Synthesis of perfectly alternating carbon monoxide/olefin polyketones using a sulfonated diphosphine catalyst system
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Summary

This thesis presents the results of a study aimed at the co- and terpolymerization of carbon monoxide, ethylene and propylene to produce alternating aliphatic polyketones.

The copolymerization of carbon monoxide and an olefin was first achieved in 1941 by Farbenfabriken Bayer. The polymer was produced by the free-radical copolymerization of ethylene and carbon monoxide and the polymer was characterized as a random (non-alternating) polyketone. The reaction conditions were extreme, i.e., 400 bar and 250 °C. The first perfectly alternating polyketone was synthesized at the Badische Anilin und Soda-Fabrik Aktiengesellschaft in 1951 (Scheme 1).

Scheme 1. Perfectly alternating ethylene carbon monoxide polyketone (poly-3-oxotrimethylene, PK-E).

Since the first synthesis of aliphatic polyketones most research in the field of olefin/carbon monoxide copolymerization has been carried out on the production of perfectly alternating ethylene/carbon monoxide copolymers (PK-E). The reasons for this focus on PK-E are:

- The base materials are readily available and ethylene and carbon monoxide are relatively low-cost monomers.
- The product PK-E is known to have interesting engineering plastic properties, typical for polymers with a high density of heteroatom functionalities.
- PK-E has unique chemical and physical properties, e.g. mechanical properties, photodegradability, biodegradability and chemical resistance.
- New materials can be derived from PK-E by functionalizing the carbonyl groups.

This polymer has been characterized as a highly crystalline material with a melting point of approximately 260 °C. However, processing of the polymer was found to be extremely difficult as the material starts to degrade at this temperature. So far, the most successful method to make PK-E more processable was achieved by incorporating propylene, thus producing a polyketone terpolymer of ethylene, propylene and carbon monoxide (PK-EP, Scheme 2).
The incorporation of propylene as comonomer lowers the melting temperature of the polyketone. For example PK-EP containing 15-20 % propylene has a melting temperature in the range of 160-170 °C. This decrease in temperature means that the polyketone can be processed at a lower temperature without significant product degradation, while the PK-EP terpolymer still has all the interesting engineering plastic properties of PK-E. Despite this significant improvement in the processing window, the synthesis of PK-EP has not been studied as extensively as PK-E. The synthesis of PK-EP introduces new challenges to the polymerization, such as lower catalyst activities due to the more difficult propylene insertion. The propylene insertion also introduces new features to the polyketone formation such as regio- and stereoselectivity.

The objective of this project was the development of an efficient and recyclable catalyst system for the copolymerization of carbon monoxide and olefins. To achieve this objective two palladium based catalyst systems, 

\[
[Pd(BDOMPP)][TFA]_2, 1,3\text{-bis(di-(o-methoxyphenyl)-phosphino)propane}
\]

and 

\[
[Pd(BDOMPP-S[H]_4)][TFA]_2, 1,3\text{-bis(di-(o-methoxy-m-sulphonatophenyl)-phosphino)propane}
\]

were studied in more detail.

In Chapter I, the current state of art of alternating polyketone synthesis was summarized. Available literature on catalyst systems, reaction mechanisms, applied reaction solvents and monomer types was reviewed.

Chapter II described the synthesis of PK-EP using the 

\[
[Pd(BDOMPP-S[H]_4)][TFA]_2
\]

catalyst system in a methanol, water, acetic acid and methyl acetate solvent mixture (the Mix). By studying the effect of these four solvents separately, and in combination, a better understanding of the solvent effect on catalyst performance was obtained.

The best catalyst performance was achieved in the Mix, i.e., 3.52 kg PK-EP (g Pd)^{-1} hr^{-1}. Not only the catalyst activity was better, but also the stability of the catalyst was observed to be better in this solvent. The experimental results showed that the highest initial activity is achieved in a solvent containing methanol and water. Methanol is needed for high monomer solubility and water for its promoting effects. But because of the low stability of the catalyst in methanol, acetic acid is needed to improve the stability needed for a high average activity.

In all the solvents the catalyst mechanism was found to be the same. The molecular weight (M_n) of the produced ter-oligomers was between 2000 and 5000 g/mole.

By studying the reaction profile a new phenomenon, so far not observed in PK-EP synthesis, was found. At a certain stage during the reaction the initially
decreasing catalyst activity started to recover to reach approximately its initial activity.

