

Random and Non-Random Hydrogenation of Polybutadiene using Homogeneous Molecular and Heterogeneous Transition Metal Catalysts



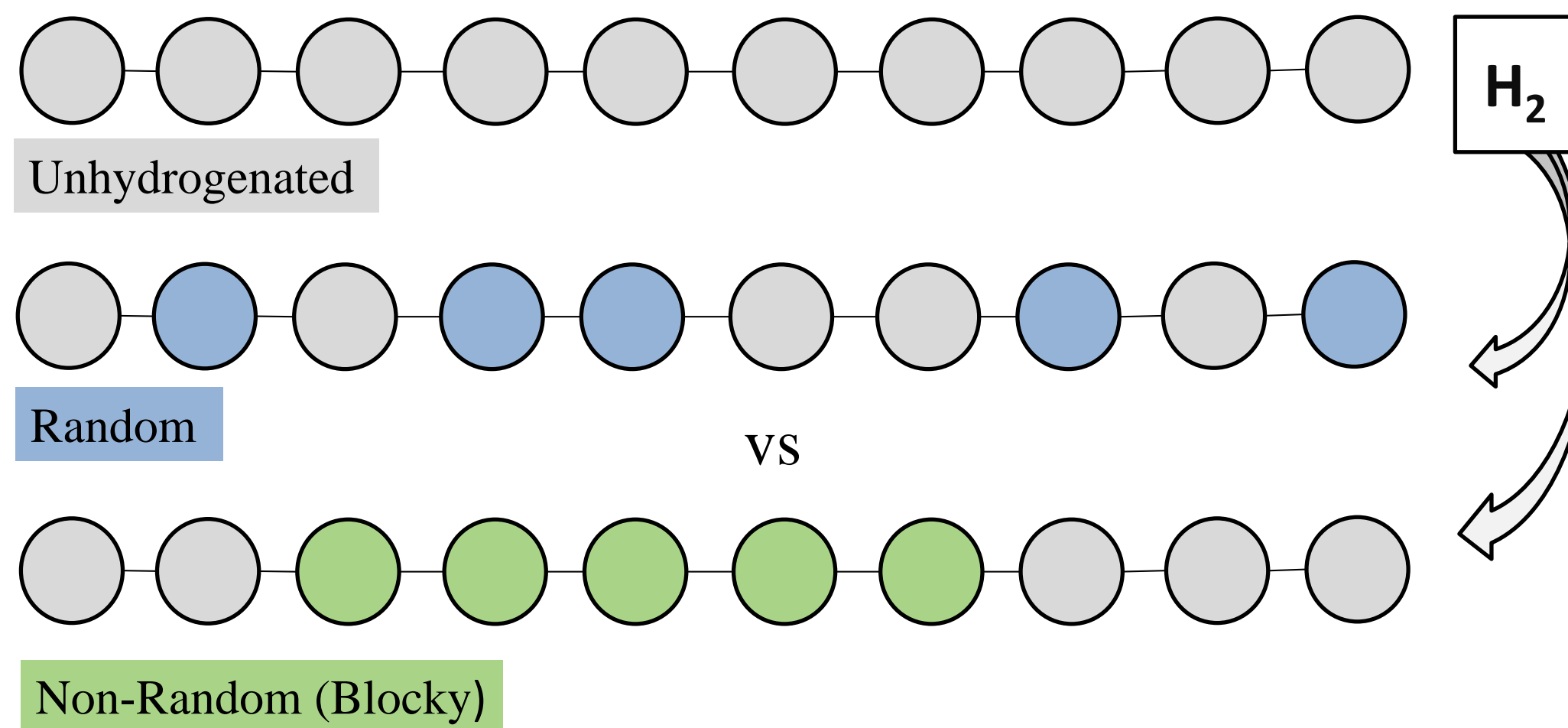
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Introduction

Catalytic hydrogenation is widely practiced in industries ranging from fuel and petrochemical to food and pharmaceutical. Unsaturated polymers have hundreds of double bonds per chain, and an important question is whether the unhydrogenated repeat units are distributed randomly along the chain or in blocks.



