Poly(propylene carbonate), old CO_2 Copolymer with New Attractiveness

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Summary: The catalytic synthesis of poly(propylene carbonate) (PPC) from propylene oxide and CO_2 is mediated by zinc glutarate and chromium salen complexes. The determined solid state structure of the zinc glutarate was taken to model the polymerisation of ethylene oxide. It has a low activation energy for a reaction path involving two zinc atoms, where one binds the nucleophilic alkoxy chain end and one activates the epoxide. A similar pathway may operate in the alternating copolymerization PO/CO_2 as is shown in the homogeneous chromium salen catalyst system. The material profile was determined of PPC with 93% carbonate linkages. A study of the transparent blend with poly(lactic acid) (PLA) shows that the polymers are not miscible, but rather compatible as they are finely dispersed and show linear behaviour in the mechanic properties. The permeability of oxygen, carbon dioxide and water of the composite PPC/PLA are also reported.

Keywords: blends; carbon dioxide; catalysis; poly(propylene carbonate)

Introduction

The alternating copolymerization of propylene oxide and carbon dioxide is a long known and ever studied reaction since the first reports by Professor Inoue at the end of the 1960s.[1] Research of this reaction has greatly intensified again after a period of little activity in the nineties in the beginning of the new century, particular in China and South Korea. This may be attributed to several factors involved with the polymer and its preparation: importantly the current interest using carbon dioxide as feed stock, the degradation in compost of PPC (poly(propylene carbonate)) and the relative simple preparation. Many issues of the copolymerization and the copolymer are in a process of becoming clarified, however, one of continuous controversy is the reaction mechanism.[2] This will be addressed in the first part. The material profile of the copolymerisates of CO_2 and propylene oxide is another topic addressed: - not always realized - it is rather dependent on the ratio of carbonate and ether linkages in the main chain. A copolymer with 93% carbonate linkages and 7% ether linkages will be introduced. This copolymer has quite different properties as the commercial QPAC which is almost perfectly alternating CO_2-PO (vide infra).

Catalysis

In the early days, only heterogeneous catalysts were known for the copolymerization. These were usually obtained from the reaction between dialkyl zinc reagents and some proton acidic compound like water, phenols or acids.[3] These catalytic solids were hard to study on the molecular level with respect to the mechanism and the alternating copolymerization remained at the level of plausible proposals. Later also homogeneous catalysts have been identified for the copolymerization in form of porphyrin complexes of aluminium[4] and chromium,[5] diketiminates of zinc[6] and

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salen complexes of cobalt[7] and others.[2,8] The new opportunity to study the dependence of the catalysis with respect to the catalyst, cocatalyst and the reagents has again intensified investigations to clear the reaction mechanism and with the desire to develop more productive systems. Until today there is an ongoing debate on the reaction order with respect the metal center.[2]

In this contribution, we argument that the most likely mechanism involves two metal centres, one for coordinating and activating an epoxide and the other holding the chain end. It is in accordance with the dependence of the polymerization rate on the concentration of neutral chromium (III) and corresponding –ate complexes. It differs from earlier studies which use chromium (III) salen systems in combination with a twofold excess of chloride (which react to give chromium ate complexes, and possibly results in a kind of saturation kinetics).[2]

The formation of PPC from PO and CO_2 can be mediated by N,N′-bis(3,5-di-t-butylsalicylidene)-1,2-diaminobenzene chromium (III) chloride in combination with a chloride as nucleophile.[9] The nucleophile is known to react with the coordinatively unsaturated chromium(III) complex to give corresponding ate complexes. It binds much better than the weakly coordinating PO. Eventually the chloride – either free or bound to chromium - acts as a nucleophile toward a coordinated PO to give an alkoxide (vide infra). This is the starting point of a copolymerization.[2] Meaningful experiments for the mechanism were performed in neat PO at a temperature of 75 °C, a CO_2 pressure of 1.4 MPa, and had a constant concentration of salen chromium (III) species but a variable –also under-stoichoimetric - amount of chloride as cocatalyst. It was found, that the highest rates are observed for system consisting of chromium salen and one a half equivalent of chloride. With increasing concentration of added chloride nucleophiles to Cr-salen the copolymerization activity decreases sharply and drops to zero. Thus a kind of parabolic dependence as shown in Figure 1 is obtained for the formation of PPC in dependence of the chromium to chloride ratio.

