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Synthesis of copolymers of ethylene with 1-alkenes and 1,4-hexadiene using metallocene catalysts

Mark Pecak

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Synthesis of Copolymers of Ethylene with 1-Alkenes and with 1,4-Hexadiene using Metallocene Catalysts

By
Mark Pecak

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

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Rochester, New York
April, 2003**

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*Synthesis of Copolymers of Ethylene with 1-Alkenes and with 1,4-Hexadiene using
Metallocene Catalysts*

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Abstract:

Metallocene catalysts have been increasingly studied by industry and academic groups, and are starting to be applied commercially to produce a variety, among which are ethylene/1-alkene copolymers. This study was primarily concerned with ethylene/1-alkene copolymerizations using dimethylsilyl-bis(2-methyl-4-phenyl-indenyl)zirconium dichloride with methylaluminumoxane as cocatalyst.

The effect of the 4-phenyl group was shown to greatly increase the polymerization activity of ethylene as well as the copolymerization of ethylene and 1-hexene copolymers. The reactivity ratios, used to calculate the necessary feed ratios needed to create a copolymer with specific characteristics were also determined. The molecular weights, melting points, and glass transitions of the resulting polymers were examined. The activities of copolymerizations of ethylene and 1,4-hexadiene were found to have a diminished activity compared to copolymerizations of ethylene and 1-hexene.

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Thesis Goal:

The goal of this thesis was to study the binary copolymerizations of ethylene with 1-alkenes using metallocene/ methylaluminoxane (MAO) catalysts, specifically rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride. The activities of metallocene catalysts were to be compared for polymerizations with two 1-alkenes, 1-hexene and 1-octene. The amount of comonomer incorporation and the reactivity ratios were of primary interest. The influence of the comonomer concentration on the polymerization and the presence of a possible comonomer effect were to be determined. The dependence of the 1-alkene incorporation on the presence of the phenyl-group at the 4-position on the indenyl-ring was investigated. In addition, the catalyst of interest was also applied to the copolymerization of ethylene with 1,4-hexadiene.

Introduction:

Polyethylene is an important industrial commodity polymer, which has been in use for over 50 years. Its versatility and ease of processing make it a valuable resource to mankind. In the year 2000, about 15.4 billion pounds of high density polyethylene, and 17.9 billion pounds of low density and linear low density polyethylene were produced in the United States alone.¹

High density polyethylene is used for a wide variety of applications, some of which include: plastic bottles, food containers, plastic sheeting, lawn furniture, packaging materials, pipes, etc. Low density polyethylene is used for soft bags, some food containers, soft toys, etc. Depending on the type of application a specific type of ethylene polymer might be more desirable. For instance, a plastic lawn chair would be made of

HDPE rather than LDPE because of the added strength, whereas a plastic bag might be made of LDPE because it is softer and more malleable.

In the 30's, polyethylene was made via radical polymerizations at elevated temperatures and pressures. This kind of polyethylene tends to have large amounts of branching due to backbiting, a chain transfer reaction. Polyethylene with branches of different sizes is referred to as low-density polyethylene (LDPE).

In the 50's Ziegler discovered that linear polyethylene, chains with no or very few branches referred to as high-density polyethylene (HDPE), could be produced at moderate temperatures and pressures using a coordination catalyst system. In order to reach a larger market, companies using coordination catalysts for the production of HDPE can polymerize with ethylene and a 1-alkene, such as 1-hexene, to produce linear low-density polyethylene (LLDPE).

The side branches cause the polymer chains to be further apart, so they cannot be packed as close to one another, thus decreasing the density. With little or no side branching, the polymer chains can form a tighter structure resulting in a higher density. Figure 1 shows the difference in the branching of the different polyethylenes. LDPE and LLDPE typically have densities around $0.91\text{-}0.93\text{ g/cm}^3$, while HDPE has densities around $0.95 - 0.97\text{ g/cm}^3$.¹ In addition to differences in density, HDPE has a higher tensile strength, stiffness, and chemical resistance.²

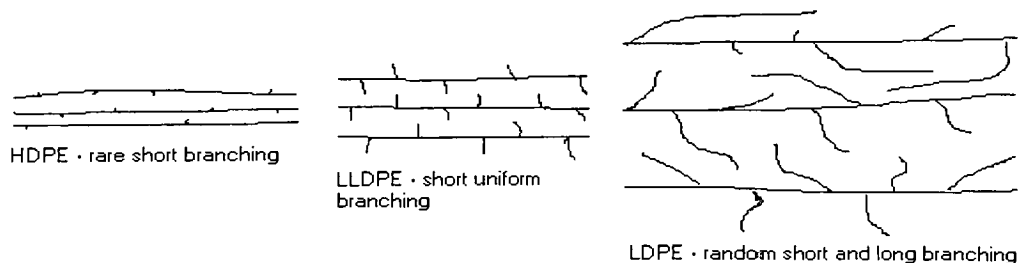


Figure 1: Branching in HDPE, LDPE, and LLDPE

Homopolymers of 1-Alkenes can have three possible orientations of the side-groups. Figure 2 shows the corresponding orientations as Fisher projections. The first possible orientation is atactic; in which the side-groups are oriented randomly. The second possibility is isotactic, in this configuration all the side-groups are attached to the backbone of the polymer in the same position. The last configuration is syndiotactic in which the position of the side-groups alternate.

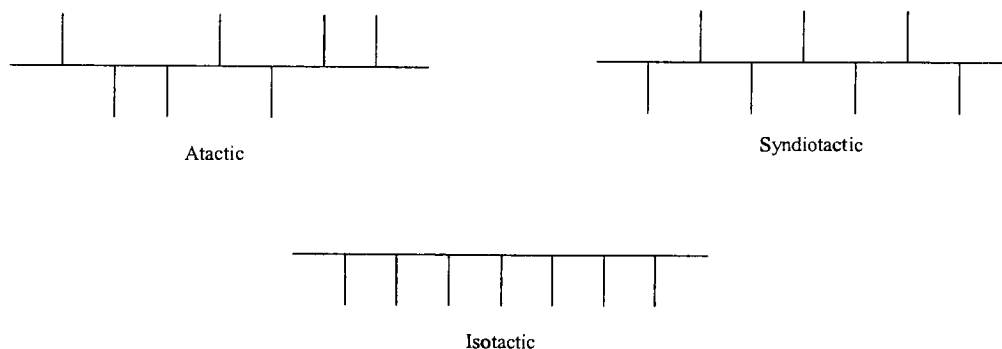


Figure 2: Side Branch Orientation Given as Fisher Projection

Polymerizing more than one type of monomer is considered a copolymerization. In our case, the polymerizations of ethylene and a 1-alkene is a binary copolymerization. The resulting polymers can have different compositions. The monomer sequence distribution is an important aspect of the composition of the copolymer. There are three classifications for the monomer sequence distribution.

| <u>Distribution Designation</u> | <u>Representative Sequence</u> |
|---------------------------------|--------------------------------|
| Alternating | ABABABABABAB |
| Random | BAABBBABABBA |
| Block | AAAAAABBBBBB |

The copolymer composition can be determined from the “copolymerization equation” of Mayo and Lewis. One form of the copolymerization equation can be seen as:

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}$$

Where F_A is the mole fraction of A in the resulting copolymer, f_A and f_B are the “feed” ratios of the monomers during the polymerization. The reactivity ratios r_A and r_B are based off the ratio of rate constants for the rate laws governing the two monomers during the polymerization. If the reactivity ratios for a given catalyst/monomer system is known, then the polymer composition can be controlled by varying the feed concentrations of the monomers.³ There is a relation between the reactivity ratio product ($r_A * r_B$) and the monomer sequence distribution:

Table 1: Reactivity Ratio Products and Monomer Sequence Distributions

| Reactivity ratio product | Monomer Sequence Distribution |
|---------------------------|-------------------------------|
| $0 \leq r_A * r_B \leq 1$ | Alternating |
| $r_A * r_B = 1$ | Random |
| $r_A * r_B > 1$ | Block |

Radical chain polymerizations of ethylene are typically run as bulk processes at high pressures (120-300 MPa) and at varying high temperatures, starting from around 140 °C to approx. 325 °C, before cooling to around 250 °C for polymer retrieval.² LDPE can be made preferably by this polymerization process due to the large amounts of chain transfer reactions possible with radical polymerizations.

High density polyethylene can be produced with catalyst systems obtained from the interaction of an organometallic compound or hydride of a group I-III metal with a halide, hydroxide, alkoxide, or other derivative of a Group IV-VIII transition metal,

known as a Ziegler-Natta catalysts or coordination catalyst.² When these catalysts are used to polymerize ethylene, more linear polymer chains are produced. This type of polymerization has become popular industrially because high temperatures and pressures are not required. For example, a gas phase process is typically run with a pressure of 2-3 MPa and temperatures in the range of 70 – 105 °C.² An issue with these conventional catalysts is that they are typically not soluble in organic solvents making the study of their reaction mechanism difficult.

One of the best reaction models for coordination catalyst polymerizations is the Cossee model.^{4,5} Cossee modeled the polymerization of propylene with a TiCl_4 catalyst in combination with Et_3Al as a cocatalyst. Figure 3 shows the steps involved in the polymerization process. For simplification, the cocatalyst has been omitted. Step I shows the catalyst with an initial polymer chain. When the polymerization is initiated, an alkyl group originating from the cocatalyst is attached to the transition metal via an alkyl exchange. There is a vacant site available for the coordination of a monomer unit indicated by the empty box. First, the complexation of a monomer unit occurs into the vacant site of the catalyst as indicated in the second figure. Then a four member, electron deficient, ring intermediate is formed between the monomer, the transition metal, and the carbon atom attached to it. The two carbons of the olefin are inserted between the metal center and the carbon of the alkyl group, thus adding another repeat unit to the growing chain. Finally, a migration step of the polymer chain back to its original position as shown in structure V takes place. This is a very rapid structural rearrangement that must occur in order for the catalyst to always attach a new monomer to the chain in the same stereochemical orientation, resulting in the formation of isotactic polypropylene. With

vanadium catalysts this last step occurs slower than the next monomer can be inserted. Due to the change in orientation of the inserted monomer a syndiotactic polymer is formed with the latter transition metal.

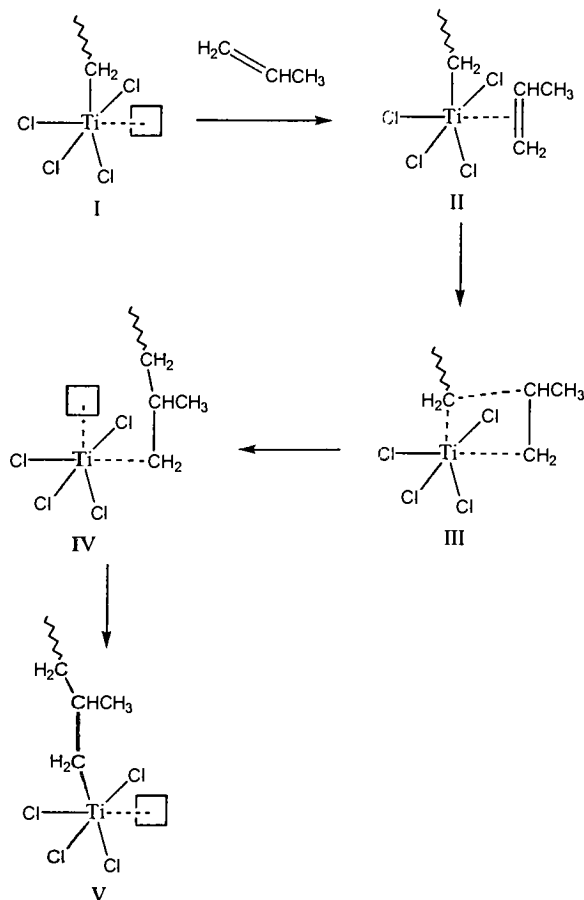


Figure 3: Cossee's Polymerization Mechanism for Titanium Coordination Catalyst²

Recently metallocene catalysts have been increasingly used to make polyethylene.⁵ One major feature of metallocenes is that they are soluble in most organic solvents. These catalysts are capable of making high-density polyethylene at high polymerization activities

Because metallocene catalysts are soluble in organic solvents, they form a homogeneous reaction mixture. They are also referred to as single-site-catalysts because

there is only one type of active catalyst center, in contrast to heterogeneous Ziegler/Natta catalysts that typically have different types of catalytic sites. This is reflected in the molecular weight distribution or polydispersity of the resultant polymers. Polymers produced with single site catalysts have polydispersities of 2-3; whereas heterogeneous catalysts typically have polydispersities of 5-20. A metallocene has at least one cyclopentadienyl ring coordinated to a transition metal center. Methylaluminoxane (MAO) is typically used as the cocatalyst.

