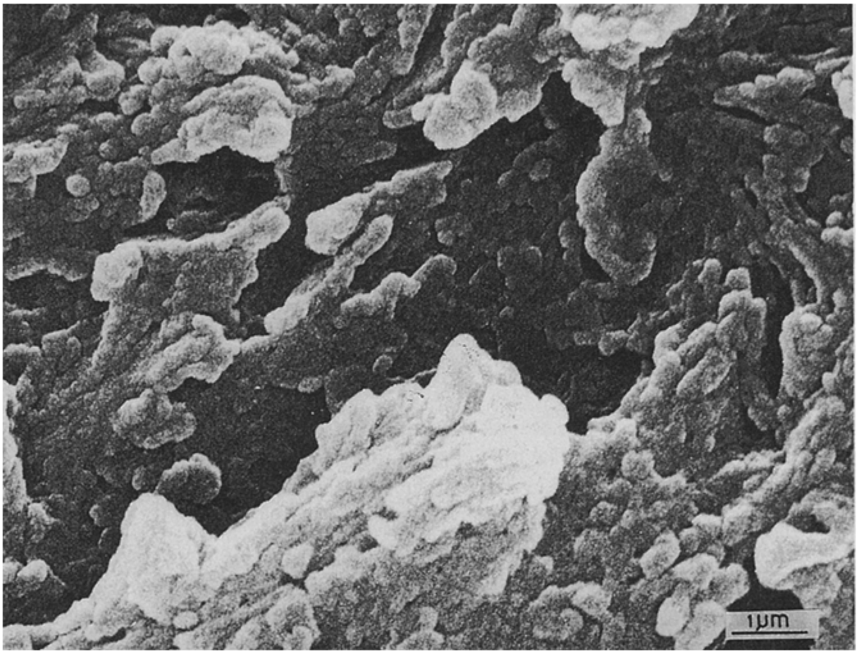


Figure 6 : SEM micrograph of the fracture surface of PLLA obtained with Sn(Oct)$_2$.

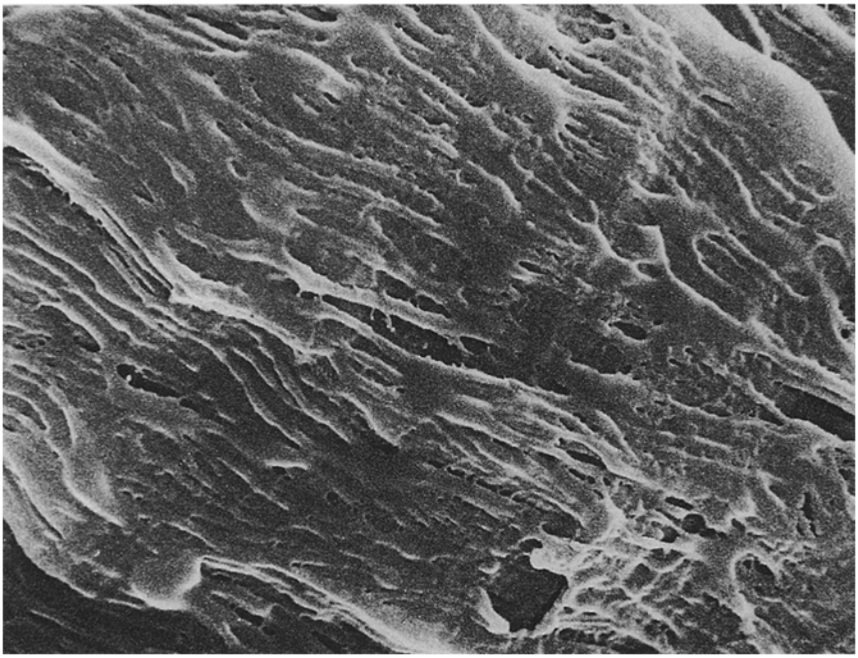


Figure 7 : SEM micrograph of the fracture surface of high crystalline PLLA obtained with $Zn(DMH)_2$.

The rate of polymerization using $Zn(DMH)_2$ as a catalyst is lower as compared to $Sn(Oct)_2$ (14). This lower rate of polymerization will probably be closer to the rate of crystallization in this system.

In this way the growing chain end is close to the crystal surface. As a result of this fact the different dangling growing chain ends will not be able to entangle, thus producing a highly crystalline material with a high concentration of tie molecules and a low concentration of entanglements.

Conclusions

The structure of as-polymerized high molecular poly(L-lactide) can be strongly influenced by the catalyst of choice.

Using $Zn(DMH)_2$ a high molecular weight nascent polymer with an extremely high value for the ΔH_m of 100 $J.g^{-1}$ is obtained. The high crystallinity caused a shift in T_g and T_m of respectively 70 °C and 13 °C, compared to nascent PLLA obtained by using $Sn(Oct)_2$ as a catalyst.

SAXS and SEM results suggest a complex structure of the ultra high crystalline material with a possible formation of fibrillar crystals.

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