The interpretation of these data is of a rate determining reaction in the alternating copolymerization between a coordinated, thus activated PO on a neutral chromium salen complex and a carbonato chain end bound to another (anionic) chromium salen generated from a chloride nucleophile after consecutive alternating PO and CO_2 insertions. At a constant sum of chromium atoms, a kind of parabolic dependence

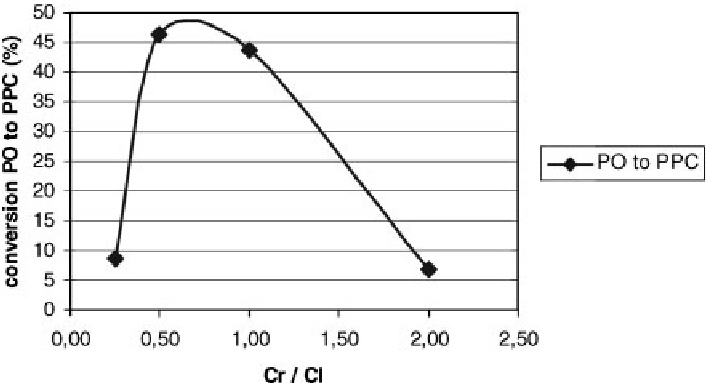
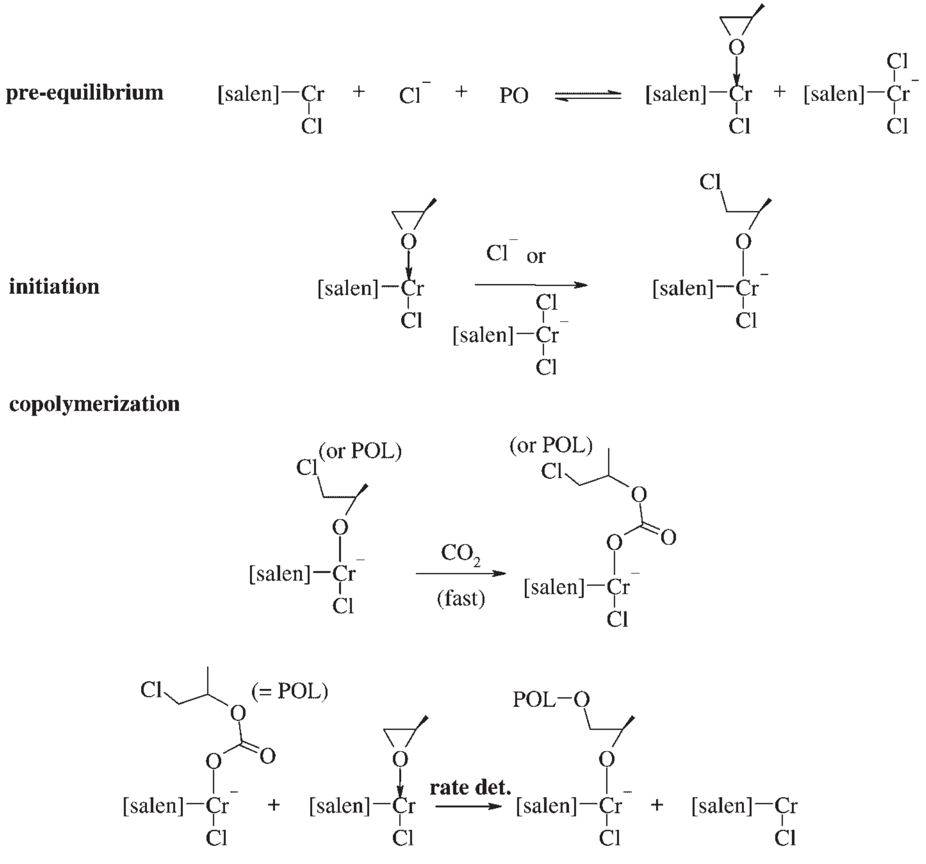


Figure 1.
Transformation of PO and CO_2 into PPC using chromium salen complex in neat PO at 75 °C and 1.4 MPa CO_2 pressure with various ratios of chloride to chromium salen at a total chromium concentration of 9.1 mmol/L; chloride as tetrabutyl ammonium salt.

arises of the copolymerization rate with the chloride concentration. The other elementary reactions are in equilibrium or fast. The following reactions pertain to the observations (see Scheme 1).



rate = k [salen-Cr-POL][salen-Cr-PO] , with inital condition of

$[\text{salen-Cr}]_0$ = [salen-Cr-PO] + [salen-Cr-POL]

Scheme 1.

