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Continuous Reactive Extrusion Polymerisation of L-Lactide - An Engineering View[‡]

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SUMMARY: Polylactides (PLA), biodegradable aliphatic polyesters, produced from renewable resources might substitute petrochemically based polymers in a broad range of applications in the near future, if we manage to produce them at lower cost and higher efficiency than nowadays. Possible applications include food packaging for meat and soft drinks, films for agro-industry and non-wovens in hygienic products. The authors developed, based on a new catalytic system, a reactive extrusion polymerisation process, which can be used to produce PLA continuously in larger quantities and at lower costs than before. This extrusion polymerisation process has been developed and tested with laboratory scale machines and has to be transferred to industrial processing equipment. This paper aims to address the problems attached with this transfer and to discuss the chances to finally achieve low cost PLA at industrial scale.

Introduction

Worldwide the problems associated with the production of large amounts of waste are one of the most important challenges to face in the following century. The average american family, for example, produces more than 3,000 kg of waste per year. In the case of plastic waste, we have to face the fact that in the US alone 35 million tons of consumer polymers have been produced in 1998. The corresponding figures for Europe and Asia are 34 million tons and 25 million tons, respectively. All this polymer has to be disposed some day. In the case of plastic waste, the preferred solution up to now is recycling, though often conducted as downcycling or incineration. Nevertheless degradable materials can offer a substantial possibility to reduce these waste disposal problems.

Polylactide (PLA), a hydrolyzable aliphatic polyester known and used for a long time for medical applications[1-4)] is one of the polymers widely accepted to play a major role as future packaging material[5,6)]. This is mainly due to the good mechanical properties of PLA, which are comparable to today's standard packaging polymer polystyrene, but also due to the fact that PLA is produced from lactic acid, which in turn can be prepared by fermentation from nearly any renewable resource such as starch, molasses, whey and sugar. After use PLA polymers can be recycled, incinerated or landfilled,

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[‡] this publication is dedicated to Prof. Fritz' 60th birthday

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though it is mainly intended for disposal by composting and in-soil degradation. Thus PLA provides a closed natural cycle, being produced from plants and crops, polymerised and processed into a packaging product and degraded after use into soil and humus, which is the basic necessity for growth of new plants and crops.

Indeed the potential market for biodegradable life respecting polymers has been estimated to be around 200,000 tons in 2005, thereof 100,000 tons are supposed to be PLA7). These large production volumes require economically viable manufacturing processes. Thus a continuous polymerisation appears to be essential to the large scale commercial production of polylactides.

Polylactide can be synthesized by two different pathways: either the step polycondensation of lactic acid, or the ring opening polymerisation (ROP) of the cyclic diester lactide. In contrast to the more traditional polycondensation, that usually requires high temperatures, long reaction times and a continuous removal of water, to finally recover quite low molecular weight polymers with poor mechanical properties, lactide ROP provides a direct and easy access to the corresponding high molecular weight polylactide. The ring opening polymerisation of lactide is known to be promoted by Lewis acid type catalysts such as metals, metal halogenides, oxides, aryls and carboxylates. The main representative of this group of catalysts is tin(II)bis(2-ethylhexanoate). The ring opening polymerisation is initiated by protic compounds such as water, alcohols, thiols and amines, which are either present as impurities in the lactide dimer or can be added on purpose.

