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## Synthesis and properties of lactide polymers

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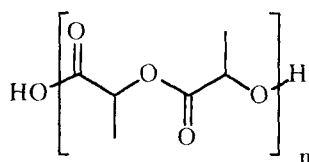
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## Summary

For decades the accent in polymer research has been on the development of materials with stable properties. For instance, the poly(ethylene) bottle of the detergent is not supposed to break up spontaneously and the car paint should not crack under the influence of sun light. However for several years now there is a growing interest in degradable polymers. This interest is partly the result of the increasing number of waste related problems, but also because these materials can have specific advantages in certain applications. At this moment several types of degradable polymers are commercially available and this number will increase in the coming years. A polymer which has been studied a lot for degradable applications is poly(lactide) which is also called poly(lactic acid) (Figure 1). Chapter 1 will go more

deeply into the development, raw materials position, production and applicability of poly(lactide). It will show that the most important reasons for the interest in this polymer are:



*Figure 1: Poly(lactide).*

① It can be produced from cheap raw materials. This can be petrochemicals or raw materials from agricultural sources.

② The polymer can be produced using well known polymerization procedures. This can be a polycondensation or a ring opening polymerization, depending on the desired properties (molecular weight).

③ The properties of poly(lactide) can be varied over a large range. This includes both the degradation characteristics and the mechanical properties.

④ The final degradation product is completely or largely made up of lactic acid. This can be converted to carbon dioxide or water in every ecological system or it can even be used as a carbon source.

Poly(lactide) is an interesting polymer in relation to its price (cheap raw materials) and its properties (variable or tuneable)

For a number of applications like films and fibres it is important that the polymer has a high molecular weight. Only then can good mechanical properties be obtained. However there is only one synthetic route for the synthesis of high molecular weight poly(lactide). In this route the lactide (the cyclic dimer of lactic acid) is polymerized at low temperatures using tin(II) bis(2-ethyl-hexanoate) as the catalyst. In chapters 2 and 3 for the first time two new catalyst

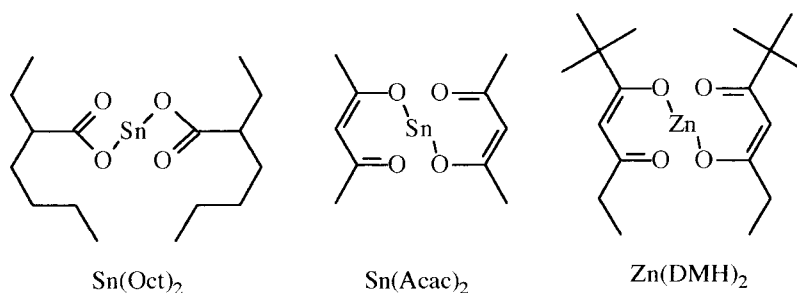


Figure 2: With these three catalysts very high molecular weight poly(lactide) can be obtained. The tin(II) salt of 2-ethyl-hexanoic acid  $\text{Sn}(\text{Oct})_2$  was known from previous literature for this application. Tin(II)-bis(2,4-pentanedionato-*O,O'*), or  $\text{Sn}(\text{Acac})_2$ , and zinc-bis(2,2-dimethyl-3,5-heptanedionato-*O,O'*), or  $\text{Zn}(\text{DMH})_2$ , are compounds with  $\beta$ -diketones and have been newly developed.

are given that can also produce high molecular weight poly(lactide). These catalysts are not salts from carboxylic acids, like tin(II) bis(2-ethyl-hexanoate), but compounds from  $\beta$ -diketonates (Figure 2). The three catalysts can all produce very high molecular weight poly(lactide), but there are large differences in the rate of polymerization. It appeared, quite unexpectedly, that the activity of the catalyst had a very large influence on the properties of the nascent polymer. The catalyst with the lowest activity produced an extremely crystalline polymer with a high melting point while the catalyst with the highest activity had the opposite effect on the properties. It is shown that during the polymerization there is a complex interplay between the rate of polymerization and the rate of crystallization and that the final polymer properties are determined largely by these two factors.

The polymerization of lactide is initiated by compounds with an active hydrogen, like water or alcohol, when the catalysts of this study are used. Because the monomer and catalyst are always contaminated with these compounds the maximum molecular weight that can be obtained is determined by the purity of the starting materials. Previous models where  $\text{Sn}(\text{Oct})_2$  was supposed to initiate the polymerization appear not to be correct.

In many cases polymer properties are adjusted for specific applications. Mostly this is done with the aid of additives, like plasticizers or fillers. Chemical modification of the polymer can also be used to induce specific properties, as for example in the vulcanization or cross-linking of (natural-) rubber.