Objective

This project looked to characterize the “blockiness” of hydrogenation from the prototypical polymer cis 1,4-polybutadiene to polyethylene with specific catalysts of interest, in order to better understand the resulting thermal properties of the polymer. The catalysts studied were:

- A homogenous ruthenium coordination complex, Ru(PPh₃)₃COHCl
- A heterogeneous catalyst formed from the reaction of organometallic Ni and Al compounds

Method

- Ru(PPh₃)₃COHCl
 - 6.5g polybutadiene (PBD) dissolved in 1.3L Toluene with 12mg butylated hydroxytoluene (BHT) and 12 mg ruthenium catalyst added to solution. Pressurized with H₂ to 400 psi at 100°C.
 - 4 hour reaction, aliquots taken every 30 minutes after 100 °C is reached.
- Nickel (II) 2-Ethylhexanoate Triethylaluminum
 - 15g PBD dissolved in 1.5L cyclohexane with 30 mg BHT to make polymer solution. Added between 104 mg and 1.04 g of nickel (II) 2-ethylhexanoate and between 1 and 10 ml of 1M triethylaluminum in order to prepare the desired amount of catalyst with a precise Al:Ni molar ratio of 4.25:1. Pressurized with H₂ to 400 psi at 100°C.
 - 1 hour reaction, aliquots taken once catalyst is injected, and then every 15 minutes after 100°C is reached.

Equipment used:
 High-Pressure Parr reactor, Perkins Elmer DSC 7, Thermo Scientific IR spectroscopy (Nicolet iS50 FT-IR) & high temperature proton NMR.



Reaction Catalyst Key:

- Ruthenium
 - NiAl: 0.235 (0.235 mmol Ni)
 - NiAl: 0.470 (Additional 0.235 mmol Ni added)
 - NiAl: 0.705 (Additional 0.235 mmol Ni added)
 - NiAl: 0.3525 (0.3525 mmol Ni added)
- Same polymer solution used