Of practical interest is also insight into the catalytic action of an active heterogeneous catalyst, zinc glutarate.[10] One especially simple preparation of PPC uses this catalyst, which is readily prepared from zinc oxide and glutaric acid. The copolymer can conveniently be isolated from the reaction mixture, for example by extraction of the catalyst with aqueous hydrochloric acid.[11] Several groups have put larger efforts in the molecular characterization of the bulk and the surface of the heterogeneous zinc glutarate. In particular the research group around Professor Ree characterized the surface using several techniques.[12] It has for example been shown that both carbon dioxide and PO coordinate to zinc at the surface and also that PO and CO_2 may insert into some surface species.[13]

A reaction pathway for the copolymerization at the catalyst surface has not been secured. We decided to use DFT quantum

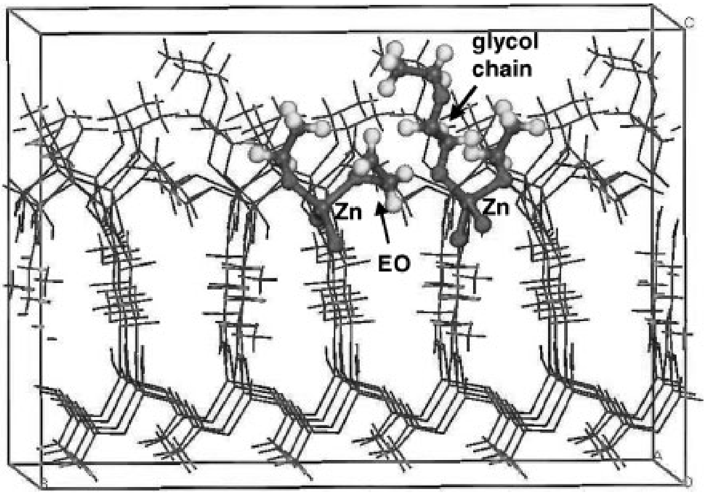


Figure 2.
The polymerization of ethylene oxide at the surface of zinc glutarate: crystal surface with coordinated ethylene oxide and glycol chain as was calculated by DFT methods (CPMD).

mechanical methods to find low energy pathways for epoxide opening reaction at the zinc glutarate surface, in our opinion the key step. In the past, we determined the crystal structure of the active catalyst using synchrotron radiation[9] and found it to be equal to the compound prepared in water[14] and to the compound prepared from glutaronitril and zinc perchlorate.[15] It consists of alternating layers of zinc dications and deprotonated glutaric acid. Zinc is tetrahedral coordinated by four oxygen atoms from four different κ^2-bridging carboxylates. Since zinc adipate and pimelate are also active catalysts, and probably have the same kind of structure,[16] we can anticipate that the catalysis proceeds at the zinc layer, in particular at the surface zinc

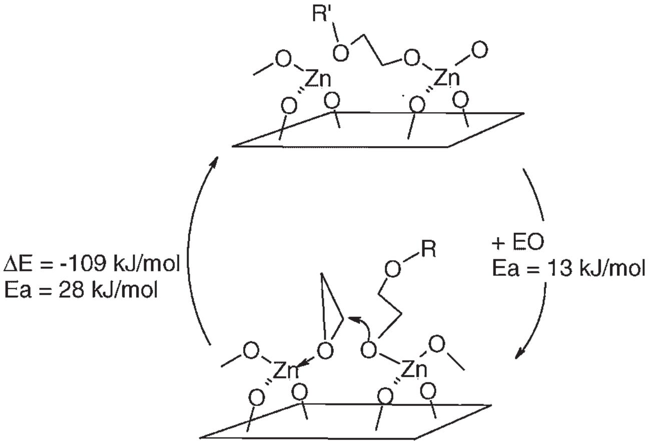


Figure 3.
The polymerization of ethylene oxide at the surface of zinc glutarate: schematic representation and calculated barriers.

atoms that have free coordination sites.[13] The ring opening of ethylene oxide in its homopolymerization was used as simplified model (Figure 2) to study reaction routes at that surface. Experimentally it is known that the zinc glutarate also catalyses the generation of polyethylene glycols from EO, and hence a certain relevance may be assumed.