Figure 4 shows a first generation metallocene which has two cyclopentadienyl rings coordinated to a zirconium center. These first generation catalysts had high activities and could be used to make HDPE, LLDPE, ethylene/propylene rubber, and atactic polypropylene. Syndiotactic or isotactic polypropylene could not be produced. The molecular weights of the resulting polymers were low compared to those made using heterogeneous catalysts, but with a much narrower molecular weight distribution.

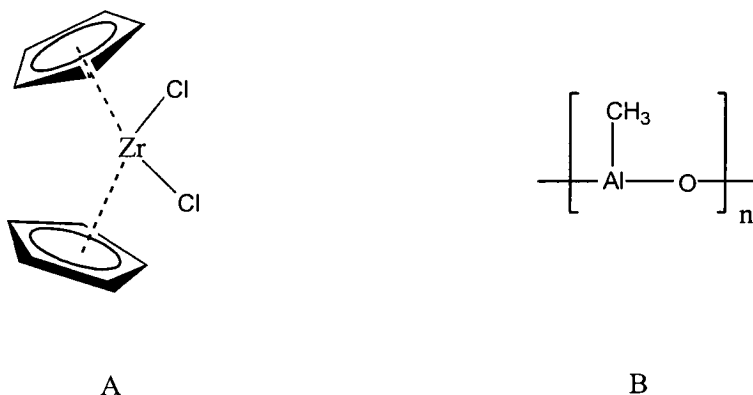


Figure 4: First Generation Metallocene (A), Bis-cyclopentadienylzirconium dichloride; and Methylaluminoxane⁶ (B) where n is ~20

Various improvements have been made to these original metallocenes, as seen in Figure 5. Instead of just cyclopentadienyl rings larger ring structures, such as indenyl groups, were coordinated to the metal center. One of the most significant additions is the

use of a bridge to keep the rings rigid around the metal center. At first an ethylene bridge was used, but it was found that a smaller bridge, such as dimethylsilylene⁵, would force the rings open wider on one side of the catalyst causing a larger “bite-angle”. This makes room for larger comonomers to gain access to the catalytic center.

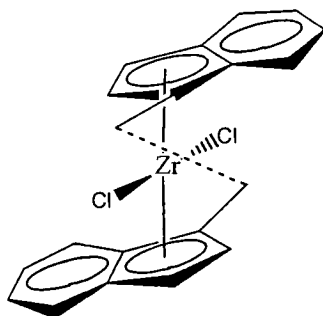


Figure 5: Modern Metallocene. Ethylene-bis(indenyl)zirconium dichloride

Rigid and chiral metallocenes capable of producing isotactic polypropylene, were found to make polymers with higher molecular weights, and incorporated comonomers much more readily.

Figure 6 depicts the insertion of a prochiral monomer, typically a monosubstituted ethylene such as propylene, unit using a rigid metallocene catalyst. Again, for simplification, the cocatalyst has been omitted. In the first structure, the growing polymer chain is on the right, and the monomer is being inserted from the left. Because of the structural orientation of the rings on the catalyst, bearing a C_2 symmetry the monomer unit is sterically guided into the catalytic center in only one direction. When the monomer is added, the entire chain moves to the left, and the next monomer comes in from the right. The monomer is added by the chiral catalyst to the polymer in the same orientation from either side of the catalyst. This leads to the formation of isotactic polymers. The meso form of the catalyst would result in mainly atactic polypropylene

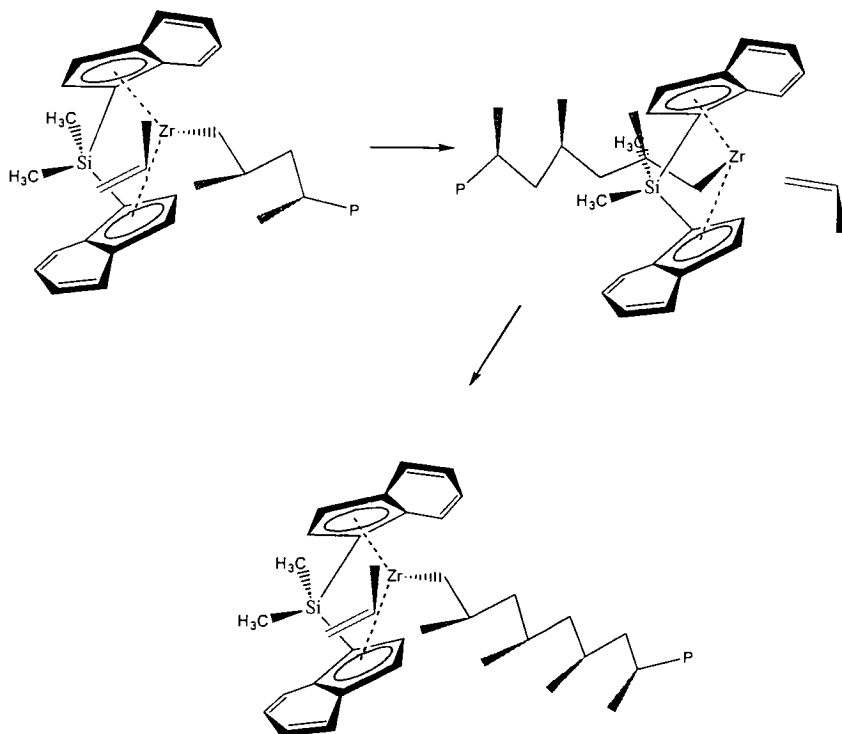


Figure 6: Monomer Insertion by a Bis(indenyl) Catalyst⁷

In the case of fluorenyl catalysts, as depicted in figure 7 which has C_2 -symmetry, the monomer comes towards the center of the catalyst from both sides, which are not stereochemically identical. As the polymer chain alternates its position from the left to the right, different enantiomeric faces of the monomer are inserted, leading to the formation of mostly syndiotactic polymers. It has been shown that if one side of this catalyst is blocked off with a bulky group, such as a *t*-butyl group, insertion occurs only on one side of the catalyst and an isotactic polymer will be formed.

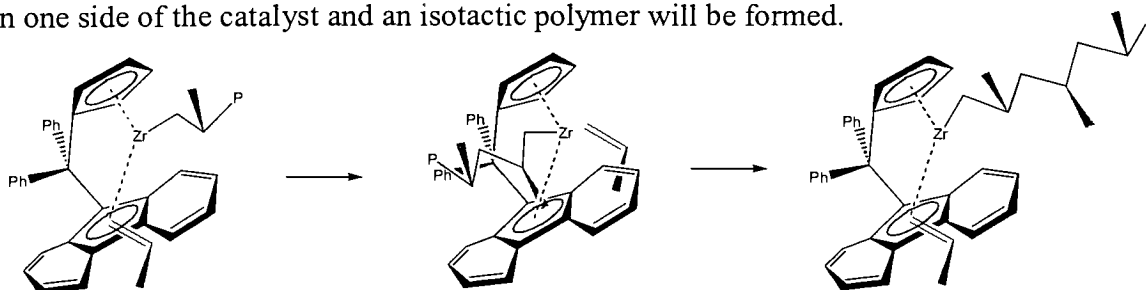


Figure 7: Monomer Addition with a Fluorenyl Catalyst⁷

Figure 8 shows the modern metallocene of primary interest used in this study. It has two indenyl groups coordinated to a zirconium center bridged with dimethylsilylene group. The indenyl groups face opposite directions, making the whole molecule chiral with a C_2 symmetry. There is also a methyl group attached to the indenyl rings in the 2-positions, which have been found to increase the molecular weights of the polymers by reducing Lewis acidity at the cationic zirconium center, thus reducing the tendency for a β -hydrogen to be abstracted.⁸ β -Hydrogen elimination is a chain transfer reaction that causes the forming polymer chains to be cut short. The phenyl groups attached at the 4-positions is assumed to aid particularly in the incorporation of larger comonomers into the polymer chains.

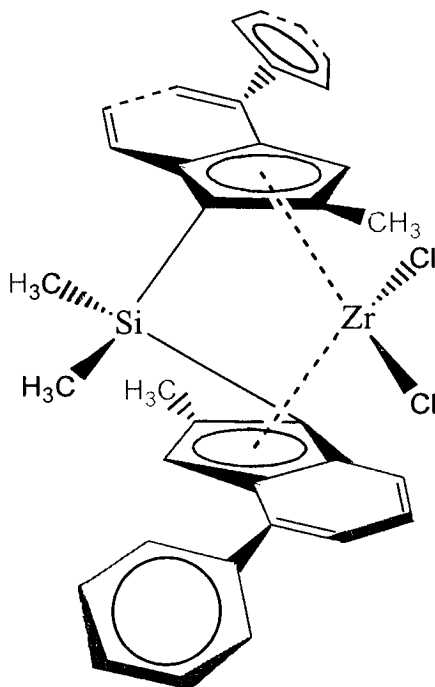


Figure 8: Rac-dimethylsilyl-bis(2-methyl-4-phenyl-indenyl)zirconium dichloride

Experimental:

Polymerizations:

A Buchi autoclave was used for the polymerizations. There are several key advantages to such a reactor. As shown in Figure 9 the reaction vessel has two parts, an inner jacket, inside of which all reactions take place, and an outer cooling jacket. By using an external water bath, the temperature of the reaction vessel can be controlled by pumping water between the outer and inner jackets. An exterior engine drives the internal stirrer magnetically. The use of a magnetically driven stirrer eliminates the need for gaskets and specialized bearings to keep the pressure constant inside the reactor, and keeps the internal atmosphere free from environmental contamination.