Little is known about the effect of cross-linking on homo- and copolymers of poly(L-lactide). For this reason several cross-link methods have been studied and described in chapter 4 and 5 (Figure 3). The first method of our study was electron beam irradiation. Although this high energy irradiation has been shown to be very effective in cross-linking a number of

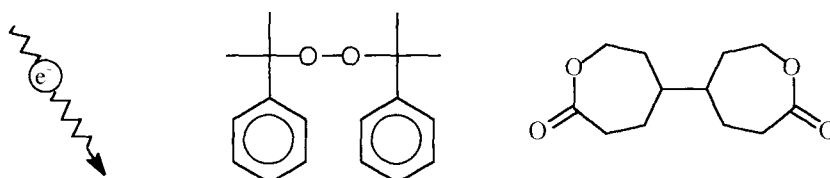


Figure 3: The cross-linking of poly(lactide) has been studied using electron beam irradiation (left), dicumyl peroxide (middle) and 5,5' bis(oxepane-2-one). Only with electron beam irradiation no cross-linking was observed. The most effective cross-linker was 5,5' bis(oxepane-2-one).

polymers it cannot be used for the cross-linking of poly(lactide). The only effect that was observed was a strong decrease of the molecular weight. Cross-linking with organic peroxides is another, but frequently used, method. It is shown that a poly(L-lactide) network can be obtained using dicumyl peroxide (DCP). A side reaction that occurs during the cross-linking is the addition of DCP fragments to the polymer. From the high concentration of peroxide that is needed to obtain a network with a low sol fraction (> 30 weight %) it can be concluded that the cross-linking reaction is not very effective. Because the degradation products that are formed during the cross-linking reaction will have to be removed the method will be suitable only for the production of small devices, fibres and films. The use of multifunctional monomers is a third method that can be used for cross-linking polymers. For this purpose a tetrafunctional monomer, 5,5'-bis(oxepane-2-one) or 5,5'-BO, has been synthesized. The cross-linker consists of two covalently linked  $\epsilon$ -caprolactone units. The effect of this cross-linker on the properties of pure poly(lactide) and poly( $\epsilon$ -caprolactone) has been studied and the same has been done for copolymers of lactide and  $\epsilon$ -caprolactone. Using these monomers weakly cross-linked materials with a high gel content can be obtained. Depending on the polymer composition a large variation in tensile strength, modulus and elongation at break can be obtained. These properties are not only determined by the lactide/ $\epsilon$ -caprolactone ratio but the influence of the cross-linker is also strong. The largest effect of the cross-linker is observed in the crystallinity, the modulus and the creep of the materials. All the semi-crystalline homo- and copolymers show a strong decrease in crystallinity when the concentration of 5,5'-BO is increased. For degradable polymers this is an important effect because the crystallinity has a large influence on the degradation. The modulus of all rubbery copolymers increases with increasing 5,5'-BO concentration and the creep of these materials strongly decreases. Especially in comparison with the linear materials the effects are very large.

At room temperature poly(lactide) is a glass like and relatively brittle polymer. The toughness of this type of polymers can be improved by blending or by block copolymerizing with a rubbery polymer. In chapter 6 blends of the low  $T_g$  poly(ethylene oxide) (PEO) and the

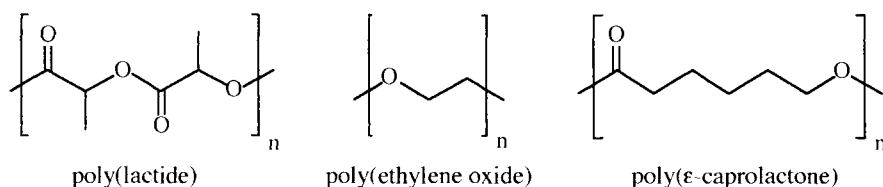


Figure 4: The toughness of poly(lactide) can be improved by blending it with poly(ethylene oxide) or copolymers of poly(ε-caprolactone). The toughness of the corresponding block copolymers is also higher in comparison with the pure poly(lactide).

glassy poly(lactide) are the subject of study. PEO is a hydrophylic and semi-crystalline polymer with a  $T_g$  of  $-60^\circ\text{C}$ . It is degradable in a biologically active environment. In this chapter it is clearly shown that these two polymers are miscible in the amorphous state. Blends with more than 10 weight % PEO are tough materials with an increased rate of degradation as a result of the hydrophylic character of the PEO fraction. These tough materials would be very suitable for packaging applications.

Blends with ε-caprolactone rubbers have also been studied (chapter 7). These materials are completely hydrolytically degradable in contrast to the blends with PEO. It was found that very tough materials can be obtained when the rubbers are partly miscible with the poly(lactide) matrix. Block copolymers of these rubbers and poly(lactide) already show good mechanical properties at low molecular weight. A further improvement of the properties is obtained with increasing molecular weight. This study shows that a rubber modified poly(lactide), composed of hydrolytically degradable polyesters, can be obtained.

The aim of this dissertation is to improve the understanding of the syntheses and properties of poly(lactide). Much attention is also paid to the effect of modifications on the polymer properties. Poly(lactide) is a very interesting material because of the potentially cheap raw materials and low production costs and also because of the ease with which the material properties can be influenced.