

# Direct Catalytic Hydrogenation of Unsaturated Diene-Based Polymers in Latex Form

by

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## Abstract

The direct catalytic hydrogenation of nitrile butadiene rubber (NBR) in latex form was studied as a model system for the development of a new latex hydrogenation process for the modification of unsaturated diene-based polymers. NBR is a synthetic rubber of copolymerized acrylonitrile and butadiene produced in latex form by emulsion polymerization. The catalytic hydrogenation of NBR is an important post-polymerization process resulting in a more stable and tougher derivative, hydrogenated NBR (HNBR), which has been widely used in the automotive and oil drilling industry. The present commercial process involves a number of cumbersome steps to obtain solid NBR from the latex and subsequent dissolution of the solid NBR in a large amount of organic solvent followed by solvent recovery after coagulation of the hydrogenated NBR. Since NBR is produced in latex form, it is very desirable to directly hydrogenate NBR in the latex form which will significantly simplify the hydrogenation process and facilitate subsequent applications. As an economical and environmentally benign alternative to the commercial processes based on the hydrogenation of NBR in organic solution, this direct latex hydrogenation process is of special interest to industry. The objective of this project is to develop an efficient catalytic system in order to realize the direct catalytic hydrogenation of NBR in latex form.

$\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was initially used as the catalyst to investigate the possibility of hydrogenation of NBR in latex form and to understand the major factors which affect the hydrogenation operation. It was found that an organic solvent which is capable of dissolving or swelling the NBR was needed in a very small amount for the latex hydrogenation using the Os catalyst, and gel occurred in such a catalytic system during hydrogenation.

Wilkinson's catalyst,  $\text{RhCl}(\text{PPh}_3)_3$ , was then used for the latex hydrogenation in the presence of a small amount of solvent successfully without gel formation. Further investigation found that Wilkinson's catalyst has a high activity for NBR latex hydrogenation without the use of any organic solvent. The influences of various operation conditions on hydrogenation rate, such as catalyst and polymer concentrations, latex system composition, agitation, reaction temperature and hydrogen pressure, have been investigated. It was found that the addition of triphenylphosphine (TPP) has a critical effect for the hydrogenation of NBR latex, and the hydrogenation rate was mainly controlled by the amount of catalyst which diffused into the polymer particles. In the presence of TPP, NBR latex can be hydrogenated to more than 95% degree of hydrogenation after about 30 hours at 160°C

using Wilkinson's catalyst with a catalyst to NBR rubber ratio of 1 wt%, without the addition of any organic solvent. The apparent activation energy for such NBR latex hydrogenation over the temperature range of 152°C to 170°C was found to be 57.0 kJ/mol.

In the present study, it was also found that there are some impurities within the NBR latex which are detrimental to the hydrogenation reaction and are suspected to be water-soluble surfactant molecules. Deliberately designed solution hydrogenation experiments were conducted to study the impurity issue, and proper latex treatment methods have been found to purify the latex before hydrogenation.

To improve the hydrogenation rate and to optimize the latex hydrogenation system, water soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst (TPPMS: monosulphonated-triphenylphosphine) was used for the latex hydrogenation of NBR. The latex hydrogenation using the water soluble catalyst with TPP can achieve more than 90% degree of hydrogenation within 20 hours at 160°C. Further experiments using  $\text{RhCl}_3$  with TPP proved that the water soluble  $\text{RhCl}_3$  can be directly used as a catalyst precursor to generate the catalytic species in situ for the latex hydrogenation, and a stable NBR latex with 96% degree of hydrogenation can be produced without any gel problem within 19 hours of reaction at 160°C.

The catalyst mass transport processes for these Rh based catalysts in the latex system were investigated in order to further optimize the solvent-free latex hydrogenation process. While maintaining the emulsified state of the original latex, the direct catalytic hydrogenation of NBR latex can be carried out efficiently without any cross-linking problem to more than 92% degree of hydrogenation within 8 hours at 160°C.

As a result of this research project, new latex hydrogenation technologies were successfully developed to fulfill all major requirements for a solvent-free polymer latex hydrogenation route, which is a significant milestone for the improvement of this polymer modification technology. The finding of TPP's role as the "catalyst mass transfer promoter" is a breakthrough for the research field related to the hydrogenation of unsaturated diene-based polymers in latex form.

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# Chapter 1

## General Introduction

Hydrogenation is an important method for polymer modification as it provides an efficient synthetic route for the production of novel polymers which have certain unusual chemical and physical properties which are not found in other available materials. The saturated materials exhibit superior stability toward thermal, oxidative, and radiation-induced degradation in comparison with their parent polymers. Early findings reported in the 1940s act as the foundation for current polymer hydrogenation technology. Researchers used supported transition metal catalysts, such as nickel-kieselguhr and palladium-calcium carbonate, to hydrogenate polybutadiene (PB) at high temperatures (150~250°C) and under moderate hydrogen pressure (3.4~7 MPa, i.e. 500~1000 psi)<sup>[1,2]</sup>. There are two critical reviews published in 1990s with respect to polymer hydrogenation<sup>[3, 4]</sup>.

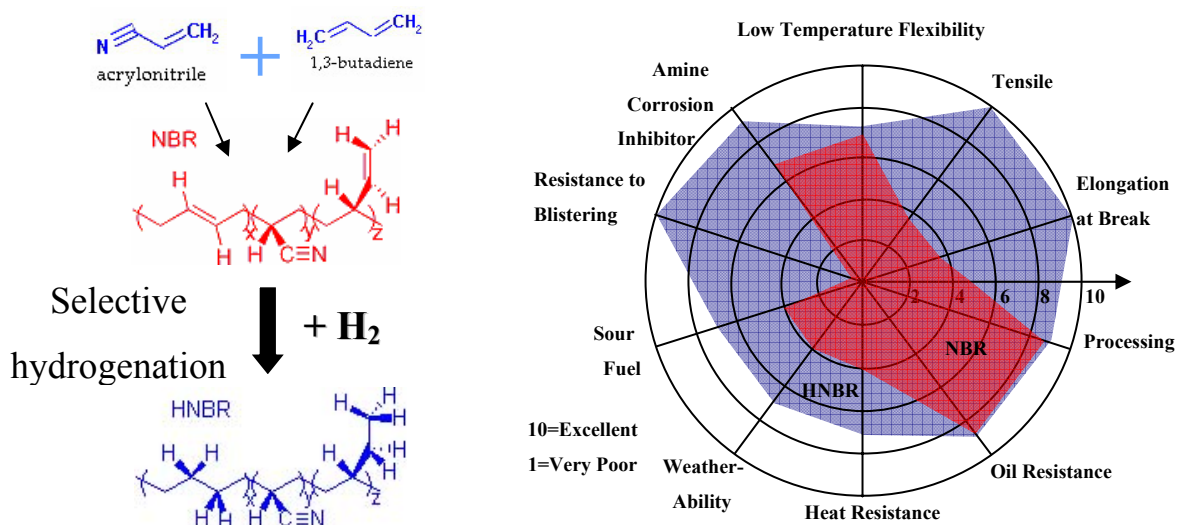
Diene polymers are polymers synthesized from monomers that contain two carbon-carbon double bonds (C=Cs), such as butadiene, isoprene and chloroprene. Diene-based polymers usually include these diene polymers and those copolymers of which at least one monomer is a diene. Diene-based polymers obtained by polymerization or copolymerization of conjugated dienes are widely utilized for many industrial applications. The common character of unsaturated diene-based polymers is that they all have residual double bonds in their polymer chains.

The chemical unsaturation, which is so important from the standpoint of permitting vulcanization to take place, is also the greatest weakness of these polymers. Residual carbon-carbon double bonds in the polymer chains are sites leading to potential degradation when exposed to oxygen, ozone and/or heat. This deficiency can be significantly improved by hydrogenating the diene-based polymers in order to eliminate the residual double bonds within the polymer chains.

Hydrogenated polymers usually exhibit improved thermal and oxidative stability compared with their precursors. Among these polymers that have been studied for hydrogenation, the hydrogenation of the butadiene units in styrene-butadiene-styrene copolymers and in nitrile butadiene rubber have been commercialized, producing the well-known Kraton G<sup>®</sup> (Shell)<sup>[ 5 ]</sup> and Therban<sup>®</sup> (Bayer/LANXESS)<sup>[6]</sup> polymers.

Nitrile butadiene rubber (NBR) is a synthetic diene-based rubber resulting from copolymerization of acrylonitrile and butadiene. It is one of a class of typical oil-resistant elastomers. A selective hydrogenation of the C=C unsaturation in NBR is an especially important commercial process

(Figure 1-1), which can increase the stability of the material, thereby extending its range and lifetime of application <sup>[7]</sup>. The hydrogenated nitrile butadiene rubber (HNBR), depending on acrylonitrile content and degree of hydrogenation, contributes to excellent mechanical properties, good hot air aging resistance, and superb resistance to oil swelling<sup>[8, 9]</sup>. NBR latex obtained by emulsion polymerization is a model latex system for the hydrogenation study of unsaturated diene-based polymer in latex form.



**Figure 1-1 Structure change and property changes <sup>[10]</sup> from NBR to HNBR**

During the 1970s, the automotive, industrial, and oil-well industries challenged the research and development community to develop an improved heat- and oil-resistant elastomer. It was essential for this new elastomer to perform at 150°C in air, oils, and other aggressive media for extended periods of time. Although many new elastomers were considered, HNBR emerged as the most promising by demonstrating a unique combination of excellent mechanical properties, good oil resistance, and high-temperature performance. HNBR was developed to bridge the price-performance gap between specialty high-performance fluoroelastomers (FKM), fluorosilicone (FMQ), and general purpose oil-resistant elastomers such as NBR, epichlorohydrin (ECO), and polychloroprene (CR). HNBR has been commercially available in bale form from Bayer and Nippon Zeon since the early 1980s. Evaluation of HNBR in the marketplace confirmed their unique balance of dynamic properties at elevated temperatures, excellent ozone resistance, superior abrasion resistance, good low-temperature

behavior, and very good hot-air resistance. The presence of the nitrile group in combination with the highly saturated nature of the elastomer is responsible for the superior resistance to aggressive fluids such as oils, fuels, and other non-polar liquids.

HNBR has been extensively used to make parts of equipment for utilization in solvent/oily/high-temperature environments, such as under-the-hood rubber components of automobiles (automobile fuel system parts and timing belts), seals or gaskets for oil drilling devices, paper industry rolls or textile rolls, tank track pads, seals for airplanes, seals for air-conditioning systems and shock absorption material <sup>[6]</sup>.

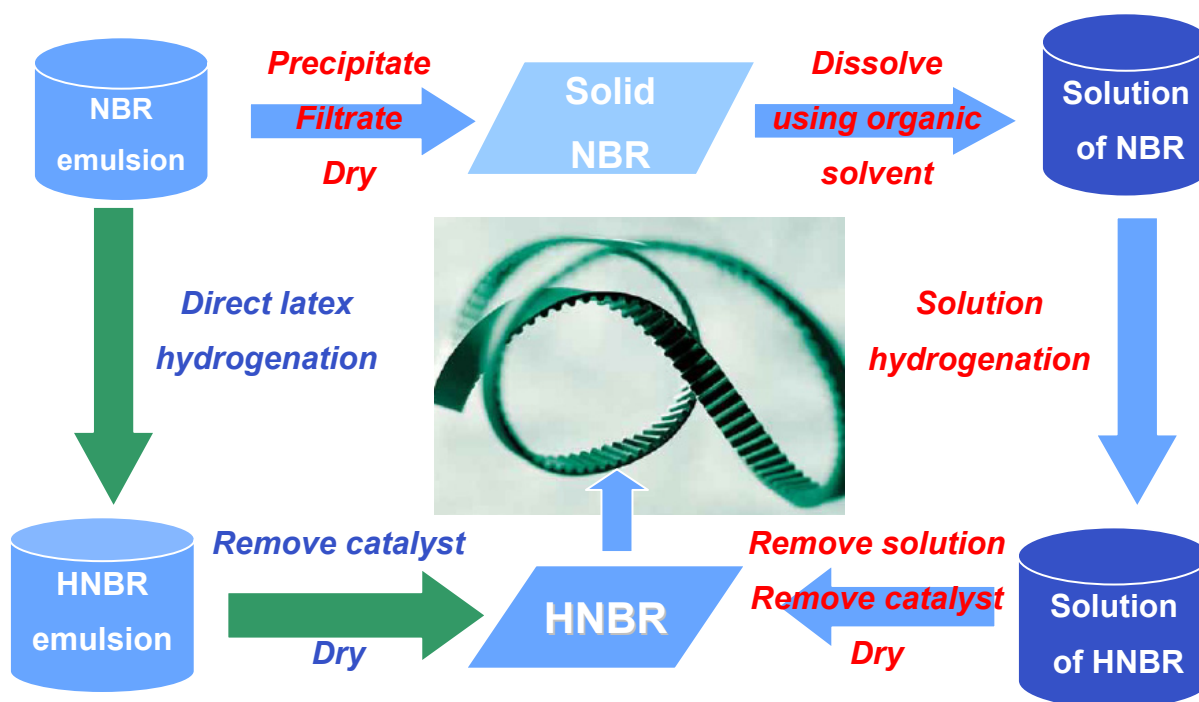
## **1.1 Present commercial process for HNBR production**

Nippon Zeon Co. Ltd., Japan, firstly commercialized HNBR under the trade name Zetpol using a heterogeneous catalytic hydrogenation process. Bayer also invented a HNBR production process by using homogeneous catalysts. Therban, the trade name for HNBR produced by LANXESS now, is currently manufactured in Orange, Texas and Leverkusen, Germany <sup>[11]</sup>. Commercial grades of HNBR generally have a level of unsaturation between 5 and 0.5% (a certain amount of, but very low, residual unsaturation is necessary for vulcanization) and a level of acrylonitrile between 34 and 45%.

Conventional HNBR manufacturing technology, developed since the 1970s, is based on the hydrogenation of NBR in non-aqueous solutions by using either a heterogeneous or a homogeneous noble metal catalyst containing rhodium or palladium <sup>[12, 13, 14, 15, 16]</sup>. NBR, produced by emulsion polymerization and standard latex coagulation and drying, is dissolved in a suitable organic solvent. Subsequently, the catalyst and hydrogen are introduced to react with the rubber in a batch reactor for a period of time (one to five hours) to reach the required hydrogenation level. The solid HNBR is obtained after removal of the solvent and the noble metal catalyst from the polymer solution <sup>[17]</sup>.

This conventional hydrogenation method is referred to as *solution hydrogenation*. The present commercial process involves a number of cumbersome steps to obtain solid NBR from the latex and subsequent dissolution of the solid rubber in a large amount of organic solvent followed by solvent recovery after coagulation of the hydrogenated polymer. This solution hydrogenation process suffers from drawbacks such as the high price for rhodium metal, the high viscosity of the reaction medium, and the cost involved in solvent recycle (shown in Figure 1-2). For improving the industrial process,

many papers have appeared reporting on the use of ruthenium or osmium based catalysts for solution hydrogenation of NBR [18, 19, 20, 21].



**Figure 1-2 Comparison of solution hydrogenation and latex hydrogenation process**

## 1.2 Direct catalytic hydrogenation of NBR latex (motivation)

NBR is synthesized commercially via emulsion polymerization and is available in the form of an aqueous latex or emulsion. It is obviously advantageous to directly hydrogenate NBR in latex form; as such a process would not only eliminate the need for a large amount of organic solvent to dissolve the solid polymer for the solution hydrogenation step, but also makes the hydrogenation process more energy favorable over the solution hydrogenation process. Therefore, it would be a very significant achievement if one could directly hydrogenate NBR in the latex form which would also help minimize negative impacts on the environment. It is especially beneficial when HNBR in the latex form is the desired end-use product, facilitating its further processing.



Two major technical routes have been reported in the literature with respect to the direct hydrogenation of NBR latex, i.e., direct hydrogenation of NBR latex by gaseous hydrogen using a Group VIII B metal complex as the catalyst<sup>[14]</sup>, and direct hydrogenation via a non-catalytic diimide route<sup>[22]</sup>.

While considerable efforts have been made to realize the direct hydrogenation of NBR latex, as yet there has been no report of a successful process for the direct hydrogenation of NBR latex in the absence of organic solvent with a conversion higher than 95% without crosslinking. A hydrogenation conversion higher than 95% without crosslinking in the resultant HNBR is a threshold that ensures high-performance applications of HNBR and guarantees excellent processibility of the final product. To realize the solvent-free latex hydrogenation process is the primary motivating force of this dissertation.

### **1.3 Scope of this research**

This research explores the feasibility of the direct hydrogenation of diene-based polymers in the latex form, and produces new knowledge for the diene-based polymer modification associated scientific field. Latex hydrogenation of NBR is chosen as the model reaction.

The objectives of this project are to develop an efficient catalytic system for NBR hydrogenation in latex form. The direct catalytic hydrogenation of NBR latex should be carried out efficiently to more than 95% conversion without any organic solvent and without any problem of cross-linking while maintaining the emulsified state of the latex system. The conducted research includes screening and developing a variety of suitable catalysts for the purpose of the latex hydrogenation, then investigating the suitable hydrogenation conditions and obtaining optimal operation conditions, and finally developing a new hydrogenation route which has the potential of being commercialized in the future.