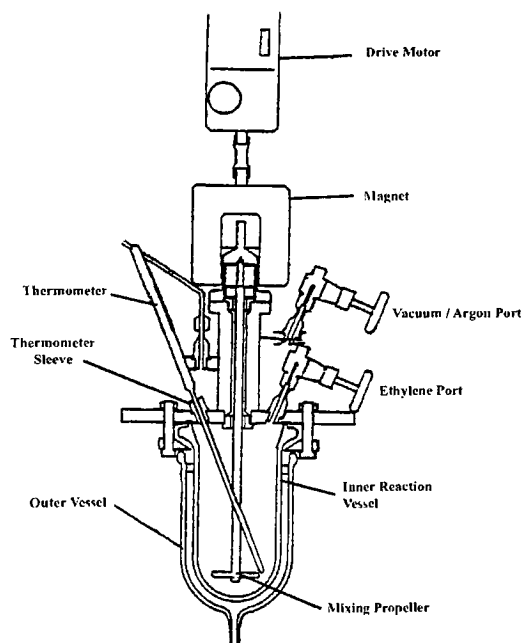


Figure 9: Buchi Autoclave used for Polymerization

A glass manifold was used to provide connections to either a vacuum or to argon gas. The vacuum was created using a standard vacuum pump connected to the manifold

through a vacuum trap. The trap was immersed in liquid nitrogen to prevent solvent fumes from being pulled into the pump and possibly destroying the gaskets and internal workings of the pump. Argon gas (99.999% from Air Products) was connected using copper tubing to an oil bubbler before being connected to the manifold. There was also a mercury pressure bubbler to keep the argon gas pressure around atmospheric pressures so that the glassware would not burst. Four fittings with glass stopcocks, which have two holes, were attached to the manifold; by turning the stopcock a vacuum or argon was applied through the fitting.

All glassware used for reactions was prepared using the following techniques. First an appropriate vessel was chosen and checked for dirt and damage. For solvent and comonomer preparation a 1000ml three-neck flask was used. The center hole being plugged by a glass stopper and the other two necks were fitted with glass stopcock adapters. High vacuum silicon grease was used to lubricate the ground glass joints. For catalyst preparation a small 50ml or 100ml single neck flask with a side stopcock attached was used. After the appropriate fittings were been attached, the flasks were attached to the vacuum/argon manifold. They were first put under a vacuum for approximately 15 minutes (depending on the volume of the flask), then backfilled with argon. This process was repeated three times. During the second or third purging, a heat gun was used to heat the glass vessel slightly. The purpose of this preparation was to remove any water and oxygen from the vessel. By heating the glass, water was forced from its surface.

The metallocene catalysts used were purchased from Boulder Scientific. The ethylene gas was purchased from Matheson. Argon was supplied by Air Products. All other chemicals used (toluene, 1-hexene, 1,4-hexadiene...) were purchased from Aldrich.

The solvent (toluene) and comonomer (1-hexene, 1-octene ...) are prepared in two separate distillations. A three-neck flask is the main reservoir, on top of which was mounted a distillation head. The distillation head has two Teflon valves, when the valve to the exit port was closed and the return valve was open, the system acted as a reflux apparatus. The toluene was refluxed overnight over sodium and benzophenone and the comonomer was refluxed over calcium hydride. The comonomer was degassed by applying a slight vacuum to the reflux system, then back filling with argon. This process removed any impurities due to oxygen or water. When the polymerization was being prepared, the return valve was closed; this allowed the solvent (or comonomer) to collect in the distillation head. To remove the solvent, the exit valve was opened. This entire operation was done with great care under argon to prevent any moisture or oxygen from being absorbed from the atmosphere.

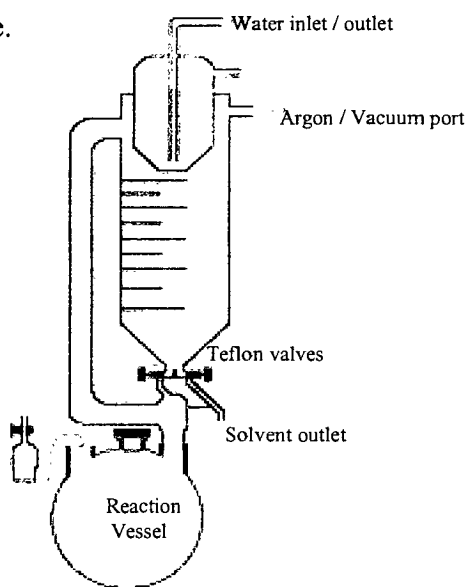


Figure 10: Solvent Still used for Purification of Toluene and Various Comonomers

The catalysts were stored in a sealed bottle under argon, in a refrigerator to prevent deterioration from atmospheric moisture. When the catalyst was to be prepared, a small glass weighing bottle was cleaned and held under a constant stream of argon, the catalyst bottle was also held under a stream of argon after opening. A small amount (approx. 0.1 g) of catalyst was transferred to the weighing bottle, and both containers were closed. The weighing bottle was massed, then the contents poured into a 50ml or 100ml prepared flask. A funnel was used, and the flask had argon running through it to keep out the atmosphere. After the contents of the weighing bottle were transferred it was massed again, the difference in weights gave the amount of catalyst transferred into the flask. A charge of 25 ml of toluene was added to the flask and agitated; then placed into the refrigerator for at least 4 hours to allow the catalyst time to dissolve. If there were solids on the bottom of the flask an additional step was added. A second small flask was prepared, and the yellow catalyst solution was carefully transferred into this new flask using a pipet. Care was taken not to suck any of the solids out of the first flask. The first flask, with solids, was closed and a vacuum applied to dry the solid at the bottom. When the solid was dry the mass of the whole flask was taken, the flask was cleaned and the mass taken again. The difference in these masses gives the amount of catalyst not dissolved, which subtracted from the first calculated weight gave the amount of catalyst actually dissolved. This gave the concentration of the solution in the second flask, which was the stock solution from which all the dilute catalyst solutions were made.

The total volume to be used in a polymerization was 250 ml this includes the solvent, catalyst, co-catalyst, and comonomer. Typically a concentration of 1×10^{-6} moles/Liter of catalyst was desired during the polymerization. An injection of 1ml of

dilute catalyst was used to begin the polymerization, with a concentration of 2.5×10^{-4} moles/Liter. One milliliter of the stock solution was diluted with approximately 5 to 10ml of toluene to achieve a concentration of 2.5×10^{-4} moles/Liter making the dilute catalyst. The stock solution was made once a week and stored in the refrigerator, whereas the dilute catalyst was made each day. By using this method of catalyst preparation, the amount of catalyst injected into the reactor was better controlled. The dilute catalyst solution goes bad after about a day, so it must be made each day. The stock solution, with its higher concentration lasts about a week if stored in a refrigerated environment.

Once the dilute catalyst was ready, the solvent and comonomer collected, the reactor was prepared, and the reaction was set up. First the argon valve was opened to the reactor. The thermometer port was removed from the reactor, and the appropriate amount of toluene was pipetted into the reactor. Then the comonomer was added in a similar fashion. 5 ml of 10 w/v % solution methylaluminoxane in toluene (MAO) was used in the reactor as co-catalyst. The thermometer sleeve was then replaced and tightened. The argon valve was closed, and the ethylene tank was opened to the reactor. The attached mass flow meter recorded the ethylene flow into the reactor. The stirrer was engaged and the ethylene was allowed to saturate the solution. When the pressure stabilized at 2 bars, and the flow of ethylene into the reactor stopped, the solution was ready to be polymerized. The thermometer was placed into the sleeve to monitor temperature. The polymerization was initiated by injecting 1ml of catalyst solution into the reactor through the injection port.

Originally 4 bars of ethylene gas was used with a temperature of 60 °C but this was reduced to better control the polymerization of ethylene and copolymerization of ethylene with small amounts of 1-alkenes.

Typically polymerizations were run for 10-30 minutes to achieve relatively low conversions, so that the monomer concentrations do not change significantly. During this time the temperature was monitored. Due to the exothermic polymerization reaction, the temperature may change rapidly. A 1 degree, or greater, temperature change was considered a rapid change, which could have lead to a loss of control of the polymerization. We tried to prevent this with the circulating water bath. If the temperature began to change too rapidly a cooling coil was placed into the water bath to reduce the temperature. If the reaction was highly exothermic, as in the case of ethylene homopolymerizations, the reaction time was reduced to 5 minutes, and the water bath was cooled as the polymerization was initiated.

To complete the polymerization the ethylene gas was turned off, and the pressure released from the autoclave. The thermometer port was then removed, and 20-mL of ethanol was added to the reaction mixture. The ethanol destroys the catalyst and terminates the polymerization. The reaction vessel was removed and the slurry was poured into a 1000-mL beaker, and approx. 200-mL of methanol was added to precipitate the polymer from the solution. The polymer was removed via vacuum filtration. The filtered polymer was placed into a clean 1000-mL beaker with 300-mL of methanol and 15-mL of 10% HCl. The polymer was stirred in this solution overnight to remove any metal residues from the polymer from either the catalyst or the MAO. The polymer was

vacuum filtered again, and placed into a tarred crystallization dish and dried in an oven for several hours.

Viscometry

Viscometric measurements of polymer solutions were done using Cannon-Fenske viscometers (figure 11). The solvent was decahydronaphthalene, stabilized with 2,6-ditertbutyl-4-methylphenol at 2 grams per liter. Four solutions of each polymer sample were made at different concentrations; approximately 40 milligrams of polymer were dissolved in 20, 40, 60, and 80mL of the stabilized solvent at 135 °C. The viscometer and solution was kept at 135 °C in a heated oil bath. The time required for each solution, including a blank, to pass through the capillary was measured.

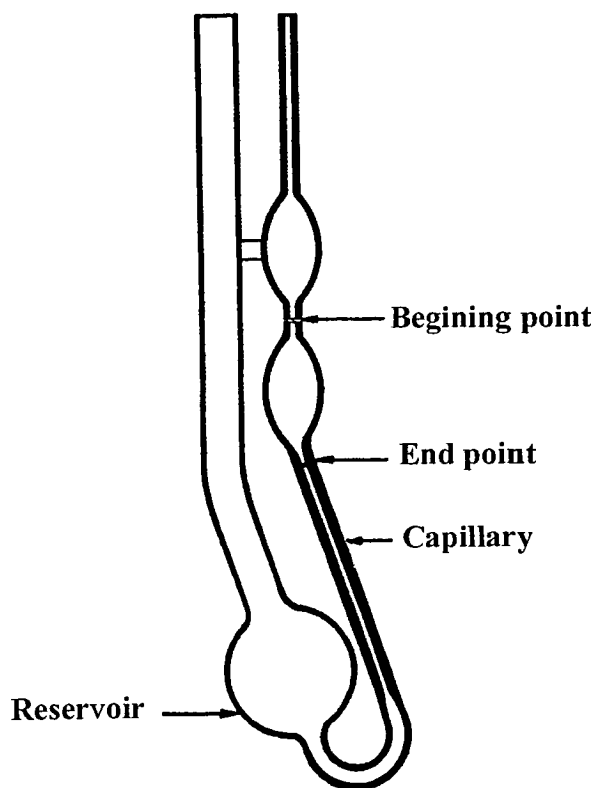


Figure 11: Cannon-Fenske Viscometer

The following formulas were used to calculate the intrinsic viscosity and viscosity average molecular weight.

$$\text{relative viscosity } (\eta_r) = \frac{t}{t_s} \quad \text{Equation 1}$$

Where t is the time measured for a solution to pass the capillary, and t_s is the time for the solvent to traverse the same capillary.

$$\text{specific viscosity } (\eta_{sp}) = \eta_r - 1 \quad \text{Equation 2}$$

$$\text{reduced viscosity } (\eta_{red}) = \frac{\eta_{sp}}{c} \quad \text{Equation 3}$$

Where c is the concentration of the solution in grams per deciliter. The intrinsic viscosity [η] was approximated using equation 4;⁹ where k_η is 0.029.

$$[\eta] = \frac{\text{avg } \eta_{red}}{1 + (k_{\eta} \times \text{avg } \eta_{red})} \quad \text{Equation 4}$$

$$M_{\eta} = \left(\frac{[\eta]}{k} \right)^{\frac{1}{\alpha}} \quad \text{Equation 5}$$

The viscosity average molecular weight (M_η) was calculated using equation 5, which is the Mark-Houwink-Sakurada equation. Where k is 4.6 x10⁻⁴ mol/g and α is 0.73 for HDPE.¹⁰ These values were used to approximate the M_η of ethylene/1-hexene copolymers since values for these types of polymers were not available.

