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Copolymerization of Ethylene and 4-Penten-1-ol Using an Aryl Sulfonate Phosphine Palladium Catalyst

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Copolymerization of Ethylene and 4-Penten-1-ol Using an Aryl Sulfonate Phosphine Palladium Catalyst

A Graduate Thesis Presented

By

Shuo Lin

Submitted to the Graduate School of Rochester Institute of Technology

in partial fulfillment of the requirements of the degree of

Master of Science

October 30, 2011

Center for Materials Science and Engineering.

College of Science
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Copolymerization of Ethylene and 4-Penten-1-ol using an Aryl Sulfonate Phosphine Palladium Catalyst

A Graduate Thesis Presented

By

Shuo Lin

Approved as to style and content by:

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Dr. KSV Santhanam, Department Head,
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Dedication

I would like to dedicate this work to my parents Mr. Jiandi Lin and Mrs. Yujing Yang Lin. It’s their love and inspirations that make me keep pursuing my academic goal.
Acknowledgements

I would like to thank Dr. Massoud (Matt) Miri. It is his help and guidance that made me able to complete my research project. His profound understanding in Chemistry and Polymer Science largely impressed me. The experience of learning chemistry and doing research with him is memorable.

I would also like to thank Dr. Kalathur (KSV) Santhanam for his time, financial support and help throughout my Master Degree study. I would also like to thank Dr. Gerald Takacs for his time, support and guidance for my research and thesis writing.

I want to thank the members of our research team: Elizabeth Bennett, Rebecca Andrew, Dieter Scheibel, and Laura Parisi, who helped me a lot in experiments and are nice people to work with, bringing me a lot of fun and introducing me the American culture. I would like to thank Dr. Sandip Sur (University of Rochester) for providing us with the 2D-NMR spectra. I am grateful to Dr. Hunaid Nulwala for his help with NMR related literature references. I would like to thank all the people in the Department of Chemistry and the Center for Materials Science and Engineering, who gave us a lot of support. I also want to thank everyone in the Chemistry Stock room who were always patient to help me to find anything I needed. I would like to thank Tom Allston for training me on the instruments, which I have largely used throughout the whole project. I would like to thank Dr. Sophia Maggelakis, Dean of the Collage of Science and Sponsored Research Services.

Finally, I want to thank my parents. It is their love, encouragement, support and help made me able to complete this Master Degree.
Abstract: Copolymerization of Ethylene and 4-Penten-1-ol using an Aryl Sulfonate Phosphine Palladium Catalyst

Our goal was to investigate the copolymerization of ethylene with 4-penten-1-ol using an aryl sulfonate phosphine catalyst. In addition to several polymerizations of ethylene, used as control runs, more than a dozen copolymerizations were conducted at reasonable yields. As a main variable in these runs, we changed the comonomer concentration (ca. 0.10 to 2.82 mol/L). However, also the influence of polymerization time (1 h versus 21 hours runs), temperature (80 versus 95 °C), and catalyst concentration (160 μmol/L versus 820 μmol/L) was determined. Activities for all the runs were determined. For the first time, the $^{13}$C NMR spectra of the copolymers were analyzed and all peak assignments made. In addition, $^1$H NMR spectra were completely analyzed. Based on these spectra, the comonomer contents in the copolymers could be determined. The reactivity ratios for ethylene and 4-penten-1-ol were determined using the methods of Fineman-Ross and Kelen-Tüdös. Molecular weight properties measured by GPC are reported, as well as DSC-based melting temperatures. Some TGA measurements were conducted to determine the heat stability and purities of the copolymers. Finally the nature of the mechanism of the polymerization, coordinative as expected or radical, has been also discussed.
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1 Introduction
Ziegler-Natta catalysts represent important coordinative polymerization initiators and facilitate polymerizations at low temperatures and low pressure. In 1952, after E. Holzkamp accidentally discovered the Ni effect\[^\text{1}\] the nature of these metal polymerization catalyst caught Karl Ziegler’s interest. They observed that the polymer obtained with the zirconium catalyst was linear. They further studied the titanium/Al-aryl catalytic system, TiCl\textsubscript{4}, and Al(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}, in a hydrocarbon solvent, which provided a much higher activity. Giulio Natta was intrigued by Ziegler’s research, and in early 1954 his group produced for the first time, isotactic polypropylene with the catalytic system, TiCl\textsubscript{3}/AlEt\textsubscript{2}Cl.\[^\text{2,3}\] In 1955 Ziegler and Natta’s group verified that the polymerization conditions can be mild in contrast to the radically initiated polymerization of ethylene.\[^\text{4}\]

The second generation of Ziegler/Natta catalysts involves the application of solid state chemistry to change β-TiCl\textsubscript{3} into δ-TiCl\textsubscript{3}, in order to get a higher stereoselectivity and activity. In 1960s, the use of MgCl\textsubscript{2} as a support was applied for the improvement of activity. Approximately 10 years after the discovery of the Ziegler-Natta catalyst, a fourth type of compound in this catalytic system was added— a Lewis base, as an electron donor. This improved the stereoregularity of the products. The Ziegler-Natta catalysts, based on all four components, are considered the third generation of this catalyst family.\[^\text{2}\]

The major disadvantage of the third generation of Ziegler-Natta catalysts is that the
active centers are not uniform. This occurs because TiCl\textsubscript{x}-type compounds have several different types of crystalline forms (TiCl\textsubscript{4} has four types, while TiCl\textsubscript{3} has three), some of them are stereoselective while some are not, and the activities of the different crystal types are different.\textsuperscript{[2]}

In contrast to the Ziegler-Natta catalysts, which one can consider “multi-site” catalysts, the metallocene or Kaminsky catalysts, which were discovered at the end of the 1990s, represent defined active species and, therefore, are called single-site catalysts. By serendipity, less-experienced students in Kaminsky’s group had moisture from the air enter their polymerization systems. However, these students obtained higher polymerization activities. Further studies by this group resulted in the use of methyl aluminoxane as a cocatalyst, resulting in polymerization activities that surpassed those of industrial catalysts known at that time.

The metallocene catalysts have several advantages compared to the traditional Zeigler-Natta catalysts. As a homogeneous catalytic system, their activities are more than 10,000 higher than the original Ziegler-Natta catalysts. They can polymerize additional types of terminal olefins and cyclic olefins such as cyclopentene. They exert higher stereoselectivity, and their selectivity can be further controlled by structural modification of the aromatic groups bonded to the transition metal. They result in much narrower molecular weight distributions, typically around 2, which was not achieved by the traditional Ziegler-Natta catalyst\textsuperscript{[2,3,5]}. 
The mechanism of metallocenes polymerizations is shown in Figure 1.1.

After forming the active species with methylalumoxane (MAO), ethylene is coordinated into the vacant site. The complexation is a relatively fast step. The double bond of the monomer undergoes a syn-addition forming a four-membered transition state. The monomer’s two carbon atoms are then inserted between the transition metal atom and the carbon atom to which the metal atom had been previously bonded. Therefore, the original $\alpha -$ agostic hydrogen becomes a $\gamma -$agostic hydrogen. At the end of the cycle, a new vacant site forms and another
insertion can proceed.

One critical problem that remained to be solved was how to copolymerize polar olefins. Due to high oxophilicity of early transition metals, metallocenes could not polymerize functional olefin. Researchers in the polymerization area turned to the Shell Higher Olefin Process (SHOP) to search for the answer. The catalyst SHOP, developed by Keim et al. [6] in the 1970s (Figure 1.2), produces oligomers of olefins. This production is due to the late transition metal catalyst generally exhibiting reduced activities for olefin insertion relative to earlier transition metal catalysts, and β-hydride elimination typically competes with chain growth, resulting in the formation of dimers or oligomers [7]. In 1985, Starzewski et al. [8] showed that the SHOP catalyst was modified into a new type of catalyst that could be used to polymerize ethylene by modifying the ligand and allowing it to have a π bond connected to the Ni metal center (Figure 1.3).

![SHOP catalyst by Keim et al.](image)
In 1995 Brookhart reported that planar Ni- and Pd-based α-diimine catalysts overcame the shortcomings of previous late transition metal SHOP catalysts not to polymerize ethylene to high molecular weight polymers. These types of catalysts possess imine bonds as part of the ligand (Figure 1.4), with bulky aryl groups connected to the N-atoms. The bulky ligand supports the coordinate sphere of the plane, thus, the growing polymer chain can stay coordinated to the metal center and reach high molecular weight. These catalyst systems still depend on MAO for activation. Also, studies showed that if no bulky groups are present, oligomers are formed.

