

# New developments on the ring opening polymerisation of polylactide<sup>1</sup>

Sven Jacobsen <sup>a</sup>, Hans-Gerhard Fritz <sup>a</sup>, Philippe Degée <sup>b</sup>, Philippe Dubois <sup>b</sup>, Robert Jérôme <sup>c</sup>

<sup>a</sup> *Institut für Kunststofftechnologie, Universität Stuttgart, Böblinger Strasse 70, D-70199 Stuttgart, Germany*

<sup>b</sup> *Laboratory of Polymeric and Composite Materials, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium*

<sup>c</sup> *Center for Education and Research on Macromolecules CERM, University of Liège, Sart Tilman B6, B-4000 Liège, Belgium*

## Abstract

Poly lactides (PLA), biodegradable aliphatic polyesters, produced solely from renewable resources may 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 as 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 the possibilities to extend this polymerisation process to lactide based blockcopolymers have been investigated.

**Keywords:** Polylactide; Ring opening polymerisation; Blockcopolymers; Reactive extrusion; Twin screw extruder

## 1. 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 3000 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 of this polymer has to be disposed of 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.

Poly lactide (PLA), a hydrolyzable aliphatic polyester known and used for a long time for medical applications (Schmitt and Polistina, 1967; Conn et al., 1974; Gilding, 1982; Heller, 1985) is one of the polymers widely accepted to play a major role as future packaging material (Narayan, 1992; Sinclair, 1996; Hakola, 1997). 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, 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 (Fig. 1).

Poly lactide 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 by demand.

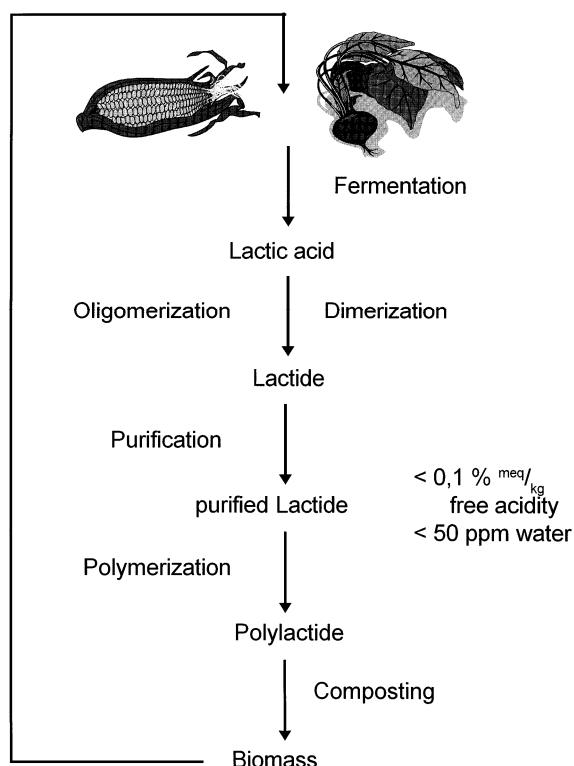
As previously mentioned, the current objectives are to make the manufacturing of PLA economically viable. In this respect, the authors developed a continuous one-stage process using reactive extrusion technology (Fritz et

---

<sup>1</sup> This publication is dedicated to Professor Fritz' 60<sup>th</sup> birthday.

al., 1996). However, this technique requires that the bulk polymerisation is close to completeness within a very short time (5-7 min), 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), can promote quite fast Lactide (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 processing (Gogolewski et al., 1993; Södergard and Näsman, 1995). 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)<sub>2</sub>), significantly enhances the lactide polymerisation rate in bulk (Degée et al., 1998a, submitted). 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 (Degée et al, 1998b, submitted). The Sn-OR bond is formed in situ by the reaction of the alcohol and the tin(II)dicarboxylate. 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 initiators (Kricheldorf et al., 1988; Löfgren et al., 1995). The addition of one equivalent of triphenylphosphine onto Sn(Oct)<sub>2</sub>, 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 inter-meshing co-rotating extruders have been achieved (Jacobsen et al., 1998, submitted) and the influence of various processing parameters on the resulting polymeric properties has been determined. However the technology developed originally for homopolymerisation of polylactide can be transferred to lactide based blockcopolymers. The technological background and two typical examples are presented within this paper.