As aforementioned, the current objectives are to make the manufacturing of PLA economically viable. In this respect, the authors have developed a continuous one-stage process using reactive extrusion technology8).However this technique requires that the bulk polymerisation is close to completeness within a very short time (5 to 7 minutes), which is predetermined by the residence time of the extrusion system, and that the polylactide stability is high enough at the processing temperature. Even though $Sn(Oct)_2$ can promote quite fast LA polymerisation, it is also known to have adverse effects on the PLA molecular weight and properties, as a result of back-biting and intermolecular transesterification reactions, not only during the LA polymerisation, but also during any further melt processing9,10). The authors therefore showed that the addition of an equimolar amount of a Lewis base, particularly triphenylphosphine onto 2-ethylhexanoic acid tin(II) salt ($Sn(Oct)_2$) in presence of an alcohol ROH, significantly enhances the lactide polymerisation rate in bulk11). This kinetic effect has been accounted for by coordination of the Lewis base onto the metal atom of the initiator, making the insertion of the monomer into the metal alkoxide bond of the initiator easier.12) The Sn-OR bond is formed in situ by reaction of the alcohol (ROH) and the tin(II)dicarboxylate13). Thus the ROP proceeds via the same coordination-insertion mechanism involving the selective O-acyl cleavage of the cyclic ester monomer, as already known from alkoxide initiators14,15).The addition of one equivalent of triphenylphosphine onto $Sn(Oct)_2$ allows for reaching an acceptable balance between propagation and depolymerisation rates, so that the polymerisation is fast enough to be performed through a continuous single-stage process in an extruder. Results obtained by the reactive extrusion polymerisation using laboratory scale closely intermeshing corotating extruders have been achieved16) and the influence of various processing parameters on the resulting polymeric properties has been determined. However the technology will have to be transferred to industrial scale processing equipment to produce PLA economically.

Materials and Methods

Materials. (L-L)-Lactide (L-LA) was purchased from Boehringer Ingelheim and used as received, having a water content < 200ppm and a remaining free acidity < 1 mequ/kg.
2-ethylhexanoic acid tin(II) salt $Sn(Oct)_2$ was purchased from Th. Goldschmidt and used without purification. Triphenylphosphine $P(\phi)_3$ was purchased from Janssen and dried by three azeotropic distillations of toluene. A 0.15 molar solution of the equimolar $Sn(Oct)_2 \bullet P(\phi)_3$ has been prepared by dilution in freshly dried toluene. Toluene was dried by refluxing over CaH_2. Ultranox 626 was provided by GE Specialty Chem. and used without further purification.
Polymerization. For reactive extrusion polymerisation the lactide is used as received without further purification. A mixture prepared of L-Lactide, stabiliser and catalytic system is transferred into a constantly nitrogen purged gravimetric feeding unit, which constantly provides the test specific throughput to the twin screw extruder used as polymerisation device. The lactide is fed into a closely intermeshing corotating twin-screw extruder of BERSTORFF (ZE 25), having a screw diameter of 25 mm and a L/D-ratio of 48. The machine is divided into 12 sections which can be temperature controlled by means of electric heating devices and water cooling. The polymerisation occurs during the extrusion process at a temperature of about 185°C. Finally at the tip of the screw the machine is equipped with a static mixer, kindly provided by SULZER, to homogenise the material and especially to improve distribution of the stabilising system in the PLA polymer. The polymer is extruded through a strand die, cooled under a constant air flow on a take-off unit and pelletised.
Analysis. L-LA conversion was calculated from FTIR spectrum of cast film on NaCl. A calibration plot of PL-LA to L-LA molar ratio versus A_{1383} to A_{935} ratio was established, where A_{1383} and A_{935} are the absorptions of bands at 1383 and 935 cm^{-1}, respectively. The absorption band at 1383 cm^{-1} corresponds to a vibration mode shared by the polymer and the monomer while the absorption band at 935 cm^{-1} is characteristic of the monomer. Practically, monomer conversion (c) was calculated on the following equation: $c = 100/([L\text{-}LA]/[PL\text{-}LA]+1)$ where

$$[PL\text{-}LA]/[L\text{-}LA] = -12.27 + 31.56\,(A_{1383}/A_{935}) - 26.76\,(A_{1383}/A_{935})^2 + 10.43\,(A_{1383}/A_{935})^3 - 1.81\,(A_{1383}/A_{935})^4 + 0.12\,(A_{1383}/A_{935})^5.$$