The α-diimine bearing catalysts also have the interesting feature to cause it
branching due to “chain walking”, illustrated in Figure 1.5\textsuperscript{[10]}. Due to $\beta$-hydrogen elimination the chain can separate from the catalyst with a double bond forming at the $\alpha$-carbon. This newly formed olefin then is inserted into the growing chain resulting in a branch. The length of the branches formed by this mechanism depends on the catalyst type and the polymerization conditions, the length of the branches varying from methyl to hexyl or even longer. By modifying the polymerization conditions, the product could be changed from highly crystalline high density polyethylene (HDPE) to amorphous polymer with glass transition temperatures of for example -50°C.

Also iron and cobalt were applied instead of nickel and palladium in catalysts with $\alpha$-diimine ligands. However, these resulted in low polymerization activities.\textsuperscript{[11]}

Figure 1.5  Mechanism of chain walking.\textsuperscript{[10]}
Gibson et al.\textsuperscript{[12]} introduced a tridental iron based bisiminopyridyl catalyst in 1998, (Figure 1.6).

The ethylene homopolymerization activity of this iron-based catalyst was relatively high and even comparable to metallocenes, using again MAO as an activator.\textsuperscript{[5]} The tridental pyridine iron catalyst also can homopolymerize polar monomers. However, this catalyst cannot copolymerize polar monomers with ethylene. When ethylene and a polar monomer such as methyl acrylate are introduced in the polymerization, a blend of the two homopolymers is produced, because each of the two monomers forms its specific type active center.\textsuperscript{[12]}

Other similar polymerization catalysts based on group 8—10 transition metals with N-N chelating ligands have been developed.\textsuperscript{[13]} None of these catalysts is able to insert polar monomers in ethylene copolymerization.

Brookhart had shown that Pd as metal resulted in higher branching than Ni. The
only difference between the Ni and Pd centers is the Pd center tends to make more branches. Boussie et al\textsuperscript{[14]} applied this catalyst to polymerize ethylene and made up a method to characterize the catalyst. By the 2000s, many groups [10, 15,16] studied the insight of the Brookhart’s N-N ligand catalysts system. The results showed that with these catalysts, the monomers with strong polar groups could be incorporated into the ethylene chain, but the functional monomer just appeared as the end-groups of the branches.

By 1998 Grubbs\textsuperscript{[16]} reported a modification of a SHOP related catalyst, derived from Klein\textsuperscript{[17]} (Figure 1.7) in which R represents a bulky aryl or aryl group.

![Figure 1.7](image-url)

Figure 1.7 The catalyst developed by Klein et al. in 1996\textsuperscript{[17]}.

Grubbs\textsuperscript{[16]} developed salicylaldiminato catalysts that were highly active for ethylene polymerization. From the previous research of Brookhart’s group, it was known that the bulky group substituted on the ketimine nitrogen and the phenolic ring could block the axial faces of the metal center, retarding the rate of associative displacement. Thus, it can slow down the deactivation process and let the catalyst
approach a longer lifetime and higher polymer molecular weight. Using phosphine scavengers, which are necessary to create vacant sites for the complexation of monomers, high polymerization activities were realized. However, the catalyst works as single component catalyst if more labile ligands such as acetonitrile are applied. Using a similarly approach, in later years Grubbs applied bulky groups on the N-atom as well as on the benzene group in the salicyl portion of the ligand. Since this time, Grubbs compound became a single-component catalyst that can copolymerize polar monomer with non-polar monomer.

![Salicylaminato Ni Catalyst](image)

**Figure 1.8** One of the salicylaminato Ni catalysts by Grubbs et al.\(^\text{[18]}\)

The Grubbs catalyst can homopolymerize ethylene in the presence of water or copolymerize ethylene with polar monomer, such as norbornene acetate and CO. Later this type of catalyst was widely studied by many groups, who applied this catalyst in ethylene/MMA copolymerization using MAO as a cocatalyst. Rodriguez et al.\(^\text{[13]}\) also tried this catalyst with MMA/ethylene copolymerization, but with Ni(COD)\(_2\) as the cocatalyst.
By 2002, Drent, Pugh et al.\textsuperscript{[19]} published the first non-alternating CO/ethylene copolymerization with a new type of catalyst, a sulfonate aryl phosphine catalyst (Figure 1.9).

![Palladium(II) sulfonate aryl phosphine catalyst](image.png)

Figure 1.9  Palladium(II) sulfonate aryl phosphine catalyst\textsuperscript{[19]}.

This catalyst follows a coordinate-insertion path in incorporating ethylene and a polar monomer, e.g. methylacrylate(MA) into the chain, and it will not perform chain-walking, which means it results in a linear product. (Figure 1.10)
This catalyst has an extraordinary functional groups tolerance and a very good lifetime. The sulfonate group seems to be unique for the functional tolerances property. For this reason, the ligand yields such a high activity for ethylene copolymerization with a polar comonomer. By comparing the Keim-type ligands, Goodall \cite{21} made the following conclusion, “the good leaving nature of sulfonate group is critical to the success of this system.”

This catalyst is currently the state-of-art late-transition-metal-polymerization catalyst. In Figure 1.11 a summary of the development of late-transition-metal catalysts leading to the Pd aryl sulfonate catalyst is presented.
The Pd aryl sulfonate catalyst induced great interest among organometallic catalyst research groups worldwide. By now this catalytic system had been applied for different types of ethylene homo and copolymerizations\textsuperscript{[19-34]}. The results show
that:

1. This catalyst has an extremely long lifetime, much longer than Brookhart’s or Grubbs’ catalysts.
2. This catalyst has an “unusual functionality tolerance”. \cite{22}
3. It is a homogeneous, single-component catalytic system, making a phosphine scavenger or activator as a cocatalyst obsolete.
4. It yields linear products.

Ethylene polymerization showed that $M_n$ is around 6000-19000 and $M_w/M_n$ lies typically around 2 \cite{23}. For this catalyst, copolymerization was achieved between ethylene and the polar monomer for polar norbornene derivative, \cite{22} CO, \cite{19,25,26} N-vinyl-2-pyrrolidinone, acrylonitrile, \cite{27} vinyl acetate, \cite{28} vinyl ketone (BPh$_3$ as an activator was applied), \cite{29} aryl vinyl ethers, \cite{30} vinyl sulfones, \cite{31} alkylacrylate, \cite{20,32} N-iso-propylacrylamide. \cite{33} Nozaki et al. demonstrated that this ligand also can be applied to a nickel center. However, the Ni sulfonate/aryl-phosphine catalyst has a low activity, and the yield for homopolymerization of ethylene is poor. \cite{34}

Currently the best catalyst for copolymerizing ethylene with polar comonomer, the Pd sulfonate/aryl-phosphine catalyst attracts our group’s attention as well. Our main goal was to find another industrially relevant polar monomer that this catalyst can copolymerize with ethylene. Copolymers of ethylene with alcohol bearing groups could be commercially quite interesting leading to applications such as adhesives,
coatings, surface modifiers and water soluble binders. One interesting type of polar monomer that has not been evaluated with this polymerization system is one bearing a hydroxyl group. The functional group has a relatively high polarity. As is well known, alcohols, such as methanol, are used to quench polymerizations to obtain defined end points. We chose 4-penten-1-ol as our comonomer, because it has a few methylene groups acting as spacer groups, which could keep the palladium center from undergoing rapid deactivation reactions with the oxygen of the hydroxyl group. The desired copolymers could be useful as adhesives, coatings, laminates and other applications of moderately hydrophilic ethylene copolymers.
2 Experimental Part

All liquids with a required amount less than or equal to 200 ml were purified using this method.

1. A 250 mL 1 neck flask was set up.

2. The flask was prepared under argon with 3 Vacuum/Argon cycles, and pyridine was introduced using a warm disposable pipet.

3. The flask was put into liquid nitrogen to completely freeze the liquid, and then the vacuum was applied.

4. After a good vacuum was obtained inside the flask, the vacuum was shut off, and the flask was taken out from the liquid nitrogen and warmed to room temperature. Steps 3 and 4 were repeated until the vacuum reading at step three was above 200 torr.

5. Dried molecular sieves were put into the pyridine and were allowed to sit overnight.
6. The degassed and anhydrous pyridine was then transferred to a Schlenk flask with a needle and was kept in the flammable cabinet.

2.2. Purification of Solvent (Toluene)

Chemicals used:\textsuperscript{[24]}

a) Toluene anhydrous (99.98%): 1 L (from Sigma-Aldrich)

b) Sodium Metal: 1-1.5 g (From Alfa Aesar)

c) Benzophenone: 1.5-2.25 g (from Sigma-Aldrich)

The dose of sodium and benzophenone depends on the need, and the weight ratio between them is 2:3, respectively.