Based on the knowledge in the literature, research in this area has focused on the design and development of efficient catalytic systems, and on improving the hydrogenation operations. A variety of catalysts have been investigated for the solution hydrogenation of diene-based polymers, including Os-, Rh-, Ru- and Ir- based catalysts. Since Rh and Os based catalysts have been found to have many advantages for solution hydrogenation of NBR, they were utilized for this research project involving the hydrogenation of NBR latex. This project began with the catalytic activity test of different

catalysts for latex hydrogenation (catalyst screening). On the basis of preliminary experimental results, a catalysis system with high efficiency for catalytic hydrogenation of NBR latex would be selected. The optimization of the catalysis system would consider the increasing of catalyst diffusion rate and the preventing of polymer cross-linking during the hydrogenation process. After the catalytic system was established, further improvements of the process were conducted.

## **Chapter 2**

### **Literature Review**

The hydrogenation of unsaturated carbon-carbon double bonds in polymers is of great importance as it provides an efficient synthetic route for the production of more stable and tougher derivatives. It also allows the introduction of functional groups that are often inaccessible by conventional polymerization techniques. Many of the natural and synthetic elastomers are available in the form of aqueous latices or emulsions (such as natural rubber (NR), styrene-butadiene rubber (SBR), and NBR). Thus it will be advantageous to hydrogenate elastomers in the latex phase as it will eliminate the need for the use of a large amount of organic solvent and dissolution of the polymer.

This chapter begins with a short review of the history of polymer hydrogenation technology. Then it focuses on the techniques used for the hydrogenation of polymer latex. Different catalytic or non-catalytic methods for latex hydrogenation are summarized and compared with respect to their efficiency and limitations. Engineering problems for latex hydrogenation, such as separation of catalysts and cross-linking of polymer chains, are also discussed. Research methodology and approaches for the hydrogenation of NBR latex are generated based on the analysis of the literature.

#### **2.1 Development of polymer hydrogenation technology**

Hydrogenation is a well-established technique for post-polymerization chemical modification of polymers [23]. Polymer hydrogenation presently is carried out using a variety of catalytic (homogeneous and heterogeneous) and non-catalytic techniques. Depending on the target polymer, desired selectivity and reaction conditions, one technique may be more beneficial than the others. Also, even with the development of latex hydrogenation, most polymer hydrogenation studies have been conducted on polymers dissolved in an appropriate organic solvent. The growth of polymer hydrogenation studies has been so extensive that it is impossible to provide a comprehensive review here. Thus the following sections shall mainly give information about hydrogenation of unsaturated diene-based polymers in organic solutions.

The importance of polymer hydrogenation in scientific and engineering applications has grown dramatically since the 1940s when several investigators began to conduct nondestructive polymer

hydrogenation (the polymer structure of polybutadiene was preserved after the hydrogenation) using nickel oxide <sup>[24]</sup>. The polymer hydrogenation studies in the 1950s using supported transition metal catalysts acted as the foundation for current polymer hydrogenation technology <sup>[25]</sup>. During that period, significant efforts were made to use heterogeneous catalysis for the hydrogenation of polymers to produce new materials with high resistance to degradation.

From an examination of the patent and publication literature, it is apparent that heterogeneous catalytic hydrogenation of NBR in solution using Pd-based catalysts was mainly studied by Nippon Zeon Co. Ltd., Japan <sup>[26, 27, 28]</sup>. The main problem with the Pd-based heterogeneous catalytic system is that a high hydrogenation degree (greater than 95%) can not be achieved.

The discovery of homogeneous catalysts for polymer hydrogenation occurred in the 1960s, which represented a most important breakthrough in this field. Numerous groups developed many types of homogeneous hydrogenation catalysts derived from organometallic and transition metal compounds. Polymer hydrogenation research shifted to develop and optimize homogeneous catalysts during 1960-70s, since these catalysts have much higher activity than the heterogeneous ones <sup>[29]</sup>. A great amount of research has been conducted using various rhodium, ruthenium, and osmium complexes for homogeneous hydrogenation of NBR <sup>[3]</sup>.

Wilkinson's catalyst, a rhodium-triphenylphosphine complex  $[\text{RhCl}(\text{PPh}_3)_3]$ , is by far the most studied and understood homogeneous catalyst for NBR hydrogenation. Professor Rempel's group <sup>[3]</sup> carried out the pioneering work of using it for polymer hydrogenation. The main advantages of Wilkinson's catalyst include its stability in air and excellent activity for NBR solution hydrogenation. It has also been found that in order to achieve quantitative hydrogenation of the C=C bonds in the presence of  $\text{RhCl}(\text{PPh}_3)_3$ , it is necessary to add an excess of free  $\text{PPh}_3$  to the polymer solution <sup>[30, 31]</sup>. Many other Rh-based complexes are also excellent catalysts for diene-based polymer hydrogenation. However, the Rh metal is always very expensive. As of 2006, rhodium costs approximately six times as much as gold, by weight. This has led to research and development of alternate catalysts based on cheaper noble metals, such as ruthenium.

Ru-based complexes are also good catalysts for polymer solution hydrogenation. Ru- $\text{PPh}_3$  complexes and  $\text{RuHCl}(\text{CO})\text{L}_2$  (L is a bulky phosphine) catalyst systems led to quantitative hydrogenation of NBR without the necessity of adding a free phosphine ligand to maintain the catalyst activity <sup>[32]</sup>. However, they are prone to gel formation and may cause a certain degree of cross-linking during hydrogenation.

Professor Rempel's group developed a series of Os-based catalysts for NBR solution hydrogenation <sup>[33]</sup>. J. S. Parent discovered that the best Os complex for NBR hydrogenation is  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  <sup>[34]</sup>. The rates of hydrogenation using this catalyst were superior to those produced by Wilkinson's catalyst over the entire range of reaction conditions studied.

The non-catalytic polymer hydrogenation technique was realized in the late 1960s when diimide ( $\text{N}_2\text{H}_2$ ) generated from *p*-toluenesulfonylhydrazide (TSH) was used to reduce residual unsaturation in polyvinylchloride <sup>[35]</sup>. For solution hydrogenation of NBR, this technique caused cross-linking reactions and the addition of sulfur containing species onto the polymer backbone <sup>[36]</sup>.

With the production of many polydiene elastomers in latex form, there has been a great interest in conducting direct polymer latex hydrogenation. To provide substantial environmental and economical benefits, the focus of polymer hydrogenation studies shifted from hydrogenation of polymers in organic solutions to the direct hydrogenation of polymer latex. However, in the latex the small polymer particles are suspended in the aqueous solution and surrounded by surfactants. Therefore, the contact between the  $\text{C}=\text{C}$  bonds within polymer particles and heterogeneous catalyst is extremely difficult due to the mass transfer limitations for latex hydrogenation. In this case, hydrogenation of latex elastomers has been exclusively reported by dissolving the oil soluble catalysts in an organic solvent then dispersing the solvent with the latex <sup>[37-43]</sup>, by using water soluble catalysts directly (biphasic catalysis) <sup>[51-58]</sup>, and by using non-catalytic methods <sup>[63-Error! Bookmark not defined.]</sup>. The following sections review research and process development related to latex hydrogenation of unsaturated diene-based polymer systems.

## 2.2 Hydrogenation of polymer latex using oil soluble catalysts

Oil soluble catalysts are homogeneous catalysts that can be dissolved in organic solvents. Researchers initially used a large amount of solvent with the oil soluble catalysts (volume of the organic solvent used was greater than the volume of the latex) for the latex hydrogenation <sup>[37-39]</sup>; then, latex hydrogenation using less organic solvent (volume of the organic solvent used is smaller than the volume of the latex) was realized <sup>[40-43]</sup>. Recently, there have been reports <sup>[45-47]</sup> on using oil soluble catalyst for latex hydrogenation in the absence of organic solvent during the reaction process.

### 2.2.1 With a large amount of solvent

Guo and Rempel <sup>[37]</sup> developed two processes for the selective hydrogenation of the C=C bonds in NBR emulsions in the presence of a number of  $\text{RuCl}_2(\text{PPh}_3)_3$  complex catalysts. One of the processes was carried out in a homogeneous system, in which an organic solvent, which can dissolve the NBR polymer and catalyst and which is compatible with the emulsion, was used. The other process was carried out in a heterogeneous system, in which an organic solvent, which is capable of dissolving the catalyst and swelling the polymer particle but is not miscible with the aqueous emulsion phase, was used. In both processes, quantitative hydrogenation of the C=C bonds of the NBR emulsion was achieved in the presence of  $\text{RuCl}_2(\text{PPh}_3)_3$ . The hydrogenation conversion could be more than 95% within 4 hours. It was also found that the addition of certain types of additives can improve the activities of the Ru-based catalysts.

A. Mahittikul et al. <sup>[38]</sup> hydrogenated natural rubber latex to produce a strictly alternating ethylene-propylene copolymer using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst in the presence of 150ml of chlorobenzene. The catalyst was capable of providing a hydrogenation level of more than 90% of C=C bonds of natural rubber latex in 4 hours. Addition of a controlled amount of acid demonstrated a beneficial effect on the hydrogenation rate.

Kubo et al. <sup>[39]</sup> hydrogenated NBR latex using a benzene solution of palladium acetate as catalyst. A benzene/acetone solution of the catalyst was added to the aqueous latex and the volume ratio of aqueous emulsion/organic solvent is less than 1:3. This ratio is important to keep the emulsion stable. 100 ml NBR latex (10% solid content, 39.4% ACN content) was placed in an autoclave and any dissolved oxygen was removed by purging with nitrogen. Palladium acetate (63.3 mg) dissolved in 160 ml of acetone/benzene (1/1) was added to the latex (emulsion/organic solvent = 1/1.6). The quantitative hydrogenation reaction was carried out at 3.0 MPa (435 psi) of hydrogenation pressure and 50°C for 6 hours to achieve more than 90% hydrogenation conversion. After completion of the hydrogenation reaction, the catalyst was removed by adding ion exchange resins to the reaction system and after absorption of the catalyst it was separated by the usual methods of filtration or centrifuging. It is also possible to allow the catalyst to remain as such in the hydrogenated polymer without removing it.

### 2.2.2 With less solvent

Previous processes of latex hydrogenation involve reactions of the polymers in the form of an aqueous dispersion in a large amount of organic solvent. Leube et al. provided a process for conducting the hydrogenation of an aqueous dispersion of the polymer that comprises not more than 20% by volume of an organic solvent <sup>[40]</sup>. They used a special catalyst solution preparation process: an autoclave with a volume of 0.3 L was charged under argon with 100g of toluene, 5.0g of ruthenium(III) tris-2,4-pentanedionate and 10.15g of tris-n-butylphosphine. Then 5 bar (72 psi) of hydrogen pressure was applied to the autoclave at room temperature, the contents were heated to 100 °C, and the hydrogen pressure was raised to 10 bar (145 psi). The hydrogen pressure and temperature were maintained for 2 hours. For hydrogenation, 45.5g of the catalyst solution prepared was added with thorough mixing to 1kg of SBR latex contained in a 2.5 L autoclave. 10 bar (145 psi) of hydrogen were applied to the autoclave at room temperature, the contents were heated to 110°C, and then the hydrogen pressure and temperature were maintained for 15 hours to achieve 95% conversion.

Krause <sup>[41]</sup> hydrogenated oil-insoluble SBR latex using  $\text{RhCl(PPh}_3)_3$ . The latex was swollen in benzene to allow the catalyst to diffuse into the polymer matrix and then the polymer was hydrogenated at temperatures ranging from 22°C to 65°C under 3.1 to 5.7 MPa (455 to 825 psi) of hydrogen for 3 to 36 hours. This emulsion of 30g [with 1.65% dispersion of SBR] was hydrogenated using  $\text{RhCl(PPh}_3)_3$  (0.05g) with 7g of benzene at 4.0 MPa (580 psi) over 18 hours at 22°C to obtain the hydrogenated SBR latex having only 0.3% residual unsaturation and an average particle size was 0.4-0.5 µm. Reactions run without a swelling medium, such as benzene, did not show any degree of hydrogenation.

Murrer et al. <sup>[42]</sup> hydrogenated an acrylonitrile-butadiene-styrene (ABS) emulsion using Wilkinson's catalyst,  $\text{RhCl(PPh}_3)_3$ . An ABS emulsion (5mL, containing 32.32% solid polymer) was placed in a rocking autoclave of 50 ml capacity. An equal volume (5mL) of water was added to the emulsion. Nitrogen was bubbled through the solution for about 10 minutes to remove oxygen. A solution of 20 mg (0.02 mole) catalyst,  $\text{RhCl(PPh}_3)_3$  in a mixture of 5 ml acetone and 5 ml toluene was added to the autoclave. Then the autoclave was flushed twice with hydrogen gas and finally pressurized at 1.5 MPa (218 psi). Hydrogenation was carried out at 70°C for 6 hours at the rate of one rocking movement per second. Infrared spectrum and NMR spectroscopy showed that 20% hydrogenation of the trans double bonds had occurred. Hydrogenation conducted at 100°C resulted in

40% hydrogenation of the trans double bonds. When the catalyst  $\text{RhCl}(\text{PPh}_3)_3$  was replaced by  $[(\text{PPh}_3)_2\text{RhCOD}]^+[\text{BF}_4]^-$  (COD = 1,5-cyclooctadiene), the trans double bonds were hydrogenated to the extent of 70%. In their experiments the organic solvents used for the catalyst were also compatible solvents for the polymer. These solvents swell the polymer particles and thereby make the double bond more accessible to the catalyst.

Ming Yao's group <sup>[43]</sup> reported that over 82% conversion was reached in 12 hours for hydrogenation of NBR in latex form based on a patented process involving an Rh-Ru bimetallic complex<sup>[44]</sup>. Organic solvent acetone/monochlorobenzene (volume ratio is 1/1) as cosolvent was added to the aqueous latex. Their results showed that 1.4 MPa (200 psi) of hydrogen pressure and 145 °C were the optimum technological parameters.

### 2.2.3 Without the presence of any solvent

There is particular interest in the possibility of carrying out catalytic hydrogenation of polymers containing unsaturated double bonds without the presence of any organic solvent.

In 1989, Gilliom <sup>[45]</sup> reported the hydrogenation of polybutadiene and butadiene-styrene triblock polymers without the presence of a solvent using either Wilkinson's catalyst,  $\text{RhCl}(\text{PPh}_3)_3$ , or Crabtree's catalyst,  $[\text{Ir}(\text{COD})(\text{PMePh}_2)_2]\text{PF}_6$  (COD = 1,5-cyclooctadiene). The dispersion of the catalyst through the polymer was achieved by dissolving the polymer with the catalyst in an appropriate solvent, such as toluene or dichloromethane, to cast a polymer film, and then removing the solvent under vacuum. The resulting polymer/catalyst mixture (9.1% by wt catalyst) was then placed under 0.38 MPa (55 psi) of hydrogen and heated to 60 °C. High conversion (80-94%) for 1,2-polybutadiene was achieved with both catalysts in less than 70 hours. Lower catalyst loadings were also investigated.  $\text{RhCl}(\text{PPh}_3)_3$  at 1.1% by wt catalyst loading was reported to afford 88% hydrogenation of the double bonds in a butadiene-styrene triblock polymer after several days of reaction. Then, Gilliom and Honnell <sup>[46]</sup> observed that the triblock copolymer polystyrene-polybutadiene-polystyrene (PS-PB-PS) was hydrogenated from the outside in, which produced a marked reaction front within the polymer solid pellet. The hydrogenation rate for the solid is limited by the diffusion of hydrogen through the polymer material to the reaction front.

Dersch <sup>[47]</sup> et al. invented a method to hydrogenate ethylenically unsaturated double bonds in SBR by reacting the aqueous dispersion of SBR with hydrogen in the presence of a ruthenium based



catalyst. The inventive method is characterized by integrating the hydrogenation catalyst into the aqueous dispersion of SBR without adding any solvent. They added ruthenium (III) tris-2,4-pentaketone into the monomer mixture before the emulsion polymerization to produce the SBR emulsion. Then distilled water was added into the emulsion to adjust the solid content to 30% and tri-n-butylphosphine was also added into the emulsion. After stirring for 16 hours at room temperature, hydrogen was introduced to 100 bar (1450 psi) pressure and the temperature was increased to 150°C. When 150°C was reached, the hydrogen pressure was increased and kept at 280 bar (4000 psi) for 15 hours for the hydrogenation reaction. A conversion of more than 95% was achieved using this hydrogenation method.

### **2.3 Hydrogenation of polymer latex using water soluble catalysts (bi-phasic catalysis)**

E.G. Kuntz<sup>[48]</sup> introduced the idea of biphasic catalysis in water, and the first industrial application of biphasic hydroformylation increased the interest in such water-soluble organometallic systems. Biphasic catalysis makes it easier for catalyst separation without destroying or transforming the catalyst. The most famous water soluble catalyst is  $\text{RhCl}(\text{TPPTS})_3$  (TPPTS = trisulphonated-triphenylphosphine) by Kuntz<sup>[49]</sup>. Following his success, several water-soluble ligands and catalyst systems were introduced in the literature. K. Nomura has summarized the transition metal catalyzed hydrogenation in water<sup>[50]</sup>. Biphasic hydrogenation is well known in synthetic organic chemistry. However, its application to hydrogenation of polymers has so far not been so successful; only a few systems were found to work for the biphasic reaction with a polymeric substrate.