**Fig. 1.** Natural cycle for the production of polylactide.



## 2. MATERIALS AND METHODS

### 2.1. Materials

(L,L)-Lactide was purchased from Boehringer Ingelheim and used as received, having a water content <math>< 200 \text{ ppm}</math> and a remaining free acidity <math>< 1 \text{ mequ kg}^{-1}</math>. Additional (L,L)-lactide was provided by 2B, Brussels, having a wafer content of <math>< 40 \text{ ppm}</math> and containing 0.2% remaining Toluene. The remaining free acidity was determined to be <math>6.5 \text{ mequ kg}^{-1}</math>.

Hydroxy terminated Polyethyleneglycol (PEG 1500) with a molecular weight of 1500 was purchased at Henkel and used as received. Hydroxy terminated Oligo- $\epsilon$ -caprolactone ( $M_n = 4000$ ,  $\delta = 1.5$ ) has been prepared in the laboratory.

2-Ethylhexanoic acid tin(II) salt  $\text{Sn}(\text{Oct})_2$  was purchased from Th. Goldschmidt and used without purification. Triphenylphosphine  $\text{P}(\phi)_3$  was purchased from Janssen and dried by three azeotropic distillations of toluene. A 0.15 M solution of the equimolar  $\text{Sn}(\text{Oct})_2 \cdot \text{P}(\phi)_3$  has been prepared by dilution in freshly dried toluene. Toluene was dried by refluxing over  $\text{CaH}_2$ . Ultrinox 626 was provided by GE Specialty Chem. and used without further purification.

## 2.2. Polymerisation

For reactive extrusion polymerisation the lactide is used as received without further purification. A total of 2 kg lactide, previously mixed with 0.5 wt% of ULTRANOX 626 stabilizer, is rapidly filled into previously flame dried and nitrogen purged 51 glass bulbs, equipped with a stopcock capped with a rubber septum. The catalyst solution is added using a syringe with stainless steel capillary. Toluene was distilled off under reduced pressure for 60 min.

The mixture prepared as such is transferred into a constant 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 co-rotating 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 180-185°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.

## 2.3. Analysis

The monomer conversion was determined by FTIR and tin residues were extracted by washing successively the organic layer once with an aqueous HCl solution (0.1 M) and twice with deionised water. Part of this solution was evaporated to dryness and the solid residue (monomer + polymer) analysed by size exclusion chromatography (SEC). The second part was precipitated in cold methanol and the polymer was filtered off and dried under vacuum to a constant weight.

## 2.4. Measurements

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 the bands at 1383 and 935  $\text{cm}^{-1}$ , respectively. The absorption band at 1383  $\text{cm}^{-1}$  corresponds to a vibration mode shared by the polymer and the monomer, while the absorption band at 935  $\text{cm}^{-1}$  is characteristic of the monomer. Practically, monomer conversion ( $c$ ) was calculated in the following equation:  $c = 100/([\text{L-LA}]/[\text{PL-LA}] + 1)$  where

$$\begin{aligned} & [\text{PL-LA}]/[\text{L-LA}] \\ &= -12.27 + 31.56(A_{1383}/A_{935}) \\ &\quad - 26.76(A_{1383}/A_{935})^2 + 10.43(A_{1383}/A_{935})^3 \\ &\quad - 1.81(A_{1383}/A_{935})^4 + 0.12(A_{1383}/A_{935}) \end{aligned}$$

Occasionally conversion was also calculated by  $^1\text{H-NMR}$  from the relative intensity of the methine group of the monomer and the polymer ( $\delta\text{CH}_{\text{PL-LA}} = 5.16$  ppm,  $\delta\text{CH}_{\text{L-LA}} = 5.02$  ppm).  $^1\text{HNMR}$  spectra were recorded in  $\text{CDCl}_3$  with a Bruker AM400 apparatus at 25°C. Solution concentration was 5 wt/v%.

