

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

8.1.1 Hydrogenation of *Cis*-1,4-Polyisoprene

Hydrogenated *cis*-1,4-polyisoprene can be produced by using Ru(II) as homogeneous catalyst. $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ functions as the most efficient catalyst system among the selected Ru complexes for the study of CPIP hydrogenation in chlorobenzene solvent. The kinetics of CPIP hydrogenation was studied by monitoring the hydrogen consumption using a computer controlled gas uptake apparatus. The process exhibited a first order dependence on concentration of Ru, carbon – carbon double bond and hydrogen pressure, and an inverse dependence on the concentration of added PCy_3 . The activation energy was determined as 51.1 kJ/mol. The proposed mechanism and the derived rate expression are consistent with the observed kinetic data. The more polar solvent increases the degree of hydrogenation and the reaction rate. The activities of the Ru based catalysts can be promoted by the addition of a small amount of acid (i.e., *p*-toluenesulfonic acid). The main polymer chain length and molecular weight were decreased during the hydrogenation due to the reaction condition (i.e., temperature) used in the catalytic process.

8.1.2 Hydrogenation of Natural Rubber

A detailed kinetic study on the hydrogenation of natural rubber catalyzed by $\text{Ru}(\text{CH}=\text{CH}(\text{Ph}))\text{Cl}(\text{CO})(\text{PCy}_3)_2$ was carried out in the presence of adding small amounts of *p*-toluenesulfonic acid as promoter. The rate of double bond hydrogenation is first order with respect to concentration of catalyst, hydrogen and carbon – carbon double bond. An inverse effect on the pseudo rate constant on the PCy_3 concentration is observed. The rate of hydrogenation increases with increasing temperature; however, the effect of temperature declined with increasing temperature above 160°C. The apparent activation energy was estimated to be 25.25 and 23.26 kJ/mol for 130 and 260 mM of olefin concentration, respectively. Comparing with CPIP hydrogenation, the apparent activation energy of NR hydrogenation shows a lower value than that of

CPIP hydrogenation. The presence of impurities and high molecular weight of NR may reduce the efficiency of Ru based catalyst. The addition of a small amount of *p*-toluenesulfonic acid could neutralize the poisonous effect of the system. The rate of hydrogenation reaction increases with increasing the concentration of acid. The molecular weight and molecular weight distribution of NR are similar to those of the hydrogenated polymer. However, the high temperature used in the hydrogenation led to polymer chain degradation.

8.1.3 Hydrogenation of Natural Rubber Latex

Natural rubber latex was hydrogenated under two different processes using Ru(CH=CH(Ph))Cl(CO)(PCy₃)₂ as catalyst. One process was carried out in a homogeneous reaction system using THF as solvent. The other was a heterogeneous system, in which MCB was used as solvent. *P*-toluenesulfonic acid was added in order to improve the activities of Ru catalysts in both systems. It was found that the homogeneous hydrogenation system yielded a much slower rate than the heterogeneous system. The kinetic studies of the heterogeneous system showed that the reaction rate was first order with respect to olefin and hydrogen concentration. The process is first order with respect to concentration of catalyst, and plateaus at high catalyst concentration. The apparent activation energy is 29.2 kJ/mol. The reaction rate increases with increasing the amount of acid addition. However, the gel formation was noticed if the molar ratio of acid to polymer was more than 7:100.

8.1.4 Thermal Analysis

Differential scanning calorimetry and thermogravimetric analysis were used to investigate the thermal properties of the hydrogenated polymer. It was found that the hydrogenation reaction has no effect on the glass transition temperature (T_g) of the hydrogenated rubber. Nevertheless, the gel formation in the polymer product led to an increase in T_g . The initial decomposition temperature (T_{id}) and the maximum decomposition temperature (T_{max}) increase as the degree of hydrogenation increase. Therefore, the hydrogenation reaction can lead to an increase in the thermal stability of the diene polymer without affecting the glass transition temperature.

8.1.5 Numerical Investigation of Continuous HCPIP Process

A dynamic model for the hydrogenation reaction coupled with mass transfer was investigated for CPIP hydrogenation in a CSTR and PFR. It is proposed that the coupling behavior was determined by the relative capacity of reaction over mass transfer, polymer loading level and the residence time in the reactor. R is the dominant factor to affect the hydrogenation processes. The reaction rate and final degree of hydrogenation increase as R decreases. However, further decreasing R is not suggested when $R < R_c$. Due to the mass transfer effect, the CSTR shows better behavior in the short period at the beginning of the hydrogenation and later the PFR is better.

8.2 Recommendations

Further study for the hydrogenation of diene polymers should be concerned with the following aspects:

1. Mechanism of Effect of Acid Addition on Catalyst Activity and Impurities in NR and NRL

The addition of small amount of acid led to a great increase in the kinetic rate for the hydrogenation of CPIP, NR as well as NRL. The study of the mechanism by which the acid affects the hydrogenation of these polymers and impurities in the natural polymer should be carried out.

2. Effect of Impurities in Natural Polymer on Hydrogenation

The presence of impurities in NR and NRL results in a dramatic decrease in hydrogenation rate. The investigation of impurity components in the natural polymer should be carried out to understand their effect of impurities on the hydrogenation reaction.

3. Properties of Hydrogenated Polymer

Upon hydrogenation, some properties such as chemical, physical, and mechanical properties of the hydrogenated polymers have changed. Properties testing of the hydrogenated product is required in order to apply the novel polymers for commercial utilization.

4. Continuous Hydrogenation of Hydrogenation Processing

Application of ideal models for CPIP hydrogenation process should be investigated. The investigation of continuous of NR and NRL hydrogenation process should be made. The design of another type of real CPIP and/or NR and/or NRL reactor such as PFR with recycle or CSTR with some bypass should be further considered.



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