Mudalige and Rempel<sup>[51]</sup> studied the hydrogenation of polybutadiene (PBD), styrene-butadiene (SBR) and NBR polymers in aqueous/organic biphasic media catalyzed by one water-soluble complex  $[\text{RhCl}(\text{HEXNa})_2]_2$  ( $\text{HEXNa} = \text{Ph}_2\text{P}-(\text{CH}_2)_5-\text{CO}_2\text{Na}$ ) at 100°C and 5.5 MPa (800 psi) of hydrogen pressure. The hydrogenations were carried out on the polymer emulsions formed by suspending a polymer solution (2g of the polymer in 10ml of toluene) in 80 cm<sup>3</sup> of distilled, deionized water (the resulting emulsion contained 2.2 wt% solids). The hydrogenation conversion obtained after 6 hours was 53% at 100°C and 5.5 MPa (800 psi). But the catalyst was extracted into the organic phase during the reaction. They also compared the experimental results with experiments

using water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst (TPPMS: monosulphonated-triphenylphosphine). Both complexes showed a reasonable catalyst activity toward polymer hydrogenation.

Lin's group in China synthesized a water soluble ligand, tri-(*p*-phenoxy-polyoxyethylene ether)-phosphine and its rhodium complex <sup>[52]</sup>. The rhodium complex was used to hydrogenate a NBR emulsion which contained 20ml of water, 2g NBR dissolved in 80ml of chlorobenzene and 0.1g of the complex. The reactions were carried out at 4 MPa (580 psi) of hydrogen and under 90°C to 154°C, and the maximum hydrogenation conversion was 65% after 2 hours. More than 96% of the initial used metal rhodium was recovered from the water phase, and no Rh metal was detected in the polymer phase (<0.1 mg/kg HNBR) according to their report.

Singha et al. <sup>[53]</sup> have explored a method whereabouts NBR latex can be directly hydrogenated using the water soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst <sup>[54]</sup>. The hydrogenation of the NBR latex was carried out over a large range of pressure, temperature and catalyst concentration. More than 60 mol% hydrogenation could be achieved at 75 °C and atmospheric hydrogen pressure after 12 hours. Hydrogenation was accompanied by an increase in the gel content of the latex. The degree of hydrogenation increases with increasing catalyst concentration but the fraction of soluble rubber decreases with the increase in catalyst concentration. With increase in temperature and hydrogen pressure the degree of hydrogenation increases but the gel content remains almost invariant. The extent of hydrogenation increases with increasing reaction time. The reasons for the insolubility of HNBR prepared using the water soluble catalyst is not clearly understood. No coagulation was observed after the hydrogenation reactions. Hydrogenation also was accompanied with no significant change in the average particle size as well as particle size distribution.

Nabeshima Yasuhiko et al. <sup>[55]</sup> used a water-soluble Rh-TPPTS compound catalyst to hydrogenate the NBR latex (solid content 11.1%). The hydrogenation reaction of such a NBR latex was performed under 0.8 MPa (116 psi) and 60°C for 24 hours. The latex obtained after the hydrogenation reaction was stable and the hydrogenation conversion was 56%.

Because of the very poor solubility of the NBR and SBR polymer chains in water, the contact between the C=Cs and water soluble catalysts during the hydrogenation of the polymer latex is limited to the interface between the water and polymer particle phase. In addition, the water soluble catalysts tend to remain on the surface of the polymer particles and to cause gel formation.

Papadogianakis et al. reported an exceptional aqueous phase hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) (PB-*b*-PEO) by using water-soluble Rh/TPPTS complexes <sup>[56]</sup>. In their hydrogenation system, mixed micelles were formed by mixing the amphiphilic PB-*b*-PEO with added cationic surfactant dodecyltrimethylammonium chloride (DTAC) and *n*-hexane. Hydrogenation conversion can go up to 100% after one hour catalyzed by Rh/TPPTS complexes ([Rh] = 10 ppm or less in aqueous phase) generated in situ from RhCl<sub>3</sub>·3H<sub>2</sub>O and TPPTS under 80 to 100°C and 20 bar (290 psi) of hydrogen pressure. Their recycling experiment showed that the catalytic activity of the anionic catalytic system, Rh/P(C<sub>6</sub>H<sub>4</sub>-*m*-SO<sub>3</sub><sup>-</sup>)<sub>3</sub>, remained high in a consecutive run. The success of this hydrogenation system is mainly due to the fact that PB-*b*-PEO is an amphiphilic starting material.

Water-soluble organometallic catalysts have also been used in non-aqueous ionic liquid systems. Rosso et al. described the biphasic hydrogenation of PB, NBR and SBR catalyzed by RhCl(TPPTS)<sub>3</sub> in ionic liquids such as *N,N'*-butylmethylimidazolium tetrafluoroborate <sup>[57]</sup>. Jin's group in China reported the bi-phasic hydrogenation of the polystyrene-*b*-polybutadiene-*b*-polystyrene (SBS) block copolymers catalyzed by Ru/TPPTS complexes in polyether modified ammonium salt ionic liquids <sup>[58]</sup>. Their experimental results showed that the hydrogenation degree can be enhanced significantly by the addition of triphenylphosphine (TPP). When the molar ratio of TPP, TPPTS and Ru is 2:5:1, a 89% hydrogenation degree can be achieved after 12 h under reaction conditions of 5.0 MPa (725 psi) hydrogen pressure and 150°C. In addition, no hydrogenation takes place on the benzene ring. The Ru catalyst immobilized in the ionic liquid can be recovered simply by phase separation and was recycled three times without any significant changes in the catalytic selectivity and activity.

## 2.4 Hydrogenation of polymer latex using non-catalytic techniques

A non-catalytic technique using diimide (N<sub>2</sub>H<sub>2</sub>) reduction of double bonds has also been applied for saturation of polydiene latex. Diimide acts as a mild reducing agent for a variety of symmetrical unsaturated bonds <sup>[59, 60]</sup>. There are several methods for generating diimide, including oxidation of hydrazine, decarboxylation of potassium azodicarboxylate, and thermolysis of *p*-toluenesulfonylhydrazide (TSH) <sup>[61, 62]</sup>.

The oxidation of hydrazine is the method most commonly utilized to produce diimide in-situ in the aqueous phase for polymer latex hydrogenation, which was firstly reported by Wideman for NBR latex hydrogenation in 1984 <sup>[63]</sup>. Parker and Roberts developed this diimide reduction process to hydrogenate SBR and BR latices as well as NBR latex <sup>[64, 65]</sup>. The chief advantage of diimide

hydrogenation over other techniques is that no high-pressure apparatus, hydrogen gas, noble metal catalysts or any organic solvents are required. However, the low efficiency of diimide utilization and latex gel formation exist in the diimide hydrogenation process.

To overcome the gel problem, Belt et al (DSM N. V.) applied several patents after 1998, which claimed that some compound containing primary or secondary amines can be added before, during or after the latex hydrogenation to break crosslinks formed during the hydrogenation <sup>[66]</sup>.

Zhang et al further proved that dropwise addition of hydrogen peroxide with post reaction at ambient temperature was the most effective way to conducting diimide hydrogenation of NBR latex. They hydrogenated NBR with a hydrogenation degree of 80% and a gel mass fraction of 3.1% was obtained <sup>[67]</sup>.

Chun Wei <sup>[68]</sup> reported that the hydrogenation extent is influenced by the particle-size of latex and more than 90% conversion can be achieved using high-soap, small particle size NBR latex.

Recently, X. Lin in Professor Rempel's group reported NBR latex hydrogenation studies via utilization of diimide with the use of boric acid as a promoter <sup>[69]</sup>. It has been found that the hydrogenation efficiency, which is defined as the ratio of the amount of hydrogen peroxide consumed for the hydrogenation to the total amount of hydrogen peroxide reacted, varies with both the type of catalyst and degree of hydrogenation. It was also found that using radical scavengers in such a latex hydrogenation process did not show any evidence in helping to suppress the degree of gel formation, which is in contradiction with that observation by Belt <sup>[66]</sup>. Therefore, gel formation in polymers that are hydrogenated via diimide has been investigated in detail through an inspection of all the chemical reactions involved in the process by X. Lin, and it was proposed that the primary radicals giving rise to crosslinking are generated in the polymer phase in situ, and the step responsible for generating these organic radicals is possibly the diimide disproportionation reaction <sup>[70]</sup>. A comprehensive simulation of the diimide hydrogenation process was carried out, and it was found that the diimide diffusion interferes with the diimide hydrogenation of the NBR latex, even though the particle diameter is as small as 72 nm. The interference of diimide diffusion makes it very difficult to achieve above 90% hydrogenation without significant gel formation <sup>[71]</sup>.

The major disadvantage of diimide hydrogenation is still its propensity to promote crosslinking of polymer chains and cause gel formation when the hydrogenation reaction reaches high conversion, which deteriorates the mechanical properties of the hydrogenated rubber, and even makes the final

product non-processible <sup>[71]</sup>. Furthermore, since this method of polymer hydrogenation is stoichiometric in nature, it is only practical on laboratory scales. Industrially, the present preferred method of polymer hydrogenation, for both economic and technical reasons, is to use transition metal catalysts in organic reaction media.

## **2.5 Other issues in the hydrogenation process**

There are also some other aspects, such as separation of the catalyst from the products and control of the cross-linking problem, to consider for further development of the catalytic hydrogenation process of the polymer latex. These aspects determine the commercial feasibility of the latex hydrogenation process.

### **2.5.1 Separation of catalyst from products**

In the development of catalytic hydrogenation processes, separation of catalysts is also important. Efficient separation of catalysts to enable their reuse for subsequent cycles of reactions presents a key challenge. Catalyst removal is especially difficult from polymer latex because of the high viscosity within the polymer particles and the good compatibility between the catalysts and the polymer. Several fundamental approaches have been studied to propose a solution to this catalyst separation problem <sup>[72, 73]</sup>.

Removal of Rh based catalyst after solution hydrogenation reaction has been realized in the industrial production of NBR as a unit operation by using ion-exchange resins. Panster et al patented the use of organosiloxane copolycondensates to recover rhodium and ruthenium catalysts from solution of HNBR, which reduced the metal residual to less than 5 ppm in solution <sup>[74]</sup>. Rhodium residues in HNBR solution can also be removed by using ion-exchange resins with thiourea functional groups <sup>[75]</sup>. Kramer et al. disclosed fast and selective recovery of rhodium-containing catalyst with various silica-based amine ion exchange resins <sup>[76, 77]</sup>. They also reported the recovery of Wilkinson's catalyst with P-donor ligands immobilized onto silica <sup>[78]</sup>. Silicates, such as calcium silicate, magnesium silicate and diatomaceous earth, have also been used as adsorbers for catalyst separation <sup>[79]</sup>.

Besides using ion-exchange resins, the concept of controlling the catalyst's phase compatibility and the use of super critical CO<sub>2</sub> (scCO<sub>2</sub>) to assist the reaction/separation has emerged as possible tools for the separation of catalyst from the latex system.

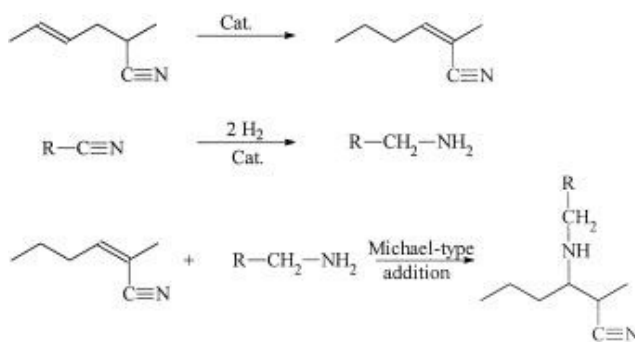
By controlling the phase compatibility, catalyst that is predominant or exclusive present in one phase is separated by mechanical operation from products in the other phase. Zilin Jin etc. reported a thermo regulated phase transfer catalyst (TRPTC) <sup>[80]</sup>. They synthesized a series of novel polyether-substituted triphenylphosphines (PETPPs). PETPPs manifest inverse temperature-dependent solubility in water that enables them to act as thermo regulated phase transfer ligands. The concept of the TRPTC, in which the catalyst transfers into the organic phase to catalyze the reaction at a higher temperature and returns to the aqueous phase to be separated from the product at a lower temperature, was successfully applied to the biphasic hydroformylation of higher olefins.

Several aqueous biphasic catalytic systems using scCO<sub>2</sub> have been developed with the catalyst immobilized in the water layer. These systems are truly biphasic (sc/l) in nature and have been mainly applied to hydrogenation reactions <sup>[81, 82]</sup>. One report has discussed enhanced catalyst reactivity and separations using water/carbon dioxide emulsions or microemulsions <sup>[83, 84]</sup>. It offers a distinct advantage over common water/oil emulsions in that it can be easily broken by simply decreasing the pressure to effect product separation and catalyst recycle. And a new inverted biphasic catalysis system using supercritical CO<sub>2</sub> as the stationary catalyst phase and water as the continuous phase was reported for Rh-catalyzed hydroformylation of polar substrates <sup>[85]</sup>. Product separation and catalyst recycling is possible without depressurizing the autoclave.

Wilkey invented a novel catalyst separation process comprising the steps of contacting a metal catalyst residue-containing polymer solution with an aqueous solution of ammonia and carbon dioxide, separating the metal residue from the polymer solution, and recovering a polymer solution comprising less than 15 ppm by weight, based on polymer, of the metal <sup>[86]</sup>.

## **2.5.2 Control of the cross linking problem**

The mechanism of crosslinking during hydrogenation of diene based polymers is not well understood; although a Michael-type addition mechanism <sup>[20]</sup> was speculated to account for this problem (Figure 2-1).



**Figure 2-1 Proposed mechanism of crosslinking during hydrogenation reactions**

It has been found that an increase in molecular weight resulting in gel formation of the hydrogenated NBR occurred during the hydrogenation reaction when using Ru catalysts <sup>[87, 88]</sup>. Rempel and Guo <sup>[89, 90]</sup> disclosed a method by which this gel formation can be avoided. An NBR emulsion (containing about 33% solid NBR having an acrylonitrile content 38%) was hydrogenated in methyl ethyl ketone (MEK) at 2.5 to 10.0 MPa (360 to 1450 psi) hydrogen pressure and 100 to 200 °C. Organic additives such as ascorbic acid, chloroacetic acid, hydroxyl acetic acid, and phenoxy acetic acid were added to the reaction. The additives had a beneficial effect in minimizing the gel content.

Belt <sup>[91]</sup> reported that cross-links can be broken by adding some chemicals such as phenylhydrazine. Wang et al. <sup>[92]</sup> found that the mass fraction of gel in the hydrogenated NBR was significantly reduced by adding hydroquinone.

## 2.6 Summary

In the stream of “green” chemistry, the latex hydrogenation process that uses no organic solvent has been increasingly appreciated. Hydrogenation of latex elastomers has been reported in the literature by dispersing oil soluble catalysts with organic solvents, by using water soluble catalysts as a biphasic catalysis process, or by using the non-catalytic diimide reduction process.

When oil soluble catalysts were used, there was a general belief that polymer latex particles must be swollen by more or less organic solvents to allow the catalyst to get into the polymer matrix and then the polymers could be hydrogenated in the latex form to a high degree of hydrogenation. So the use of organic solvents seems indispensable.

Using of water soluble catalysts may eliminate the need for solvents. However, there are two major problems associated with water soluble (bi-phasic) catalysts compared with using oil soluble catalysts: low final hydrogenation conversion and gel formation.

The hydrogenation of polymer latex via diimide is another very attractive method. Unfortunately, serious crosslinking always accompanies it and limits the end-use properties of the polymers.

Among all these previous latex hydrogenation studies, there is one report that peeled back the surface layers of the complicated latex hydrogenation problem and provided us the opportunity to figure out a solution: Gilliom described the bulk hydrogenation of olefinic polymers using molecular catalysts<sup>[45, 46]</sup>, which introduced the idea that homogeneous catalysts can be utilized to hydrogenate C=C in polymer chains without the use of any organic solvent. Actually, in their study an organic solvent was used initially to disperse the catalyst into the polymer matrix, with subsequent removal of the solvent before the hydrogenation. Although an organic solvent was involved in their process, their study really presented a rare example of polymer hydrogenation occurring in a pure polymer matrix without the presence of any solvent during the reaction. *This confirms that the catalytic ability of the homogeneous catalyst does not depend on the presence of solvents. So, it inspired us to discover and develop a catalytic system using homogenous catalysts for the hydrogenation of NBR latex in the absence of organic solvent.*

One important fact about Gilliom's study is that the hydrogenation of 1,2-polybutadiene was performed at temperatures above the polymer glass transition temperature,  $T_g$ , allowing for mobility of the catalyst. So, it is interesting to investigate whether the mobility of homogeneous catalysts within the NBR polymer particle phase was sufficient to permit effective hydrogenation of the NBR latex without using organic solvents. *The sufficient mobility of homogeneous catalysts within the polymer particle phase should be the key to successfully realize the solvent-free polymer latex hydrogenation process.* Based on this idea, which was initiated by the analysis of research results from the literature, a strategy for the whole project was developed, and successful latex hydrogenation was achieved.



## **Chapter 3**

### **Research Methodology and Approaches**

The motivation of this dissertation was to develop a new latex hydrogenation process for diene-based polymers by exploiting highly efficient catalytic systems, and to optimize the process for potential commercial production. The hydrogenation of NBR latex was chosen as the model system. In the long term, we aim at polymer latex hydrogenation processes which are “greener” and more economical. The conducted research of this work has been arranged into the following seven chapters and three appendices, which are briefly summarized below in this chapter.