Procedure:

(Refer to Figure 2.1)

1. Toluene was used as the solvent for all the polymerization runs and for dissolving the catalyst. Because the catalyst is air sensitive, the toluene was distilled before use.
2. A two-liter, three-neck flask and a one-liter three neck flask are prepared with three times Vacuum/Argon cycles. The two-liter flask was used as the reflux flask while the one-liter flask was used as the collecting flask. A straight up reflux condenser was setup on the reflux flask.

3. About 1 L of toluene (1.5 L the first time the flask was filled) was introduced to the reflux flask together with the needed 2:3 ratio of sodium metal and benzophenone.

4. The toluene was heated to about 150 degree C to allow it to boil. The heat was provided by a heating mantel. Variac and Mental Minder were used to control the heating mantel’s temperature.

5. A bubbler was connected to the condenser in order to prevent the system from exceeding its maximum pressure limit.
6. The toluene refluxing was then run overnight (for at least 18 hours). The toluene was then collected and put in the receiver flask for distillation also via the reflux condenser (Figure 2.1). After the a sufficient amount was collected the toluene was transferred into a Straus flask for long term storage.

Figure 2.1  Toluene distillation apparatus.\cite{23,24}
2.3. Synthesis of the Palladium Aryl Sulfonate Catalysts:

All chemicals used in this thesis were all supplied by Sigma-Aldrich, unless it is specified.

During the entire procedure, it was important to keep in mind that this catalyst is very air sensitive. Therefore, before any experiments, the apparatus went through three Argon/vacuum cycles to clean out all the air in the system. During the experiments, it was critical to always use argon as the protection gas for any operation.

**Step 1: Synthesis of Lithiation of Anisole for Synthesis of Palladium Aryl Sulfonate Catalysts**

\[
\text{LiC}_6\text{H}_{13} \quad \text{TMEDA} \quad \text{MTBE} \\
\text{Anisole} \quad \text{Lithiated anisole}
\]

82 g (=0.76 mol) of anhydrous anisole was added to the flask, then 9.47 ml (=0.063 mol) tetramethyethylene diamine (TMEDA), and 100 ml anhydrous methyl-tert-butylether (MTBE). A solution of 254 ml hexyllithium (= 0.63 mol, 2.5 M in hexane) in 125 ml MTBE was added dropwise to the anisole solution while cooling the reaction flask to 0 °C. After the addition of the hexyllithium was
completed, the temperature was slowly brought to the reflux temperature (= boiling point of MTBE = 55.2 °C) and allowed to reflux for 8 hours.

After reflux, the solution was cooled down to room temperature. The solution was filtered using an air-free filter and the solid dried in the vacuum.

Product yield: 58.77g

Yield percentage: 81.8%

**Step 2: Synthesis of Aminophosphine for the Synthesis of the Palladium Aryl Sulfonate Catalysts**

![Reaction diagram]

This reaction is quite vigorous and needs to be carefully controlled. About 415 ml of anhydrous hexane were added to the reaction flask, followed by 86 ml phosphorous trichloride (= 0.983 mol). A solution of dried diethyl amine (= 1.97 mol) in 200 ml anhydrous hexane was added dropwise while cooling and staying close to 0 °C. (The total volume of hexane should then be 615 ml). The reaction temperature was raised to room temperature. The solution was stirred for another 2 hours.
The product flask was then separated under argon flow, and 175 ml hexane is added to the produced salt and the filtrate collected. The salt was washed repeatedly with hexane and added to the main filtrate.

A distillation apparatus was used to first remove the lower boiling by-products (the excess diethylamine, phosphorous trichloride, and hexane). The main product is then distilled under oil pump vacuum at 67°C. The final product will appear as a clear liquid.

Product yield: 87.19g
Yield percentage: 51.0%

**Step 3: Synthesis of N,N-diethylamino-bis(2-methoxyphenyl)phosphine (An₂PNEt₂)**

Produced by lithiated anisole (Step 1) reacts with aminophosphine (Step 2.)

Sixty-five g (= 0.57 mol) lithiated anisole was added to a reaction flask and dissolved
in 100 ml anhydrous methyl tert-butyl ether (MTBE). Then 39 ml (= 0.267 mol) Cl$_2$PNEt$_2$ was added in about 200 ml anhydrous MTBE through a drop funnel. A water/ice bath is then applied for cooling so the temperature in the reaction flask did not exceed 25 °C. The solution was stirred for another 4 hours at 25 °C (or room temperature).

In the reaction flask, 250 ml distilled water was added to the solution. A separatory funnel was used to extract the product with 2 x 100 ml regular MTBE. The combined organic layers were then washed with 2 x 100 ml distilled water.

The solvent was removed under vacuum using a rotovap. Then the product was further dried at ca. 50 °C under reduced pressure.

Product yield: 36.00 g
Yield percentage: 94.5%

Step 4: Synthesis of bis(2-methoxyphenyl)methoxyphosphine (An$_2$PO(OMe))

The An$_2$PNEt$_2$ was broken into smaller pieces, and 72.0 g of it (= 0.228 mol) were
placed into a reaction flask. 140 ml anhydrous methanol was added while stirring. Then the solution was refluxed for 4 hours. After cooling, the solvent was removed using a rotovap.

Product yield: 31.24g
Yield percent: 99.2%

Step 5: Synthesis of 2-(bis(2-methoxyphenyl)methoxyphosphino)benzenesulfonic acid – the main ligand

(Produced by reaction of benzene sulfonic acid with the product from Step 4.)

9.14 g (=0.0578 mol) of previously dried benzene sulfonic acid were added to a reaction flask and then 106 ml anhydrous THF while stirring. A solution of 44.0 ml of a 2.5 M hexyllithium (= 0.11 mol) was slowly added through the dropfunnel to cool the solution with an ice bath at about 0 °C. After the addition of the
hexyllithium solution was completed, the solution warmed up to room temperature and continued to be stirred for 20 hours.

A solution of 16.0 g (= 0.0579 mol) An$_2$P(OMe) in 35 ml anhydrous THF was prepared in a flask and added dropwise to the reaction flask at 20 °C and stirred for 16 hours.

To the reaction product 6 g (= 0.112 mol) ammonium chloride was added while stirring. The solvent was removed using a rotovap. 176 ml of distilled water was added to the product and the mixture transferred into a separatory funnel. Then the mixture was washed with 2 x 70 ml regular MTBE. The mixture was acidified to a pH of 2 by adding dropwise concentrated HCl. The product was then extracted with two portions each of 105 ml dichloromethane, CH$_2$Cl$_2$ (total: 210 ml). The product was dried over anhydrous MgSO$_4$ overnight and the solution filtered. The filtrate is then placed into a freezer at max. -20 °C and the solution allowed to crystallize in the freezer for two days. The color of the product is an opaque white.

Product yield: 3.72 g

Yield percentage: 16.8%
Step 6: Synthesis of Palladium Anisole Sulfonate Catalyst complex

(Produced by reaction of product from Step 5 with TMEDAPdMe₂ and Pyridine.)

All operations were performed under argon. All solvents and liquid reactants were degassed before starting this step. To a 100 ml flask 0.73 g (= 1.82 mmol) of the main ligand was added (the product of the step 5) along with 22.5 ml of THF, and it should be stirred so a suspension is formed. To this suspension 0.5 g (= 1.98 mmol) (TMEDA)PdMe₂ was added. The solution stirred for 30 minutes and then 0.67 ml (= 0.66 g = 8.33 mmol) pyridine was added to the reaction flask. The solution stirred for another 30 minutes. Precipitation of the product as an off-white solid may already occur. To cause further precipitation of the product, ca. 20 ml diethylether was added. Then the product was washed with diethyl ether. The flask is then placed in the freezer overnight. All solvents were removed and the product dried using an oil pump.

Product yield: 0.45g
Yield percentage: 40.7%

2.4. Polymerization Procedure

The polymers were prepared by a slurry process (for low comonomer concentration) or a solution process (high comonomer concentration) due to the solubility of the copolymers.

Procedure:

Scheme for copolymerization

Figure 2.2  Scheme for copolymerization

1. The reactor was purged three times with Argon/vacuum cycles at 80 °C.
2. The required volume of distilled toluene was transferred to the autoclave reactor (120 ml for total volume, 110 ml initially, another 10 ml used as the solvent for catalyst).

3. A dispersion of the catalyst (typically 20 mg for copolymerizations, 10 mg for ethylene homopolymerizations) was prepared in a separate flask in 10 ml toluene and stir for a couple of minutes.