Occasionally conversion was also calculated by ^1H NMR from the relative intensity of the methine group of the monomer and the polymer ($\delta CH_{PL\text{-}LA} = 5.16$ ppm, $\delta CH_{L\text{-}LA} = 5.02$ ppm). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ with a Brucker AM400 apparatus at 25°C. Solution concentration was 5wt/v %.
Size exclusion chromatography (SEC) was carried out in $CHCl_3$ at 35°C using a WATERS 610 liquid chromatograph equipped with a WATERS 410 refractometer index detector and two STYRAGEL columns (HR1, HR5E). Molecular weight and molecular weight distribution of polylactides were calculated in reference to a polystyrene calibration and corrected to an absolute basis using an universal calibration curve ($K_{PS} = 1.67 \cdot 10^{-4}$, $a_{PS} = 0.692$, $K_{PLA} = 1.05 \cdot 10^{-3}$, $a_{PLA} = 0.563$ in the $[\eta] = K \cdot M^a$ Mark-Houwing relationship).

Laboratory scale production

In this frame a closely intermeshing twin screw extruder, type ZE 25 of Berstorff company has been used as polymerisation equipment. This twin screw extruder is characterised by a screw diameter of 25 mm and an L/D ratio of 48. Because of the large L/D ratio and therefore the long possible residence times, this type of extruder is especially suited for reactive extrusion processes[17-21)]. The self cleaning screw profile ensures a proper transport of the polymer inside the extruder and prevents the accumulation of degradation by-products along the screw. Of great importance for the course of the polymerisation reaction are the processing parameters residence time, residence time distribution, temperature development and degree of mixing. Especially the degree of mixing has a huge influence on a diffusion controlled polymerisation reaction such as the ROP of lactide. The degree of mixing can be widely influenced by the design of the screw. Due to the extremely low viscosity of the dimeric basic material lactide, there will be no dissipative energy introduction at the initial part of the extrusion process. Thus, the lactide has to be melted and heated to reaction temperature solely by heat transfer from the extruder barrel. Because of the existing boundary conditions a processing concept has been developed according to Fig 1. The powdery crystalline lactide is mixed with the catalytic system $Sn(Oct)_2{\bullet}P(\phi)_3$ dissolved in toluene and the toluene is extracted using vaccum.The powdery Ultranox 626 stabilizer is then added to the such prepared lactide and the mixture is homogenized in a tumble mixer. This premix is added into the entrance section of the extruder using a gravimetric loss weight feeder system. The lactide is melted, heated to reaction temperature, polymerised to polylactide and the final polymer is extruded through a static mixer at the die section of the extruder. The static mixer will ensure the proper dispersion of the stabilizer inside the formed polymer. The screw configuration used during the extrusion experiments is shown in Fig.2.