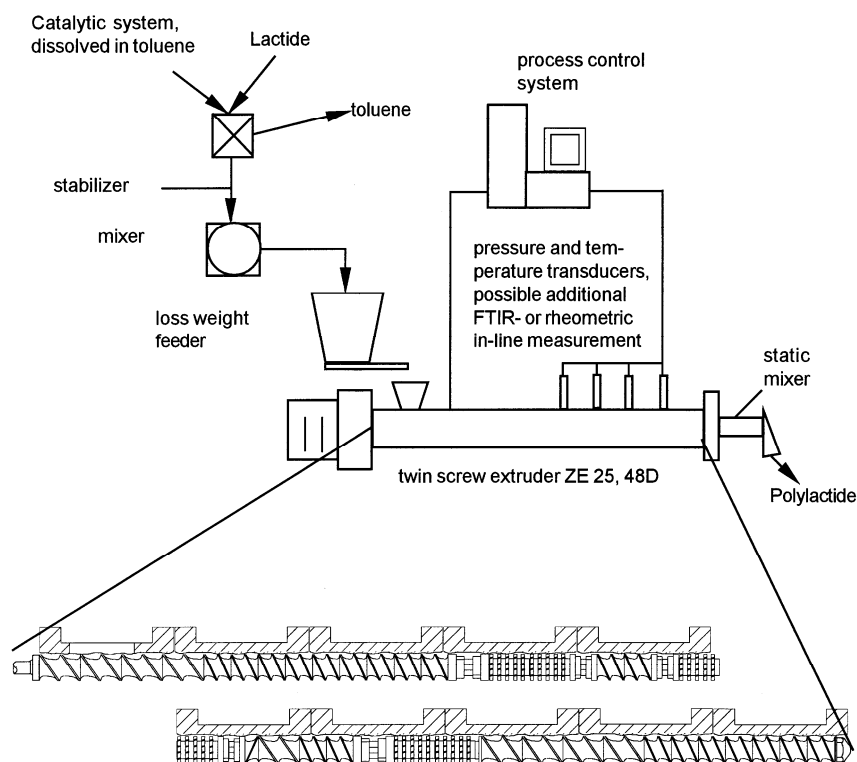
SEC was carried out in  $\text{CHCl}_3$  at 35°C using a WATERS 610 liquid chromatograph equipped with a WATERS 410 refractometer index detector and two STYRAGEL columns (HR1, HR5E). Molecular weight and molecular weight distribution of polylactides were calculated in reference to a polystyrene calibration and corrected to an absolute basis using an universal calibration curve ( $K_{\text{PS}} = 1.67 \times 10^{-4}$ ,  $a_{\text{PS}} = 0.692$ ,  $K_{\text{PLA}} = 1.05 \times$

$10^{-3}$ ,  $a_{\text{PLA}} = 0.563$  in the  $[\eta] = K \times M^a$  Mark-Houwink relationship).

### 3. RING OPENING POLYMERISATION OF LACTIDE USING REACTIVE EXTRUSION

The technology of reactive extrusion polymerisation, which has been used for a broad range of chemical reactions (Illing, 1969; Goyert et al. 1985; Sneller, 1985; Stuber and Tirrell, 1985; Anderlik, 1994), is conducted in a closely intermeshing co-rotating twin screw extruder with the processing and screw concept shown in Fig. 2. The previously prepared monomer-catalyst-stabiliser mixture is transferred into a gravimetric feeding system. This feeding system is constantly purged with dried nitrogen and provides the entrance section of the extruder, which is also constantly flushed with dried nitrogen to avoid unnecessary contact of the lactide with the moist air of the surroundings, with a constant throughput rate. The used twin screw extruder has a screw diameter of 25 mm and an L:D-ratio of 48, being one of the longer extruders, traditionally used in reactive processing. The extruder contains a modular screw and consists of several barrel parts. The first two barrel sections are not heated, so that the solid dimer is pushed relatively fast into the extruder. This is done using screw elements with a large helix angle. Within the third barrel section, combined with screw elements and with smaller helix angles, an increased temperature is used to melt the dimer and to disperse the catalyst and stabilising agent within the low viscous material. Within these first three-barrel sections, no significant polymerisation occurs, as the temperature is not high enough for a fast polymerisation. Starting with the 4th barrel section, the whole twin screw extruder until the screw tips is heated to a temperature of 180°C. The material inside the extruder will not have this temperature, but will have a temperature spectrum, which is in a range to deliver acceptable polymerisation conditions. Within the following screw part, the oligomerisation or prepolymerisation occurs. In that purpose, three combinations of shearing and kneading elements are included. Each of these combinations includes a large kneading element, which enhances the thermal polymerisation conditions by energy dissipation, followed by elements working similar to counter-rotating scissor blades.

**Fig. 2.** Processing and screw concept for the production of polylactide using reactive extension technology within a closely intermeshing co-rotating twin screw extruder.