Reaction Kinetics

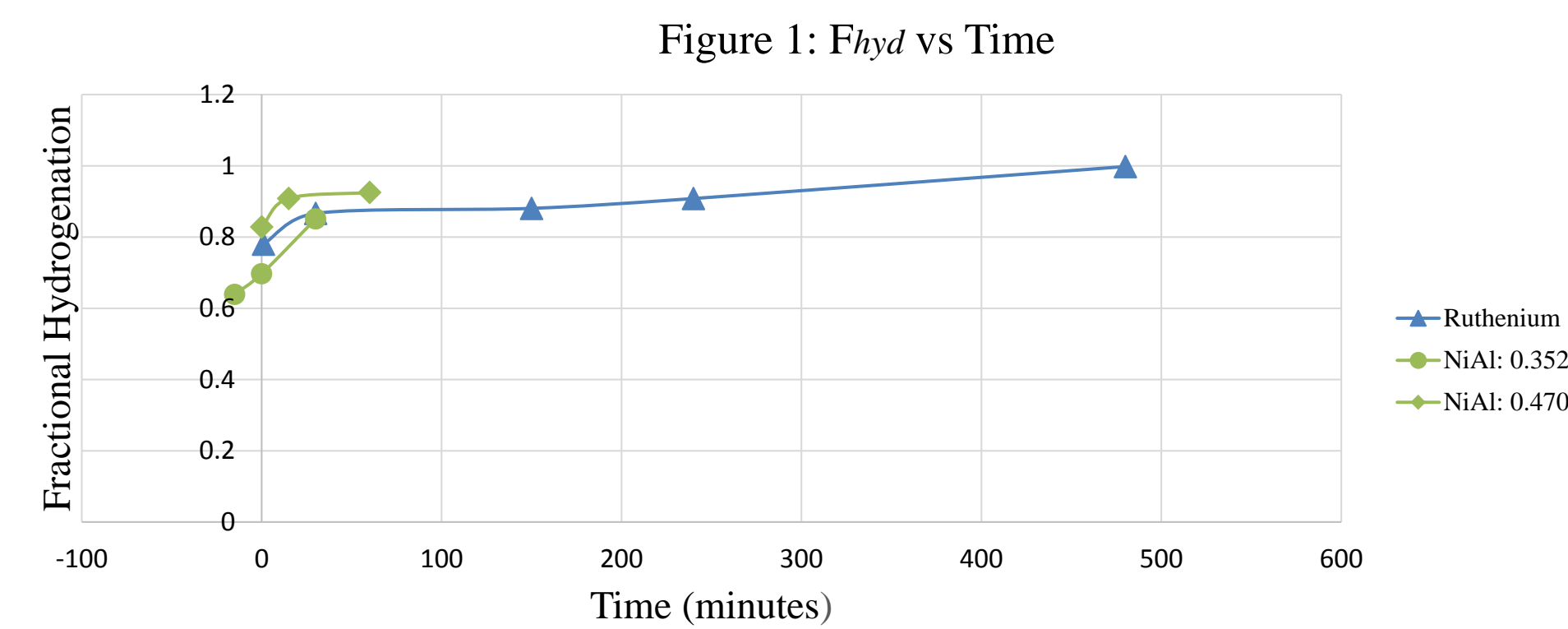


Figure 1 illustrates a visual representation of the rate of the hydrogenation reaction for different ratios of catalyst to polymer. The fractional hydrogenation was calculated from NMR. Values before time 0 represent samples taken after catalyst injection but before the temperature reached 100 °C.

Data Analysis

In Figure 3 and Figure 5, the graphs use data obtained by high temperature proton NMR analysis (Figure 2) where a ratio of olefinic to aliphatic peaks were used to calculate F_{hyd} . Figure 4 is data from an IR spectrum, where a ratio of C-C double bonds to single bonds was obtained through peak area calculations. Although both methods can calculate F_{hyd} , the NMR method is more precise and therefore gives more reliable results. The different slopes represent the variation seen within random (based on the lower melting temperatures at higher F_{hyd} values) and non-random hydrogenation patterns (based on the higher melting temperatures at higher F_{hyd} values, meaning thicker crystals which occur with blocky hydrogenation).

Figure 2 (below). Ruthenium Sample 5 proton NMR spectra.

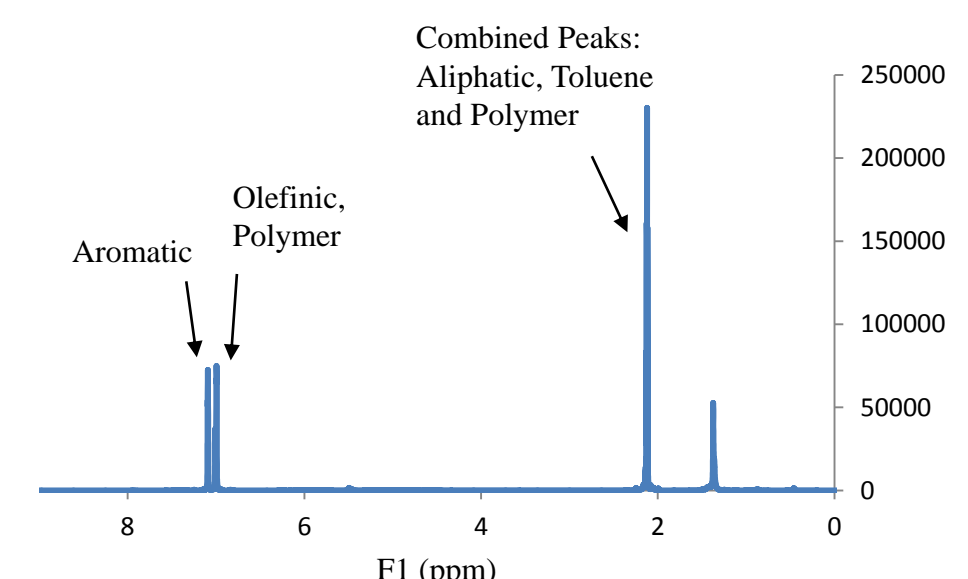


Figure 4 (below). Ruthenium Sample 5 IR spectra.