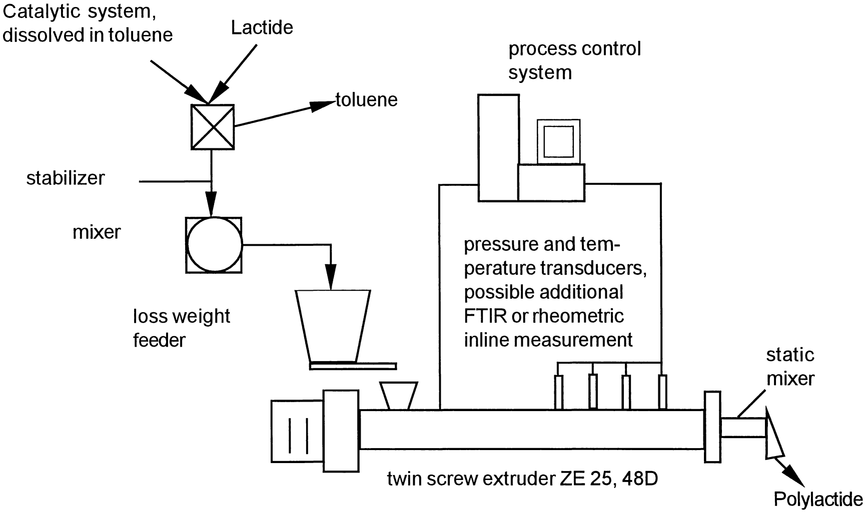

Fig 1: Processing concept for the ring opening polymerisation of PLLA

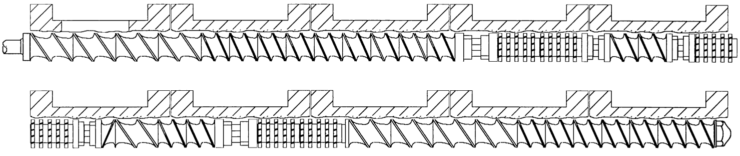

Fig.2: Screw configuration for the ring opening polymerisation of PLLA

The mechanisms apparent during reactive extrusion processes can be subdivided into three major groups. These mechanisms are the flow-, the heat transport and the reaction mechanism. They all are closely related to each other, influence each other and predetermine the processing behaviour of the extruder system and thus the quality of the final product.

The mechanism of flow influences the degree of mixing, the residence time and thus the course of the polymerisation reaction. In addition it influences the heat transport phenomena by dissipation and convection. On the other hand the mechanisms of reaction and heat transport influence the flow, as the thermal and chemical conditions determine the flow behaviour of the melt. Finally reaction and heat transport phenomena will influence each other, as the reaction rate is a function of temperature, on the other hand the reaction enthalpy produced will alter the thermal condition of the melt. In principal these facts can be described by the four fundamental equations of

- continuity $$\frac{\partial \rho}{\partial t} + \vec{v} \cdot \mathrm{grad}\rho + \rho \cdot \mathrm{div}\vec{v} = 0 \quad ,$$

  where ρ is the density of the polymer
  v is the velocity vector
  t is the time

- impulse $$\rho \frac{D\vec{v}}{Dt} = \rho \cdot \vec{g} + \nabla \underline{\underline{\sigma}} \quad ,$$

  where g is the vector of the gravitational forces

  σ is the force tensor

- energy $$P_{Eng} - (\dot{H}_{Ex} - \dot{H}_{In}) + \dot{Q}_H - \dot{Q}_C - \dot{Q}_{Loss} - \dot{H}_R = 0$$

  where P_{Eng} is the power of the extruder engine

  H_{Ex} is the enthalpy flow of the material exiting the extruder

  H_{In} is the enthalpy flow of the material entering the extruder

  Q_H is the heat flow provided by heating through the barrel

  Q_C is the heat flow provided by cooling through the barrel

  Q_{Loss} is the heat flow lost to the surroundings

  H_R is the enthalpy of the polymerisation reaction and

- reaction kinetics $u = f(T,p,t)$,

  where u is the conversion

  T is the temperature

  p is the pressure.

The first three equations describe the general behaviour of any polymer melt inside the extrusion system. In principal these equations can be modified and simplified by boundary conditions or rheological laws for the flow behaviour of these polymer melts, so that the state of the system can be determined mathematically. In the case of reactive extrusion the fourth equation describes the development of the reaction as a function of temperature, pressure and time. Here it is impossible to combine all four equations to describe the state of the process numerically in a simple way. First, in this special case of polymer synthesis it is impossible to simplify especially the flow behaviour of the melt by a single equation, second the exact course of the used ring opening polymerisation reaction is still not described in every detail. Indeed the kinetic reaction behaviour will be different in the extruder to any kinetics developed under model or laboratory conditions. Therefore one is limited to qualitative suggestions for the screw design. Besides traditional requests like constant material feeding and sufficient pressure build up to overcome the die resistance, the following demands have to be considered:

- Considerably fast melting of the monomer and fast heating to reaction temperature.
- Avoidance of leakage of the low molecular weight monomer through the gaps between the modular barrels.
- High degree of mixing and sufficient residence time within the reaction zone.
- Melt temperature in the area of highest reactivity has to be controlled.
- Avoidance of peak temperatures in the reaction zone, to prevent side or degradation reactions.
- Homogeneous introduction of the stabiliser into the resulting polymer.
- Constant material transport within the extrusion system in spite of increasing viscosity.
- Avoidance of transport and reaction pulsation, combined with varying product quality.