GPC:

GPC experiments were performed at Dow Chemical Company. Samples were prepared by dissolving 15mg of copolymer in 13mL of 1,3,5 trichlorobenzene with 300

ppm w/w Ionol. The solutions were shaken at 160 °C for two hours. The hot solutions were filtered using a 0.5 micron steel filter.

A polystyrene/polyethylene universal calibration was carried out using polystyrene standards with narrow molecular weight distributions.

DSC:

A Differential Scanning Calorimeter (DSC) by TA Instruments was used to determine thermodynamic properties, specifically melt temperatures and glass transition temperatures of varying polymers. Samples of approximately 5mg were prepared in sealed aluminum pans. For very amorphous and sticky samples, liquid nitrogen was first used to cool the sample into a more solid state so that a piece could be removed.

The nitrogen flow through the instrument was set at 100 ml/min. The thermal history of the sample was removed by heating it to 200 °C at 30 °C/min, held for 5 minutes, and then cooled to -150 °C at 30 °C/min. The sample was then allowed to equilibrate at this temperature. Once the sample and instrument equilibrated, the sample was evaluated from -150 °C to 200 °C heating at a rate of 10 °C/min, and held at 200 °C for 5 minutes.

Results/Discussion:

Table 2 shows the effect of varying comonomer concentration on the copolymerization of ethylene/1-hexene and ethylene/1-octene.¹¹ The ethylene pressure was 4 bars, resulting in a concentration of 0.36 M ethylene in the toluene solution. The cocatalyst concentration was 3.0×10^{-2} M and the catalyst ($\text{Me}_2\text{Si}-[2\text{-Me-4-Ph-Ind}]_2\text{ZrCl}_2$) concentration was 1×10^{-6} M. The polymerization was run at a temperature of 60 °C.

Table 2: Influence of Comonomer Type and Concentration on Polymerization Activity using $\text{Me}_2\text{Si}-[2\text{-Me-4-Ph-Ind}]_2\text{ZrCl}_2$

| 1-Olefin, Type | 1-Olefin, M | Activity | Induction Period, min | $R_{p,\max} 10^{-5}$ | 1-Olefin in polymer, mol-% |
|-------------------|----------------|---|-----------------------------|--|----------------------------------|
| | | $\frac{\text{Kg polymer}}{\text{mol Zr} \times \text{h} \times [\text{mon}]}$ | | $\frac{\text{g ethylene}}{\text{min.} \times \text{mol Zr}}$ | |
| -- | 0 | 96 800 | 2 | 6.00 | 0 |
| 1-Hexene | 0.32 | 28 000 | 2 | 3.20 | 16 |
| 1-Hexene | 0.64 | 13 300 | 24 | 2.72 | 21 |
| 1-Hexene | 1.92 | 4 500 | 39 | 1.20 | 50 |
| 1-Hexene | 3.20 | 4 500 | 40 | 1.12 | 55 |
| 1-Octene | 0.32 | 16 800 | 10 | 2.00 | 20 |
| 1-Octene | 0.64 | 13 500 | 23 | 1.92 | 23 |
| 1-Octene | 1.92 | 2 800 | 42 | 1.00 | 45 |
| 1-Octene | 3.20 | 1 900 | 38 | 0.60 | 53 |

The activity was calculated using equation 6, where h is the polymerization time in hours and [mon] is the total monomer concentration.

$$\text{Activity} = \frac{\text{Kg polymer produced}}{\text{mol Zr} \times \text{h} \times [\text{mon}]} \quad \text{Equation 6}$$

The induction period is the time between the catalyst injection and onset of polymerization activity determined by the first sign of ethylene consumption recorded by the mass flow meter, see Figure 12.

Initially, the mol-% of 1-alkene in the polymer was estimated from the amount of polymer produced minus the amount of ethylene consumed by the polymerization. The maximum rate of polymerization ($R_{p,\max}$) was calculated using equation 7 from the plateau of the ethylene curve.

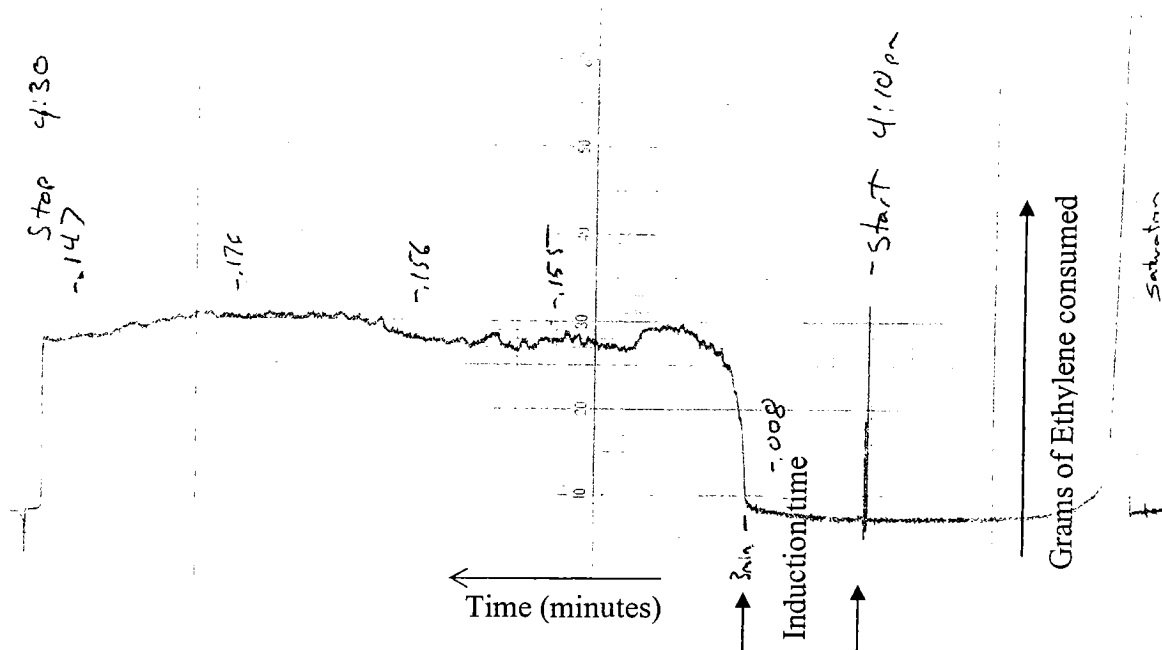


Figure 12: Ethylene Mass Flow Chart. Grams of Ethylene per Minute.

$$R_p = \frac{\text{g ethylene}}{\text{min} \times \text{mol Zr}} \quad \text{Equation 7}$$

As seen in Figure 13, the general trend is for the activities to decrease as the comonomer concentration is increased. Also the activities for copolymerizations using 1-octene are lower than the activities for copolymerizations using 1-hexene.

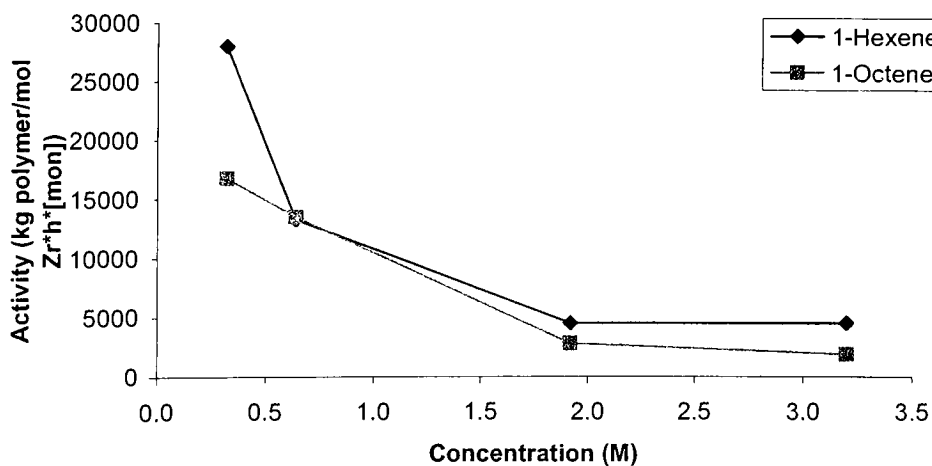


Figure 13: Effect of Increased Comonomer Concentration on Activities

Table 3 shows the effects of premixing the catalyst ($\text{Me}_2\text{Si}[\text{2-Me-4-Ph-Ind}]_2\text{ZrCl}_2$) and the cocatalyst (methylaluminoxane) as opposed to adding the cocatalyst to the reaction mixture before the catalyst is added. The ethylene pressure was two bars, resulting in an ethylene concentration of 0.23M in solution. The cocatalyst concentration was $3.6 \times 10^{-2}\text{M}$ with a catalyst concentration of $1 \times 10^{-6}\text{M}$. The polymerization was conducted at 40 °C. Premixing time was 20 minutes.

Table 3: Effects of Premixing Catalyst and Cocatalyst on Copolymerization of Ethylene/1-Hexene

| Premix catalyst & co-catalyst | 1-Hexene concentration M | Induction time Min | Activity |
|-------------------------------|-----------------------------|-----------------------|----------------------------------|
| | | | kg polymer mol Zr * h * [mon] |
| Yes | 0.22 | 0.5 | 308 411 |
| Yes | 0.45 | 0.5 | 160 107 |
| Yes | 0.67 | 1.5 | 80 548 |
| Yes | 1.34 | 5.0 | 19 217 |
| No | 0.22 | 0.5 | 780 720 |
| No | 0.45 | 0.5 | 316 870 |
| No | 0.67 | 0.5 | 317 876 |
| No | 1.34 | 0.85 | 81 848 |

The induction period was again taken from the mass flow chart as the time between the catalyst injection and first sign of ethylene consumption. The activity was calculated using equation 6 from above. With the premixed catalyst/cocatalyst there was a longer induction period with increase 1-hexene concentrations, which was significantly greater than the induction periods for the unpremixed polymerizations. The activities were also much lower with the premixed catalyst system.

Table 4 shows the activities of ethylene homopolymerizations and ethylene /1-hexene copolymerizations using different racemic mixtures of dimethylsilyl-bis(2-methyl-4-phenyl-indenyl) zirconium dichloride.¹¹ Ethylene pressure was 2.5 bars, resulting in a 0.26 M concentration of ethylene. The comonomer concentration was 3.2

$\times 10^{-2}$ M with a catalyst concentration of 1×10^{-6} M except for Exp. No. 3 which had a catalyst concentration of 1×10^{-7} M for better control.

Table 4: Activities and Related Data Obtained for the Polymerization of Ethylene and 1-Hexene using Different Racemic Mixtures of $\text{Me}_2\text{Si}[-2\text{-Me-4-Ph-Ind}]_2\text{ZrCl}_2$

| 1- Hexene M | rac:meso of metallocene \geq | Activity | Induction period, min | $R_{p, \max} 10^{-5}$ | 1-Hexene in polymer mol-% |
|----------------|--|----------------------------------|-----------------------------|----------------------------|---------------------------------|
| | | kg polymer mol Zr * h * [mon] | | g ethylene min * mol Zr | |
| 0 | 30:1 | 50 800 | 1 | 2.20 | 0 |
| 0.26 | 30:1 | 32 500 | 2 | 1.76 | 14 |
| 0 | 49:1 | 1 169 000 | 1 | 60.8 | 0 |
| 0.26 | 49:1 | 477 000 | 1 | 13.0 | -- |

The catalyst that had a racemic to meso mixture of 49:1 was much more active than the 30:1 mixture.