#### **3.1 Introduction and objective of the project**

It has been indicated in previous chapters that there are two major concerns associated with the present hydrogenation methods and technologies for the modification of diene polymers, i.e., the requirement for the use of a large amount of organic solvent, and the complicated post treatment operations. These drawbacks significantly increase the production cost, and raise serious concerns about the impact of any residual organic solvent and catalyst in the polymers on the environment.

In order to improve the present commercial process for the production of high performance elastomers, quite a few approaches have been reported in the literature to overcome these problems. Research in this area over the past 30 years has focused on the design of efficient catalytic systems and on improving the hydrogenation operations. However, these previously obtained results were generally associated with using a considerable amount of organic solvent, low catalytic efficiency and/or the occurrence of crosslinking before a suitable hydrogenation degree was achieved, which significantly deteriorates the post-processing properties.

The present research aims at inventing highly efficient catalytic systems to “green” the hydrogenation technologies by developing a new organic solvent-free polymer latex hydrogenation route, which can provide the industry with significant economical benefit and favorable environmental impact.

Particularly for NBR hydrogenation, the new latex hydrogenation process should meet the following technical demands for producing HNBR latex and/or solid products:

- Selectively hydrogenate C=C bonds only -- preserve the –CN groups within the polymer chains during the hydrogenation reaction to maintain good oil-resistance properties of NBR;
- Hydrogenation conversion higher than 95% -- decrease the level of unsaturation to less than 5%, which is a threshold that ensures high-performance applications of the HNBR products;
- Maintain the polymer in a stable latex form throughout the whole reaction -- directly produce HNBR latex in one step, simplifying the production process and facilitating latex applications;
- No cross-linking or gel problem in the final product -- control the physical properties of the material and guarantee excellent processibility;
- No residual solvent in the product or totally eliminate the use of organic solvents -- significantly reduce the cost for solvent and meet environment requirements.

Therefore, the objective of the present research is to discover and develop an efficient catalytic system for the organic solvent-free hydrogenation of NBR latex, which can fulfill these desirable technical requirements and act as an important milestone for the scientific field of the direct catalytic hydrogenation of unsaturated diene-based polymers in latex form.

## 3.2 Experimental Methods

In this chapter only general investigation methods, experimental procedures, and characterization methods used for the research work are described. Details for special chemicals and modified experimental processes are listed in corresponding chapters.

### 3.2.1 Materials and experimental setup

**Nitrile Butadiene Rubber Latex:** The commercial NBR latex (VPKA 8817, 12 g polymer solid per 100 ml of latex) used in this investigation, which contained 62 % butadiene (80 % trans, 15 % cis, 5 % vinyl C=C) and had an  $M_n = 70,000$  with a polydispersity of 3.6, was provided by LANXESS Inc. Another NBR latex, with the grade name of Perbunan and with a solid content of 15 g polymer per 100 ml of latex, was also provided by LANXESS Inc. (more details about the particle size and pH values of these latices are listed in Chapter 8).

**Solvent:** Reagent grade tetrahydrofuran (THF), ethanol, toluene, monochlorobenzene (MCB) and methyl ethyl ketone (MEK) were all purchased from Fisher Scientific Ltd. All solvents were used as received.

**Reaction Gas:** Hydrogen gas and nitrogen gas used for the hydrogenation studies were oxygen-free being of ultra high 99.999% purity provided by Praxair Inc.

**Catalysts and co-catalysts:** Discussed in corresponding chapters

**Other Chemicals:** Reagent grade potassium hydroxide (KOH), sodium dodecyl sulfate (SDS), ammonium sulfate, ferrous sulfate and citric acid were obtained from Sigma-Aldrich Ltd. (additional lists of used chemicals can be found in the experimental sections of corresponding chapters)

The reactions were carried out in a 300 ml Parr 316 Stainless Steel reactor system, which has a catalyst addition device installed in the head of the reactor for the addition of catalyst at a controlled time in solid powder form or in catalyst solution form. The Parr reactor system also has a dip tube for sampling at intervals during the reaction. By manually opening the sampling valve which connects a tube outside the reactor to the dip-tube inside the reactor, the latex samples were pushed out of the reactor and were released into sample vials, since there was hydrogenation gas on top of the liquid phase of the reaction system. Because the dip-tube sometimes might be blocked by the rubber residue remained inside the tub, it might fail to obtain latex samples during certain periods of some hydrogenation reactions. Therefore, it appears in the following chapters that some conversion-time curves have different sampling time.

### **3.2.2 Solution hydrogenation process**

Solution hydrogenation means that a polymer is dissolved in organic solvents and is hydrogenated by oil soluble catalysts in a whole homogeneous organic phase. Solution hydrogenation of NBR has been successfully developed into commercial production, and the solution hydrogenation technique is the foundation of this latex hydrogenation research.

The hydrogenation reaction was carried out in a 300 ml Parr reactor. A certain amount of weighed NBR solid was dissolved in a certain volume of organic solvent and some other chemicals may be added into this solution as desired; then, the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The solution was purged by bubbling hydrogen gas at about 200 psi through the reaction solution for 20 minutes at room temperature. After that the system

was heated to the desired reaction temperature with an agitation speed of 600 rpm. When the temperature of the reactor was stabilized for 30 minutes, the weighed catalyst solid powder (or the catalyst dissolved in solution) was pressurized into the reaction system by high pressure hydrogen gas. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to obtain the final product and to clean the reactor.

### **3.2.3 Latex hydrogenation process with the use of solvent**

The hydrogenation reaction was carried out in a 300 ml Parr reactor. A measured volume of NBR latex was mixed with a certain amount of organic solvent and some other chemicals may be added into this mixture as desired; then, the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The mixture was purged by bubbling hydrogen gas at about 200 psi through the latex system for 20 minutes at room temperature. After that, the system was heated to the desired reaction temperature with agitation. When the temperature of the reactor was stabilized for 30 minutes, the catalyst solid powder or the catalyst dissolved in a small volume of solution was pressurized into the reaction system by high pressure hydrogen gas. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to obtain the final product and to clean the reactor.

### **3.2.4 Latex hydrogenation process without the use of solvent**

The hydrogenation reaction was carried out in a 300 ml Parr reactor. A measured volume of NBR latex was mixed with a certain amount of additional water in order to adjust the solid content of the latex system. Some other chemicals, such as more surfactants and co-catalyst ligands, might be added into this mixture as desired, and then the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The mixture was purged by bubbling nitrogen gas at low pressure through the latex system for 20 minutes at room temperature. After that the system was heated to the desired reaction temperature with agitation. When the temperature of the reactor was stabilized for 30 minutes, the catalyst solid powder was pressurized into the reaction system by high pressure

hydrogen gas. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to isolate the final product and to clean the reactor.

### **3.2.5 Characterization**

In order to investigate the conversion and rate of the hydrogenation reaction the system was periodically sampled at various time intervals during the reaction.

A Bio-Rad FTS 3000MX spectrometer was used for Fourier transform infrared (FTIR) analysis of samples. The degree of hydrogenation was calculated based on the peak strength from the IR spectra according to the American Standard Test Method (ASTM) D5670-95. For FT-IR analysis, the latex samples may be prepared by directly casting the latex on Zn-Se plates and drying to obtain a film for FTIR scans. Also, the polymer samples in latex form may be precipitated by slowly dropping 50 ml of methanol from a dropping funnel into the latex sample under agitation with a magnetic stirrer; after the solvent was decanted, the precipitated rubber was washed with 50 ml of methanol and dried under vacuum; the dried solid rubber was re-dissolved in 10 ml of methyl ethyl ketone; and a polymer film was cast onto a potassium bromide disc for FT-IR analysis (More details about the process to prepare samples for IR analysis and determine the degree of hydrogenation can be found in Appendix A).

Crosslinking (gel formation) was judged by checking if the resultant HNBR was totally soluble in MCB or MEK at room temperature by the naked eye. When gel was found, the gel content was tested for some samples according to ASTM D3616-95.

The particle size distribution of the latex, before and after hydrogenation, was determined at room temperature using a Nanotracs NPA250 particle size analyzer (Microtrac Inc.) based on dynamic light scattering measurement principles.

### **3.3 Approach strategies**

The research project was guided by the following methodology: this work began with measurements for the performance of different catalysts in latex hydrogenation process (catalyst screen). By comparing the initial experimental results, a primary catalytic system with high efficiency for catalytic hydrogenation of NBR latex was chosen. After the selected catalysis system was further

studied under different operation conditions, improvement of the process was conducted in order to successfully establish the latex hydrogenation process. The optimization of the catalytic system took into account the aspects of improving activity of the catalyst, increasing mass transfer rates, and preventing the cross-linking.

### 3.4 Outline of the thesis

This dissertation is organized according to the research progress of the project guided by the approach strategies. The motivation of Chapter 3 is not only to give information about general operating procedures for hydrogenation experiments and characterization methods used for this research project, but also to outline how the research results are presented in the following chapters.

Chapter 4 starts with the NBR latex hydrogenation experiments using the  $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$  catalyst. The preliminary studies of the reaction variable effects were carried out to gain a fundamental understanding of the latex hydrogenation process. Initial studies were completed on understanding the important aspects of latex hydrogenation in an effort to accumulate knowledge and techniques for further study.

Chapter 5 focuses on the latex hydrogenation study using Wilkinson's catalyst,  $\text{RhCl(PPh}_3\text{)}_3$ , by exploring how each factor, such as co-catalyst, system composition, agitation, temperature or hydrogen pressure, influences the hydrogenation rate in isolation. The data presented in Chapter 5 represents the first published report of the successfully realized direct catalytic hydrogenation of acrylonitrile-butadiene rubber latex in the absence of any organic solvent with a conversion of higher than 95 % without crosslinking of the polymer <sup>[93]</sup>.

In Chapter 4 and Chapter 5, the principal factors of interest are the influence of the concentration of the catalyst, NBR polymer concentration and hydrogen pressure on the rate of hydrogenation. The other factors of interest are the effect of varying the reaction temperature and solvent type on hydrogenation. In these sections of work, efforts were made to use Os or Rh complexes as the catalyst with or without solvent to carry out the latex hydrogenation reaction. Research results from Chapter 4 and Chapter 5 are the foundation of this dissertation, which suggests that  $\text{RhCl(PPh}_3\text{)}_3$  is the right catalyst for latex hydrogenation. Each subsequent chapter, which developed better catalytic systems based on Rh complexes, is related with the methods described in these two chapters.

Chapter 6 utilizes the knowledge employed in the previous chapters to successfully develop a latex hydrogenation system which exhibits a much higher hydrogenation rate. After it was found that Wilkinson's catalyst was suitable for latex hydrogenation, modification of the catalyst by using water soluble ligands was carried out in an attempt to develop a better catalysis system. The performance of water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst is compared to that of Wilkinson's catalyst. Effects of adding a surfactant on the latex hydrogenation is also presented.

With the better understanding of the latex hydrogenation process, Chapter 7 reports on an investigation on the use of Rh salts directly for latex hydrogenation. It also contains a method for the in-situ synthesis of preferred catalysts for latex hydrogenation by using different Rh salts. Attempts to use Rh colloids as the latex hydrogenation catalyst were also carried out in Chapter 7.

Chapter 8 begins with an analysis of problems which emerged from the research progress made in using both the Os based catalyst and the Rh based catalysts. The effects of polymer latex change, latex impurity issues and polymer chain crosslinking problems are discussed. This chapter is useful for further development of the latex hydrogenation process.

Chapter 9 analyzes the mass transfer steps in the latex hydrogenation system for hydrogen and catalysts. Based on the study of the catalyst transportation into the TPP phase and an analysis of Rh metal resided in polymer particle phase, different catalyst mass transport processes are proposed for latex hydrogenation using different Rh complex catalysts. With a better understanding of the catalyst mass transfer, better hydrogenation results were obtained by the optimization of the latex hydrogenation process.

Finally, Chapter 10 briefly summarizes all the experimental results and the new knowledge gained from this research work for the hydrogenation of unsaturated diene-based polymer latex. The efficiency of different catalysts is compared. Based on these achievements through the whole research project, recommendations for further studies are listed.

## Chapter 4

### Hydrogenation of NBR Latex Using $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$

Although the rhodium-triphenylphosphine complex known as Wilkinson's catalyst (i.e.,  $\text{RhCl(PPh}_3\text{)}_3$ ) is most widely employed for polydiene hydrogenation and used for the industrial HNBR production process, one drawback with the Rh based catalyst is the relatively high cost of Rh metal. To circumvent this economic problem, catalysts based on other cheaper transition metals in the platinum group have been utilized for hydrogenation of diene-based polymers. One osmium based catalyst,  $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$ , was found to have comparable catalytic activity to the Wilkinson's catalyst [18]. This present chapter reports on a study of the hydrogenation of NBR latex catalyzed by  $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$ .

#### 4.1 Introduction

This research began with exploratory experiments using  $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$  as the catalyst.  $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$  has demonstrated excellent catalysis performance for solution hydrogenation of NBR at temperatures above 130°C. Compared with the  $\text{RhCl(PPh}_3\text{)}_3$  catalyst which is used industrially for NBR solution hydrogenation, the Os catalyst has high activity at lower temperature without any need for addition of free phosphine ligand which is required for the Rh catalyst, and the Os catalyst is cheaper than the  $\text{RhCl(PPh}_3\text{)}_3$  catalyst. So the Os catalyst was the first catalyst considered for the latex hydrogenation experiments.

Based on other researchers' methodology [37-43], a small amount of an organic solvent was also added for the latex hydrogenation. The idea of using some organic solvent is to help in making the carbon-carbon double bonds more accessible to the catalyst. This approach was adopted initially in the present research.

#### 4.2 Experimental

Catalyst:  $\text{OsHCl(CO)(O}_2\text{)(PCy}_3\text{)}_2$  was prepared by refluxing  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  with  $\text{PCy}_3$  (both obtained from Strem Chemicals) in methoxyethanol according to the synthetic procedure of



Esteruelas and Werner <sup>[94]</sup>. The corresponding dioxygen adduct,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$ , was prepared by exposing a suspension of  $\text{OsHCl}(\text{CO})(\text{PCy}_3)_2$  in hexane to pure  $\text{O}_2$  as detailed by Esteruelas et al. <sup>[95]</sup>

NBR Latex: VPKA 8817 latex was the only latex used with the Os catalyst (obtained from LANXESS).

The hydrogenation reaction was carried out in a 300 ml Parr reactor. A measured volume of NBR latex was directly mixed with a certain amount of organic solvent with the possible addition of some other chemicals into this mixture as desired; then, the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The mixture was purged by bubbling hydrogen gas at about 200 psi through the latex system for 20 minutes at room temperature. Subsequently, the system was heated to the desired reaction temperature and hydrogen pressure under agitation. When the temperature of the reactor was stabilized for 30 minutes, the catalyst solid powder or the catalyst dissolved in a small volume of solution was pressurized into the reaction system by high pressure hydrogen gas to initiate the hydrogenation. Agitation speed (600rpm), hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to obtain the final product and to clean the reactor.

Further information on general experimental procedures was reported in Chapter 3.

## **4.3 Results and discussion**

Weight ratios of the Os catalyst to NBR between 0.0015 and 0.0220 were used in the following sets of experiments.

### **4.3.1 Effect of organic solvents**

The research goal in this study involves carrying out hydrogenation efficiently while maintaining the emulsified state of the system. According to previous studies by other researchers, added organic solvents seem to play some role in the hydrogenation since the solvent molecules potentially coordinate or solvate the metal complexes. Also, the utilization of some small amount of solvent is

regarded as a requirement in order to make the carbon-carbon double bonds more accessible to the oil soluble Os catalyst.

In the preliminary study, an organic solvent capable of dissolving or swelling polymer particles in the NBR latex was added in varying amounts to the aqueous emulsion. Tetrahydrofuran (THF), toluene and mono chlorobenzene (MCB) were used in different catalytic hydrogenation systems (Rh, Ru, Pd or Os complex based catalysts) for hydrogenation of NBR solutions. A series of experiments using these solvents was carried out for the latex hydrogenation. The effects of solvent on the hydrogenation of NBR latex are compared in Table 4-1 below.

**Table 4-1 Effect of organic solvent on NBR latex hydrogenation**

(Solid content of VPKA latex is 12g rubber solid/100 ml, 800 psi of H<sub>2</sub>, catalyst was added as solid powder, gel content was not tested)

#	Solvent (ml)	T (°C)	Os cat.* (g)	NBR (ml)	Water (ml)	Conversion (time)
0	No solvent	130	0.05	110	0	0% (6hr)
1	MCB 90	130	0.016	20	0	52% (3hr)
2	MCB/THF 80/10	130	0.029	20	0	43% (3hr)
3	THF 40	130	0.011	70	0	0% (3hr)
4	MCB 40	130	0.014	70	0	12% (2hr)
5	MCB 40	130	0.011	70	0	25% (4hr)
6	THF 10	130	0.014	100	0	gel (4hr)
7	MCB 10	130	0.012	100	0	18% (5hr)
8	THF/MCB 5/5	130	0.014	100	0	gel (4hr)
9	Toluene 5	130	0.038	100	0	9% (4hr)
10	MCB 5	130	0.014	100	0	13% (4hr)
11	Toluene 10	100	0.012	50	50	5% (5hr)
12	MCB 10	100	0.012	50	50	32% (5hr)
13	THF 5	100	0.050	20	50	33% (23hr)
14	MCB 5	100	0.050	20	50	79% (23hr)

\*: OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>

It was found that no hydrogenation reaction occurred in the absence of added organic solvent in these preliminary studies using the Os catalyst. The NBR latex is a polar material and it can be dissolved in a number of polar non hydroxylic solvents. Since tetrahydrofuran (THF) is a fairly strong polar solvent, THF can also destroy the latex, cause gel formation and result in unsuccessful hydrogenation (such as in Exp. #6 and Exp. #8 of Table 4-1. In many other experiments the latex was separated into two phases when THF was used). No effective hydrogenation results were achieved

even if THF was used in a very low amount or used as a co-solvent with other solvents. Toluene is not a very good solvent for HNBR, and hydrogenation results using toluene were not as good as the results when the more polar MCB solvent was used. So, MCB appeared to be the best solvent of those used in the latex hydrogenation system, which is consistent with the results from known solution hydrogenation results. Therefore, MCB was always used in the following sets of experiments with the Os catalyst.