The general request for constant material feeding is realised by extrem cooling of the feeding barrel by means of cold water (T_W ~ 10°C), to ensure transport of solid material in the entrance section. The contradictory request on fast melting of the monomer and temperature increase to reaction temperature can only be realised by setting all barrel temperatures to reaction temperature starting with the second barrel. Because of the low viscosity of the monomer, no temperature increase due to dissipative effects can be expected, and thus the complete heat to melt and heat the monomer to reaction temperature has to be provided through the barrel by heat conduction. Only after the start of the polymerisation reaction the dissipated energy of the now higher viscous material and the produced reaction enthalpy (~ 29 J/g) will enhance the thermal development of the reactive material, so that even heat has to be removed out from the melt over the barrel, to avoid peak temperatures in the reaction zone and to prevent inter- and intramolecular transesterification reactions. Because of these two main reasons, the heating and cooling performance of the extrusion equipment has to be extremely high. Leakage of the extremely low viscous monomer through the gaps of the modular barrel system can be avoided by adding PTFE films in between the barrel section.

The request to homogeneously incorporate and disperse the stabiliser into the final polymer is realized by adding a static mixer in front of the die. Unfortunately it was not possible to distribute the stabilizer inside the polymer within the screw length, as it dissolves readily and stays preferably in the monomer phase before moving into the polymer only after a certain monomer conversion is reached. Among the most important requests high mixing efficiency and sufficiently long residence time inside the reaction zone, to achieve high monomer conversion are key parameters. As ROP of lactide is solely diffusion controlled above conversion levels of ~80%, the mixing is even more important at the end of the reaction.This intensive mixing is ensured by adding three similar combinations of screw elements within the reactive zone. Each of these combinations consists of a broad conveying kneading element, which introduces shear energy into the reactive mixture, followed by toothed elements, which ensure an intensive distributive mixing by cutting and rejoining the material flow. Each of these combinations of kneading and shearing elements are finished off with counter conveying elements to increase the degree of fill within these screw sections. The more advanced the reaction is, the more intensive the mixing has to be, and this is done by stronger counter conveying elements downstream in the extruder. The initial counter conveying kneading block has been supplemented by an additional counter conveying screw element in the second combination and exchanged by a blister disk in the last combination. Finally to ensure constant transport characteristics and to prevent pulsation in transportation and reaction it is necessary to bring process parameter modifications only slowly to avoid instable process conditions.

Tab. 1 shows two typical Poly-L-Lactides. One of them (Tab. 1, entry 2) is produced following this new developed reactive extrusion polymerisation method, using a barrel temperature of 180°C. The second (Tab. 1, entry 1) is polymerised using the more conventional batch polymerisation technique. Both polymerisations have been promoted by the new developed catalytic system $Sn(Oct)_2 \bullet P(\phi)_3$. Although the same starting polymerisation conditions have been used, direct comparison between two polymers, produced using such different technologies is very difficult. Furthermore the cleanness and drynesswithin an extruder never reaches the one of a chemical batch reactor, which lead to a reduction in number average molecular weight available. At nearly similar monomer conversion (~99%), the time needed for reaching this conversion is 40 minutes within the batch process, while the time required using the reactive extrusion process is nearly reduced by a factor of five. The residence time of the material inside the extruder has been deducted using the free volume of the extruder used and the throughput rate. This sharp reduction in polymerisation time can be related to the consequent and efficient mixing inside the extrusion equipment.

Tab.1: Comparison between Poly(L-Lactides) as produced in traditional batch processing and in reactive extrusion polymerisation in corotating closely intermeshing twin screw extruders, both using an equimolar $Sn(Oct)_2 \bullet P(\phi)_3$ complex with a $[L\text{-}LA]_0/[Sn]$ ratio of 5000, at 180°C polymerisation temperature.

entry	process	conversion [%]	time[min] for conversion	$M_n \bullet 10^{-3}$	M_w/M_n
1	batch	98.5	40	246.0	1.9
2	reactive extrusion	99.0	~7	91.1	1.8

Influence of process parameters on the resulting polymer

Detailed information about the influence of different process parameters on the molecular properties of the resulting polymers has been published elswhere(16). One of the process parameters with the most important influence is the throughput rate. Using the above stated process and screw concept, L-Lactide has been continuously polymerised. The throughput rate has been increased from 0.75 kg/h to 1 kg/h and further to 1.25 kg/h (Fig 3).