Table 5 shows the effect of the 4-phenyl group on polymerization activity. Polymerizations were conducted at 2 bars of ethylene (0.23 M in solution) and a temperature of 40 °C. The catalyst concentration was 1×10^{-6} M and cocatalyst concentration of 3.6×10^{-2} M. The catalysts were identical except for one did not have the 4-phenyl ring. As can be seen, the activity for the dimethylsilylbis-2-methyl-indenylzirconium dichloride catalyst was significantly lower than the activity for dimethylsilylbis-2-methyl-4-phenyl-indenylzirconium dichloride.

Table 5: Effect of 4-Phenyl Group on Polymer Activity

| 1-Hexene M | Activity | Activity |
|---------------|---|--|
| | $\text{Me}_2\text{Si}[-2\text{-Me-Ind}]_2\text{ZrCl}_2$ | $\text{Me}_2\text{Si}[-2\text{-Me-4-Ph-Ind}]_2\text{ZrCl}_2$ |
| 0 | 56 348 | 2 796 522 |
| 0.22 | 30 665 | 780 720 |

Table 6 displays the weight average (M_w), number average (M_n), and viscosity average (M_v) molecular weights of polyethylene and ethylene/1-hexene copolymers. The intrinsic viscosity $[\eta]$ was calculated from measurements done using capillary viscometry.

Table 6: Molecular Weight Properties of Polyethylene and Ethylene/1-Hexene Copolymers Produced with Me₂Si-[2-Me-4-Ph-Ind]₂ZrCl₂.

| 1-hexene | | M _n | M _w | M _n | M _w /M _n |
|----------|------|----------------|----------------|----------------|--------------------------------|
| M | [η] | g/mol | g/mol | g/mol | |
| 0 | 4.86 | 325 000 | -- | -- | -- |
| 0.32 | 2.69 | 144 000 | 247 000 | 117 000 | 2.11 |
| 0.64 | 1.84 | 86 000 | 222 000 | 80 200 | 2.76 |
| 1.92 | 1.26 | 51 200 | 114 000 | 36 400 | 3.13 |
| 3.20 | 0.65 | 20 200 | -- | -- | -- |

M_w and M_n were determined by GPC performed for us by Dow Chemical Co. As can be seen in the table, the approximations used to calculate M_n are acceptable because M_n still falls between M_w and M_n. The molecular weight distribution (M_w/M_n) is close to 2, which is the expected value for polymers produced with metallocene catalysts.

Table 7 shows the effects of different comonomers on the molecular weight and molecular weight distribution of the resulting polymers.¹¹ As can be seen, the molecular weight decreases as the amount of comonomer increases. The molecular weight distribution also increases slightly with the increased comonomer concentration.

Table 7: Effects of Varying Comonomers on Molecular Weight and Molecular Weight Distribution of Ethylene/1-Alkene Copolymers

| 1-alkene Type | 1-alkene M | M _w g/mol | M _n g/mol | M _w /M _n |
|---------------|------------|----------------------|----------------------|--------------------------------|
| -- | 0 | 477 000 | 181 000 | 2.63 |
| 1-Hexene | 0.32 | 213 000 | 79 100 | 2.68 |
| 1-Hexene | 0.64 | 182 000 | 65 500 | 2.78 |
| 1-Hexene | 1.92 | 103 000 | 29 900 | 3.43 |
| 1-Hexene | 3.20 | 96 400 | 29 500 | 3.27 |
| 1-Octene | 0.32 | 200 000 | 72 600 | 2.90 |
| 1-Octene | 0.64 | 173 000 | 59 500 | 2.90 |
| 1-Octene | 1.92 | 148 000 | 38 100 | 3.87 |
| 1-Octene | 3.20 | 140 000 | 41 600 | 3.37 |

Table 8 displays the DSC data for some of our polymer samples. The glass transition temperature (T_g) measured for polyethylene (-128°C) is slightly lower than the accepted value of -125°C found in the polymer handbook.¹² The melting temperature (T_m) of the polyethylene sample (136.8°C) was comparable to the accepted value of

137°C. The T_g of poly(1-hexene) was found to be -57.7°C, there was no measurable melting point though. Consulting the accepted values from the polymer handbook where the T_g of poly(1-hexene) was found to be -58°C and the T_m was listed as -55°C. Because these values are so close to one another, it is likely that the instrument was not able to differentiate between the glass transition and melting point temperatures. Although no accepted values for T_g and T_m of poly(1-octene) were available, the data was found to follow a similar trend as that of the 1-hexene copolymers.

Table 8: Glass Transition and Melting Point Data for Polyethylene and Ethylene/1-Alkene Copolymers

| Type of Polymer | Ethylene in Copolymer, Mol % | T_g °C | T_m °C |
|-------------------|------------------------------|----------|----------|
| Polyethylene | 100 | -128.0 | 136.8 |
| Ethylene/1-hexene | 89 | -54.1 | 91.7 |
| Ethylene/1-hexene | 85.1 | -58.5 | 77.1 |
| Ethylene/1-hexene | 74.9 | -65.4 | |
| Poly-1-hexene | 0 | -57.7 | |
| Ethylene/1-octene | 91 | -56.9 | 90.7 |
| Ethylene/1-octene | 86.8 | -59.9 | 79.4 |
| Ethylene/1-octene | 74.9 | -70.5 | |
| Poly-1-octene | 0 | -69.0 | - |

Table 9 has the feed and copolymer composition data from which reactivity ratios were determined using a non-linear, iterative method.³ Polymerizations were performed at 60 °C with $\text{Me}_2\text{Si}[\text{-2-Me-4-Ph-Ind}]_2\text{ZrCl}_2$. Figure 14 shows the resulting copolymerization diagram.

Table 9: Feed and Copolymer Composition and Reactivity Ratios for Ethylene/1-Hexene and Ethylene/1-Octene Copolymerizations¹¹

| Comonomer | Mol% C ₂ H ₄ In reaction | Mol% C ₂ H ₄ In copolymer | Reactivity ratios And R (or SSD) |
|-----------|--|---|----------------------------------|
| -- | 100.0 | 100.0 | |
| 1-Hexene | 69.2 | 89.0 | $r_e = 3.95$ |
| 1-Hexene | 52.9 | 85.1 | $r_h = 0.04$ |
| 1-Hexene | 36.0 | 74.9 | $R = 3.6 \times 10^{-4}$ |
| 1-Hexene | 15.8 | 59.0 | |
| 1-Hexene | 0 | 0 | |
| -- | 100.0 | 100.0 | |
| 1-Octene | 69.2 | 91.0 | $r_e = 4.75$ |
| 1-Octene | 52.9 | 86.8 | $r_o = 0.07$ |
| 1-Octene | 36.0 | 74.9 | $R = 3.5 \times 10^{-4}$ |
| 1-Octene | 15.8 | 56.8 | |
| 1-Octene | 0 | 0 | |

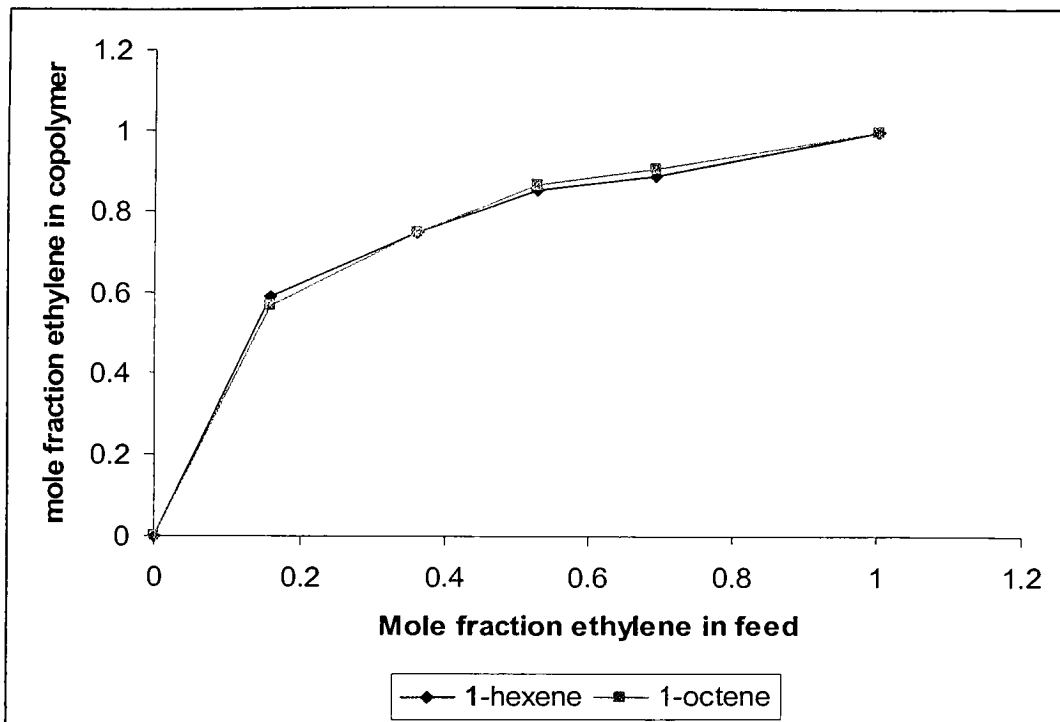


Figure 14: Copolymerization Diagrams for Ethylene/1-Hexene and Ethylene/1-Octene Copolymers

Table 10 shows the effect of 1,4-hexadiene on the rate of polymerization between catalysts. 1,4-hexadiene was used instead of 1,5-hexadiene, because the later would have two terminal double bonds, which would likely result in small cyclic molecules instead of long polymer chains. The rate of polymerization drops for each of the catalysts as the 1,4-hexadiene concentration is increased, however the decrease in the polymerization rate using the modern rigid catalysts with the 1,4-hexadiene is much larger than that of the zirconocene catalyst.

Table 10: Comparison of Feed and Copolymer Composition Using Varying Metallocenes for the Copolymerization of Ethylene and 1,4-Hexadiene¹¹

| Metallocene | $R_p \times 10^{-5}$ g C ₂ H ₄ / (min * mol Zr) | | |
|---|--|---|---|
| | 0 mol% C ₆ H ₁₀ in feed | 25 mol% C ₆ H ₁₀ in feed | 50 mol% C ₆ H ₁₀ in feed |
| Me ₂ Si-[2-Me-4-Ph-Ind] ₂ ZrCl ₂ | 32 | 0.50 | 0.12 |
| Me ₂ Si-[Ind] ₂ ZrCl ₂ | 1.7 | 0.48 | n.d. |
| Cp ₂ ZrCl ₂ | 8.4 | 1.12 | 0.72 |

Conclusions:

The study of dimethylsilylbis-2-methyl-4-phenyl-indenylzirconium dichloride has resulted in a number of interesting discoveries. The effect of the 4-phenyl group on polymerization activity is remarkable. The phenyl substituted catalyst is almost 50 times as active as the unsubstituted catalyst for ethylene homopolymerization and over 25 times as active when copolymerizing ethylene and small amounts of 1-hexene.