These elements will cut the material flow in ever-new single flows creating new neighbourhoods within the melt. These shearing and mixing combinations are blocked against the flow direction. The further the advancement of

the polymerisation, the more powerful the restriction element is chosen. In the first combination, a counter conveying kneading element; in the second combination, a counter conveying standard screw element is added and finally, a blister is chosen as flow restriction element. These blocking elements are used to increase the degree of fill and the residence time of the material inside the mixing and kneading elements, which in turn will lead to a better mixing. With increasing conversion, the viscosity of the melt will increase, and therefore the mixing of the melt becomes more relevant for the polymerisation advancement, as the potential reactive partners become more rare. Therefore, it was decided to choose stronger flow restriction elements with increasing conversion.

After a last pressure reduction, the melt enters a partially filled zone using screw elements with a larger screw volume. Within this part, a devolatilisation of remaining monomer or low molecular weight components from the polymer would be possible, which has proven not to be necessary in this case. Within the last two barrel sections, screw elements with a smaller helix angle provide a pressure build up to push the polymer through the static mixer in front of the screw tips and through the die. In this section, the final polymerisation proceeds under increased pressure of 30-40 bars. In the optimum case, the polymerisation is continued, until the thermodynamic equilibrium is reached. It has to be noted that the state of equilibrium, due to the enhanced pressure level and the thermo-mechanical energy input, does not necessarily have to be the same as in similar polymerisation experiments conducted in glass ampoules under the same starting polymerisation conditions.

Within the static mixer the stabilizer system ULTRANOX 626 (bis(2,3-di-*t*-butylphenyl) pentaerythritol diphosphite used as antioxidant) is finally dispersed within the polymer. 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. The extruded high viscous polymer is cooled down by an air-cooled conveying belt and pelletised afterwards.

In Table 1, poly-L-lactides produced in glass ampoules using bulk batch polymerisation technology and in single-stage continuous reactive extrusion polymerisation are compared on the basis of molecular parameters. The comparison of two polymers polymerised under such different conditions is very difficult, although the same starting polymerisation conditions were used. The resulting conversions of 98.5 and 99% show that, in both cases, the polymerisation reaction has been finished, though for the bulk batch polymerisation in a glass ampoule, the time required to reach this conversion is approximately 40 min, compared with only 7-8 min in the reactive extrusion process. This difference can be explained by the fact that as soon as a high molecular weight, i.e. a high melt viscosity is reached, the speed of the reaction is limited not by the reactivity of the chemicals, but by the diffusion of the dimers or low molecular weight compounds inside the high viscous melt to find a reactive partner. This physical movement is limited to the Brownian movement in the glass ampoule, but is supported in the twin-screw extruder by the mixing elements and by the shearing of the polymer inside the inter-meshing zone.

The low molecular weight distribution (MWD) values smaller than 2 in both cases show that intermolecular transesterification reactions have been very limited, which is due to the use of triphenylphosphine as a co-catalyst, as well as due to the use of ULTRANOX 626 as stabilising agent.

The difference in molecular weight can be explained by the fact that the lactide for the polymerisation in the glass ampoule has been recrystallised, while it has been used as received for the reactive extrusion polymerisation, and by the fact that contact of the lactide with humid air can not be totally avoided during the transfer of the lactide from the gravimetric feeder to the twin-screw extruder.