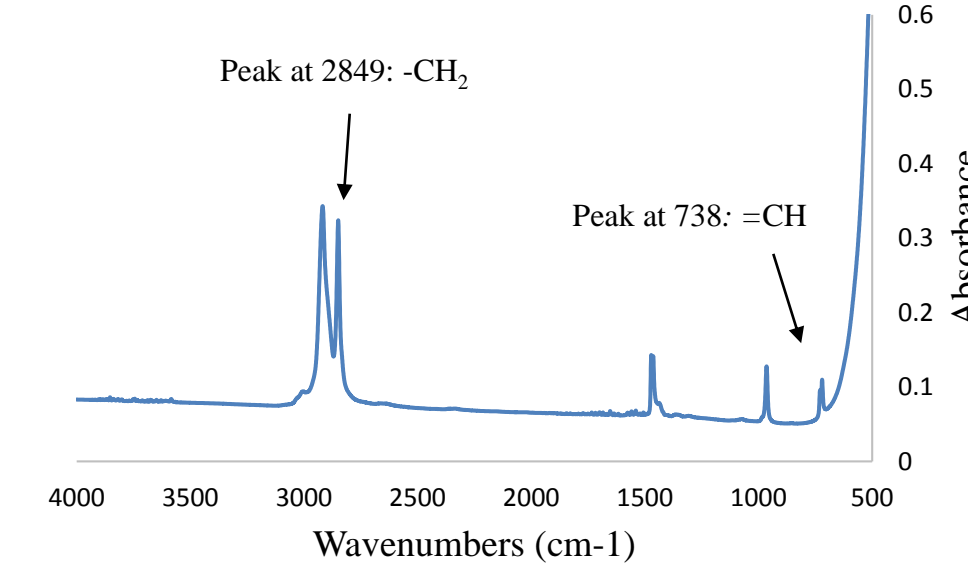


Figure 3: T_m vs F_{hyd}

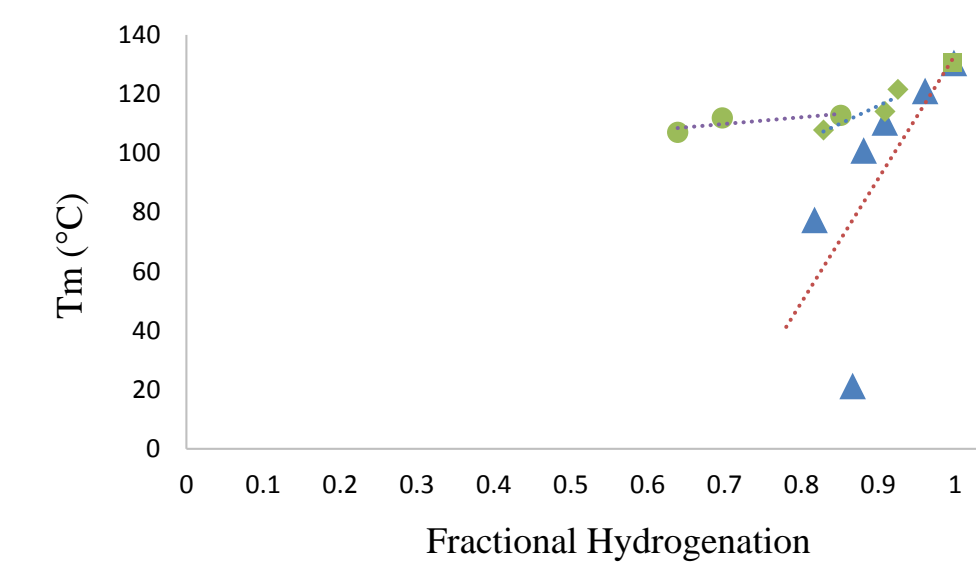


Figure 5: ΔH_m vs F_{hyd}

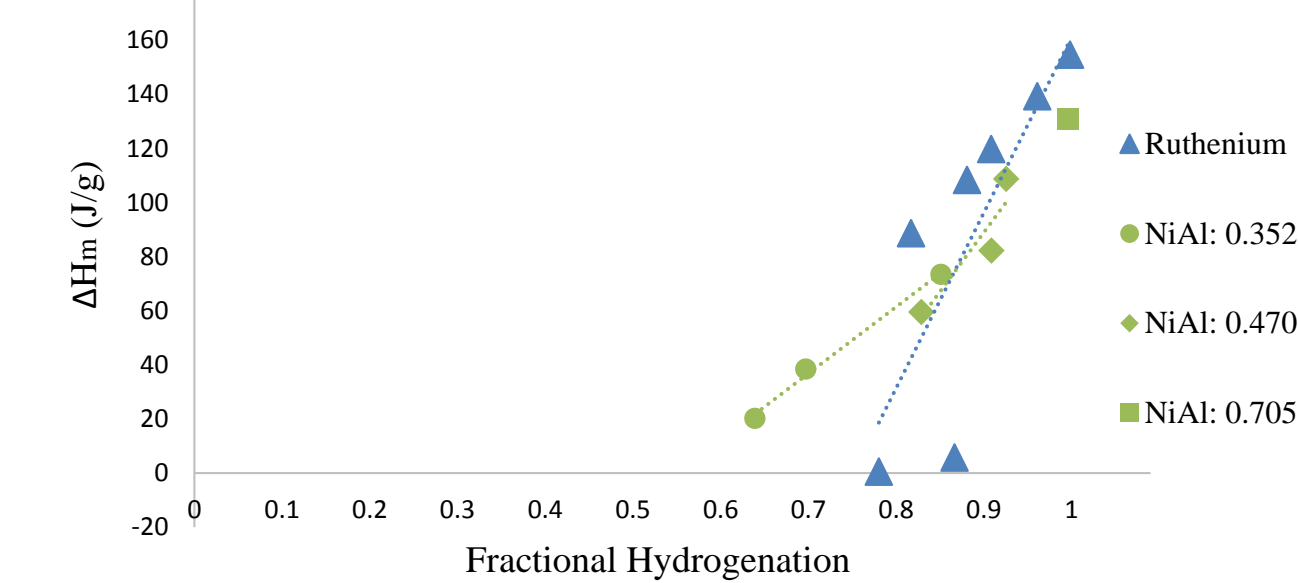


Figure 6 is an example DSC curve from which the melting enthalpy and peak temperatures were obtained. Figure 7 represents the different patterns seen between random (based on a literature comparison) and modified non-random hydrogenation catalysts (based on the higher melting temperature for a given melting enthalpy).

Figure 6 (below). Ruthenium Sample 5 DSC Curve.