The monomer conversion drops from 99% at 0.75 kg/h to 94% at the highest throughput rate of 1.25 kg/h. The number average molecular weight increases by 4000 g/mol and the molecular weight distribution is slightly lower, while increasing the throughput rate from 0.75 kg/h to 1 kg/h. A further increase to 1.25 kg/h results in drastic reduction of number average molecular weight and a broadening of the molecular weight distribution.

A significant element changing with the throughput rate is the mean residence time inside the extruder. The extruder residence time can be directly compared with the reaction time in a batch process. Using bulk batch polymerisation the monomer conversion will increase fast with increasing reaction time, slow down and continue to rise to asymptotical approach the 100% conversion. The molecular weight of the resulting polymer will similar increase fast with increasing reaction time, will reach a maximum at a certain level of conversion and will decrease again with longer reaction times as side and degradation reactions become more significant. Finally a specific level of molecular weight will be reached, as the conversion approaches 100% and a Polymerisation depolymerisation equilibrium is reached.

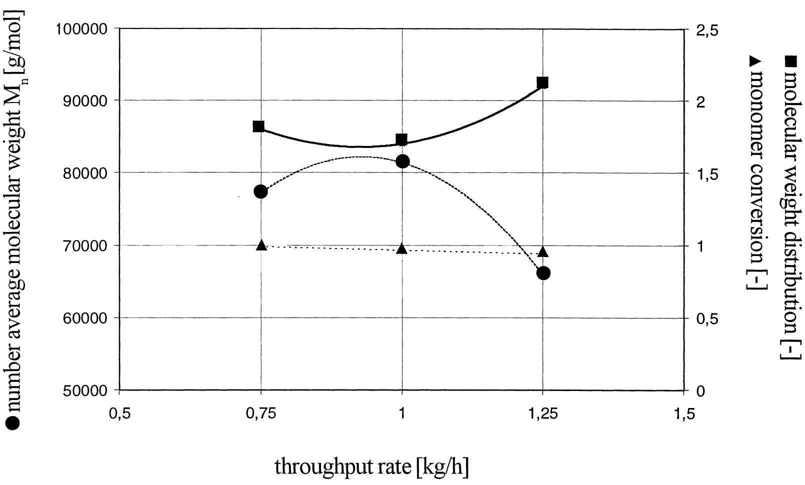

Fig.3: Influence of the throughput rate on the molecular parameters of the resulting polymer

At a throughput rate of 0.75 kg/h the chemical equilibrium of the polyreaction has been reached at the end of the extruder, the maximum of the molecular weight has been exceeded and first degrading transesterification reactions take place, which lead to a broadening of the molecular weight distribution. At a higher throughput rate of 1 kg/h the extruder residence time is shorter and the state reached at the end of the extruder is similar to the situation at the maximum of the molecular weight development. Here the chemical equilibrium has also been reached, though an additional increase in monomer conversion will result in molecular weight degradation. Further increase in throughput rate to 1.25 kg/h reduces the remaining residence time further, so that the polyreaction inside the extruder is not finished, the monomer conversion is dramatically reduced and the molecular weight is still in the phase of building up.

Transfer to production units and associated problems.

As aforementioned the process has been developed on a laboratory type extruder with an average throughput rate of 1 kg/h. If we think of 300 working days per year and an average of 8 hours production per day this would result in 2.4 tons of polymer per year. Even an extrapolation to 24 hour production a day would results in only 7.2 tons per year. To produce the anticipated 100.000 tons per year of PLLA polymer, large production facilities would be necessary and the process will have to be transferred to production machinery. The main difference between industrial production and laboratory scale extruders is the higher channel depth and the therefore larger free volume within the production extruder. In addition to that, the free volume per extruder length unit will increase with increasing screw diameter. This influence can be seen in Fig 4.