#### **4. INFLUENCE OF PROCESS PARAMETERS ON THE FINAL POLYMER PROPERTIES-MASS FLOW RATE**

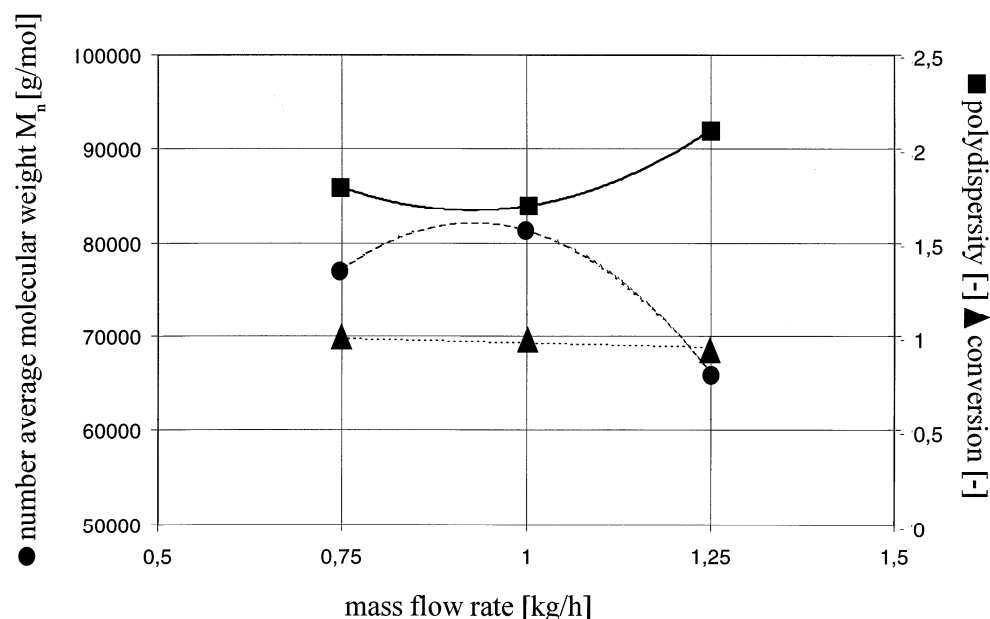
As a typical example for the influence of different processing parameters on the properties of the achieved polymer, the influence of the mass flow rate through the extruder on the resulting polymer parameters has been determined. More detailed information on the processing parameters is published elsewhere (Jacobsen et al., 1998, submitted). Using the above specified processing and screw concept for the continuous polymerisation of poly-L-lactide, the mass flow rate has been changed from 0.75 to 1 kg h<sup>-1</sup> and further to 1.25 kg h<sup>-1</sup>. For these experiments, a lactide supplied from Brussel Biotech has been used, all other processing parameters have been kept constant and especially the screw speed, always remaining at 50 rpm. In Fig. 3, the results of this set of experiments are shown. The conversion decreases from 99% at a mass flow rate of 0.75 kg h<sup>-1</sup> over 97 to only 94% at the highest flow rate of 1.25 kg h<sup>-1</sup>. This fact can be explained by the effective residence time of the material inside the extruder. The residence time will be reduced with increasing throughput, which results in a

polymerisation, which has not reached the equilibrium state at the end of the die. A further increase in the throughput would result in a dramatic decrease of conversion, as the viscosity of the resulting material would be too low to provide a successful pressure build up at the die, which in turn would result in an even lower residence time and thus even lower conversion and lead to a complete break down of the reaction. The molecular weight increases by 4000 and the molecular weight distribution decreases slightly, while increasing the mass flow rate from 0.75 to 1 kg h<sup>-1</sup>, which can be explained by already starting degradation reactions at the experiment with 0.75 kg h<sup>-1</sup> mass flow rate, reducing the chain length again, after reaching the maximum conversion. If the throughput is further increased to 1.25 kg h<sup>-1</sup>, as already described, the state of equilibrium cannot be reached anymore, resulting not only in reduced conversion, but also, in a dramatically reduced molecular weight and in a broader molecular weight distribution, due to the appearance of shorter chains, which are still in the chain growing phase.

**Table 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)<sub>2</sub> · P(φ)<sub>3</sub> complex with a [L-LA]<sub>0</sub>/[Sn] ratio of 5000, at 180°C polymerisation temperature

Entry	Process	Conversion [%]	Time[min] for conversion	M <sub>n</sub> ×10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>
1	Batch	98.5	40	246.0	1.9
2	Reactive extrusion	99.0	≈7	91.1	1.8

**Fig. 3.** Resulting molecular parameters of poly-L-lactide as received by reactive extrusion polymerisation—average molecular weight, conversion and polydispersity as a function of mass flow rate through the extruder.



## 5. TRANSFER OF THE DEVELOPED PROCESS TO OTHER POLYMERS, COPOLYMERS AND ESPECIALLY BLOCKCOPOLYMERS

The above mentioned process to enhance the reactivity of the slowly proceeding ring opening polymerisation of lactide within a twin screw extruder, lead it to the reactions equilibrium within the extrusion system and thus, continuously produce polymer, can be transferred under certain circumstances to similar polymers and copolymers with comparable monomers or comonomers. A number of such monomers are presented in Fig. 4. They include not only lactones such as ε-caprolactone, but also dilactones as glycolide. Basic necessities to transfer the developed process to other monomers are:

- Sufficient fast reaction kinetics, which can be further enhanced within the extrusion system using diffusion controlled polymerisations, such as the ROP of lactide.

- The equilibrium of reaction is close to complete monomer conversion, to ensure the production of high molecular weight and high viscosity polymers.
- Side- and degradation reactions can be suppressed by the use of suitable stabilizer systems or conditions of reaction.