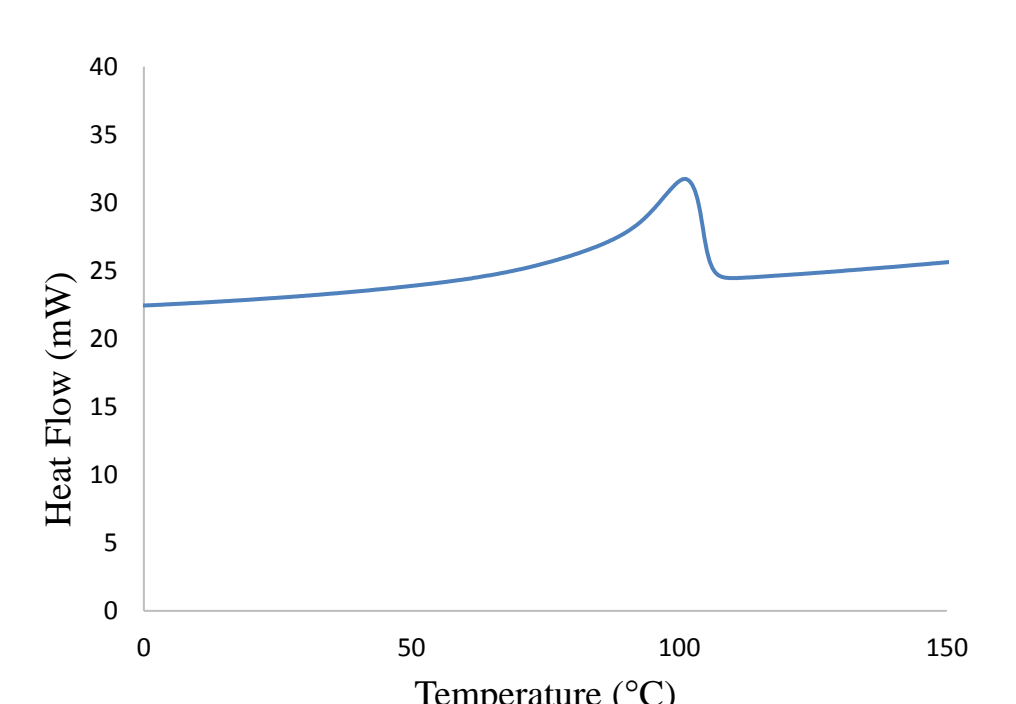
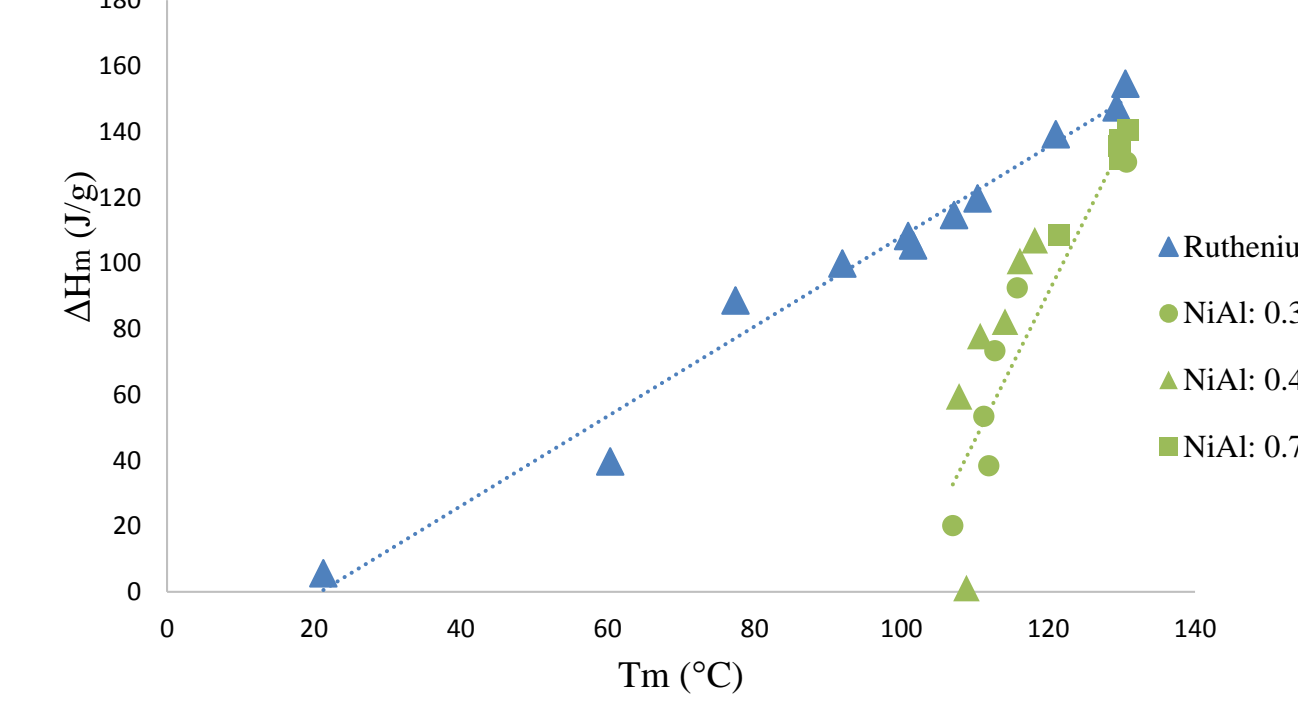