4. While gently stirring, the catalyst solution was transferred via a 10 ml pipette to the reactor.

5. The required volume of comonomer to the reactor was added.

6. The addition of the ethylene was immediately started at 600 RPM stirrer speed.

7. The polymerization time for the runs was set to be one hour or 21 hours. The ethylene flow and the reactor temperature (shown on the display of the electric thermometer placed in the thermometer sleeve) was recorded once every minute for the polymerization. Also, the appearance and color of the solution was monitored in the beginning and when it changed.
8. To terminate the polymerization: ca. 15 ml methanol was added to the solution and stirred.

9. The polymer solution was poured into a beaker with about 300 ml methanol and stirred overnight.

10. The polymer slurry was filtered using a Buchner funnel. While the polymer was still wet, it was washed twice with methanol. Then the polymer was dried on the filter paper before it was placed into the oven at 60 °C.

2.5. Polymer Characterization.

NMR Spectroscopy (300 MHz, Bruker):

$^1$H Proton NMR spectrum and $^{13}$C Carbon NMR spectrum were acquired for all the polymers and the catalysts synthesized. H/H COSY are used for the selected sample, which had large amounts of 4-penten-1-ol comonomer added. A Bruker Avance 300 DRX is a 300 MHz with a 7 mm coil. Catalysts and ligands synthesized also were characterized using deuterated chloroform as the solvent. For polymers, about 100 mg of polymer was dissolved in d$_2$-1,1,2,2-tetrachloroethane. The probe temperature was about 120°C.
Differential Scanning Calorimetry

DSC 2010 by TA Instrument was used to determine the thermal properties of the polymers. The first cycle was done by ramping the sample 10 K/min to 165°C and was then kept isothermal for 2 minutes. The second cycle was recorded at 20 K/min to lower the temperature from 165°C to 20°C and at 10 K/min from 20°C to -165°C (or to 0°C if the Tg was not believed to be detectable) and was kept isothermal for 2 minutes. The third cycle was to raise the sample again from -165°C (or from 0°C) to 165°C. The third cycle was recorded at 10 K/min.

Fourier Transform Infrared Spectroscopy:

A Shimatzu IR Prestige-21 ATR was used to obtain a FTIR spectrum for certain polymer samples to determine and confirm the composition which was then compared to a known sample.

GPC Data:

The molecular weight and molecular number average data were provided by DOW Chemical Corporation. They were run in 1,2,4 trichlorobenzene at 150 °C. Polystyrene was used as the calibration standard and data are reported as polyethylene-apparent molecular weights.

The final catalyst product was tested with ¹H NMR Bruker 300MHz, with
chloroform-d\textsuperscript{1} as the solvent:

MePd(pyr)P(\text{-3-Me-6-SO}_3\text{C}_6\text{H}_3)(\sigma\text{-OMe-Ph})\text{2 catalyst:}

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \text{δ} 8.78 – 8.72 (s, 2H), 8.23 – 8.13 (m, 1H), 7.82 – 7.75 (s, 1H), 7.73 – 7.33 (m, 6H), 7.31 – 7.22 (m, 1H), 7.09 – 6.76 (m, 5H), 3.65 – 3.58 (s, 6H), 2.27 – 2.18 (s, 1H), 0.27 – 0.20 (d, J = 2.8 Hz, 3H).
3 Results and Discussion
3.1. Activity

Activity is here defined as weight of the product (in kg) of the run over the catalyst amount (in mol) times the polymerization time (in hour).

In Table 1 the information about the polymer synthesis is provided.

Table 1  Polymerization conditions, yields and activities.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (µmol/L)</th>
<th>Comonomer (mol/L)</th>
<th>Polymerization time (h)</th>
<th>Yield (g)</th>
<th>Activity kg/(mol Pd x h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1</td>
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<td>1.08</td>
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<tr>
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<tr>
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<tr>
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<td>1</td>
<td>0.23</td>
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</tr>
<tr>
<td>8</td>
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<td>20</td>
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<td>45</td>
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<tr>
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<td>25</td>
</tr>
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</tr>
<tr>
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<td>0.40</td>
<td>21</td>
<td>3.89</td>
<td>6</td>
</tr>
<tr>
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<td>4.41</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>1</td>
</tr>
<tr>
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<td>281</td>
<td>0.58</td>
<td>1</td>
<td>0.78</td>
<td>23</td>
</tr>
</tbody>
</table>

Ethylene: 7.6 bar; solvent: toluene; solution volume: 120 ml; Temperature: 80°C, except Entry 2 and Entry 9 at 95°C; Entry 17: run with 553 µmol/L galvinoxyl.
The main condition which was changed was the comonomer concentration. We used the ethylene polymerizations with the Pd-catalyst mainly as control runs for the copolymerizations. As expected, the run at the higher temperature (95°C) is more active, by about a factor of 4.

Figure 3.1 (a) shows the plot of the activity as a function of comonomer (4-penten-1-ol) concentration for 1h runs. An increase in the comonomer concentration results in a lower activity. This is mainly because the comonomer is less reactive than ethylene and lowers the rate of the copolymerization. A secondary effect of the comonomer is that its oxygen atom could react with the palladium center and deactivate a smaller portion of the catalyst.

In Figure 3.1 (b) change of the polymerization activity in dependence of the comonomer concentration is shown for the 1 hour runs (a) and the 21 hour runs (b). In both cases the activity drops as more comonomer is added; increased addition of relative small amounts of comonomer result in a more marked decrease in activity, while at high comonomer concentrations the activity is relatively low but stays almost constant as more comonomer is added.
From Table 1 the effect of a temperature increase from 80 to 95 °C results in an increase in activity. However, this increase for copolymerizations with 0.58 mol/L
comonomer (Entry 5 and Entry 9) is only by a factor of 1.6 and, therefore, not as high as in the case of the ethylene homopolymerizations (Entry 1 and Entry 2) for a factor of 4.13.

A tripling of the catalyst concentration causes a decrease of the polymerization activity by about 29%. This decrease is due to the definition of the activity. Since the catalyst amount is in the denominator of the unit of the activity, generally a sufficiently large increase in the catalyst concentration results in a decrease of activity, because polymer is not produced proportionally.

Interestingly, using approximately two equivalents of galvinoxyl, which typically reacts as radical scavenger, under conditions similar to one of the copolymerizations (Entry 5) led to only about a 18 % lower yield and activity (Entry 17). This can be used as evidence that the polymerization mechanism is proceeding as intended rather by a coordinative than by a radical mechanism.

The ethylene consumption versus the polymerization time for Entry 5 is shown in Figure 3.2. These curves resulted from the data obtained with a mass-flow meter measuring the ethylene flow during each polymerization.
a. 1 h run

![Graph showing ethylene consumption rates for Entry 5 and 16.](image)

b. 21 h run

![Graph showing ethylene consumption rates for Entry 5 and 16.](image)

Figure 3.2   Ethylene consumption rates for Entries 5 and 16 (a and b, respectively).

From Figure 3.2.a, it is obvious that the ethylene flow rate is very high at the beginning and decreases as copolymerization continues to reach a minimum after which the rate stays relatively constant. The high flow rate in the beginning comes
from the ethylene saturation process for the autoclave. After the toluene is saturated with ethylene (after the first 5-10 min), it was observed that the catalyst nearly maintained a constant activity throughout the whole polymerization process. This curve shows that the catalyst will get slightly deactivated as the copolymerization continues.

Polymerization activities were also monitored for the 21 hour runs. As shown in Figure 3.2.b the activity during this longer run gradually decreases over the first 3 to 4 hours after which it reaches a lower level. However, polymerization also continues after 10 hours and up to 21 hours.

3.2. Evaluation of $^1$H and $^{13}$C NMR Spectra and Determination of 4-Penten-1-ol Content in Copolymers

There was only one $^1$H NMR spectrum of ethylene/4-penten-1-ol copolymer found in the literature.$^{[37]}$ It was produced with a salicylaldiminato nickel catalyst using Al(isoBu)$_3$. The aluminum alkyl had to be added as protective agent to mask the oxygen of the alcohol from the nickel catalyst center. The copolymer in this case contained less than 2 mol% comonomer and was highly branched. No $^{13}$C NMR spectrum of the copolymer has been reported in the literature.

3.2.1. $^1$H NMR Spectrum of Polyethylene obtained with Pd-Catalyst
To make the peak assignments, it is first necessary to determine the peaks that are obtained in the $^1$H NMR spectrum for the polyethylene with the Pd-catalyst. Figure 3.3 shows such a spectrum for the polyethylene produced at 80 °C.