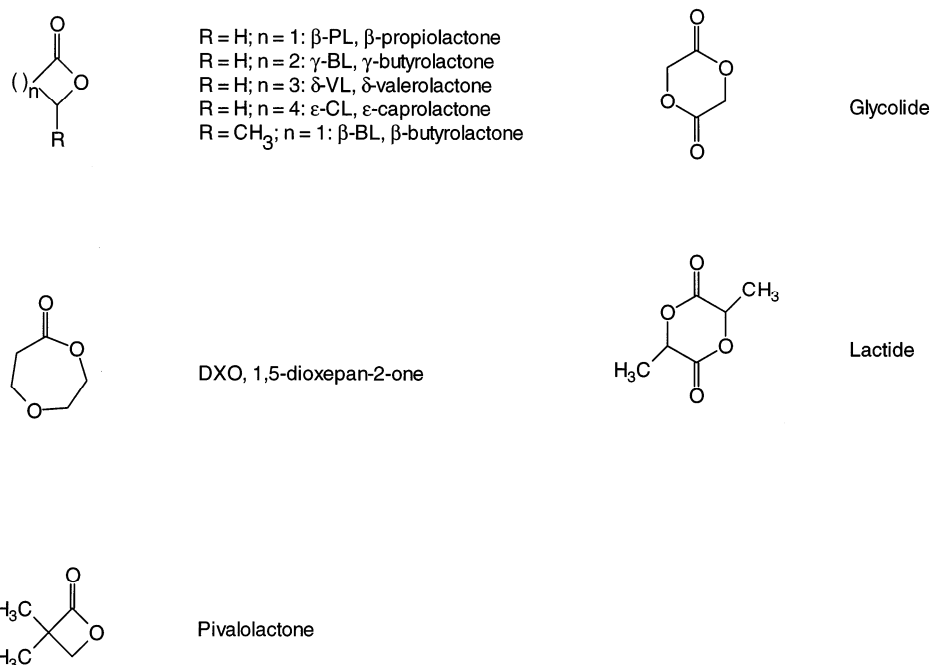
Due to these boundary conditions the number of possible polymers to be produced in this way is greatly reduced, though in most cases a modification of the reaction kinetics by choosing a suitable catalytic system is plausible, so that it might be possible to generate these polymers by reactive extrusion. If one wants to additionally generate copolymers from different monomers, the following additional boundary conditions have to be disregarded:

- The reaction kinetics of both monomers is similar and can be enhanced using the same catalytic system.
- Both monomers are consumed completely or nearly completely during the copolymerization reaction.

These additional boundary conditions restrict the number of possible copolymers further, especially as the reaction kinetics of both monomers is different in most cases due to steric hinderance, so that usually one monomer homopolymerises readily, while the second remains nearly unaffected by the polymerisation reaction.

An alternative to the described copolymerisation of two or more monomers is the possibility to incorporate pre-oligomerised, hydroxy-terminated blocks as starter molecules to a second type of monomer. Thus the homopolymerisation of this second monomer will start at both ends of the oligomers and incorporate them as blocks of predefined size into the polymer (Fig. 5) Using this technique, one can generate a blockcopolymer of defined composition and with defined blocklength of the second monomer. This technology has been described by Stevels et al. (1996) using large amounts of prepolymers and  $\text{Sn}(\text{Oct})_2$  as catalyst. Here, similar experiments using small amounts of prepolymer have been conducted to determine the influence of the prepolymers on the course of reaction using  $\text{Sn}(\text{Oct})_2 \cdot \text{P}(\phi)_3$  as catalytic system. First positive results have been made with the homopolymerisation of polylactide using prepolymerised oligomers of poly- $\epsilon$ -caprolactone and polyethylenglycol.

