

Catalytic Hydrogenation of Grafted Natural Rubber in the Presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$

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Introduction

Natural rubber (NR), *Hevea Brasiliensis*, is a natural biosynthesis polymer containing 93–95 wt % of cis-1,4-polyisoprene. One type of chemical modification of natural rubber involves the grafting of vinyl monomers onto the rubber backbone. This reaction has gained significance by modifying the NR structure to provide more desirable properties. After the grafting of a vinyl monomer onto NR, the grafted NR may be degraded when exposed to sunlight due to the residual double bond content. The chemical modification of unsaturated polymers via catalytic hydrogenation offers a potentially useful method for improving the unsaturated polymer properties toward greater stability against thermal, oxidative, and radiation-induced degradation [1, 2]. This work focused on hydrogenation of purified PMMA grafted natural rubber in the presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$. The effect of catalyst, rubber, poly(methyl methacrylate) (PMMA) and p-toluenesulfonic acid concentration, hydrogen pressure, and temperature on hydrogenation rate were studied. The mechanistic aspects of this catalytic process are discussed based on the kinetic results observed. The thermal properties of grafted NR (GNR) and the hydrogenated grafted NR (HGNR) were also investigated.

Materials and Methods

The purified PMMA grafted NR was dissolved in monochlorobenzene in the presence of $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ as a catalyst. The kinetic data were obtained using a gas uptake apparatus [3]. The amount of hydrogen consumed as a function of time and the solution temperature were recorded using a gas-uptake monitoring program. The degree of hydrogenation was confirmed by ¹H-NMR spectroscopic analysis.

Results and Discussion

An olefin conversion profile versus reaction time is shown in Figure 1. The conversion plot exhibits an apparent first-order with respect to double bond concentration. Hydrogenation of grafted NR also exhibited a first-order dependence on catalyst concentration. A first-order to zero-order dependence on hydrogen pressure was found. The addition of a small amount of acid and poly(methyl methacrylate) demonstrated a beneficial effect on the hydrogenation of grafted natural rubber. It can be postulated that PMMA addition possibly affected the chain orientation in polymer solution because of the attraction and repulsion in polymer coils. The rate of hydrogenation was dependent on reaction temperature and the apparent activation energy over the range of 120–160°C was found to be 70.3 kJ/mol. The proposed mechanism and the rate expression for the hydrogenation of grafted NR were consistent with the kinetic data. The thermal stability of hydrogenated grafted NR was improved without affecting its glass transition temperature.

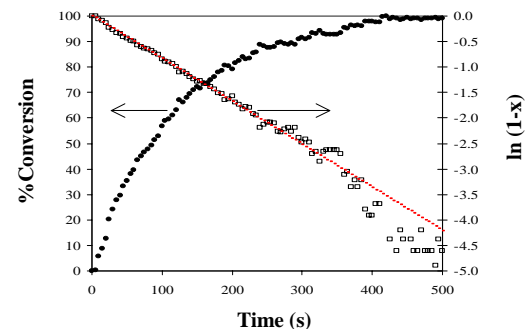
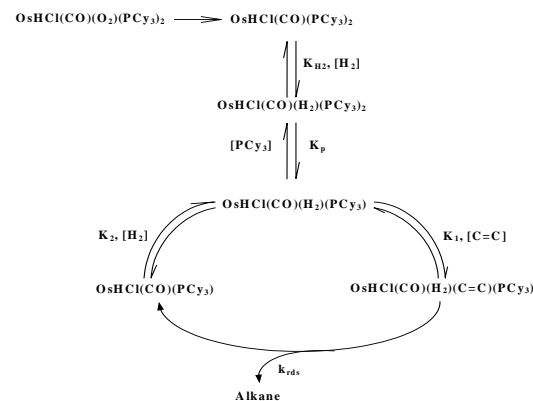


Figure 1. Olefin conversion profile and First-order $\ln(1-x)$ vs time plot (---- Linear regression model). $[\text{Os}] = 100 \mu\text{M}$; $[\text{C}=\text{C}] = 100 \text{ mM}$; $[\text{p-TSA}] = 2 \text{ mM}$ in monochlorobenzene; $P_{\text{H}_2} = 27.2 \text{ bar}$ and $T = 140^\circ\text{C}$.

Significance

For hydrogenation of grafted NR using $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$, more than 97% hydrogenation was achieved under optimum conditions. Mechanistic aspects of the hydrogenation of grafted NR were derived from the kinetic results as shown in Scheme 1.



Scheme 1. Proposed catalytic mechanism for hydrogenation of grafted NR

References

1. Singha, N. K., De, P. P., and Sivaram, S. *J. Appl. Polym. Sci.* 66, 1647 (1997).
2. Sarkar, M. D., Mukunda, P. G., De, P. P., and Bhowmick, A. K. *Rubber Chem. Tech.* 70, 855 (1997).
3. Mohammaddi, N. A., and Rempel, G. L. *Comput. Chem. Eng.* 11, 27 (1987).