Besides the main peak at about 1.28 ppm, it also contains smaller peaks at 1.17 and 0.96 ppm, respectively. The peak at 1.17 ppm is caused by methine proton, whereas the triplet at 0.96 ppm results from the presence of the methyl protons. Based on this spectrum the total number of methyl groups (at the chain ends and along the chain) amounts to ca. 3 branches per 1000 C-atoms, as also was reported earlier.
Furthermore Drent reported these H NMR chemical shifts for possible end-groups:

![Chemical shifts](image)

Figure 3.4 The starting group and the endgroup values from Drent.\cite{20}

3.2.2. $^{13}$C NMR Spectrum of Polyethylene

In Figure 3.5 the $^{13}$C NMR spectrum of polyethylene produced with the Pd-catalyst is shown.

![C NMR spectrum of polyethylene](image)

Figure 3.5 $^{13}$C NMR spectrum of polyethylene (Entry 1)\cite{23,34}
The smaller peaks for carbons 10 and 11 are for simplicity not shown in Figure 3.5. They form smaller peaks at a lower field at 139 and 114 ppm, respectively.

3.3. NMR Predictions, Literature Spectra and Model Substances to Determine Peak Assignments for the Ethylene/4-Penten-1-ol Copolymers

3.3.1. NMR Predictions

We initially used NMR prediction programs to make rough assignments of the peaks in the $^1$H and $^{13}$C NMR spectra for our ethylene/4-penten-1-ol copolymer, using Chemdraw, nmrdb.org (H NMR only), and MestReNova, with 4-heptacosyl-31-methyldononacont-91-en-1-ol (detail structure see Appendix I, Figure 5.1.1) to predict the chemical shifts in the main structures of our copolymers. In the following the chemical shifts for $^1$H NMR are given in regular font, and those for $^{13}$C NMR in italic font. The MestReNova predicted peaks assignments are shown below.

![MestReNova prediction peak assignment for ethylene/4-penten-1-ol](image_url)
copolymers 4-penten-1-ol pendent group segment.

3.3.2. Literature Spectra and Model Substances

We were able to find the $^1$H and $^{13}$C NMR chemical shifts for a set of dendrons shown in Figure 3.7 and Figure 3.8, which are very similar to the relevant segment of our ethylene/4-penten-1-ol copolymers.$^{[40]}$

![Diagram of NMR chemical shifts](image)

Figure 3.7 $^1$H and $^{13}$C NMR chemical shifts for a smaller dendron with similar structures as the ethylene/4-penten-1-ol copolymers.$^{[40]}$
Figure 3.8 $^1$H and $^{13}$C NMR chemical shifts for another larger dendron with a structure resembling ethylene/4-penten-1-ol copolymers.$^{[40]}$

The structure in Figure 3.8 is also useful because it has a longer chain resembling the main chain in the copolymer. It appears that the chemical shift of the tertiary proton decreases as longer chains are formed.

Also the following ethylene/1-hexene copolymer structure in Figure 3.9 is useful for identifying that the chemical shifts in the $^{13}$C NMR spectra for our copolymer’s ethylene main chain in the region close to the pendent group.
Figure 3.9 Chemical shifts for ethylene/1-hexene copolymer\textsuperscript{[38]}

For the confirmation of the chemical shifts of the nuclei closer to the hydroxyl group of the comonomer, the chemical shifts for 1-decanol, we obtained and used as model compound, given in Figure 3.10 can be used.

Figure 3.10 Chemical shifts for 1-decanol\textsuperscript{[41]}

A substance very similar to the copolymer of interest, which presents a structure, and which would be typical for a saturated chain-end segment by the comonomer is 4-methyl-decan-1-ol. This structure would be a result of a 2,1-addition of the
comonomer to a Pd-H species. The chemical shifts for the $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of this compound have been identified in reference 41 and are shown in Figure 3.11.

Figure 3.11 $^1\text{H}$ and $^{13}\text{C}$ NMR assignments for 4-methyl-decan-1-ol. Chemical shifts for $^{13}\text{C}$ NMR spectra given in italics.$^{[41]}$

To determine the possibility of unsaturated end-groups, formed by β-H elimination, we ran the NMR spectra of cis-4-decen-1-ol, and obtained the results shown in Figure 3.12.
Figure 3.12 $^1$H and $^{13}$C NMR chemical shifts for cis-4-decen-1-ol.$^{[41]}$

Because the incorporation of the comonomer is relatively low (max. 10%), most of the comonomer units can be expected to be incorporated as isolated units between ethylene units. The presence of homo $n$-ads, e.g. homotriads, of the comonomer, therefore should be less relevant, and the structure in the Nomenclature used for labeling the peaks in the H and C NMR spectra of the ethylene/4-penten-1-ol copolymer should represent the expected copolymer well. With Mestrec it can be predicted that a homodyad of the 4-penten-1-ol, indicating of a random monomer distribution, should produce a peak at about 39.4 ppm.
Figure 3.13  Nomenclature used for labeling the peaks in the H and C NMR spectra of the ethylene/4-penten-1-ol copolymer

Based on the polyethylene spectra and shown model compounds, the following peaks can be expected for the NMR spectra. In the $^1$H NMR spectra, H5 should appear at the lowest field among the protons of saturated groups at about 3.65 ppm. The polyethylene-related protons are expected to be again close to 1.28 ppm. Methyl protons should appear around 0.86 ppm. The assignments for the peaks for H2, H3, and H4 require further information.

In the $^{13}$C NMR spectra the peak for C3 again should be distinguished since it is the closest to the hydroxyl group and should appear at about 63 ppm. No major changes are expected for the chemical shifts of $S_{\beta\delta^+}$, $S_{\gamma\delta^+}$, and $S_{\delta^+\delta^+}$, which are in the main chain and further apart from the comonomers pendant chain. For the assignments of the chemical shifts for C1, C2, $T_{\delta^+\delta^+}$ and $S_{\alpha\delta^+}$ further data are
required.

3.2.3. DEPT-135 and DEPT-90 NMR

A DEPT-135 and a DEPT-90 spectra were taken to distinguish secondary carbons (here as positive peaks) from primary and tertiary carbons (here negative peaks) as given in Figure 3.14.

![Figure 3.14](image)

Figure 3.14  The stack plot of $^{13}$C NMR spectrum, DEPT-135 Spectrum, and DEPT-90 spectrum of an ethylene/4-pentene-1-ol copolymer (Entry 16)

The DEPT-135 spectrum together with the DPET-90 spectrum clearly indicates that the peak close to 38 ppm is due to a tertiary carbon, which is most likely the tertiary carbon formed by the comonomer. The tertiary carbon due to the presence of methyl groups and present in polyethylene is only showing faintly in this spectrum.
The methyl group at close to 14 ppm due to regular end groups can be also differentiated.

3.2.4. 2D NMR Spectra

3.2.4.1. COSY NMR

COSY NMR spectrum of ethylene/4-penten-1-ol copolymer (Entry 16) represents the COSY NMR plot for the copolymer with the highest content of comonomer (2.82 mol/L).

Figure 3.15  COSY NMR spectrum of ethylene/4-penten-1-ol copolymer (Entry 16)
An apparent relation exists between the peaks at about 3.70 ppm and 1.65 ppm. Since we are quite certain that the peak at 3.70 ppm is due to the methylene protons labeled as H5, we can conclude that the peak at 1.65 ppm is caused by the methylene protons H4. The integrals for these peaks have accordingly a 1:1 ratio. The only other peak that also has a 1:1 ratio with H5 and H4 and shows some relation to H4, is the peak at 1.28 ppm which therefore would represent the methylene protons H3. There is some interaction between the peak at 1.28 and the one at 1.18, the latter representing H2. Both H3 and H2 protons show interaction with the main proton H1. Finally the H5 protons at 3.70 ppm do show some interaction with the weakly presented peak at 2.20 ppm, indicating the latter being due to the proton of the hydroxyl group.

3.2.4.2. DQF-COSY NMR

To further study the region between 1.3 and 1.5 ppm in the H NMRs, the peaks of the main ethylene protons appear (H1) and overlap with the protons in their vicinity (at H2 and H3). A DQF COSY NMR also was taken, as shown in Figure 3.16.
In addition, some of the findings from the regular COSY NMR, the DQF COSY, indicate relation of the peak at 1.65 representing H4 protons with the main peak at 1.35 to 1.45 for H1, as well as the peak at ca. 2.20 ppm for the proton of the hydroxyl group (H6).

3.2.4.3. HSQC NMR

The influences between protons associated with directly bonded carbons in the copolymer can be studied using the HSQC NMR spectrum given in Figure 3.17.
The HSQC confirms that the protons at 3.70 ppm (H5) are connected to the secondary carbon bonded to the hydroxyl group (C3) at 63.0 ppm.