Using the reported ROP of lactide the reactive extrusion process can be separated into three extruder sections, requiring different scale up considerations. These sections are respectively the melting zone(to melt the monomer and to heat it to reaction temperature) the section to start the reaction and finally the polymerisation section. There is no need for a special part for degassing and pressure build up, as they are already included within the polymerisation section.

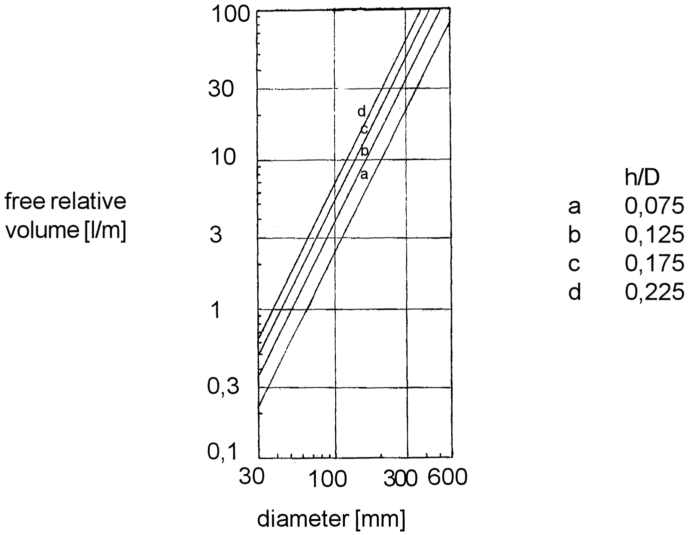

Fig 4: Influence of the screw diameter on the free volume using various channel depths h.

To make a scale up calculation from laboratory extruders to production extruders, different approaches are used in literature[22-24)], depending on the type of extruder used and depending on the limitations of the process. For this example of reactive extrusion, where low viscosity monomers are transformed into high molecular weight polymers, no up scaling rules are existing so far. In principle the two limitation can be seen by the fact that the heat transfering surface area of the extruder increases by approximately the square of the diameter (depending on the type of extruder used) and that the free volume of the extruder or the capacity increases by the cube of the diameter. The reality will be somewhere in between these upper and lower boundaries. To illustrate this difference in up scaling possibilities, Fig. 5 shows the relative throughput rate as a function of the diameter applying different scale up suggestions. The example has a reference diameter of 50mm (throughput = 1). The large differences in reachable throughput rates becomes apparent, depending on the approach used. These differences can be important for the economic efficiency of the process and thus for the success of a specific extrusion problem.
Within the melting section of the extruder all comes back to the aforementioned equation of energy. If we propose that losses are neglectable, that no reaction occurs within this section and that due to the low viscosity of the monomer only a neglectable part of energy is introduced by disspative effects, the

necessary heat to melt and heat the monomer to the polymerisation temperature will have to be introduced solely by the heating energy of the barrel. This implies a approximately square scale up calculation with respect to the screw diameter which could prevent economic production. Thus it might be necessary to introduce the monomer in its molten liquid state and at the determined reaction temperature directly into the extruder, either prepared in batch systems or within an additional single screw extruder. The very short section of reaction initiation can be triggered using a blister element, which should be able to introduce the energy necessary to start up the reaction. The remaining segments of the screw length can therefore be used for the actual polymerisation reaction. If one starts from a proposed isothermal temperature field throughout the polymerisation reaction and neglects losses, one has to take away the heat produced from dissipative effects and the polymerisation reaction heat through the barrels. It has to be noted that the reactive heat generated within a certain screw length increases with the third power of the diameter and that the dissipative heat generated is additionally dependent on the screw speed, while the heat transferring surface increases only by the square of the diameter. In spite of the low reaction heat of this ROP of lactide, the heat deduction can be the critical element using large production extruders. It can affect the homogeneity of the product and enhance degradation reactions inside the extruder. Using special construction features it can be possible to enhance the heat transfer of the barrel, so that no temperature increase occurs in the melt. As an example the usage of stainless steel barrels should be avoided due to heat conductivity reasons. To suppress side or degradation reactions a higher amount of stabiliser might be necessary as well as a reduction of the amount of tin-based catalyst, which reduces the polymerisation rate but also prevents transesterification reactions from taking place.