Figure 7: ΔH_m vs T_m



Data Comparison

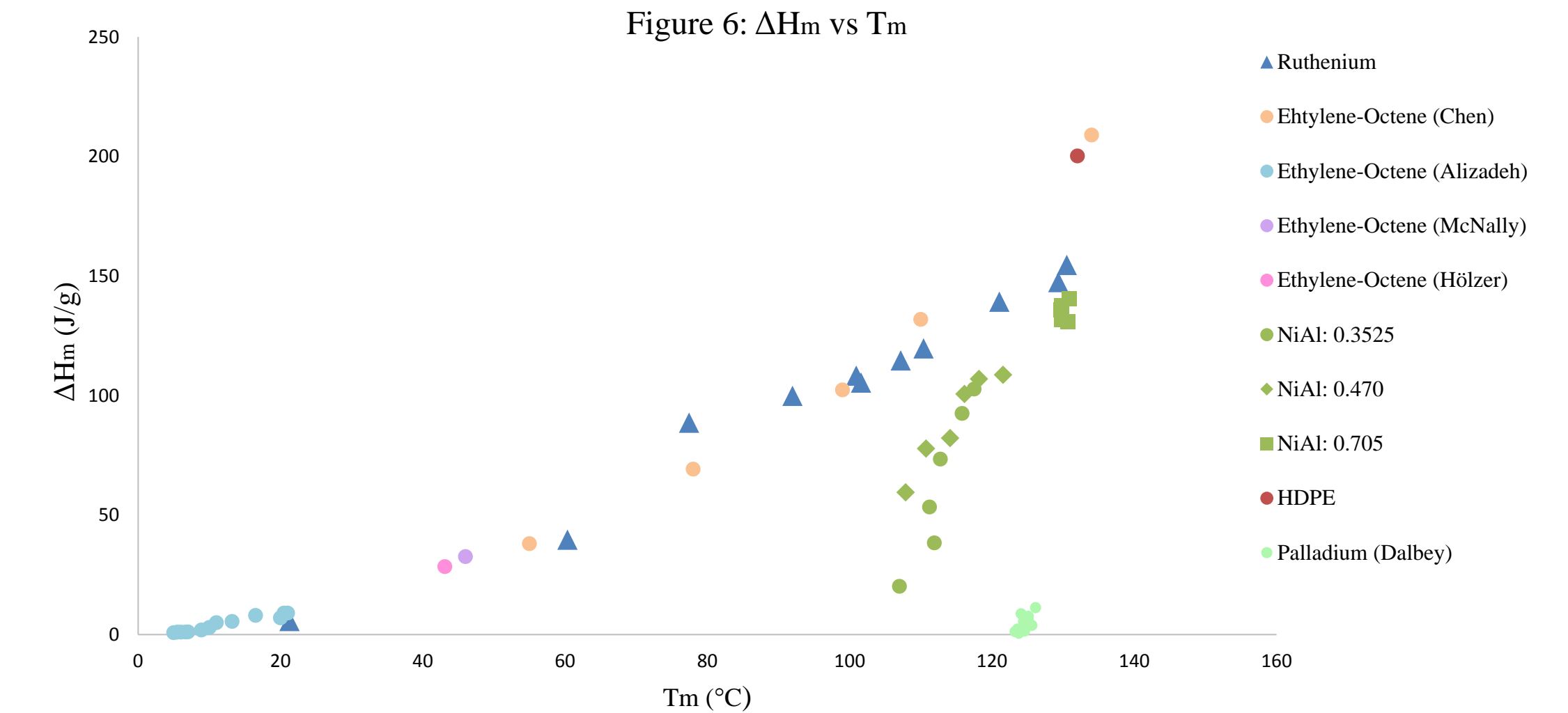
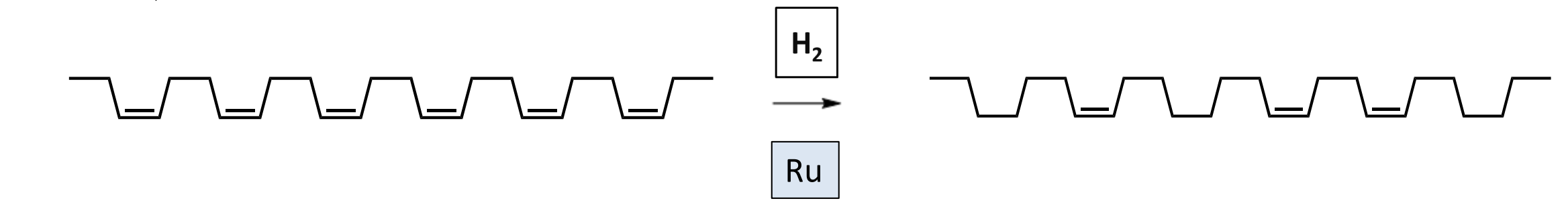