3.2.4.4. HMBC NMR

HMBC NMR provides information of interactions between protons and carbons, which are bonded but more than one or more atoms apart from each other. The HMBC NMR of the ethylene copolymer with the highest 4-penten-1-ol content is
shown in Figure 3.18.

Figure 3.18  HMBC NMR spectrum of ethylene/4-penten-1-ol copolymer (Entry 16).

From the HMBC it can be detected that the peak at 3.65 due to H5 interacts over the bonds of the pendant comonomer group with the peak at 29.5 ppm caused by the ethylene carbon atoms in the main polymer chain. It also can be observed that there is interaction between the peaks of the protons at 1.65 ppm and 1.28 ppm with the peaks at 29.5 ppm from the carbon atoms in the main chain (interaction going over two and one C-atom(s), respectively). There is also interaction between H4 (at 1.65) and the directly bonded C3 at 63.5 ppm. However, this effect is not produced when the HMBC spectrum of a copolymer with lower comonomer content is taken (1.53
mol/L, Entry 15) as shown in Figure 3.19.

![HMBC NMR spectrum of an ethylene/4-pent-1-ol copolymer produced with 1.53mol/L comonomer (Entry 15).](image)

Figure 3.19  HMBC NMR spectrum of an ethylene/4-pent-1-ol copolymer produced with 1.53mol/L comonomer (Entry 15).

3.2.5. Peak Assignments for $^1$H and $^{13}$C NMR Spectra of Ethylene/4-Penten-1-ol Copolymers

3.2.5.1. $^1$H NMR Spectra

In Figure 3.20 the $^1$H NMR spectrum of the ethylene/4-penten-1-ol copolymers with relatively high comonomer content and peak assignments are presented.
Peak Assignments:

Figure 3.20 $^1$H NMR spectrum of ethylene/4-penten-1-ol copolymer (Entry 16)

The peak integrals with ratios of 1:1 for the methylene protons in the pendant comonomer group verify the assignments. However, the integral for the methylene protons closest to the polymer’s main chain (H3) cannot be separated well from the
adjacent large peak and are, therefore, not as reliable. Also, the integral of the hydroxyl proton is lower than expected.

The $^1$H NMR peak for the copolymer with the highest comonomer content also shows small intensities in the lower field at about 4.90 ppm, which is indicative of some unsaturated chain ends of the type that also occur in polyethylene, and at about 5.35 ppm which could correspond to chain ends terminated by the comonomer.

3.2.5.2. $^{13}$C NMR Spectra

The peak assignments for the $^{13}$C NMR spectrum of the ethylene copolymer are presented in Figure 3.21.
Figure 3.21  Peaks assignments for 4-penten-1-ol/ethylene copolymer

Figure 3.22  Enlarged region of 27.6-32.4 of Entry 16 $^{13}$C NMR spectrum
Here the ratio for the integrals for C3 and $T_{5+6+}$ are as expected, 1:1. The peaks for C2 and C1 are so close to the main peak at ca. 29.5 ppm that their integrals cannot be clearly separated. However, the integral for C1 is only slightly larger than for C3. Since no peak at 33.15 ppm can be observed, the comonomer does not start a chain, resulting in the saturated structure shown in Figure 3.11. The relatively low intensities at ca. 129 and 131 ppm are indicative of the formation of unsaturated chain ends of the type shown in Figure 3.12.

3.3. Determination of reactivity ratios for the copolymerizations (at 80°C)*. [42]

Due to their different chemical structures, when two monomers copolymerize, their activities will be different. The monomer reactivity ratio is the coefficient, which is used to evaluate the copolymerization activity of each monomer, and represents the ratio of the related rate constants in a terminal copolymerization model. They are defined as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, in which 1 and 2 represent the monomers in a binary copolymerization process.

A summary of the feed ratios and monomer ratios in the copolymer is given in Table 2.
Table 2  Copolymerization data for the 80°C*.

<table>
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<tr>
<th>Entry</th>
<th>mol(ethylene) : mol(4-penten-1-ol)</th>
</tr>
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<tbody>
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<td></td>
<td>Feed</td>
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<tr>
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<tr>
<td>16a</td>
<td>0.072 : 0.34</td>
</tr>
</tbody>
</table>

*  Runs with other than 20 mg catalyst and 80 C temperature not included; these ratios are based on the average monomer ratios obtained from $^1$H and $^{13}$C NMR spectroscopy; $^a$: 21 hour runs.

3.3.1. Application of Fineman-Ross Method
If the reactivity of ethylene is set to be \( r_1 \) and the reactivity of 4-penten-1-ol to be \( r_2 \), then by the definition of the reactivity ratio of chain terminal model:\[^3\]

\[
y = x^{\frac{r_1+1}{r_2+x}}
\] (1)

When \( x \) is set to be the mol ratio of the two monomers at the start of the polymerization and the \( y \) is designated as the mol ratio of the two monomers at the polymerization product, using equation 1, a plot can be used to get the ratio of \( r_1 \) and \( r_2 \). Transforming equation 1:

\[
yr_2 + yx = x^2r_1 + x
\] (2)

Then:

\[
yr_2 = x^2r_1 + x(1 - y)
\] (3)

Then:

\[
r_2 = \frac{x^2}{y}r_1 + \frac{x(1-y)}{y}
\] (4)

Set \( F = \frac{x^2}{y} \) and \( G = \frac{x(y-1)}{y} \), so we get: \( G = Fr_1 - r_2 \) (5)

Therefore, \( F \) and \( G \) will be as follows:

<table>
<thead>
<tr>
<th>Table 3</th>
<th>( F ) and ( G ) value for 1h and 21h runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry</td>
<td>x value</td>
</tr>
<tr>
<td>4</td>
<td>1.652374</td>
</tr>
<tr>
<td>5</td>
<td>1.039956</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>0.782704</td>
</tr>
<tr>
<td>7</td>
<td>0.391352</td>
</tr>
<tr>
<td>10⁰</td>
<td>2.974273</td>
</tr>
<tr>
<td>11⁰</td>
<td>1.652374</td>
</tr>
<tr>
<td>12⁰</td>
<td>1.487137</td>
</tr>
<tr>
<td>13⁰</td>
<td>1.039956</td>
</tr>
<tr>
<td>14⁰</td>
<td>0.782704</td>
</tr>
<tr>
<td>15⁰</td>
<td>0.391352</td>
</tr>
<tr>
<td>16⁰</td>
<td>0.213057</td>
</tr>
<tr>
<td>Pure comonomer hypothesis run</td>
<td>0</td>
</tr>
</tbody>
</table>

a. 21h runs.

Plot G via F:
Figure 3.23  Fineman-Ross curve of the copolymerization system.

From Figure 3.23, for 1h runs: the \( r_1 \) is 39.715 and the \( r_2 \) is 0.0806. To enhance the accuracy of reactivity ratio results, the Kelen-Tüdős method was introduced.

3.3.2. Application of Kelen-Tüdős method

The Kelen-Tüdős method\(^{[42]}\) was implemented to help increase the accuracy of the reactivity ratio calculation results. The Kelen-Tüdős method was derived from the Fineman-Ross method. Thus, set (3) \( \eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha} \), \( \eta = \frac{G}{\alpha + F} \), and \( \xi = \frac{F}{\alpha + F} \).

Then plot \( \eta \) with \( \xi \), \( r_1 \) and \( r_2 \) can be calculated, and \( \alpha \) here is equal to \( \sqrt{F_{\text{Max}}F_{\text{Min}}} \).