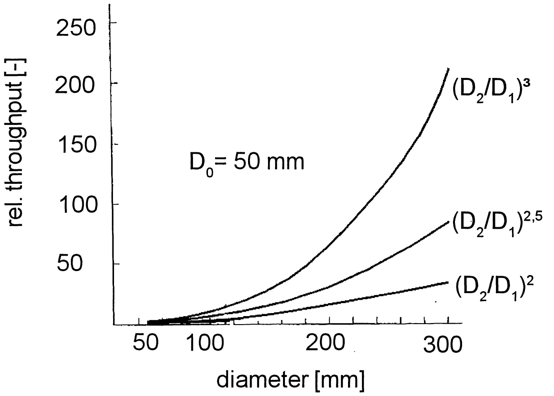

Fig 5: Calculated throughput as a function of screw diameter D using various upscaling factors Reference diameter D_0=50mm (throughput=1).

If too high peak temperatures occur, one might think of the introduction of additional cold monomer directly into the zone of highest reactivity using a side stream feeder or to coextrude an inert, non reactive filler, which evaporates at a certain temperature. In this case an additional degassing zone has to be installed. Finally the screw speed has to be adopted relative to the extruder size to ensure that the residence time is sufficient for the polymerisation to be concluded. Fig. 6 shows a proposed large scale production scheme including the discussed features.

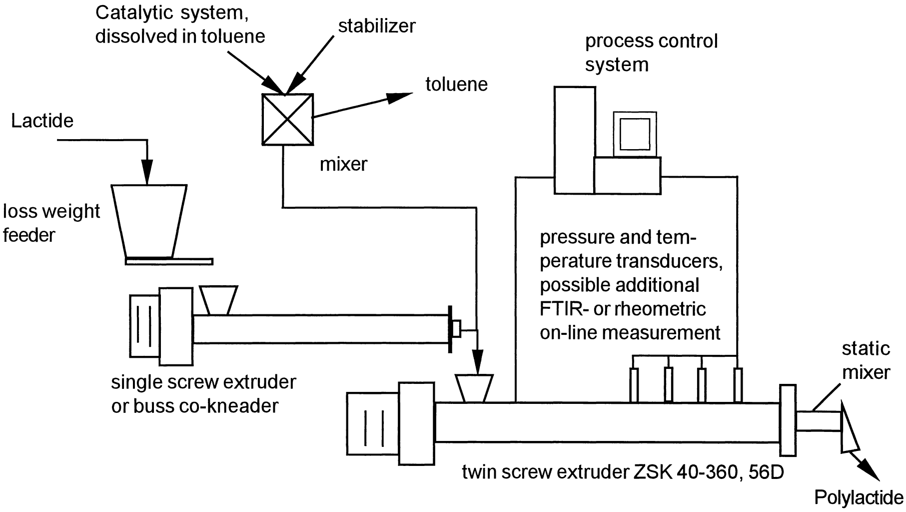

Fig 6: Production scheme for large scale production of Poly-L-lactide

Conclusion

In conclusion a new process has been developed for the production of poly-L-lactide using reactive extrusion polymerisation based on a new tin-based catalytic system. The influence of different process parameters on the properties of the resulting polymers has been examined soas one can foresee in a quite short term a large scale industrial continuous single step production of poly-L-lactide using reactive extrusion on corotating closely intermeshing twin screw extruders. The process boundary conditions and related up- scaling problems have been determined and suggestions to solve these problems have been given. Finally a production scheme has been presented to economically produce semi-crystalline poly-L-lactide, which is thermally stable, displays a number average molecular weigth of approximately 90,000 and has accordingly acceptable mechanical properties.

Acknowledgement

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