#### 4.3.2 Effect of catalyst addition method

Since an organic solvent was still used for these initial experiments, the catalyst can be added into the latex system in two different physical forms, i.e. in solid powder form and in solution form (catalyst dissolved in the solvent). The different hydrogenation results obtained for the nature of the catalyst addition method are compared in Table 4-2.

**Table 4-2      Effect of catalyst addition method on latex hydrogenation**

(Solid content of VPKA latex is 12g rubber solid/100 ml, 800psi of H<sub>2</sub>, 100°C, gel content was not determined)

#	NBR(ml)	Water(ml)	MCB(ml)	Os Cat. addition method	Conversion
1	20	50	10	0.050g added as solid	78% (22hr)
2	20	50	10*	0.044g dissolved in MCB	90% (21hr)
3	20	50	10*	0.042g dissolved in MCB	92% (22hr)

\*: 10ml of MCB was used to dissolve the catalyst and was added into the system as catalyst solution.

It can be concluded that the preferred catalyst addition method is to add the catalyst in solution form. The catalyst was added as a catalyst solution for all following sets of latex hydrogenation experiments using the Os catalyst.

#### 4.3.3 Effect of system composition

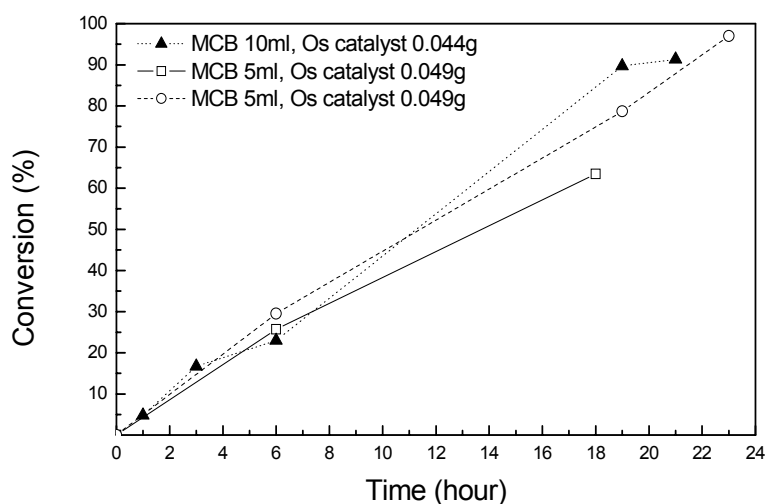
NBR latex is an aqueous dispersion of nitrile butadiene rubber with a complex chemical composition. Research has focused on finding suitable polymer concentrations and a volume ratio of emulsion to solvent in the reaction system for the latex hydrogenation. A series of experiments has been carried out using different NBR emulsion/MCB ratios, varying from (20ml emulsion/90ml MCB) to (105ml

emulsion/5ml MCB), in an attempt to find a volume ratio range of the aqueous emulsion to the organic solvent, in which hydrogenation can still be conducted while maintaining an emulsified state and system can be retained in an stable emulsified state even after hydrogenation. Some experimental results are selectively shown in Table 4-3 and Figure 4-1. It was found that a high degree of hydrogenation can be achieved only at a special range of system composition, and the optimal ratio is 70ml emulsion (20ml latex + 50ml water)/5~10ml MCB (3g NBR solid content in a 70ml latex vs. 5~10ml MCB). The latex hydrogenation using the Os catalyst is sensitive to the change of the latex system composition.

**Table 4-3 Effect of system composition on latex hydrogenation**

(Solid content of VPKA latex is 12g rubber solid/100 ml, 800psi of H<sub>2</sub>, 100°C)

#	NBR(ml)	Water(ml)	MCB(ml)	Os Cat.(g)	Conversion	Gel %
1	60	40	10	0.013	23% (19hr)	N/A
2	50	50	20	0.016	42% (19hr)	N/A
3	20	50	10	0.044	<b>90% (21hr)</b>	<b>73%</b>
4	20	50	5	0.049	<b>64% (18hr)</b>	<b>62%</b>
5	20	50	5	0.049	<b>97% (23hr)</b>	<b>80%</b>



**Figure 4-1 Effect of system composition on latex hydrogenation using OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>**

(Reaction conditions are listed in Table 4-3)

Compared with the solution hydrogenation of NBR, the reaction time required to achieve more than 90% conversion was long, and the reaction rate seems to have a zero-order relationship with respect to  $[C=C]$  during the process of the hydrogenation of the latex. This might be a result of transport limitations. The other possibility is that certain chemical components (i.e. impurities) within the NBR latex may have a negative effect on the Os catalyst. From the gel content information, the impurity problem is more likely to be the main reason (more discussion of the impurity issue can be seen in Section 8.4).

According to the results obtained, we have some ideas as to the way in which a high degree of hydrogenation can be achieved for the hydrogenation of NBR latex. However, there are still many problems including the impurity issue, which need to be solved by further research and are discussed further in Chapter 8.

#### 4.3.4 Effect of reaction temperature

Reaction temperature is a very important factor for the hydrogenation process. Temperatures of 100°C to 150°C were used for the NBR solution hydrogenation process. For the NBR emulsion system, 70 °C, 100 °C, 130 °C and 150 °C have been used. It was found that the NBR VPKA 8817 latex can not withstand temperatures above 150 °C for a long reaction time, so only experimental results using 70 °C, 100 °C and 130 °C are included in Table 4-4.

**Table 4-4 Effect of reaction temperature on NBR latex hydrogenation**

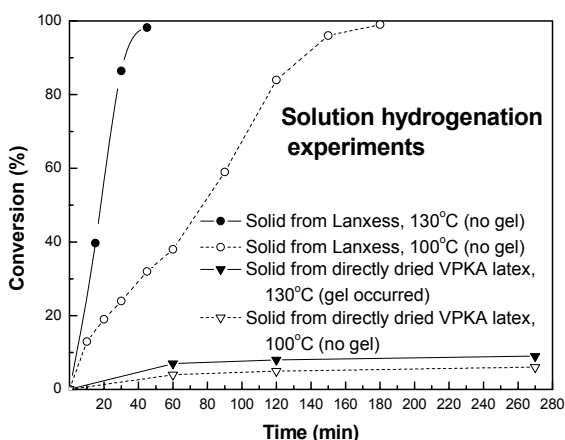
(Solid content of VPKA latex is 12g rubber solid/100 ml, 800psi of H<sub>2</sub>)

#	T (°C)	NBR (ml)	Water (ml)	MCB (ml)	Os cat.* (g)	Conversion (time)
1	130	50	50	10	0.012	27% (5hr)
2	100	50	50	10	0.011	33% (5hr)
3	130	50	50	5	0.029	7% (4hr)
4	100	50	50	5	0.038	9% (4hr)
5	130	20	50	10	0.055	15% (4hr)
6	100	20	50	10	0.048	23% (4hr)
7	130	20	50	5	0.048	59% (22hr)
8	130	20	50	5	0.049	46% (19hr)
9	100	20	50	5	0.050	79% (20hr)
10	100	20	50	5	0.024	39% (20hr)
11	100	20	50	10	0.044	51% (17hr)
12	70	20	50	10	0.043	14% (19hr)

\*: OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>

A temperature of 70°C appears to be too low to fully activate the Os catalyst as only 14% conversion can be achieved after 19 hours. The Os catalyst should have higher activity when used at a higher reaction temperature. However, it was found that hydrogenation rate decreases when the reaction temperature was increased from 100°C to 130°C. 100°C appears to be an optimal reaction temperature for these initial experimental conditions.

So it was estimated that there are some compounds (i.e. impurities) which have a more negative effect on the catalyst at higher reaction temperatures (more discussion about this impurity issue can be seen in Section 8.4). In order to improve the catalyst system, research is needed to find those compounds and ways to eliminate their influence. Some experiments for the solution hydrogenation of NBR have been carried out at 100°C and 130°C to investigate this unexpected result (shown in Figure 4-2). For NBR solids directly dried from the latex, all chemicals within the NBR VPKA latex were left in the obtained NBR solid. For NBR solids provided directly from LANXESS, the NBR latex was processed with the company's standard operation in their production line to obtain the NBR solid, which certainly removed some chemicals used in the synthesis of NBR latex by emulsion polymerization. It was found that the experiment using such a solid at 130°C gave rise to gel while the experiment using the same kind of solid at 100°C did not result in gel. This confirms that there are impurities within the latex and such impurities may become more active towards decreasing the hydrogenation reaction rates and causing gel formation at higher temperature (130 °C). A more detailed study and results are provided in Chapter 8.



**Figure 4-2 Effect of temperature on solution hydrogenation of different NBR solids**

(NBR solid 3.58g, MCB 150ml, [Os] 0.09mM, 600psi of H<sub>2</sub>)

### 4.3.5 Effect of additives

Some additives (such as SDS) may be beneficial for the hydrogenation of NBR latex as they may improve the stability of the emulsion. Some other salts (such as potassium hydroxide) may be used to increase the hydrogenation rate as they may minimize the negative influence of certain chemicals within the latex. Selected results regarding the use of such additives are listed in Table 4-5.

**Table 4-5 Effect of additives on NBR latex hydrogenation**

(Solid content of VPKA latex is 12g rubber solid/100 ml, 800psi of H<sub>2</sub>)

#	Additive (g)	Os cat.* (g)	NBR(ml)	Water (ml)	MCB (ml)	T(°C)	Conversion (time)
1	SDS 0.394	0.018	100	0	10	110	16% (3hr)
2	SDS 0.246	0.013	100	0	10	110	31% (3hr)
3	No Additive	0.012	50	50	10	100	32% (5hr)
4	SDS 0.267	0.012	40	60	10	100	26% (5hr)
5	SDS 0.329	0.012	20	80	10	100	25% (5hr)
6	KOH 0.029	0.027	10	100	5	130	25% (6hr)
7	KOH 0.058	0.029	50	50	5	130	15% (4hr)
8	No Additive	0.044	20	50	10	100	11% (22hr)
9	KOH 0.058	0.044	20	50	10	100	12% (25hr)
10	KOH 0.174	0.044	20	50	10	100	9% (22hr)

\*: OsHCl(CO)(O<sub>2</sub>)(PCy<sub>3</sub>)<sub>2</sub>

It is found that the stability of latex is improved upon the addition of SDS in that no phase separation occurred after the hydrogenation reaction. However, it can be seen from a comparison of Exp. #1 with #2 in Table 4-5 that the reaction rate decreases with an increase in SDS concentration in the emulsion probably due to the fact that less catalyst can be transferred into the polymer particles if more surfactant is used. The NBR solid content was decreased from Exp. #3 to Exp. #5 (catalyst/rubber ratio increased) while the hydrogenation rate decreased. This confirms that higher concentration of surfactants has negative effects on the latex hydrogenation rate.

The results obtained using KOH as an additive or pH adjuster compared with those without addition of KOH show no significant effect of KOH on hydrogenation rate. The pH value of the aqueous system is important for the stability of the latex. Ammonium sulfate, ferrous sulfate and citric acid were also used as additives. But the latex tended to coagulate even when a very limited amount of such a salt or acid was added. So such experiments were regarded as being unsuccessful.

## 4.4 Summary

NBR in the form of an aqueous emulsion has been successfully hydrogenated to a high conversion in the presence of  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  as catalyst. MCB was found to be the best solvent for the hydrogenation process, and was used at a very low volume ratio for the hydrogenation experiments. It has been found that using MCB at an appropriate level is crucial for the hydrogenation of NBR latex. The influences of various operation conditions, such as the system composition, catalyst addition method and hydrogenation temperature, were also studied. More than 90% degree of hydrogenation can be achieved by using the Os catalyst with suitable system compositions (volume ratio of latex/added water/MCB is 20/50/5~10) and experimental conditions (100°C, 800 psi of hydrogen).

Both solid Os catalyst and Os catalyst solution (in MCB) were used in experiments. Experimental results confirmed that it's better to use the Os catalyst solution addition method. Since the Os catalyst is soluble in the organic solvent, it is preferable, from the viewpoint of the efficiency and operation of the hydrogenation, to add the hydrogenation catalyst dissolved in an organic solution to the aqueous emulsion. Different weight ratios of Os/NBR (between 0.0015 and 0.0220) have been used, and it seems that the apparent reaction rate has a zero-order relationship with  $[\text{C}=\text{C}]$  for the latex hydrogenation process.

According to the experimental results obtained in this study, it can be concluded that there is a certain chemical within the latex which is detrimental to hydrogenation. Different additives have been used in the system to test its effect in an attempt to neutralize negative effects of impurity in the latex with respect to the hydrogenation process. It was found that a higher concentration of surfactant decreases the hydrogenation rate. More research work regarding the impurity issue was conducted later on and is reported in Chapter 8.



## Chapter 5

### Hydrogenation of NBR Latex Using $\text{RhCl}(\text{PPh}_3)_3$

Based on preliminary experimental results (Chapter 4), it is now known that the NBR latex can be successfully hydrogenated to high conversion in the presence of an Os complex; however, using the Os catalyst still needs the use of a small amount of organic solvent. To develop a solvent-free “green” latex hydrogenation process, the research work in this chapter focuses on using another promising catalyst, which is Wilkinson’s catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$ .

#### 5.1 Introduction

Among all the investigated homogeneous catalysts for hydrogenation, Wilkinson’s catalyst is considered the most preferred catalyst for the hydrogenation of diene-based polymers, since it provides high selectivity towards the olefin double bonds with minimal crosslinking problems. The only problem for using Wilkinson’s catalyst is the current high cost for Rh metal.

When Wilkinson’s catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  is used, addition of  $\text{PPh}_3$  ligand (also note as TPP) has a positive effect on the homogeneous solution hydrogenation process, although a large excess of TPP has an inverse effect on the rate of hydrogenation. The present of free TPP ligand is essential to prevent the formation of a bridged dimer  $\{\text{Rh}[\mu\text{-Cl}][\text{PPh}_3]_2\}_2$ , which is inactive for hydrogenation<sup>[14]</sup>. The optimum ligand concentration for small molecule hydrogenation is about  $[\text{PPh}_3]/[\text{Rh}] = 3$ <sup>[96]</sup>.

Wilkinson’s catalyst has excellent catalytic performance for solution hydrogenation of NBR, and is used in the industrial process for NBR solution hydrogenation at temperatures above 130°C (the weight ratio of added TPP to Wilkinson’s catalyst is about 15~20:1). Professor Rempel’s group has carried out systematic research on homogeneous solution hydrogenation of C=C bonds in polymers<sup>[97, 98]</sup>. Detailed hydrogenation mechanisms and kinetic models have been reported for the solution hydrogenation of NBR catalyzed by Wilkinson’s catalyst (Figure 5-1)<sup>[7]</sup>.

Inspired by Gilliom’s research<sup>[45, 46]</sup> using Wilkinson’s catalyst for bulk hydrogenation, a series of latex hydrogenation experiments was carried out.

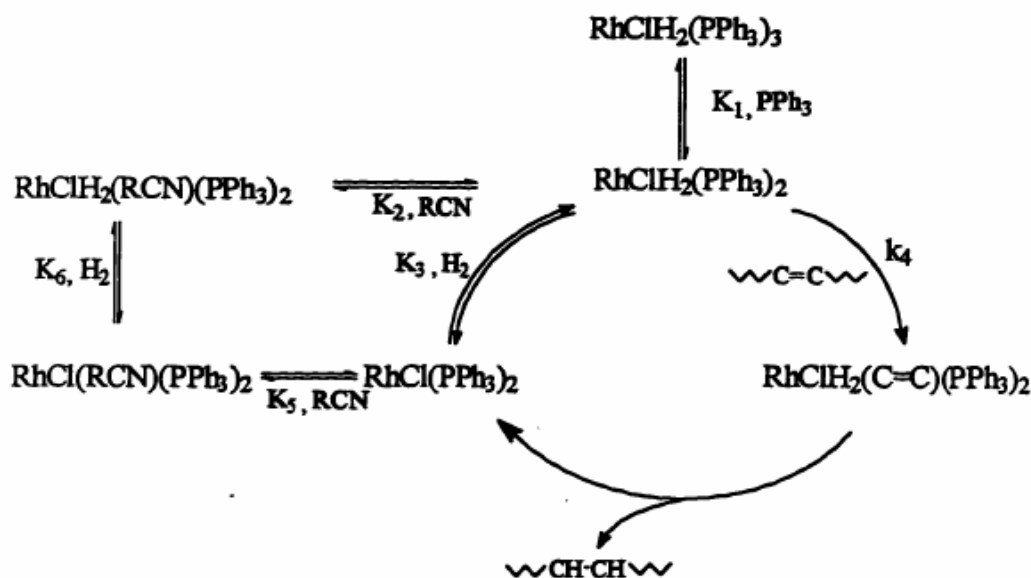


Figure 5-1 Reaction mechanism for the solution hydrogenation using Wilkinson's catalyst

## 5.2 Experimental

Catalyst:  $\text{RhCl}(\text{PPh}_3)_3$  was prepared by refluxing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (Strem Chemicals) with recrystallized triphenylphosphine (TPP) in ethanol (all obtained from Strem Chemicals) according to the synthetic procedure of Osborn and Ahmad et al. <sup>[99, 100]</sup> TPP was used as the required additive for hydrogenation using Wilkinson's catalyst. TPP was recrystallized from ethanol before use.