No comonomer effect was found with this catalyst,¹³ even though similar catalysts have been shown to have such an effect.^{14,15} Since there is no satisfactory reason for the comonomer effect has been agreed upon by the scientific community it is difficult to explain why our catalyst does not show such an effect.

The creation of high molecular weight copolymers between ethylene and 1-alkenes with narrow molecular weight distributions are easily accomplished at moderate temperatures and pressures using dimethylsilyl-bis-2-methyl-4-phenyl-indenylzirconium dichloride. However, the copolymerization of 1,4-hexadiene and ethylene met with little success. Using Cp_2ZrCl_2 a copolymer was formed, showing that there was nothing wrong with the comonomer (impurities and such), it simply would not polymerize efficiently using dimethylsilylbis-2-methyl-4-phenyl-indenylzirconium dichloride. Possibly the diene diminishes the catalytic center of the complex, chiral catalyst.

References:

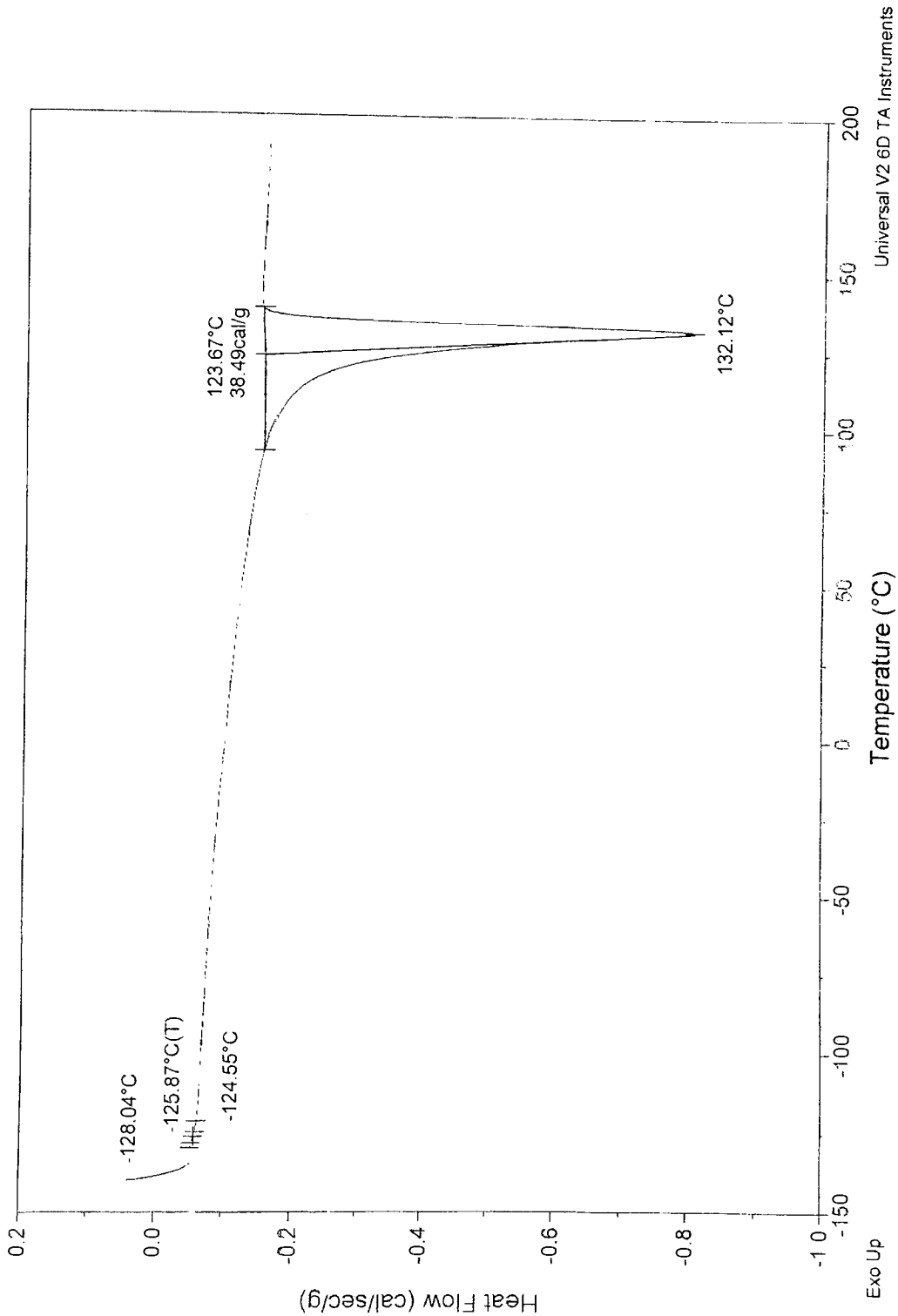
- ¹ C&EN June 25, 2001 pg. 47
- ² G. Odian, *Principles of polymerization 3rd ed.*; John Wiley & Sons, Inc.: New York 1991; 304-305, 627, 635, 656
- ³ M. Miri, J Morales-Tirado, "Tool for Understanding Copolymerization and Monomer Sequence Distribution of Copolymers," J. Chem. Edu., Webware, (Accepted 2002)
- ⁴ Cossee, P.J., J. Catalysis, 3, 80 (1964)
- ⁵ J. A. Ewen, "New Chemical Tools to Create Plastics",
<http://www.sciam.com/0597issue/0597ewen.html>
- ⁶ W. Kaminsky, M. Miri; "Ethylene Propylene Diene Terpolymers Produced with a Homogeneous and Highly Active Zirconium Catalyst", J. Poly. Sci. **23**: 2151-2164 (1985)
- ⁷ M. Arndt, Dissertation, University of Hamburg, 1993
- ⁸ W. Spaleck, M. Antberg, W. Herrmann; "High Molecular Weight Polypropylene through Specifically Designed Zirconocene Catalysts", Angew. Chem. Int. Ed. Engl., **31**, 1347-1350 (1992)
- ⁹ G. Schulz, F. Blascke; J. Prakt. Chem., **158**, 130 (1941)
- ¹⁰ A. Ahlers, W. Kaminsky; Makromol. Chem., **9**, 457 (1988)
- ¹¹ M. Miri, D. Hetzer, M. Pecak, "Ethylene/ α -Olefin Copolymerization with Dimethylsilyl-bis(2-methyl-4-phenyl-indenyl)zirconium dichloride and Methylaluminoxane: Influences on Polymerization Activity and Molecular Weight," in *Metalorganic Catalysts for Synthesis and Polymerization*, edit. W. Kaminski, 1999; 509-515
- ¹² Polymer Handbook, 4th ed.; J. Brandrup, E.H. Immergut, and E.A. Grulke; New York, Wiley, c1999
- ¹³ M. Miri, B. Culbertson, A. Evans, M. Pecak, "Metallocene Catalyzed Ethylene Copolymers with 1-olefins and dienes," Polymeric Materials: Sci. Eng., **4**, 757-758 (2001)
- ¹⁴ N. Herfert, P. Montag, G. Fink, "Ethylene, α -olefin and norbornene copolymerizations with the stereorigid catalyst systems $iPr[FluCp]ZrCl_2/MAO$ and $Me_2Si[Ind]_2ZrCl_2/MAO$
- ¹⁵ J. Chien, T. Nozaki; "Ethylene-Hexene Copolymerization by Heterogeneous and Homogeneous Ziegler-Natta Catalysts and the Comonomer Effect," J. Poly. Sci., **31**, 227-237 (1993)

Appendices:

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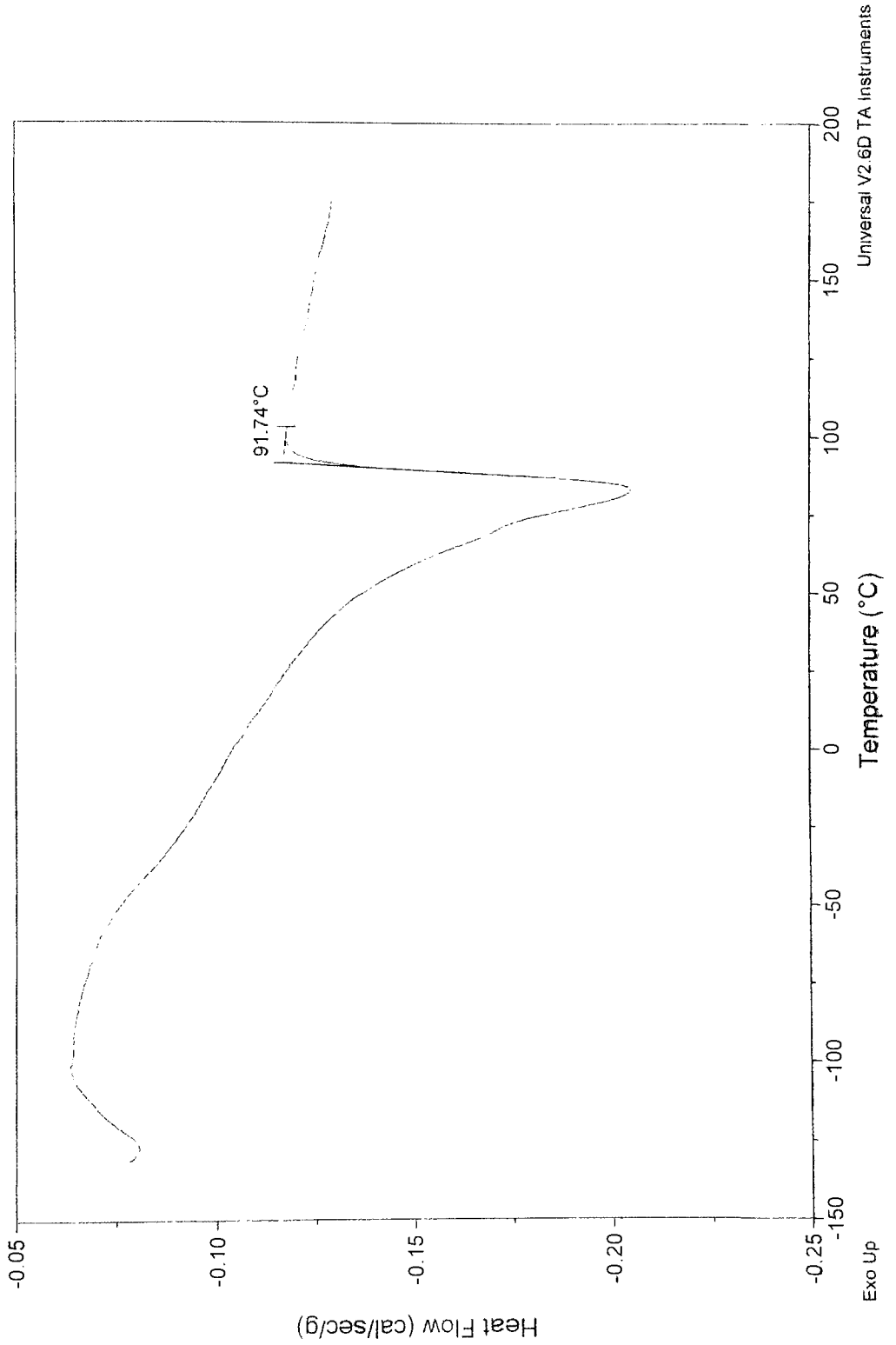