The synthesis of PK-EP was further studied using the \([\text{Pd}(\text{BDOMPP}-\text{S}[\text{H}_4])][\text{TFA}]_2\) catalyst system in the Mix under different reaction conditions in Chapter III. A more detailed study was carried out to understand the catalyst recovery phenomenon observed in Chapter II. The parameters investigated were: palladium concentration, reaction time, reaction temperature and HTFA concentration.

A higher palladium concentration increases the productivity and leads to a sooner recovery of the catalyst activity. As expected the reaction time also affects the recovery process.

A decrease in reaction temperature from 96 to 85 °C did not affect the catalyst activity. Interestingly, the polymer microstructure and the molecular weight of the polymer were altered by the decrease in temperature.

At TFA/Pd molar ratio’s of 0, 4 and 30 the average catalyst activity is respectively 3.09, 3.52 and 2.79 kg PK-EP (g Pd)\(^{-1}\) hr\(^{-1}\). Interestingly the catalyst remains active without any addition of acid counter-anion.

Chapter IV presents the results of studies aimed at creating basic understanding concerning the phenomenon that the addition of particular salts to the reaction system enhances the activity of the used catalyst. The salts were varied in type of cation and anion, and in ion-charge. This salt effect was studied with the \([\text{Pd}(\text{BDOMPP}-\text{S}[\text{H}_4])][\text{TFA}]_2\) and \([\text{Pd}(\text{BDOMPP})][\text{TFA}]_2\) catalyst systems in different solvents.

The results showed that the addition of salts like \(\text{Na}_2\text{CO}_3\), \(\text{Li}_2\text{SO}_4\), \(\text{FeSO}_4\) and \(\text{Na}_2\text{SO}_4\) to the reaction in the Mix have the capability of increasing the average catalyst activity from 3.52 (no salt) to 5.29 (\(\text{Na}_2\text{CO}_3\)) kg PK-EP (g Pd)\(^{-1}\) hr\(^{-1}\). When the catalyst activity profiles of these experiments were studied an important observation was made. The average catalyst activity was essentially equal for most of the salts, although the activity profiles were not. The initial activities were different, which had an effect on the time required before the catalyst activities started to recover. The addition of crown-ether to the reaction mixture showed that this salt enhancement effect is mainly induced by the anion of the salt.

In general, the salts did not have a significant effect on the microstructure of the ter-oligomers; however the anions had an effect on the molecular weight of the ter-oligomers.

A similar salt effect was observed in other solvents such as methanol and a water/acetic acid solvent mixture.

Interestingly the salts did not have an effect on the performance of the non-sulfonated \([\text{Pd}(\text{BDOMPP})][\text{TFA}]_2\) catalyst system in the Mix.

In Chapter V, five different catalyst systems based on BDOMPP-type ligands were studied in the synthesis of PK-EP. These catalyst systems were \([\text{Pd}(\text{BDOMPP})][\text{TFA}]_2\), \([\text{Pd}(\text{BDOMPP})(\text{Bipy})][\text{PF}_6]_2\), \([\text{Pd}(\text{BDOMPP}-\text{S}[\text{H}_4])][\text{TFA}]_2\) and \([\text{Pd}(\text{CH}_3)(\text{CH}_3\text{CN})(\text{BDOMPP-S}[\text{Na}_4])][\text{PF}_6]\) or \(-[\text{OTf}]\). The performance of the catalyst systems and their effects on polymer microstructure and molecular weight was studied in a methanol/water/acetic acid/ methyl acetate solvent mixture (Mix) and in a methanol/water (MeOH/H\(_2\)O) solvent mixture.
In MeOH/H$_2$O the sulfonated catalyst systems were much more active than the non-sulfonated ones, while in the Mix the results were opposite. The performance of the combined catalyst system containing Bipy was identical to that of the regular BDOMPP catalyst. The microstructure of the polymers was essentially the same with all the five catalyst systems and in both the solvents, while the molecular weight was altered.

The alternating copolymer of propylene and carbon monoxide, PK-P, (poly-(1-oxo-2-methyltrimethylene) is another type of polyketone with interesting physical properties, Scheme 3. PK-P has a lower processing temperature compared to PK-E and PK-EP, which is interesting for industrial applications.

![Scheme 3. Copolymerization of propylene and carbon monoxide into PK-P.](image)

Chapter VI describes the preparation of PK-P with the BDOMPP and BDOMPP-S[H]$_4$ based palladium catalyst systems in methanol and the Mix.

Both catalyst systems showed a higher catalyst activity and stability in the Mix than in methanol. With both BDOMPP and BDOMPP-S[H]$_4$ as the catalyst system, in both the solvents, the catalyst mechanism remained the same. The molecular weight of the copolymers was higher in the Mix than in methanol with both catalyst systems.