NBR Latex: VPKA 8817 latex and Perbunan latex were used at different periods of time (both obtained from LANXESS).

The hydrogenation reaction was carried out in a 300 ml Parr reactor. A measured volume of NBR latex was mixed with a certain amount of additional water in order to adjust the solid content of the latex system. Some other chemicals, such as TPP as the co-catalyst ligand, may be added into this mixture as desired, and then the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The mixture was purged by bubbling nitrogen gas at low pressure through the latex system for 20 minutes at room temperature. Subsequently, the system was heated to the desired reaction temperature under agitation. When the temperature of the reactor was stabilized for 30 minutes, the catalyst as solid powder (or catalyst solution when solvent was used) was pressurized

into the reaction system by high pressure hydrogen gas. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to obtain the final product and to clean the reactor.

Normally, the reaction was initiated by the addition of Wilkinson's catalyst. However, some latex hydrogenation experiments used the catalyst pre-dispersion method. The pre-dispersion method means that the catalyst powder was added into the latex in the reactor with TPP in the beginning. The reactor was purged with nitrogen, and the whole latex system was raised to the desired catalyst pre-dispersion temperature under nitrogen. The latex system was kept at the desired temperature for a certain period of time, and then the temperature was adjusted to the reaction temperature before introducing H<sub>2</sub> to initiate the reaction. This is called the catalyst pre-dispersion method because there was an induction period for the mass transfer of catalyst before the initiation of hydrogenation, i.e., counting of the reaction time began once the H<sub>2</sub> was introduced into the latex system.

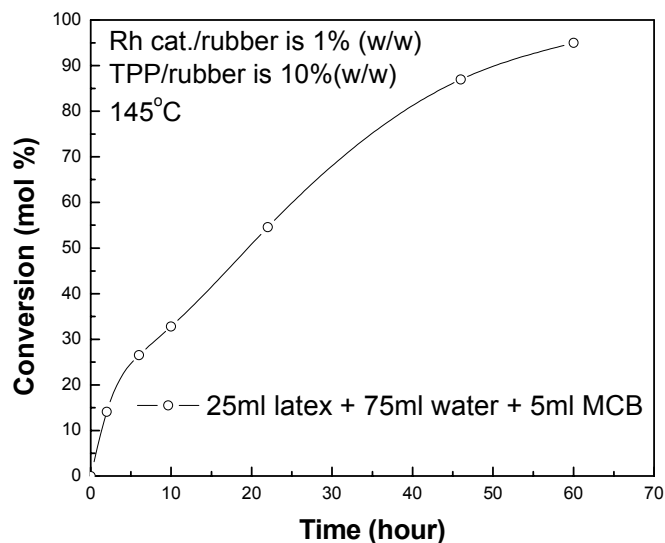
Other relevant experimental information is provided in Chapter 3.

## **5.3 Results and discussion**

### **5.3.1 Latex hydrogenation using RhCl(PPh<sub>3</sub>)<sub>3</sub> with solvent**

From the latex experiments using the Os catalyst, the best system composition is 20 ml of latex with 50 ml of added water and 5-10 ml of MCB. In preliminary experiments using Wilkinson's catalyst, a small amount of MCB was also used to assist the Rh catalyst to contact the C=C bonds within the latex particles. It was indeed found that Wilkinson's catalyst can also work for the hydrogenation of NBR latex in the presence of a small amount of organic solvent as shown in Figure 5-2.

The degree of hydrogenation was more than 95% after 60 hours using Wilkinson's catalyst in solid powder form for 100 ml NBR emulsion with 5 ml MCB. The final hydrogenation product can be totally dissolved in MCB and MEK at room temperature quickly, which suggests that there is no gel problem after hydrogenation.



**Figure 5-2 Hydrogenation of VPKA latex using Wilkinson's catalyst with MCB**

(Solid content of Perbunan latex is 15g rubber solid/100ml, MCB 5ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C, 1000psi of  $\text{H}_2$ )

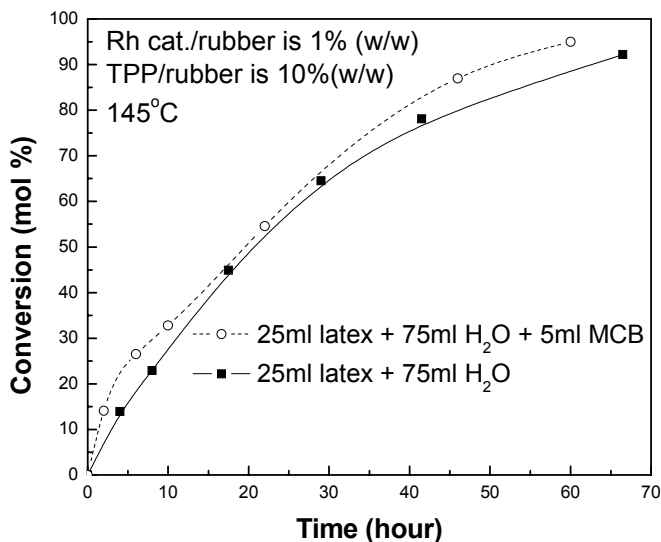
### 5.3.2 Latex hydrogenation using $\text{RhCl}(\text{PPh}_3)_3$ without solvent

The ultimate goal of this project was to develop a process for the latex hydrogenation in which no organic solvent was used. Therefore, using the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst in powder form without organic solvent has been tried and the experimental result is compared with the one using MCB as shown in Figure 5-3.

It was found that although the reaction rate is slightly slower than the one using MCB, the NBR latex can be hydrogenated to more than 90% conversion using the Wilkinson's catalyst without any organic solvent, and no gel formation was observed.

This is a very important milestone: it confirms that the catalytic ability of Wilkinson's catalyst for NBR latex is not highly dependent on the presence of solvents; with its own sufficient mobility under suitable experimental conditions, Wilkinson's catalyst without the help of any organic solvent has the chance to contact C=C bonds within the polymer particles which are suspended in the NBR

latex. This finding could be the key to successfully realizing the solvent-free polymer latex hydrogenation process.



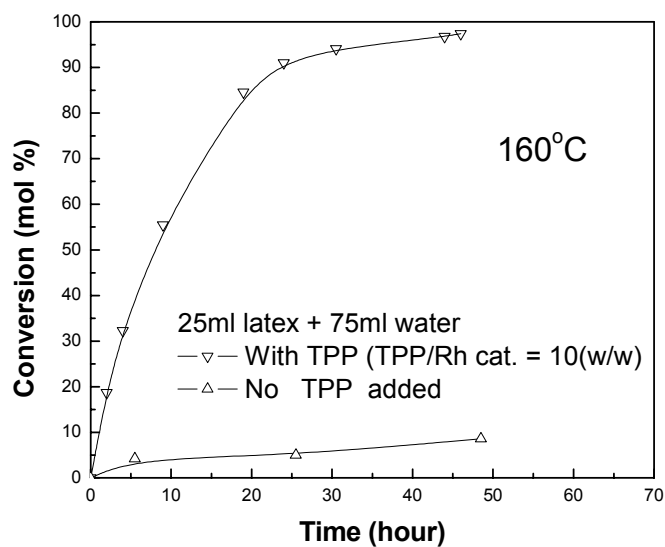
**Figure 5-3 Hydrogenation of NBR latex using Wilkinson's catalyst without MCB**

(Solid content of Perbunan latex is 15g rubber solid/100ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C, 1000psi of  $\text{H}_2$ )

The following experiments using Wilkinson's catalyst for latex hydrogenation were all carried out without the use of any organic solvent.

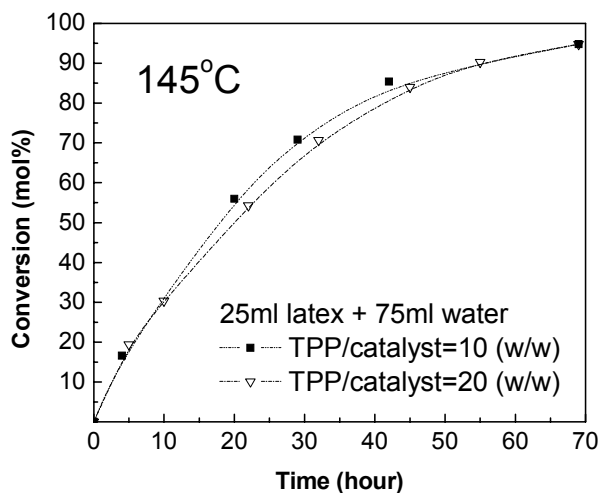
### 5.3.3 Effect of added $\text{PPh}_3$

From solution hydrogenation studies, it is known that the addition of  $\text{PPh}_3$  as a co-catalyst ligand with Wilkinson's catalyst is needed in order to maintain Wilkinson's catalyst's high catalytic activity<sup>[96]</sup>. It is interesting to investigate the effect of using TPP on the latex hydrogenation (experimental results are shown in Figure 5-4 and Figure 5-5).



**Figure 5-4 Latex hydrogenation using Wilkinson's catalyst with/without TPP**

(Solid content of Perbunan latex is 15g rubber solid/100ml,  $\text{RhCl(PPh}_3)_3/\text{NBR}$  is 1% (w/w), 600 rpm of agitation, 160°C, 1000psi of  $\text{H}_2$ )



**Figure 5-5 Effect of added TPP on latex hydrogenation**

(Solid content of Perbunan latex is 15g rubber solid/100ml,  $\text{RhCl(PPh}_3)_3/\text{NBR}$  is 1% (w/w), 600 rpm of agitation, 145°C, 1000psi of  $\text{H}_2$ )

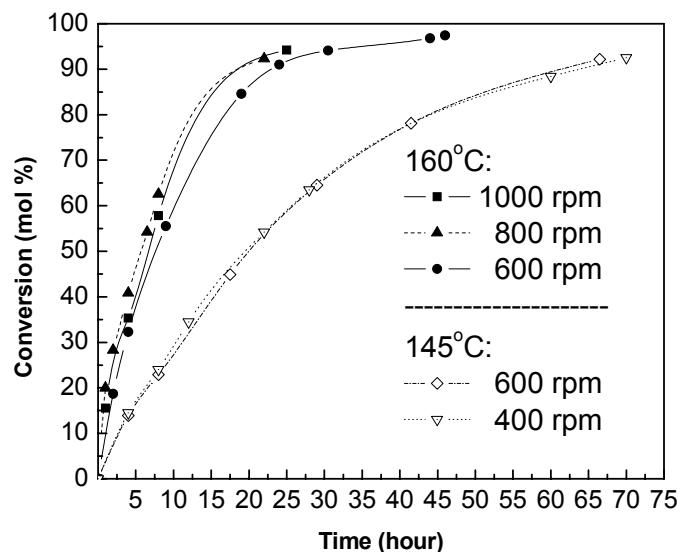
It was found that the latex hydrogenation rate was extremely low if TPP was not added into the latex hydrogenation system, even though Wilkinson's catalyst was used at higher temperature (160°C). The added TPP has a significant positive effect for the hydrogenation of NBR in latex form, which is consistent with hydrogenation results obtained from other catalytic studies using Wilkinson's catalyst <sup>[7]</sup>. Also, it seems that as long as there is added free TPP ligand (TPP/catalyst  $\geq$  10 w/w) in the latex hydrogenation system, the rate of latex hydrogenation does not appear to be strongly affected by the amount of TPP initially added. Therefore, the added TPP to catalyst ratio was usually 10(w/w) for the following experiments.

Actually, with the progress of this research project, more interesting and important roles of the added TPP for the latex hydrogenation were revealed, which will be discussed in detail in Chapter 9.

### **5.3.4 Effect of agitation on hydrogenation**

Changing the rotational speed of the agitator is often a standard technique used to study the influence of external mass-transfer resistance (the gas-liquid transport resistance). Agitation speeds of 400 rpm to 1000 rpm have been used in experiments at 145°C and 160°C. For the 300ml Parr reactor, 1000 rpm is its upper speed limitation. Experimental results using different agitation speeds are listed in Figure 5-6.

For experiments using a different agitation speed at 145°C, it was found that the hydrogenation rates were almost the same when the agitation speed increased from 400 rpm to 600 rpm. It was also found that from 600 rpm to 1000 rpm, these hydrogenation conversion-time curves are similar to each other at 160°C. It appears that an agitation speed of 600 rpm is sufficient to overcome resistance resulting from external mass transfer at these experimental conditions provided above. So an agitation speed of 600 rpm was used for most of the following latex hydrogenation experiments, except for some specially noted cases.



**Figure 5-6 Effect of agitation at 145°C and 160°C on latex hydrogenation**

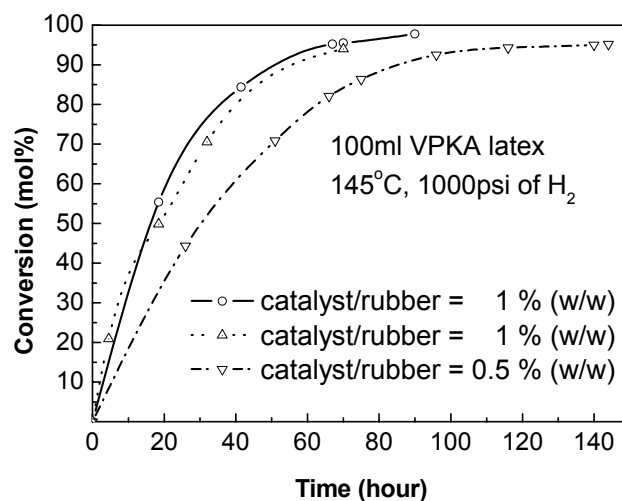
(Solid content of Perbunan latex is 15g rubber solid/100ml, Perbunan 25ml, added H<sub>2</sub>O 75ml, Rh catalyst/rubber is 1% (w/w), TPP/rubber is 10% (w/w), 1000 psi of hydrogen)

### 5.3.5 Effect of catalyst/rubber ratio

The catalyst/rubber ratio is an important factor for solution hydrogenation of NBR. For latex hydrogenation, the effect of the catalyst to rubber ratio was studied and the results obtained are shown in Figure 5-7 and Figure 5-8<sup>[101]</sup>.

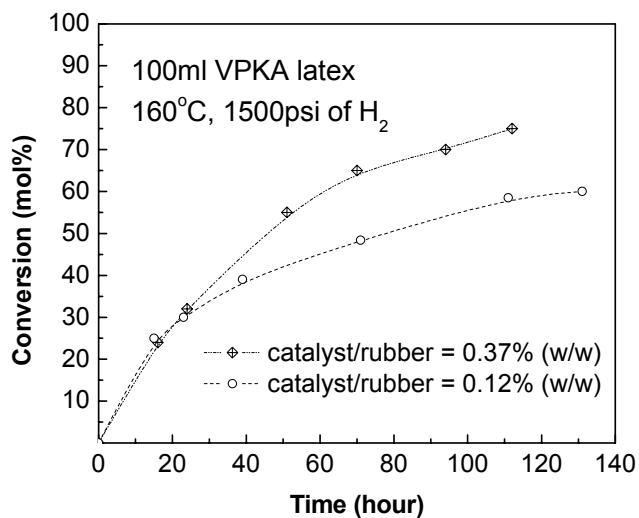
From Figure 5-7, it can be seen that when the catalyst/rubber ratio was 1 wt%, these two latex hydrogenation experiments have good reproducibility. More discussions about the reproducibility of latex hydrogenation experiments are provided in Section 8.3.3.