Universal V2.6D TA Instruments

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DSC

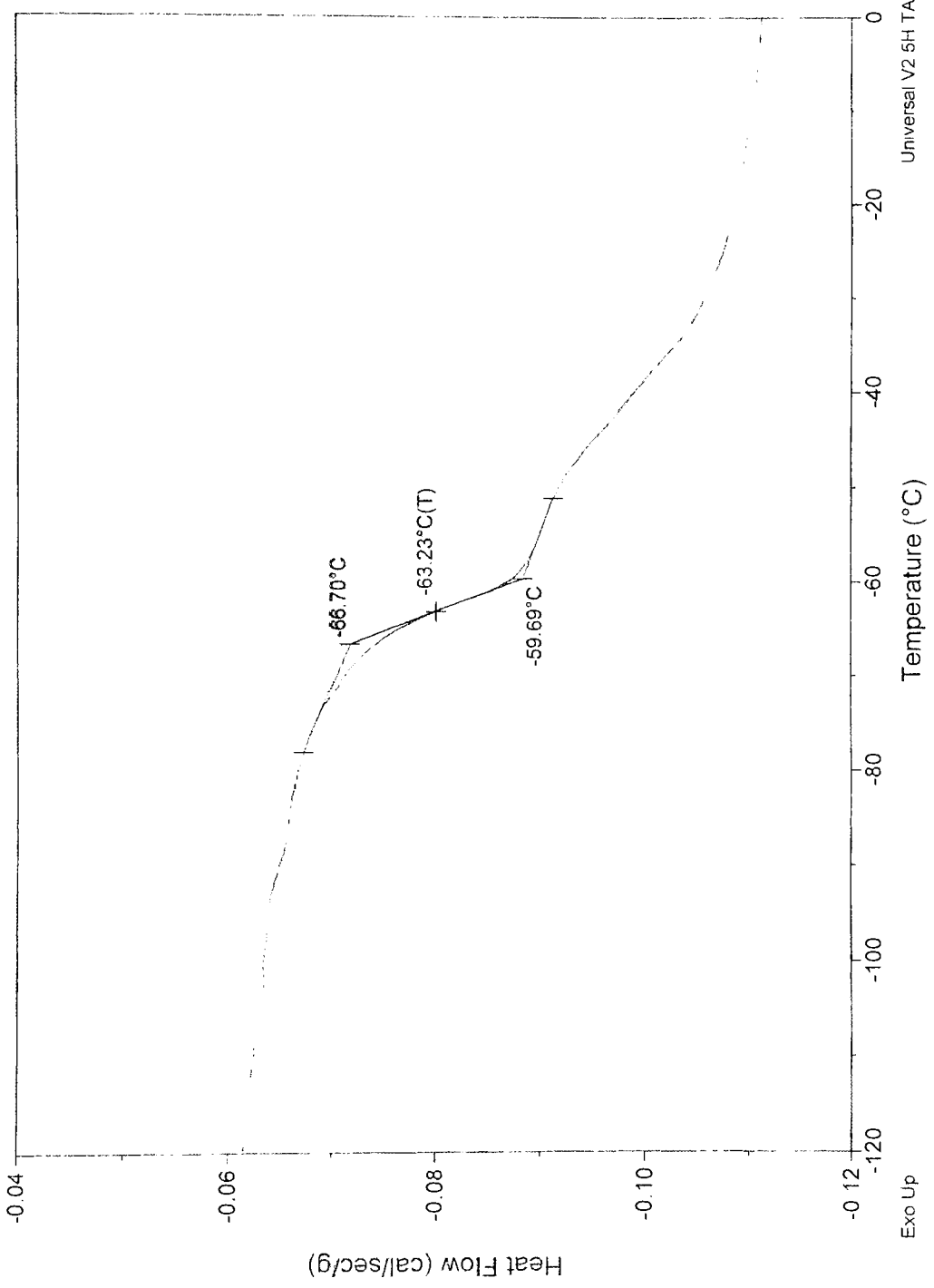
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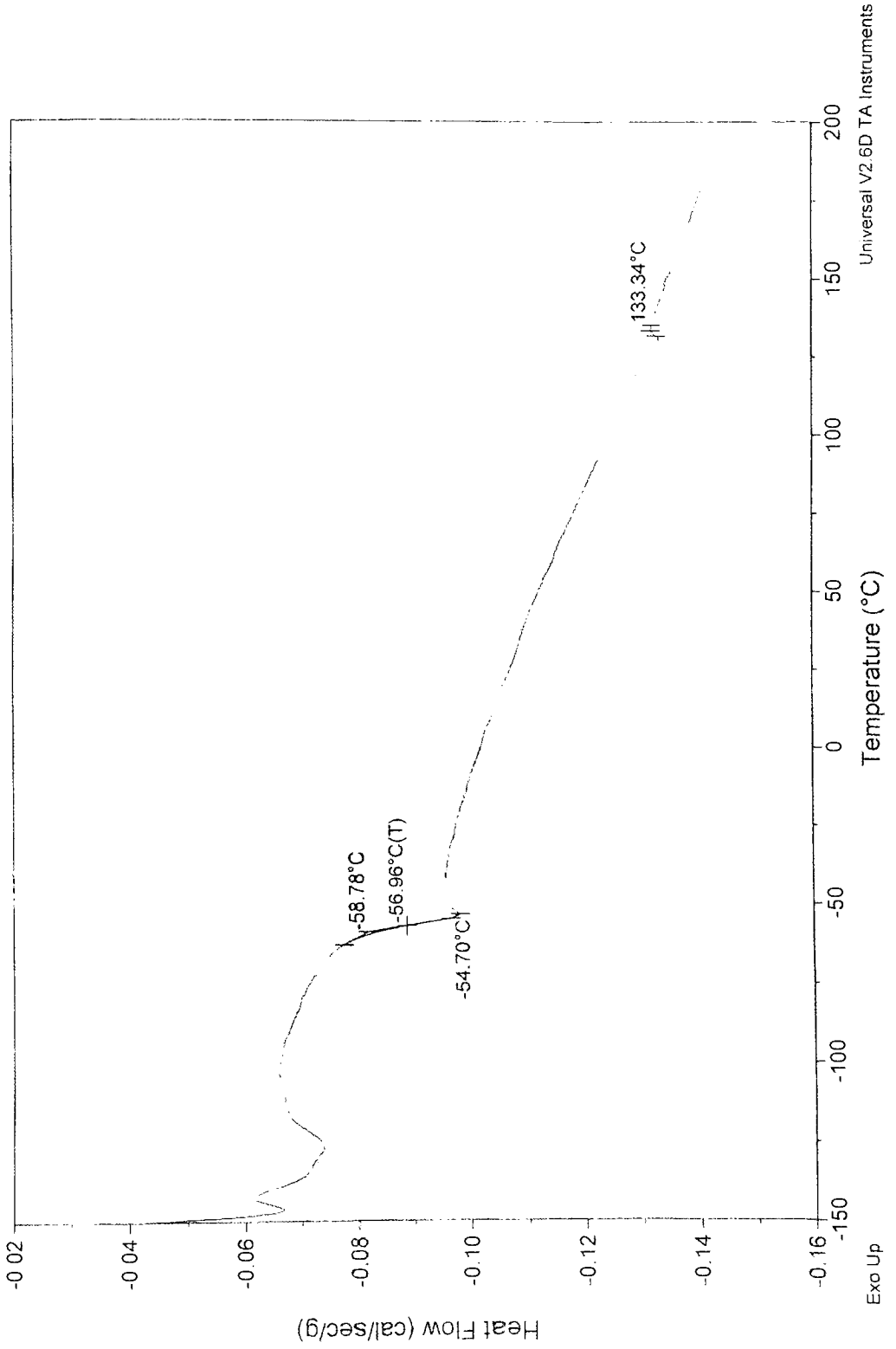
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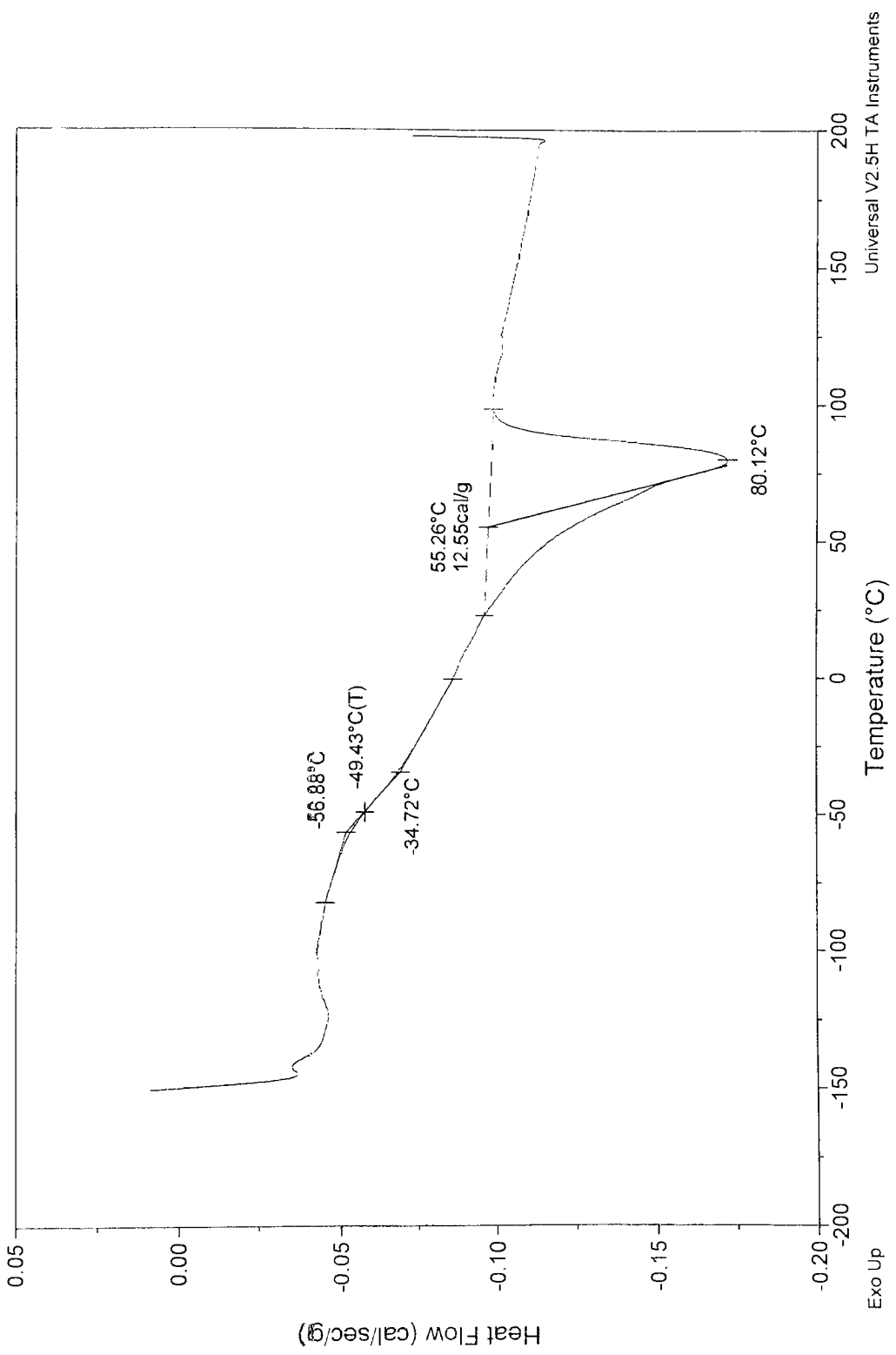