As a first approximation for the catalysis at the surface, a bridging carboxylate was removed and replaced by an oxygen coordinating ethylene oxide on one zinc, and an ethyleneglycol ethoxide on the open coordination site of the neighbouring atom. CPMD optimization of the structure was performed, resulting in the starting situation as depicted in Figure 2. A reaction coordinate was defined between the alkoxide oxygen and an ethylene oxide carbon atom; the system was allowed to equilibrate in all other coordinates. An attractive low energy pathway could be found for a typical propagation step of ‘‘ethylene oxide insertion’’ starting from a zinc alkoxide – representing the growing chain end – and a coordinated ethylene oxide on a neighbouring zinc centre. The nucleophilic attack of the alkoxide at the backside of the coordinated ethylene oxide was calculated at an activation energy of 28 kJ/mol (Figure 3; the reaction is exothermal by 109 kJ/mol). The subsequent decoordination of an ether functionality and coordination of a new ethylene oxide also had a low barrier (13 kJ/mol). The formation of PPC can be envisioned by the same mechanism, where the alkoxide intermediately takes up a carbon dioxide and is transferred into a carbonate nucleophile. This is the subject of ongoing studies.

We thus strongly favour a copolymerization mechanism with the involvement of two metal centers, one to activate the epoxide for nucleophilic attack and one to bind the nucleophilic chain end to keep it from decomposing. Quantum mechanical calculations show in several cases the presence of low energy pathways – contrasting the situation for a direct epoxide insertion[17] – and secondly, the complex kinetics of the copolymerization mediated by chromium salen complexes in combination with a nucleophile generating cocatalyst shows that the reaction is not simple.[2] In addition, epoxides are usually reacting spontaneously only with strong nucleophiles (alkoxides amides hydroxide) but not with carbonates, or after formation of a free cation, like in a cationic polymerisation.[18]

Material Properties

PPC (PPC93) with a molar carbonate linkage percentage of 93% was prepared from PO and CO_2 mediated by a zinc glutarate in toluene at 80 °C and at 4.5 MPa CO_2 pressure. The rest of the linkages between the former PO molecules are ether entities. This is established by NMR techniques on basis of the resonances of the methyl groups. It also follows from the NMR data that the ether linkages are randomly distributed along the chain. Material properties were determined and are summarized in Table 1. The material properties of a PPC are dependent on the microstructure and in particular on the regioerrors in form of ether linkages. It should therefore be accurately determined

Table 1.
Material Properties of PPC with 93 mol% of carbonate linkages.

Glas temperature	35 °C	Processing temp.	165–175 °C
Tensile strength	13–20 MPa	Elastic modulus	~600 MPa
Elongation @ break	~600%	Refractive index	1.46
Mn	50–70 kDa	Mw	300–600 kDa
Permeability of H_2O ASTM F-1249	1.15 10^3 g · μm/m^2/d	Permeability of CO_2 ASTM D 1434 82	2 10^3 cm^3 · μm/m^2/d/bar
Surface resistance (500 V)	2 * 10–14 Ω	Log E-$t_{1/2}$ (Charge build-up)	>5.9

