

CHAPTER VI

CONCLUSION

6.1 Conclusion

Cis-1,4-poly(isoprene) can be hydrogenated using $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$, $\text{RuCl}(\text{CO})(\text{styryl})(\text{PCy}_3)_2$, and $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. $\text{RhCl}(\text{PPh}_3)_3$ is an efficient catalyst for hydrogenation of most olefin polymers, but the activity is rather low for hydrogenation of cis-1,4-poly(isoprene). $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ has been shown to be the most active catalyst for the hydrogenation of cis-1,4-poly(isoprene) in toluene. Kinetic studies by gas uptake measurement showed that the process was first order with respect to $[\text{Os}]$ and $[\text{C}=\text{C}]$. A second order to zero order dependence on hydrogen pressure was found. The apparent activation energy was found to be 109.32 kJ/mol. The proposed mechanism and the rate expression for hydrogenation of cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ were consistent with the kinetic data. The viscosity of dilute solutions of fully saturated hydrogenated cis-1,4-poly(isoprene) was measured at 35°C using an Ubbelohde viscometer. The relative viscosity of hydrogenated products indicated the crosslinking effect in the polymer structure. Uniform viscosity of hydrogenated cis-1,4-poly(isoprene) suggested that there was possibly no degradation and crosslinking effect over the range of conditions used for the hydrogenation process.

In monochlorobenzene, $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ is an efficient catalyst precursor for the hydrogenation of cis-1,4-poly(isoprene). The reaction rate was first order to zero order with respect to concentration of catalyst, implying that the active complex is mononuclear. A first order dependence on hydrogen pressure and carbon double bond concentration were observed. The apparent activation energy was found to be 79.8 kJ/mol. The rates of hydrogenation in the presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ are superior to those obtained with $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ over the range of conditions studied. The proposed mechanism and the rate expression for hydrogenation of cis-1,4-poly(isoprene) using $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ were consistent with the kinetic data. The relative viscosity of the hydrogenated product indicated that there was possibly no degradation and crosslinking in the polymer structure.

Natural rubber can be quantitative hydrogenated using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ in presence of acid. An acid-induced selective entrapment of the phosphine ligand from $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ was found to give a substantial rate increase toward the hydrogenation of natural rubber. Strong acidity of acid and the high coordinating power of solvent increase the degree of hydrogenation and reaction rate. Uniform viscosity of hydrogenated natural rubber suggested that there was possibly no degradation or crosslinking over the range of hydrogenation conditions. The hydrogenation of natural rubber using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ by gas uptake measurement showed that the reaction was first-order with respect to carbon-carbon double bond.

Thermogravimetric analysis and differential scanning calorimetry were used to characterize the thermal properties of hydrogenated cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$. The increase in the degradation temperature (T_{id} and T_{max}) of hydrogenated cis-1,4-poly(isoprene) demonstrates that hydrogenation increases the thermal stability of cis-1,4-poly(isoprene). The glass transition temperature (T_g), measured from DSC, is consistent with the compositional analysis from TGA. A single T_g value of hydrogenated cis-1,4-poly(isoprene) suggested that there was possibly no side reaction during the hydrogenation process. The hydrogenation reaction did not affect the T_g value of the hydrogenated cis-1,4-poly(isoprene).

6.2 Recommendation

For the hydrogenation of rubber, further study should be given to the following aspects:

- 1) Kinetics studies of cis-1,4-poly(isoprene) using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ and $[\text{Ir}(\text{COD})\text{py}(\text{PCy}_3)]\text{PF}_6$ would possibly provide further insight into the hydrogenation of natural rubber. The kinetics study of natural rubber hydrogenation by gas uptake should be further studied.
- 2) The acid-promote hydrogenation of natural rubber demonstrated the short reaction time with small amount of homogeneous catalyst. Other types of acid, such as Lewis acids, etc., should be further investigated.
- 3) The presence of non-rubber contaminants such as, protein, etc., could affect the hydrogenation of natural rubber. These contaminants, which may act as inhibitors can stop the activity of catalyst. Therefore, the effect and elimination of non-rubber

contaminants such as proteins from natural rubber prior to hydrogenation should be further studied.