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 propylicyal polymer cis 1,4-polybutadiene to polycrylene 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)2(H2O)
- A heterogeneous catalyst formed from the reaction of organometallic Ni and Al compounds.

Method

- Ru(PPh3)2(H2O): 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.
- Nickel (II): 2-Ethylhexanoate Triethylnalumminium
  - 15 mg 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 triethylnalumminium 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 every 30 minutes after 100°C is reached.

Reaction Catalyst Key:
- Ruthenium: NIA: 0.235 (0.235 mmol Ni)
  - NIA: 0.470 (additional 0.235 mmol Ni added)
  - NIA: 0.705 (additional 0.235 mmol Ni added)
  - NIA: 0.3525 (0.3525 mmol Ni added)

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 was used to calculate Fiso. 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 Fiso, 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 Fiso values) and non-random hydrogenation patterns (based on the higher melting temperatures at higher Fiso values, meaning thicker crystals which occur with blocky hydrogenation).

Data Comparison

Figure 6 represents data points obtained from experimentation as well as points from literature sources for ethylene-octene copolymers. By making an analogy between random hydrogenation sites of polybutadiene and random copolymers of ethylene-ctene, 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 (Pd/PaCO3) 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-ethylhexanoato triethylnalumminium 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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