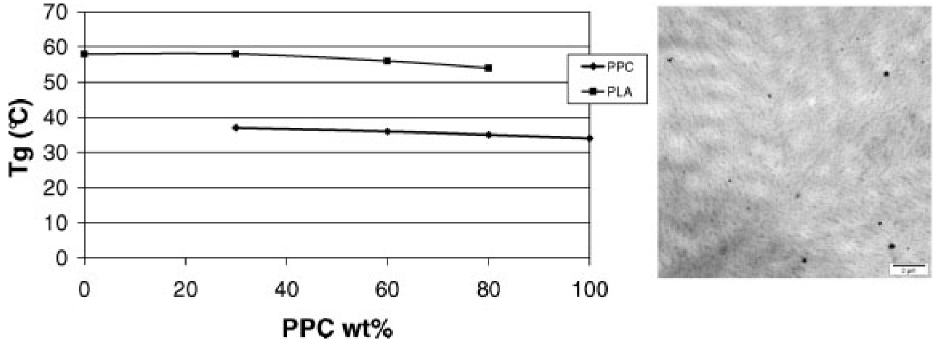


Figure 4.
Glass temperatures in composites of PPC and PLA and TEM picture of a PPC/PLA 20/80 blend (bar corresponds to 2 μm).

in order to allow a comparison between various studies on poly(propylene carbonate).[19,20]

The PPC93 with a glass temperature of 35 °C is neither a typical engineering plastic nor a rubber. It has a favourable large elongation at break, which makes it potential suitable as a blend component in brittle plastics. Of particular interest here is a blend obtained from PPC and PLA (poly(lactic acid)). Composites with various ratios of PPC to PLA were prepared in a two screw extruder and the physical properties were studied. It was found that the polymers are not miscible as follows from two separate and more or less composition indifferent glass transitions (Figure 4; PPC with Mw of 250 kDa and PLA with Mw of ±150 kDa). No evidence for transesterfication reactions between PPC and PLA is found. The molecular weights and distributions of the composites are simply the sum of the individual components within experimental error. The TEM analysis of the material shows a fine dispersion of PLA in PPC and visa versa, indicative of a high compatibility (Figure 4). The mechanical properties of the blend – tensile strength, tensile modulus, yield strength – vary linear with composition between the extremes of the pure polymers.[21] This is all reminiscent of fairly compatible polymers. The latter is perhaps not too surprising since the molecular structures are very similar.

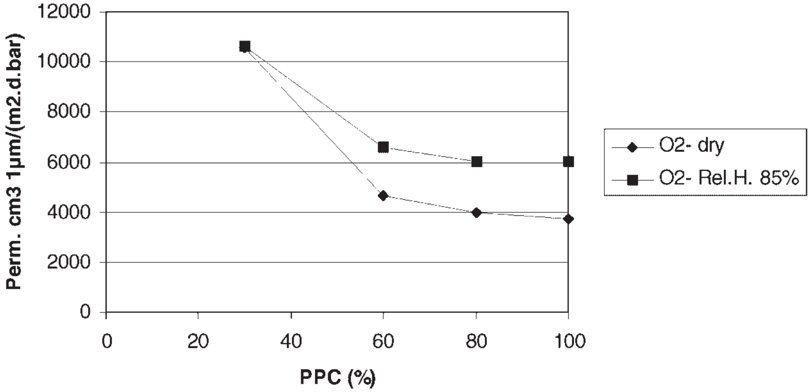


Figure 5.
Permeability of oxygen (dry and at a relative humidity of 85%) through films of PPC/PPLA.

The composites appear clear and transparent on account of a coincidental refractive index, a particular useful property for application as packaging material. For that reason, the permeability toward oxygen, carbon dioxide and water were determined. In PPC rich compositions, the permeability of oxygen changes moderately and about linearly (Figure 5), and starts to increase rapidly as PLA becomes the major compound. This probably illustrates a change in the continuous phase. A similar behaviour is found for water and carbon dioxide.

Thus a toolbox for a composite dependent adjustment of properties is found in the PPC/PLA blend. It has a large sustainable component making it attractive in the current view of renewable chemistry: PLA is prepared from an agricultural source and about 60% of the mass of PPC results from either oxygen or CO_2.

Conclusions

In light of the current interest on sustainable and biodegradable polymers, PPC has gained new interest. The catalytic process mediating the alternating copolymerization is understood in a more detailed fashion, as probably the controlled ring opening of epoxides involves coordination to metal centre followed by a backside attack of a *metal* coordinated nucleophilic chain end. The material properties of PPC can be extended by forming a transparent composite with PLA.

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