**Fig. 4.** Cyclic monomers or dimers to be used for ring opening polymerisation using reactive extrusion technology.

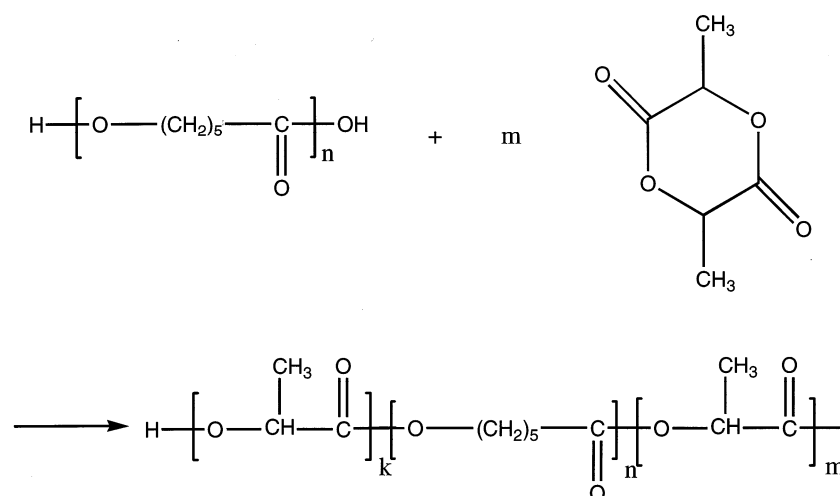


We were able to show that small amounts (1 and 2 wt%) of pre-oligomerised Poly- $\epsilon$ -caprolactone blocks ( $M_n = 4000 \text{ g mol}^{-1}$ ,  $\delta = 1.5$ ; Table 2, entries 2 and 3) have no significant influence on the propagation of the polymerisation reaction of polylactide during reactive extrusion. The reactive extrusion has been conducted using a barrel temperature of  $180^\circ\text{C}$ , a throughput rate of  $1 \text{ kg h}^{-1}$  and a screw speed of 100 rpm. As catalytic system the already proposed  $\text{Sn}(\text{Oct})_2 \cdot \text{P}(\phi)_3$  has been used with a molar monomer-tin(II)-ratio of 5000. After exiting the extruder, all materials have reached the equilibrium of reaction. The monomer conversion showed no significant indication of a negative influence of the oligomers on the reaction kinetics. The average molecular

weight decreases with increasing content of caprolactone blocks, which can be explained by the increased amount of potential starter molecules for the polymerisation reaction.

Similar results have been obtained using prepolymerised hydroxyterminated polyethyleneglycol (PEG) (Table 3). Some 2 and 5 wt% of polyethyleneglycol were added to the L-lactide feed. The reactive extrusion has been conducted using a barrel temperature of 185°C, a throughput rate of 1 kg h<sup>-1</sup> and a screw speed of 50 rpm. As catalytic system the already proposed Sn(Oct)<sub>2</sub> · P(φ)<sub>3</sub> has been used with a molar monomer-tin(II)-ratio of 5000. Again, there is no negative influence of the oligomers on the course of polymerisation detectable. The conversion within the residence time inside the extrusion equipment is close to completeness and the average molecular weight decreases from 93 000 without polyethyleneglycol to 70 000 with 5 wt% of added PEG with increasing oligomer content, while, at the same time, the molecular weight distribution becomes smaller.

**Fig. 5.** Reaction scheme for blockcopolymerisation using pre-oligomerised blocks of one monomer (here ε-caprolactone) and a second monomer (here lactide).



**Table 2:** Influence of the presence of hydroxy terminated oligo-ε-caprolactone (OCL,  $M_n = 4000 \text{ g mol}^{-1}$ ,  $\delta = 1.5$ ) on the polymerisation of L-lactide using reactive extrusion technology with a reaction temperature of 180°C

Entry	Content OCL	Conversion [%]	Time [min] for conversion	$M_n \times 10^{-3}$	$M_w/M_n$
1	0	94.0	≈7	87.0	1.7
2	1	97.0	≈7	66.6	1.3
3	2	95.0	≈7	43.8	1.4

**Table 3:** Influence of the presence of hydroxy terminated polyethyleneglycol (PEG,  $M_n = 1500 \text{ g mol}^{-1}$ ) on the polymerisation of L-lactide using reactive extrusion technology with a reaction temperature of 180°C

Entry	Content OCL	Conversion	Time [min] for conversion	$M_n \times 10^{-3}$	$M_w/M_n$
1	0	97.0	≈6	93.3	1.9
2	2	99.0	≈6	83.3	1.6
3	5	99.0	≈6	70.6	1.4



## 6. CONCLUSION

In conclusion a new process has been developed for the production of polylactide using reactive extrusion polymerisation based on a new catalytic system, which not only enhances the ring opening polymerisation kinetics of L-lactide but also suppresses side and degradation reactions such as intermolecular transesterification reactions. Thanks to this catalytic complex of Lewis base and Lewis acid, it was possible to design a suitable processing and screw concept using closely intermeshing co-rotating twin screw extruders. The lactide ring opening polymerisation reaction reaches the state of equilibrium within the residence time of the reactive material inside the extrusion system and can thus be used for further melt processing using any polymer processing device. Indeed it was possible to reduce the amount of catalyst so far, that the catalytic system can remain inside the polymer without having negative effects on the melt stability of the resulting polymer during further melt processing. An additional stabiliser, which does not influence the course of the polymerisation reaction, enhances the melt stability of the resulting polymer further. Thus a polymer is achieved, which can be used as received and does not have to be recrystallised by means of expensive solvent recrystallisation.