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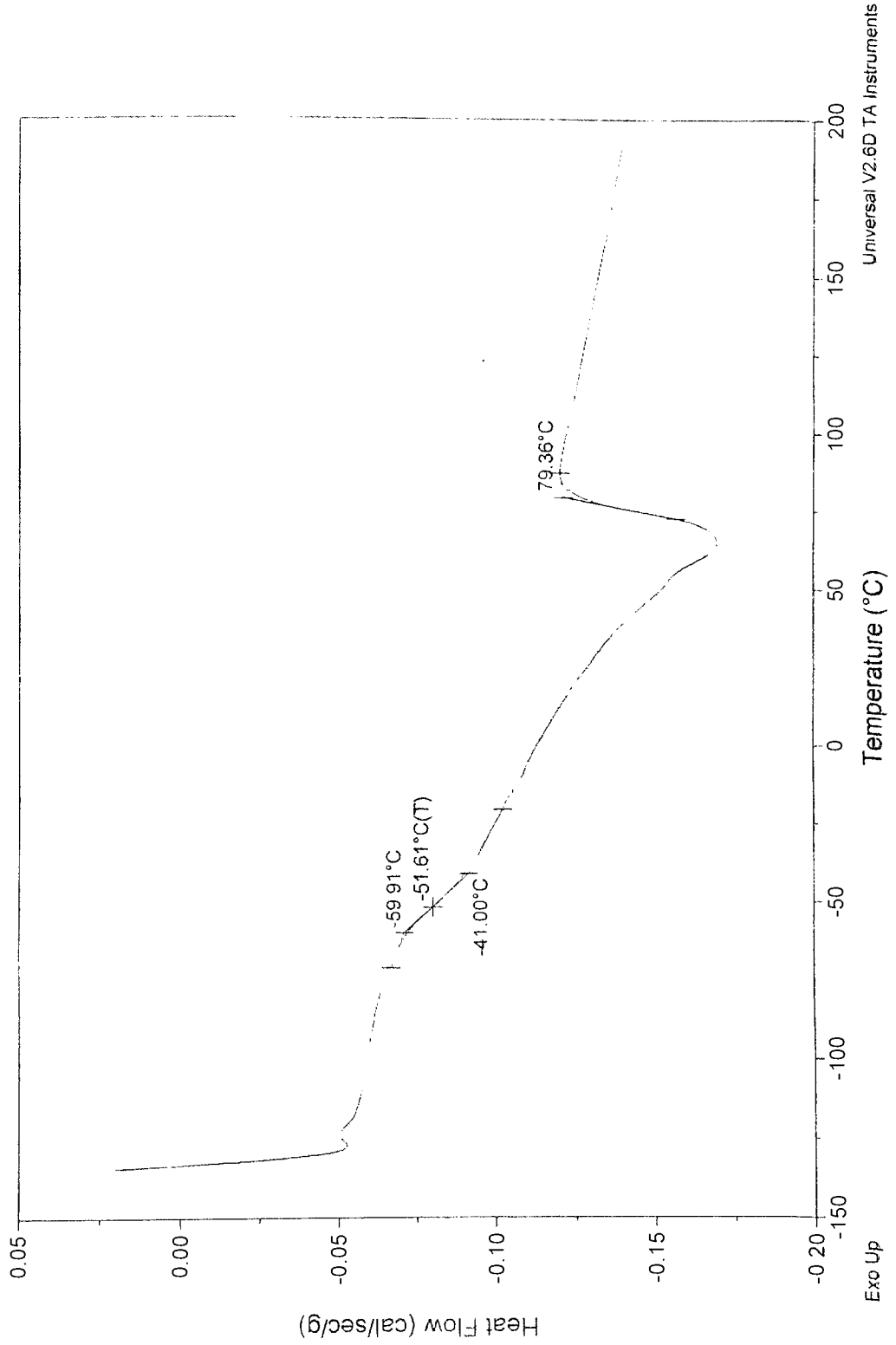


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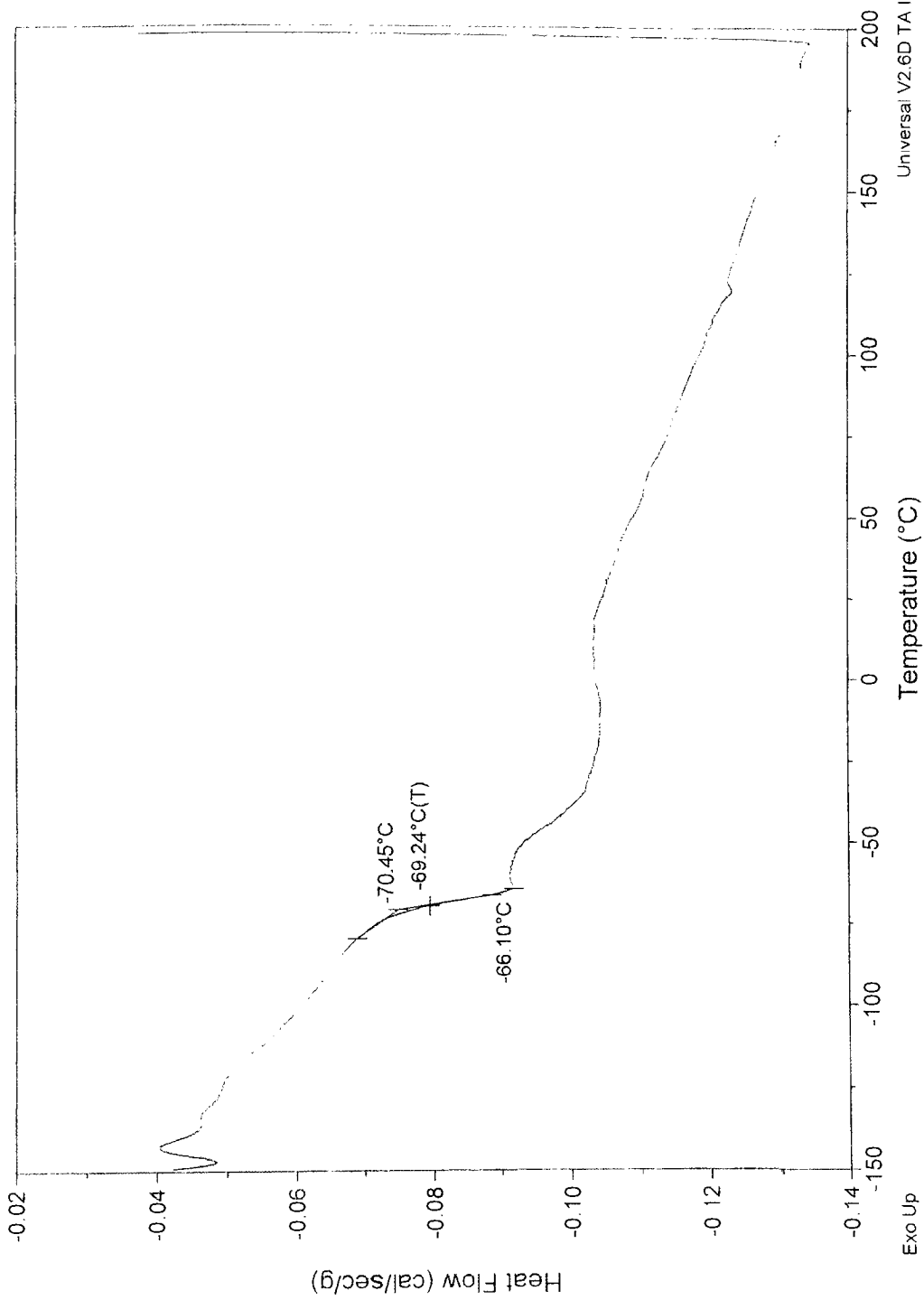
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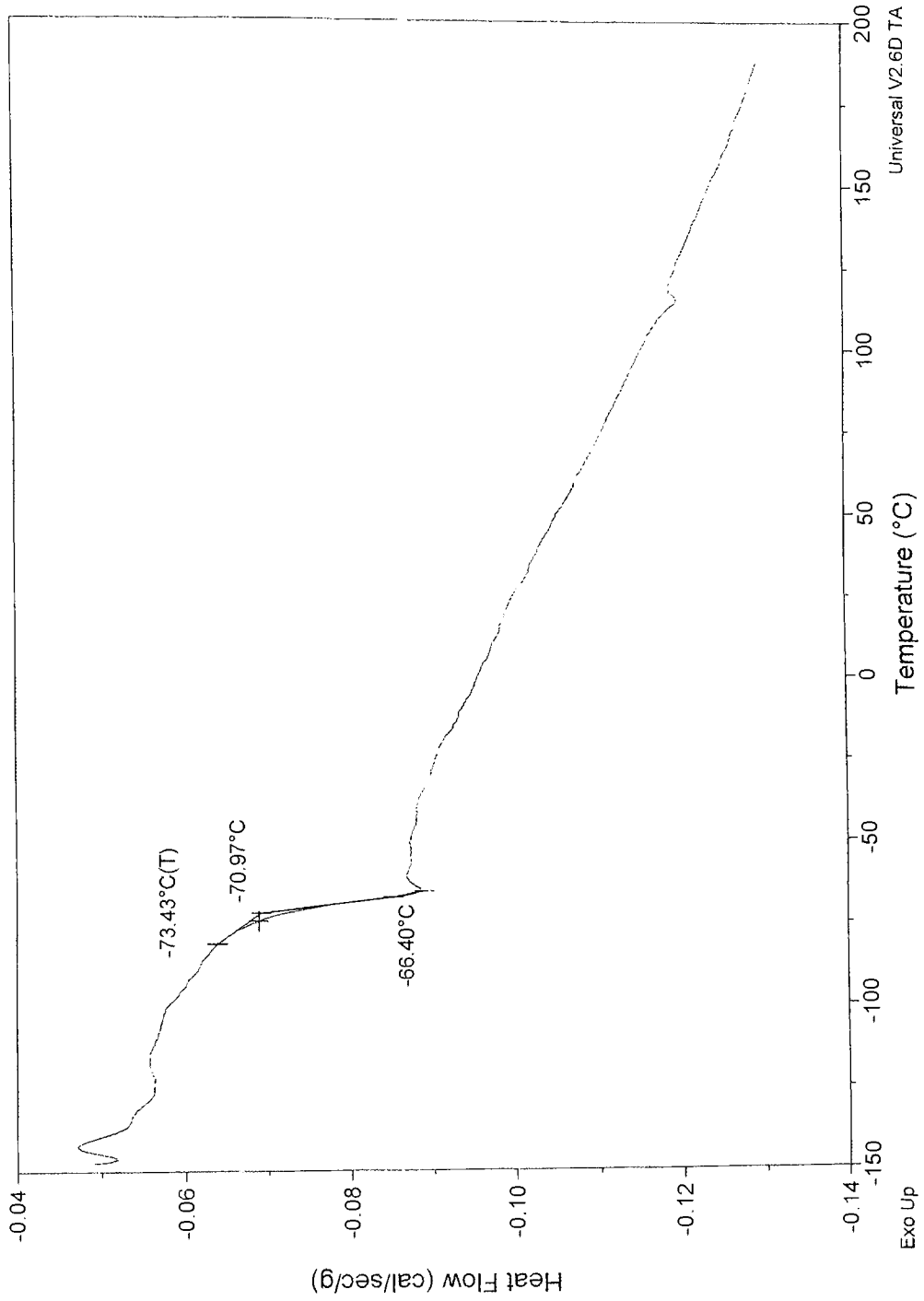
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