From the previous F values obtained for all the runs the \( \alpha \) for this system is 0.0196436.
Therefore with the previous F and G values, $\eta$ and $\xi$ will then be (Table 4):

Table 4. The $\eta$ and $\xi$ values for all the runs:

<table>
<thead>
<tr>
<th>Entry</th>
<th>G</th>
<th>F</th>
<th>$\xi$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.628539</td>
<td>0.039384</td>
<td>0.667215</td>
<td>27.589357</td>
</tr>
<tr>
<td>5</td>
<td>1.014340</td>
<td>0.026639</td>
<td>0.575577</td>
<td>21.916035</td>
</tr>
<tr>
<td>6</td>
<td>0.752968</td>
<td>0.023274</td>
<td>0.542294</td>
<td>17.54457</td>
</tr>
<tr>
<td>7</td>
<td>0.368355</td>
<td>0.009000</td>
<td>0.314198</td>
<td>12.860131</td>
</tr>
<tr>
<td>10\textsuperscript{a}</td>
<td>2.949229</td>
<td>0.074489</td>
<td>0.791319</td>
<td>31.330726</td>
</tr>
<tr>
<td>11\textsuperscript{a}</td>
<td>1.625336</td>
<td>0.044678</td>
<td>0.694603</td>
<td>25.268990</td>
</tr>
<tr>
<td>12\textsuperscript{a}</td>
<td>1.459800</td>
<td>0.040653</td>
<td>0.674216</td>
<td>24.210456</td>
</tr>
<tr>
<td>13\textsuperscript{a}</td>
<td>1.012013</td>
<td>0.029059</td>
<td>0.596664</td>
<td>20.779380</td>
</tr>
<tr>
<td>14\textsuperscript{a}</td>
<td>0.751333</td>
<td>0.024554</td>
<td>0.555552</td>
<td>16.999375</td>
</tr>
<tr>
<td>15\textsuperscript{a}</td>
<td>0.364592</td>
<td>0.010473</td>
<td>0.347740</td>
<td>12.106195</td>
</tr>
<tr>
<td>16\textsuperscript{a}</td>
<td>0.188743</td>
<td>0.005180</td>
<td>0.208681</td>
<td>7.603301</td>
</tr>
</tbody>
</table>

\textsuperscript{a}. 21h runs.

Plot the $\eta$ and $\xi$ using the values shown above:
Therefore, the copolymerization reactivity ratios result in $r_1 + \frac{r_2}{\alpha} = 38.607$ and $\frac{r_2}{\alpha} = 1.109$. Therefore, $r_2=0.021785$, and $r_1=37.498$.

3.3.3. Summary and Copolymerization Diagram

Table 5 The final results of reactivity ratios calculation.

<table>
<thead>
<tr>
<th></th>
<th>$r_1$</th>
<th>$r_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineman-Ross curve</td>
<td>39.715</td>
<td>0.0806</td>
</tr>
<tr>
<td>Kelen-Tüdős curve</td>
<td>37.498</td>
<td>0.021785</td>
</tr>
</tbody>
</table>

The reactivity ratios determined by the Kelen Tudos method are generally considered more reliable than those determined by the Fineman-Ross method.
ratio product, $r_1 \times r_2$, is equal to 0.82, which is close to 1 and means that the monomer sequence distribution is essentially random. The presence of the peak at 39.4 ppm indicative of a homodyad also indicates that the copolymer is not alternating.

The incorporated comonomer mol fraction is plotted via the comonomer mol fraction in feed to get the copolymerization diagram of this catalytic copolymerization system. The data for the incorporated comonomer represent the averages from the $^1$H and $^{13}$C NMR measurements.

Table 6  Data for copolymerization diagram for 1 h runs

<table>
<thead>
<tr>
<th>Entry</th>
<th>Comonomer mol fraction in feed (mol%)</th>
<th>Comonomer incorporated mol fraction (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.377</td>
<td>0.018800</td>
</tr>
<tr>
<td>5</td>
<td>0.490</td>
<td>0.025500</td>
</tr>
<tr>
<td>6</td>
<td>0.561</td>
<td>0.036600</td>
</tr>
<tr>
<td>7</td>
<td>0.719</td>
<td>0.055500</td>
</tr>
<tr>
<td>10\textsuperscript{a}</td>
<td>0.252</td>
<td>0.008350</td>
</tr>
<tr>
<td>11\textsuperscript{a}</td>
<td>0.377</td>
<td>0.016100</td>
</tr>
<tr>
<td>12\textsuperscript{a}</td>
<td>0.402</td>
<td>0.018050</td>
</tr>
<tr>
<td>13\textsuperscript{a}</td>
<td>0.490</td>
<td>0.026166</td>
</tr>
<tr>
<td>14\textsuperscript{a}</td>
<td>0.561</td>
<td>0.038536</td>
</tr>
<tr>
<td>15\textsuperscript{a}</td>
<td>0.719</td>
<td>0.064002</td>
</tr>
<tr>
<td>16\textsuperscript{a}</td>
<td>0.824</td>
<td>0.102430</td>
</tr>
</tbody>
</table>

\textsuperscript{a}. This run is a 21h run.
From Table 5 we can have the calculated results of the reactivity ratios of this copolymerization system. We can make the theoretical copolymerization diagram with the average values from Table 5, then put the data listed in Table 6 into the plot and see how them fit:

![Copolymerization Diagram](image)

Figure 3.25  The copolymerization diagram for all the runs at 80°C and [catalyst]~275μmol/L

From 0 it is observed, with the calculated reactivity ratio values from section 3.3, the theoretical copolymerization diagram fits very well with our real experimental data, which indicated that the reactivity ratio values gained in section 3.3 truly reflected this copolymerization system.

3.4. Polymer Properties

The properties of all polymers are given in Table 7.
3.4.1. Comonomer Content

From Table 1 and Table 7, we can see that with varying amounts of the catalyst, this catalyst tend to yield a higher comonomer incorporation. Due to the larger catalyst addition amount, entry 8 has a lower activity while having a higher yield than entry 5.
Table 7 The comonomer incorporation, molecular weights, and melting temperatures for all the runs.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Comonomer (mol/L)</th>
<th>Comonomer content (mol%)</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>Polydispersity index (PDI)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>28540</td>
<td>11750</td>
<td>2.4</td>
<td>132.5</td>
</tr>
<tr>
<td>2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.00</td>
<td>0.00</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>130.5</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.47</td>
<td>21960</td>
<td>11200</td>
<td>2.0</td>
<td>127.8</td>
</tr>
<tr>
<td>4</td>
<td>0.36</td>
<td>1.88</td>
<td>9880</td>
<td>3940</td>
<td>2.5</td>
<td>119.6</td>
</tr>
<tr>
<td>5</td>
<td>0.58</td>
<td>2.55</td>
<td>8030</td>
<td>4030</td>
<td>2.0</td>
<td>117.0</td>
</tr>
<tr>
<td>6</td>
<td>0.77</td>
<td>3.66</td>
<td>4380</td>
<td>1750</td>
<td>2.5</td>
<td>110.8</td>
</tr>
<tr>
<td>7</td>
<td>1.53</td>
<td>5.55</td>
<td>6170</td>
<td>2850</td>
<td>2.2</td>
<td>102.3</td>
</tr>
<tr>
<td>8</td>
<td>0.58</td>
<td>3.21</td>
<td>6960</td>
<td>3440</td>
<td>2.0</td>
<td>114.5</td>
</tr>
<tr>
<td>9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.58</td>
<td>3.87</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>109.7</td>
</tr>
<tr>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.20</td>
<td>0.84</td>
<td>18290</td>
<td>9160</td>
<td>2.0</td>
<td>126.7</td>
</tr>
<tr>
<td>11&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.36</td>
<td>1.61</td>
<td>12130</td>
<td>5380</td>
<td>2.3</td>
<td>121.7</td>
</tr>
<tr>
<td>12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.40</td>
<td>1.81</td>
<td>8580</td>
<td>3720</td>
<td>2.3</td>
<td>120.2</td>
</tr>
<tr>
<td>13&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.58</td>
<td>2.62</td>
<td>6820</td>
<td>2740</td>
<td>2.5</td>
<td>117.1</td>
</tr>
<tr>
<td>14&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.77</td>
<td>3.85</td>
<td>4580</td>
<td>1890</td>
<td>2.4</td>
<td>111.8</td>
</tr>
<tr>
<td>15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.53</td>
<td>6.40</td>
<td>2190</td>
<td>1120</td>
<td>2.0</td>
<td>102.3</td>
</tr>
<tr>
<td>16&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.82</td>
<td>10.24</td>
<td>1360</td>
<td>820</td>
<td>1.7</td>
<td>60.07</td>
</tr>
<tr>
<td>17</td>
<td>0.58</td>
<td>2.02</td>
<td>5735</td>
<td>2583</td>
<td>2.2</td>
<td>115.7</td>
</tr>
</tbody>
</table>

a: Runs with the polymerization temperature at 95°C; b: 21 hour runs.

Entries 3--7 and entries 10--16 were designed to examine the effects of comonomer concentration on catalyst behavior in different polymerization running times. In this way it can be observed how the reaction time affects the polymerization results and
specifically how reaction time affects the catalyst lifetime and comonomer incorporation.

3.4.2. Molecular Weight Properties

From Table 7 it can be seen that the PDI values obtained coincide well with the ideal scenario of the catalytic polymerization, which were expected to result in an average value for $M_w/M_n$ of 2. Figure 3.25 and Figure 3.26 were obtained by plotting the number average molecular weights and the weight average molecular weights of the 1h and the 21h samples.