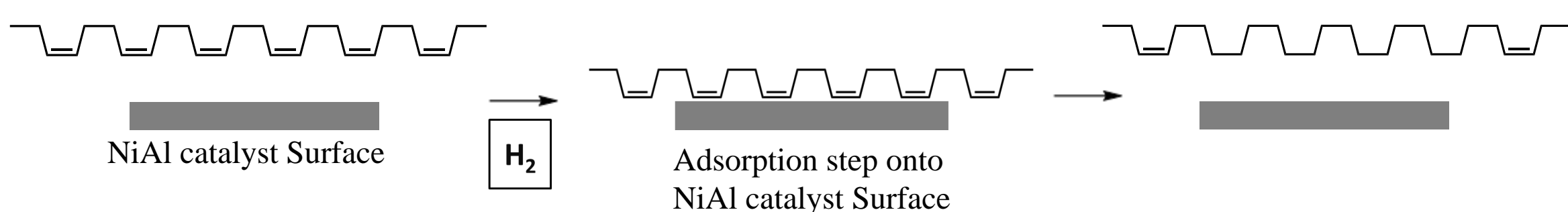
Figure 6 represents data points obtained from experimentation as well as points from literature sources from ethylene-octane copolymers. By making an analogy between random hydrogenation sites of polybutadiene and random copolymers of ethylene-octane, we were able to verify our hydrogenation trends with published data. Additionally we were able to compare Ni-Al catalyst data to the non-random palladium (Pd⁰/CaCO₃) hydrogenation catalyst.

Conclusion

Through our comparative analysis method, we were able to confirm the random hydrogenation pattern of the homogenous ruthenium catalyst (mechanism shown below).



After numerous trials of various catalyst-to-polymer ratios, we were also able to conclude that the heterogeneous nickel (II) 2-ethylhexanoate triethylaluminum catalyst hydrogenates in a modified non-random pattern. This is because the Ni-Al behaves similarly to non-random catalysts, but with slight variations seen in random catalysts (mechanism shown below).



References

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