**Figure 5-7 Effect of catalyst/rubber ratio on latex hydrogenation (1)**

(Solid content of VPKA latex is 12g rubber solid/100ml, TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C, 1000psi of H<sub>2</sub>)



**Figure 5-8 Effect of catalyst/rubber ratio on latex hydrogenation (2)**

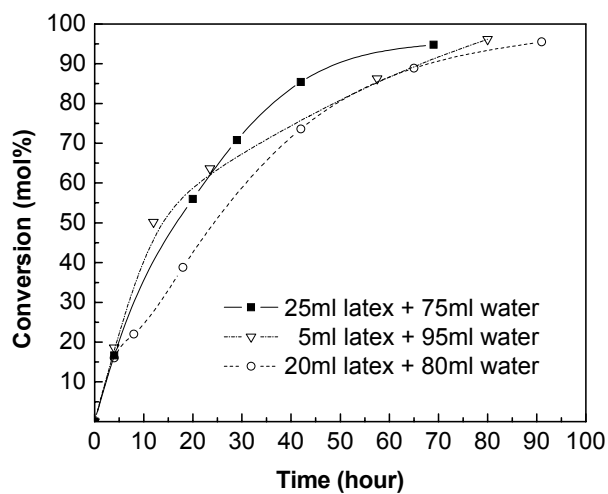
(Solid content of VPKA latex is 12g rubber solid/100ml, TPP/rubber is 10% (w/w), 600 rpm of agitation, 160°C, 1500psi of H<sub>2</sub>)

Thus from these results, it can be concluded that the catalyst/rubber ratio plays an important role for latex hydrogenation. It can be seen that the amount of catalyst has a major effect on the degree of hydrogenation. At 145°C, the degree of hydrogenation attained to more than 90% within 70 hours when the catalyst/rubber ratio was 1 wt%, while more than 90 hours were needed to achieve the same degree of hydrogenation when the catalyst/rubber ratio was 0.5 wt%. Even at a higher temperature and a higher pressure (160°C, 1500 psi of H<sub>2</sub>), the degree of hydrogenation was less than 80% after 120 hours when the ratio decreased to 0.37 wt%; With a very low amount of catalyst (catalyst/rubber = 0.12 wt%), the conversion was only 60% after 130 hours <sup>[101]</sup>.

It is quite likely that suspected impurities, which were found to affect the latex hydrogenation when the Os catalyst was used (see Section 4.3.4), also have negative influences on the latex hydrogenation when Wilkinson's catalyst was used. Therefore, with a decreased catalyst/rubber ratio, although at a higher temperature and higher hydrogen pressure, the hydrogenation rate decreased significantly. A high degree of hydrogenation could not be achieved if the catalyst was used in a very small amount. Further investigations were conducted and the results obtained are presented in Chapter 8.

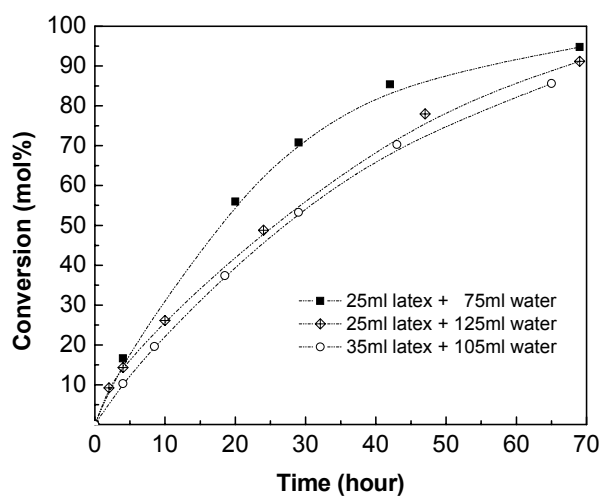
### **5.3.6 Effect of system composition on hydrogenation**

In previous experiments using the Rh catalyst, 25ml of NBR latex with 75ml added water was the commonly used latex/water ratio since that ratio was found to be the best for latex hydrogenation using the Os catalyst. To further investigate the hydrogenation of NBR latex using Wilkinson's catalyst, experiments with different system compositions (i.e., dilute the original latex with more or less added water before hydrogenation) were carried out. The experimental conditions used are shown below together with the experimental results as shown in Figure 5-9 and Figure 5-10.



**Figure 5-9 Hydrogenation of Perbunan latex with different system compositions at 145°C**  
(1)

(Solid content of Perbunan latex is 15g rubber solid/100ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C, 1000psi of  $\text{H}_2$ )



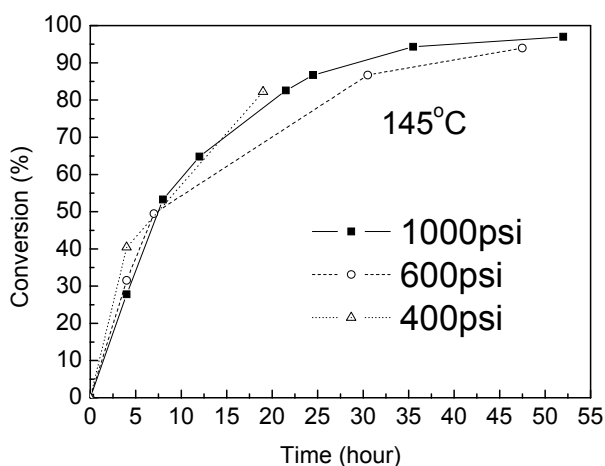
**Figure 5-10 Hydrogenation of Perbunan latex with different system compositions at 145°C**  
(2)

(Solid content of Perbunan latex is 15g rubber solid/100ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C, 1000psi of  $\text{H}_2$ )

In the experiments just shown, the  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  ratio was kept at 1% (w/w) and the TPP/rubber ratio was kept at 10% (w/w), although the NBR solid content changed in these latex systems. For the run with 5ml of latex and 95ml of added water, which means less than 0.008 g of Wilkinson's catalyst and less than 0.08g TPP were used, more than 96% degree of hydrogenation was achieved after 81 hours of reaction. Compared with the hydrogenation experiments with (25ml latex + 75ml water) and with (20ml latex + 80ml water), it appears that the hydrogenation reaction using Wilkinson's catalyst is not so sensitive to the change of latex system composition, while the 25ml latex with 75ml added water is still the preferred system composition at 145°C for hydrogenation (shown in Figure 5-9). It can be seen from Figure 5-10 that hydrogenation rate decreased when the total NBR emulsion volume increased from 100ml to 140ml or 150ml.

### 5.3.7 Effect of hydrogen pressure on hydrogenation

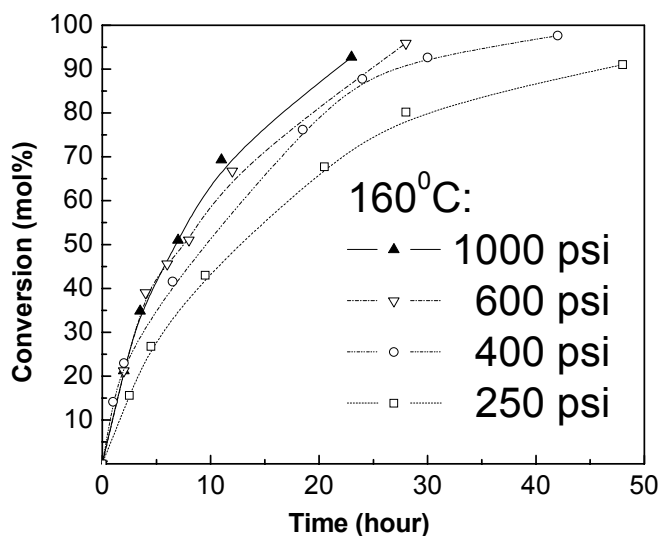
The solution hydrogenation system using the Rh catalyst exhibits a first- to zero-order dependence on  $[\text{H}_2]$  as the system pressure is increased <sup>[7]</sup>. The influence of hydrogenation pressure on the latex hydrogenation reaction was also examined. The conditions used and the experimental results obtained are shown in Figure 5-11 and Figure 5-12.



**Figure 5-11 Hydrogenation of VPKA latex under different hydrogen pressure**

(Solid content of VPKA latex is 12g rubber solid/100ml, 25ml latex, 75ml  $\text{H}_2\text{O}$ ,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C)

It can be seen from Figure 5-11 that as the hydrogen pressure was varied over the range of 400psi to 1000psi, it had little influence on the rate of the hydrogenation reaction at 145°C. It may be concluded that for the studied hydrogenation conditions at 145°C, the hydrogenation rate was mainly controlled by the amount of catalyst used and the reaction was probably controlled by the catalyst mass transfer within the latex particles.



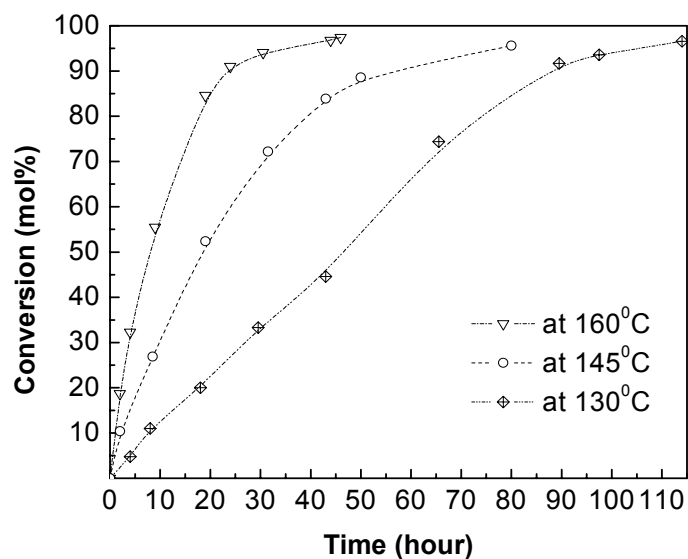
**Figure 5-12 Hydrogenation of Perbunan latex under different hydrogen pressure**

(Solid content of Perbunan latex is 15g rubber solid/100ml, 25ml latex, 75ml H<sub>2</sub>O, RhCl(PPh<sub>3</sub>)<sub>3</sub>/NBR is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 145°C)

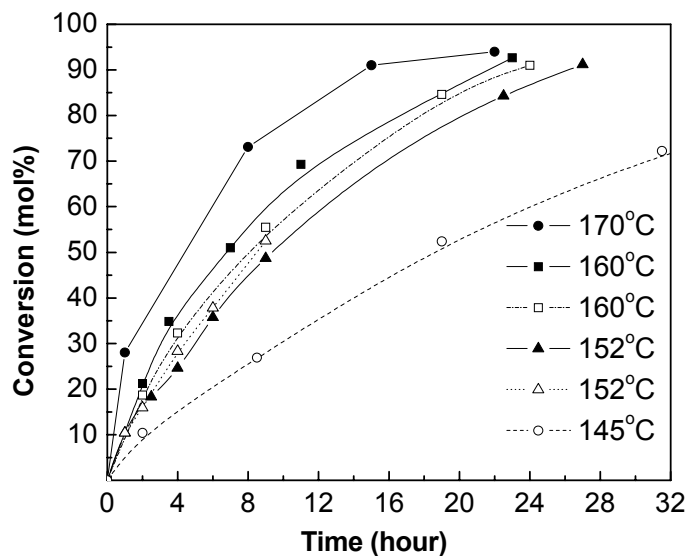
It was found that the hydrogenation rate increased with increasing hydrogen pressure at 160°C, while the reaction rate appears to be independent of H<sub>2</sub> pressure at 145°C. At 160°C and above about 600 psi, the reaction rate appears to be less sensitive to further increases of hydrogen pressure.

### 5.3.8 Effect of temperature on hydrogenation

Hydrogenation of diluted Perbunan latex (water added into the original latex) was carried out at 130 °C, 145°C, 152°C, 160°C and 170°C with a catalyst/rubber ratio of 1% (w/w) as shown in Figure 5-13 and Figure 5-14. The hydrogenation rate increases with increasing temperature as expected when the diluted Perbunan latex was used for hydrogenation.



**Figure 5-13 Hydrogenation of diluted Perbunan latex at 130°C, 145°C and 160°C**  
 (Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  
 $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 1000psi of  $\text{H}_2$ )



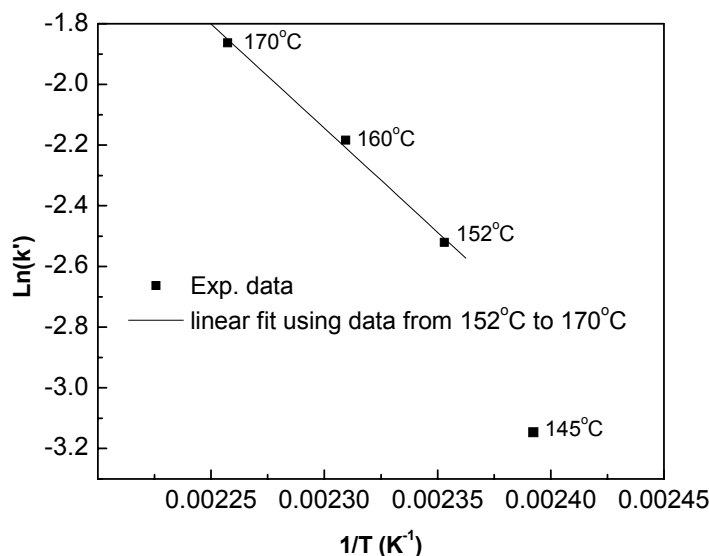
**Figure 5-14 Hydrogenation of diluted Perbunan latex at different temperatures**  
 (Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  
 $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), agitation is 600 rpm, 1000psi of  $\text{H}_2$ )

It can be seen from Figure 5-13 that even at 130°C Perbunan latex can be hydrogenated to a degree of 96% after 114 hours, and that the hydrogenation rate increases significantly at higher temperatures. The hydrogenation conversion-time curve at 130°C is like a zero-order reaction curve, which is similar to the latex hydrogenation results obtained using the Os catalyst at 100°C and 130°C (See Chapter 4). This seems to imply that the catalyst is susceptible to a mass transfer limitation.

In Figure 5-14, the repeated hydrogenation reactions at 152°C and 160 °C have good reproducibility. For latex hydrogenation at 170°C, it was found that 94% degree of hydrogenation was achieved within 22 hours, and the final product was a stable latex without any gel problem. The conversion profiles at 145 °C, 152 °C, 160 °C and 170°C were found to adhere to a first-order rate model with respect to olefin.

Based on the first-order assumption, the Arrhenius plot ( $\ln[k'] \sim 1/T$ ) provided in Figure 5-15 is obtained by using the experimental data from 145°C to 170°C and with regression provides estimates of  $k'$ . It was found that a linear response can be observed over the range of 152°C~170°C using Wilkinson's catalyst. From Figure 5-15, it also can be seen that the data point obtained from the experiment at 145°C is off the linear relationship zone existing from 152°C to 170°C. Therefore, the apparent activation energy (152°C to 170°C) for the NBR latex hydrogenation using Wilkinson's catalyst is derived to be 57.0 kJ/mol.

J. S. Parent studied the solution hydrogenation of NBR using Wilkinson's catalyst at experimental conditions without mass transfer limitation <sup>[7]</sup>. He found that the activation energy over the range of 130°C to 170°C for Wilkinson's catalyst is 73.5 kJ/mol. Compared with his result, the apparent activation energy (57.0 kJ/mol) of the NBR latex hydrogenation for Wilkinson's catalyst shows that the latex hydrogenation experiments were not carried out under the same rate limiting steps as for solution hydrogenation, especially when the reaction temperature is below 152°C.



**Figure 5-15 Arrhenius plot for the hydrogenation of diluted Perbunan latex (145°C~170 °C)**  
 (Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  
 RhCl(PPh<sub>3</sub>)<sub>3</sub>/NBR is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 1000psi of H<sub>2</sub>)

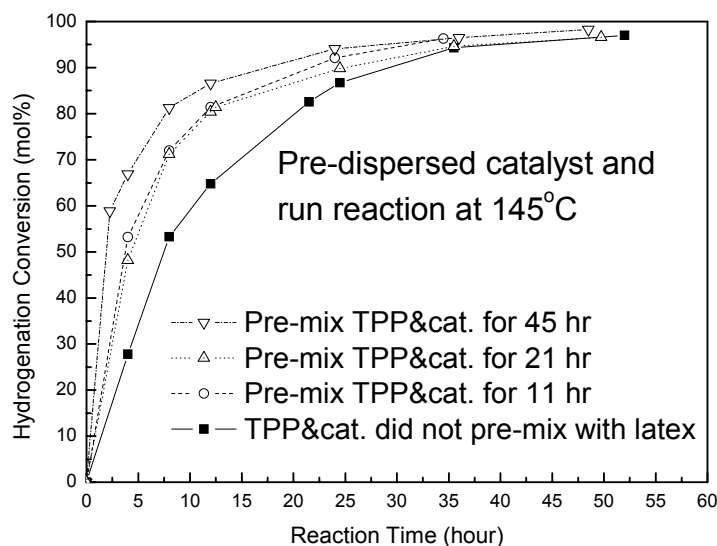
### 5.3.9 Effect of catalyst pre-dispersion on hydrogenation

Although high hydrogenation conversion can be achieved using Wilkinson's catalyst without solvent, the hydrogenation rate is low compared to solution hydrogenation of NBR. Based on previous observations, it is estimated that the transfer of the catalyst from outside the polymer particles into the polymer particles is the limiting step for the latex hydrogenation. Therefore, several comparison experiments were carried out to investigate the potential effect of catalyst pre-dispersion on the hydrogenation rate.