Figure 3.25 1h runs number average molecular weight verses 4-penten-1-ol concentration.
Figure 3.26 21h runs number average molecular weight verses 4-penten-1-ol concentration.

From the Figure 3.25 and Figure 3.26 it can be seen that as the amounts of 4-penten-1-ol increases, the copolymers tend to have lower number average molecular weight and lower weight molecular weight.

3.4.3. Melting Temperature

From Table 7, we can have the plots below:

For 1h runs
Figure 3.27 shows also that the melting temperature is lower as the comonomer incorporation rises. The higher incorporation mol percent of 4-penten-1-ol, the lower the degree of crystallinity the product achieves, resulting in a lower melting temperature.

For 21h runs
From Figure 3.28 it is easy to see that the melting temperatures obtained for the 21h runs have the same pattern as the 1h runs, which means that the amount of 4-penten-1-ol determines how much comonomer can be incorporated into the chain. As incorporation of the comonomer is increased, the regularity of the product chain is reduced, thus lowering the melting temperature.

3.4.4. Thermal Stability and Purity
Figure 3.29  TGA of a polyethylene sample produced with the Pd-catalyst (Entry 1).
From Figure 3.29 it is apparent that the catalytic system doesn’t yield much residue, which is expected. Because this catalyst can yield 1g and more product for only 20mg catalyst, and most of the catalyst residue were washed away by methanol washes after polymerization. The only residue left in the polymer is the Pd residue from the dead catalyst itself.

3.5. Coordinative versus radical polymerization mechanism

A free radical 4-penten-1-ol/ethylene copolymerization was attempted with AIBN
(azobisisobutyronitrile) as initiator. The reaction conditions were as follows:

Ethylene: 7.5 atm
4-Penten-1-ol: 1.5 ml
AIBN: 283 mg
Toluene: 200 ml
T = 60 °C
t = 18 h

No polymer was obtained in this run. Therefore it appears highly unlikely that the copolymers produced with MePd(pyr)P(-3-Me-6-SO3C6H5)(o-OMe-Ph)2 would be formed by a radical mechanism.

Also, the entry 17 run can serve as good evidence that the 4-penten-1-ol/ethylene copolymerizations followed a coordination copolymerization process. The entry 17 is a run with the same conditions as the entry 5, except 28 mg galvinoxyl was added as radical scavenger. The presence of galvinoxyl radical scavenger slightly lowered the comonomer incorporation (the entry 5 run resulted in ca. 2.55 mol % comonomer). The activity as well as the molecular weight were also lower. However, the galvinoxyl radical scavenger did not inhibit the formation of copolymer. Therefore, the copolymerization system is most likely following the coordinative mechanism, and not a radical mechanism.\[29\]
4 Conclusion
Copolymerizations of ethylene with 4-penten-1-ol were conducted, resulting in reasonable activities even when about 10 mol% of the alcohol were incorporated. As in the case of polyethylene activities are stable over a long time (> 20 h). At higher temperature (95°C versus 80°C) the catalyst is more active, resulting in higher comonomer incorporation and lower molecular weight. Also, a triple fold increase in catalyst concentration led to an increase in the comonomer content and drop in molecular weight.

Complete $^1$H and $^{13}$C NMR peak assignments have been made for these copolymers indicating that most of the comonomer is copolymerized by insertion. From the reactivity ratios of 4-penten-1-ol and ethylene, it can be affirmed that ethylene reacts about 37 times faster with its own kind than with the comonomer and that the monomer sequence distribution is random. Polyethylene-based weight average molecular weights are in the 10,000s at low comonomer content and decrease by a magnitude with increasing comonomer content. The polydispersity index is close to 2 as is typical for most single-site catalyzed polymers.

A copolymerization using galvinoxyl in addition to the palladium catalyst was conducted resulting in a moderately lower yield of a copolymer with the same properties as the control run. A separate attempt to copolymerize the monomers using a radical initiator did not yield any product. Both experiments indicate that the copolymers are formed as intended by a coordinative polymerization
mechanism.
5 References


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6 Appendix
5.1. Appendix 1: MestReNova NMR simulations model compounds

Figure 5.1.1 Structure of 4-heptacosyl-31-methyldononacont-91-en-1-ol
5.2. Appendix 2. $^{13}\text{C}$ NMR tests for all the samples:

Figure 5.1.2 $^{13}\text{C}$ NMR spectrum for the entry 1.

Figure 5.1.3 $^{13}\text{C}$ NMR spectrum for the entry 2.
Figure 5.1.4 $^{13}$C NMR spectrum result for the entry 3

Figure 5.1.5 $^{13}$C NMR spectrum result for the entry 4.
Figure 5.1.6 $^{13}$C NMR spectrum result for the entry 5.

Figure 5.1.7 $^{13}$C NMR spectrum result for the entry 6.
Figure 5.1.8 $^{13}$C NMR spectrum result for the entry 7.

Figure 5.1.9 $^{13}$C NMR spectrum result for the entry 8.
Figure 5.1.10 $^{13}$C NMR spectrum result for the entry 9.

Figure 5.1.11 $^{13}$C NMR spectrum for the entry 10:
Figure 5.1.12 $^{13}$C NMR spectrum for the entry 11:

Figure 5.1.13 $^{13}$C NMR spectrum for the entry 12.
Figure 5.1.14 $^{13}$C NMR spectrum for the entry 13.

Figure 5.1.15 $^{13}$C NMR spectrum for the entry 14.
Figure 5.1.16  $^{13}$C NMR spectrum for the entry 15

Figure 5.1.17  $^{13}$C NMR spectrum for the entry 16.
Figure 5.1.18  
$^{13}$C NMR spectrum for the entry 17.

Figure 5.1.19  
$^{13}$C NMR spectrum of cis-4-decen-1-ol
13C NMR (75 MHz, CD2Cl2) δ 130.68 – 130.39 (s), 128.83 – 128.56 (s), 74.30 – 73.32 (m), 62.46 – 62.20 (s), 32.85 – 32.59 (s), 31.36 – 31.10 (s), 29.16 – 28.90 (s), 27.09 – 26.83 (s), 23.62 – 23.36 (s), 22.25 – 21.99 (s), 13.57 – 13.30 (s). The peaks in 74.30 – 73.32 (m) are the peaks of the solvent as 1,1,2,2-tetrachloroethane.

5.3. Appendix 3. 1H NMR spectra for all the samples

Figure 5.3.1 1H NMR spectrum for the entry 1.
Figure 5.3.2 $^1$H NMR spectrum of the entry 2

Figure 5.3.3 $^1$H NMR spectrum of the entry 3.
Figure 5.3.4 $^1$H NMR spectrum of the entry 4.

Figure 5.3.5 $^1$H NMR spectrum of the entry 5.
Figure 5.3.6 $^1$H NMR spectrum of the entry 6.

Figure 5.3.7 $^1$H NMR spectrum of the entry 7.
Figure 5.3.8 $^1$H NMR spectrum of the entry 8.

Figure 5.3.9 $^1$H NMR spectrum of the entry 9.
Figure 5.3.10 $^1$H NMR spectrum of the entry 10.

Figure 5.3.11 $^1$H NMR spectrum of the entry 11.
Figure 5.3.12 $^1$H NMR spectrum of the entry 12.

Figure 5.3.13 $^1$H NMR spectrum of the entry 13.
Figure 5.3.14  $^1$H NMR spectrum of the entry 14.

Figure 5.3.15  $^1$H NMR spectrum of the entry 15.
Figure 5.3.16 $^1$H NMR spectrum of the entry 16.

Figure 5.3.17 $^1$H NMR spectrum of the entry 17.

Figure 5.3.18
5.4. Appendix 4. the DSC plots of all the samples.

Figure 5.4.1 the DSC plot of the entry 1.

Figure 5.4.2 the DSC plot of the entry 2.
Figure 5.4.3  the DSC plot of the entry 3.

Figure 5.4.4  the DSC plot of the entry 4.
Figure 5.4.5 the DSC plot of the entry 5.

Figure 5.4.6 the DSC plot of the entry 6.
Figure 5.4.7 the DSC plot of the entry 7.

Figure 5.4.8 the DSC plot of the entry 8.
Figure 5.4.9  the DSC plot of the entry 9.

Figure 5.4.10  the DSC plot of the entry 10
Figure 5.4.11  the DSC plot of the entry 11.

Figure 5.4.12  the DSC plot of the 12.
Figure 5.4.13  the DSC plot of the entry 13.

Figure 5.4.14  the DSC plot of the entry 14.
Figure 5.4.15    the DSC plot of the entry 15.

Figure 5.4.16    The DSC plot of the entry 16.
Figure 5.4.17  The DSC plot of the entry 17.