The influence of different process parameters on the properties of the resulting polymers has been determined and thus it now is possible to design a suitable processing and screw concept not only for any type of polylactide needed but also to adopt the developed polymerisation process to similar ring opening polymerisations using other monomers or even to copolymerisation reactions. Within this paper, some typical examples for the production of blockcopolymers made of hydroxyterminated pre-oligomerised blocks of one monomer and lactide as second monomer have been presented. By adopting the length of the pre-oligomerised blocks as well as the total amount of blocks added, a multitude of possible blockcopolymers can be generated with the same processing concept and equipment to receive polymers with different mechanical, physical, thermal and biodegradable properties for different applications.

## Acknowledgements

The authors are grateful to the European Commissions AIR-project 'Development of Innovative Biodegradable Polylactic Acid-Polymers, Based on Agricultural Raw Materials for New Industrial Applications' and to the FAIR-project 'Biodegradable Films and Bottles made of Polylactic Acids Polymer' for financial support.

## References

- Anderlik, R., 1994. Herstellung thermoplastischer Elastomere auf der Basis silanvernetzter Polypropylen/Ethylen-Propylen-Elastomermischungen, PhD-thesis, IKT, University of Stuttgart.
- Conn, J., Oyasu, R., Welsh, M., Beal, J.M., 1974. *Amer. J. Surg.* 128, 19.
- Degée, Ph., Dubois, Ph., Jérôme, R., Jacobsen, S., Fritz, H.G., 1998a. *J. Polym. Sci. Polym. Chem.*, submitted.
- Degée, Ph., Dubois, Ph., Jérôme, R., Jacobsen, S., Fritz, H.G., 1998b. *Macromol. Symp.*, submitted.
- Fritz, H.G., Jacobsen, S., Degée, Ph., Dubois, Ph., Jérôme, R., 1996. *DE 196 (284) 72.4.*
- Gilding, D.K., 1982. In: Williams, D.F. (Ed.), *Biocompatibility of Clinic Implant Materials*. CRC Press, Boca Raton, p.9.
- Gogolewski, S., Janovico, M., Perren, S.M., Dillon, J.G., Hughes, M.K., 1993. *Poly. Degrad. Stab.* 40, 313.
- Goyert, W., Grimm, W., Awater, M. et al., 1985. *Thermoplastische Chemiewerkstoffe und Verfahren zu ihrer Herstellung*, Bayer AG, Leverkusen, DEOS 2854406.
- Hakola, J.S., 1997. *Industrial Business Opportunities for Poly(-Lactic Acid) Biopolymers as a Non-food Application of Agricultural Production in Europe. Renewable Bioproducts-Evaluating the Current Status in Industrial Markets and Research*, EUR 18034 EN.
- Heller, J., 1985. *CRC Crit. Rev Ther. Drug Carrier Syst.* 1, 39.
- Illing, G., 1969. *Mod. Plastics* 8, 70-76.
- Jacobsen, S., Fritz, H.G., Degée, Ph., Dubois, Ph., Jérôme, R., 1998. *Polymer*, submitted.
- Kricheldorf, H.R., Berl, M., Schamagl, N., 1988. *Macromolecules* 21, 286.

Löfgren, A., Albertsson, A.C., Dubois, Ph., Jérôme, R., 1995. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* C35, 379.

Narayan, R., 1992. Biomass (renewable) resources for production of materials, chemicals and fuels — a paradigm shift. In: Rowell, R.M., Schultz, T.P., Narayan, R. (Eds.), *Emerging Technologies for Materials and Chemicals from Biomass*, ACS Symp. Ser. 476, p. 1.

Schmitt, E.E., Polistina, R.A., 1967. US Patent 3,297,033.

Sinclair, R.G., 1996. *J. Macromol. Sci. Pure Appl. Chem.* A33, 585.

Sneller, J.A., 1985. *Mod. Plastics Intl.* 8, 42-46.

Stevens, W.M., Bernard, A., Van de Witte, P., Dijkstra, P.J., Feijen, J., 1996. *J. Appl. Polymer Sci.* 62, 1295-1301.

Stuber, N.P., Tirrell, M., 1985. *Polymer Process Eng.* 3, 71-83.

Södergard, A., Näsman, J.H., 1995. *Polymer Degrad. Stab.* 46, 25.