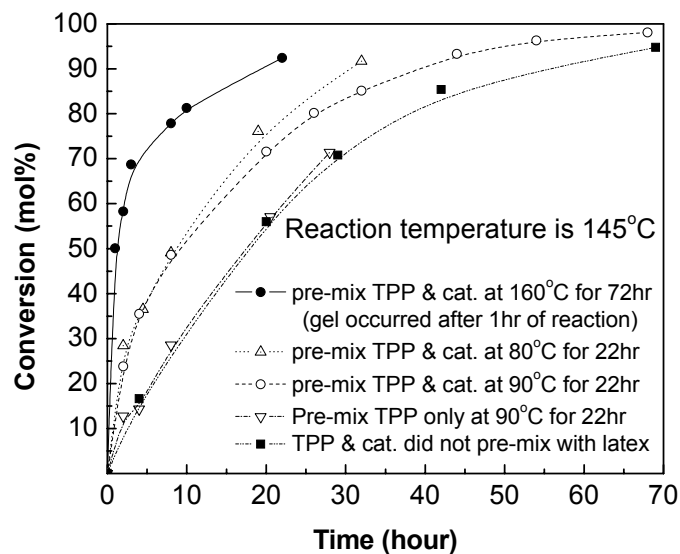
Usually, the hydrogenation was initiated at  $t = 0$  by adding catalyst into the latex system under H<sub>2</sub>. Another way, called the pre-dispersion method, is to have a certain introduction period before the initiation of hydrogenation, i.e., the catalyst was pre-mixed with the latex system under N<sub>2</sub> at the reaction temperature for several hours before adding H<sub>2</sub>. The catalyst pre-dispersion method could perhaps be beneficial to improve the hydrogenation rate, since the catalyst was already dispersed into polymer particles before the reaction began. These experimental results are shown in Figure 5-16 (using VPKA latex), Figure 5-17 and Figure 5-18 (using Perbunan latex).



It can be seen from Figure 5-16 that higher hydrogenation rates can be obtained, especially before reaching 80% conversion, if the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst is pre-dispersed within the latex before introducing hydrogen gas into the reaction system. So, the pre-dispersion of catalyst really helps the transport of the catalyst into the polymer particles. However, the reaction rate decreased after a certain conversion (about 80%), because the catalyst has a problem in contacting the remaining  $\text{C}=\text{C}$  bonds within the polymer particles although the catalyst was pre-dispersed at  $145^\circ\text{C}$ . Finally, more than 95% conversion can be achieved using almost the same reaction time as in experiments without pre-dispersion of the Rh catalyst.

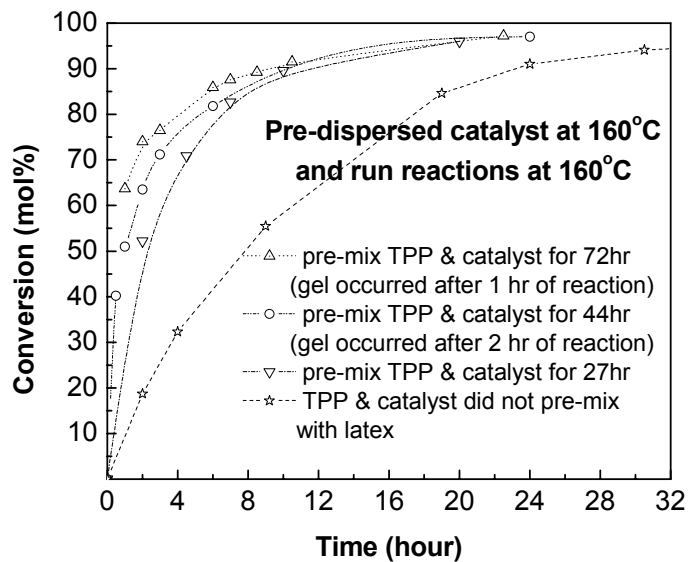


**Figure 5-16 Effect of catalyst transfer on hydrogenation of VPKA latex at  $145^\circ\text{C}$**   
 (VPKA latex 25ml (solid content is 12g/100ml), added water 75ml,  
 $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 1000psi of  $\text{H}_2$ )



**Figure 5-17 Effect of catalyst transfer on hydrogenation of Perbunan latex at 145°C**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 1000psi of  $\text{H}_2$ )



**Figure 5-18 Effect of catalyst transfer on hydrogenation of Perbunan latex at 160°C**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 600 rpm of agitation, 1000psi of  $\text{H}_2$ )

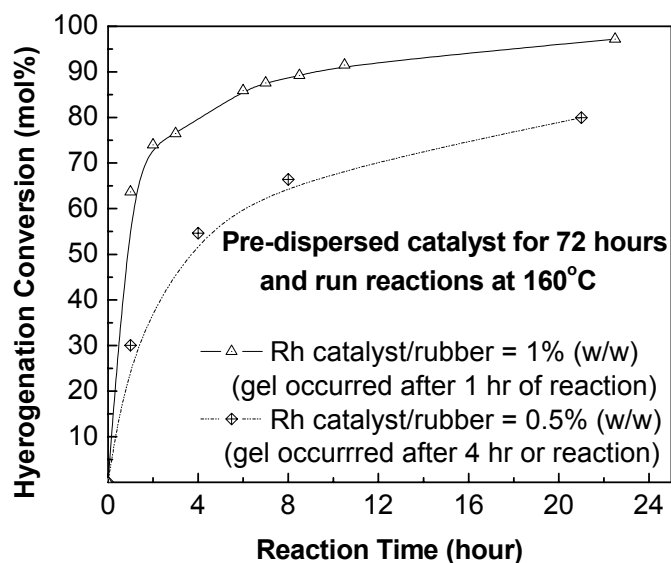
As shown in Figure 5-17, when TPP was pre-mixed with latex while the catalyst was not pre-mixed, the hydrogenation rate did not increase compared to the hydrogenation result of the experiment without pre-dispersion of TPP. The hydrogenation rate increased appreciably if both TPP and catalyst were pre-mixed with the latex before the reaction. For experiments with pre-dispersed catalyst at temperatures below 100°C, the reaction rate decreased after a certain conversion like in Figure 5-16, and these reactions still took a long time to achieve more than 95% conversion. However, when the catalyst and TPP were pre-dispersed with latex at 160°C for 72 hours and then reacted at 145°C, it was found that the hydrogenation rate increased considerably for the whole reaction period and that more than a 92% degree of hydrogenation was achieved after 22 hours (gel occurred after one hour of reaction). This confirms that catalyst transport is the limiting step for latex hydrogenation, and the pre-dispersion process provides higher concentration of Wilkinson's catalyst inside the polymer particles. Also, Wilkinson's catalyst has higher mobility in the NBR rubber network at higher temperature, so the pre-dispersion of the catalyst at 160°C can significantly short the hydrogenation time to less than 30 hours compared to the long reaction time required for hydrogenation at the same conditions without the pre-dispersion of the catalyst.

The curves in Figure 5-18 suggest that at 160°C the hydrogenation is still under catalyst transport control, since the hydrogenation rate also increased a lot if the catalyst was pre-mixed with the latex. More than 91% degree of hydrogenation was achieved within 10 hours when the catalyst and TPP were pre-dispersed with latex at 160°C for 72 hours and the reaction was carried out at 160°C. Compared to the experiment at 160°C without the pre-dispersion of the catalyst, it can be observed that the hydrogenation rates increased a lot for the whole reaction period when the catalyst pre-dispersion technique was used, but the high hydrogenation conversion was achieved using a similar reaction time no matter whether a longer or shorter pre-dispersion time was used.

According to these experimental results, the pre-dispersion of the catalyst under N<sub>2</sub>, before introducing H<sub>2</sub> to initiate the hydrogenation reaction, really improves the hydrogenation rate by transferring more catalyst into the polymer particles before the reaction begins. Based on these catalyst pre-dispersion experiments, it was confirmed that the latex hydrogenation rate mainly depends on the amount of Wilkinson's catalyst which can successfully diffuse into the polymer particles. So improvement of the catalyst mass transport into the latex particle is the key to developing a successful catalytic latex hydrogenation system.

When the catalyst was pre-dispersed with NBR latex at 160°C for 72 hours and then reacted at 145°C, there was no gel problem. However, gel occurred after 2 hours or after 1 hour of reaction for the experiments running at 160°C in which the Rh catalyst was pre-dispersed into the latex at 160°C for 44 hours or for 72 hours respectively. This suggests that higher temperatures may promote cross-linking, and after pre-dispersion of the catalyst for 44 hours at 160°C, the concentration of the catalyst inside polymer particles was high enough to promote cross-linking of the NBR polymer chains at 160°C.

To study the gel formation in these experiments with long catalyst pre-dispersion time, one catalyst pre-dispersion experiment using a reduced amount of the catalyst was conducted at 160°C as shown in Figure 5-19.



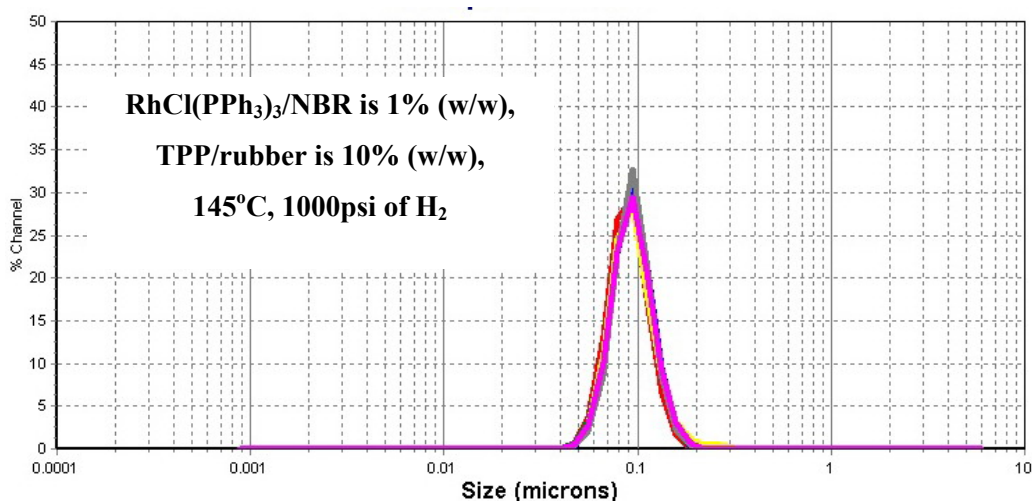
**Figure 5-19 Effect of catalyst pre-dispersion with reduced catalyst amount at 160°C**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w), 600 rpm of agitation, 160°C, 1000psi of H<sub>2</sub>)

It appears that gel still occurred, even when less catalyst was pre-dispersed with the latex for 72 hours at 160°C. The reaction rate decreased a lot when the added catalyst amount was lower (catalyst/rubber ratio is 0.5 wt%); however, the hydrogenation rate was higher than the run in which the catalyst/rubber ratio was 1 wt% without the pre-dispersion of catalyst.

## 5.4 Analysis of hydrogenation products

During all hydrogenation operations using the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst, except for those pre-dispersion experiments, no coagulation of the latex was observed even for the experiments in which very long operational periods were involved at high temperature. The average particle size of the latex before and after hydrogenation remained almost unchanged as shown in Figure 5-20. This indicates that for latex hydrogenation, the Wilkinson's catalyst has no adverse effect on the latex particle size or stability.



**Figure 5-20 Particle size analysis for Perbunan latex before and after hydrogenation**

(Including original latex before reaction, and latex products from the following experiments:  
five experiments using Perbunan latex 25ml (solid content is 15g/100ml) with added water 75ml,  
one experiment using Perbunan latex 35ml with added water 105ml,  
and one experiment using Perbunan latex 20ml with added water 80ml)

To detect whether any crosslinking had occurred in the resultant HNBR, the hydrogenated latex product was dried and then re-dissolved in monochlorobenzene. It was found that all of the HNBR latices produced by the direct hydrogenation using the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst (except for some products from pre-dispersion experiments) were completely soluble in monochlorobenzene, and no visible gel was observed. Therefore, the processibility of the hydrogenated rubber will not be adversely affected by this hydrogenation operation.

There is no characteristic signal for primary or secondary amines at around  $3500\text{ cm}^{-1}$  in the IR spectra of the hydrogenated NBR (See Appendix A). This implies that the catalytic hydrogenation was selective towards the C=Cs.

## 5.5 Summary

NBR in the form of an aqueous emulsion has been successfully hydrogenated to high conversion by using Wilkinson's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  with or without organic solvent. It has been found that the use of triphenylphosphine (TPP) as the co-catalyst ligand for Wilkinson's catalyst is crucial for the hydrogenation of NBR latex to provide a high degree of hydrogenation. In the presence of TPP, NBR latex without the addition of organic solvents can be hydrogenated to a degree of >90% after about 80 hours at  $145^\circ\text{C}$  using Wilkinson's catalyst at a catalyst to NBR rubber ratio of 1 wt%. The final product was stable HNBR latex without gel formation. The influence of the catalyst/rubber ratio, system composition (rubber solid content) and various operation conditions, such as agitation speed, hydrogen pressure and reaction temperature, were studied.

It appeared that the resistance to external mass transfer is not significant for latex hydrogenation when an agitation speed of above 600 rpm is used in the reaction. Therefore, an agitation speed of 600 rpm was used for most latex hydrogenation experiments.

The catalyst/rubber ratio has a profound influence on the latex hydrogenation rate. When the catalyst/rubber ratio was too low, a high degree of hydrogenation could not be achieved due to the impurity problem. With a high enough catalyst/rubber ratio (more than 0.005), it was found that the NBR polymer can be hydrogenated to high conversion over wide range of system composition, from 5ml latex with 95ml added water to the use of original latex without adding water. However, using additional water to dilute the original latex is still recommended for shortening the reaction time as it reduces the concentration of impurities.

Different hydrogen pressures have been used at  $145^\circ\text{C}$  and  $160^\circ\text{C}$  for latex hydrogenation. The hydrogen pressure has little influence on the rate of the reaction at  $145^\circ\text{C}$ , while the hydrogenation rate increased with increasing hydrogen pressure at  $160^\circ\text{C}$ .

Reaction temperature is another very important factor for the latex hydrogenation reactions. Latex hydrogenation reactions at  $130^\circ\text{C}$ ,  $145^\circ\text{C}$ ,  $152^\circ\text{C}$ ,  $160^\circ\text{C}$  and  $170^\circ\text{C}$  have been studied. The hydrogenation conversion-time curve at  $130^\circ\text{C}$  seems like a zero-order reaction with respect to

[C=C]. The conversion profiles at 145 °C, 152 °C, 160 °C and 170 °C were found to adhere to a first-order rate model with respect to olefin. With the presence of Wilkinson's catalyst, the apparent activation energy for the NBR latex hydrogenation over the range of 152 °C to 170 °C was found to be 57.0 kJ/mol, which suggests the hydrogenation is probably under mixed control.

It was found that higher latex hydrogenation rates can be obtained, especially before reaching 80% conversion, if the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst is pre-mixed into the latex with TPP before introducing hydrogen gas to initiate reaction. More than 92% degree of hydrogenation can be achieved within 22 hours by using this catalyst pre-dispersion method at 160 °C. Based on this observation, it is estimated that the transfer of the catalyst from outside of the polymer particles into the polymer particles and the transfer of the catalyst within the particles are the rate limiting steps for the latex hydrogenation process.

## Chapter 6

### Hydrogenation of NBR Latex Using Water Soluble Rh Catalysts

As discussed in Chapter 5, a solid powder form of Wilkinson's catalyst was used for latex hydrogenation. Wilkinson's catalyst does not dissolve in water and is only suspends in the water phase, which causes difficulties for the catalyst transport into the polymer particles. One would expect that the hydrogenation rate should be significantly increased if the catalyst transfer rate from bulk water phase to polymer particle phase could be increased. Guided by this idea, water-soluble Rh catalysts were tried for the latex hydrogenation and are reported in this chapter. A much higher latex hydrogenation rate was achieved using this approach.

#### 6.1 Introduction

Use of water-soluble catalysts for latex hydrogenation has been reported by other research groups <sup>[48-55]</sup>; however, no researchers this far have achieved high conversion. Actually, the water-soluble catalysts  $\text{RhCl}(\text{TPPMS})_3$  (TPPMS: monosulphonated-triphenylphosphine) and  $\text{OsHCl}(\text{TPPTS})_3$  (TPPTS: trisulphonated-triphenylphosphine) were also used for the hydrogenation of NBR latex in our group <sup>[101]</sup>. The conditions used for these experiments and results are listed in Table 6-1.

**Table 6-1 Hydrogenation of VPKA latex with water-soluble catalysts**

(solid content of VPKA latex is 15g/100ml, 145°C, 1250 psi of  $\text{H}_2$ )

<i>Catalyst</i>	<i>Latex (ml)</i>	<i>Water (ml)</i>	<i>Time (hour)</i>	<i>Conversion</i>
$\text{RhCl}(\text{TPPMS})_3$ 0.0386g	50	50	18.5	30% (gel occurred)
$\text{OsHCl}(\text{TPPTS})_3$ 0.0190g	50	50	22	0% (gel occurred)

When using  $\text{RhCl}(\text{TPPMS})_3$ , after 18.5 hours the hydrogenation conversion was only about 30% and at that time crosslinking had already occurred. It took several days to dissolve the polymer sample in MEK. When the  $\text{OsHCl}(\text{TPPTS})_3$  catalyst was used with additional water-soluble TPPTS,



there was no hydrogenation at all even after 22 hours and the final product could not be dissolved in MEK.

These results show that water-soluble catalysts are more prone in activating crosslinking than oil-soluble catalyst species. The possible reason is that when the catalyst molecule diffuses onto the surface of the polymer particles, the water-soluble ligands tend to stay at the interface between the aqueous phase and polymer phase, while the metal center of the catalyst may diffuse into the polymer phase. Hence, the water-soluble ligands may dissociate from the metal center to remain in the aqueous phase, and the dissociated transition metal inside the polymer particles promotes the cross-linking.

For latex hydrogenation using Wilkinson's catalyst, the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst may aggregate together suspended in the aqueous phase, so not all the catalyst molecules can be diffused to the surface of the polymer particles. Based on this fact, if a water-soluble Rh catalyst is used with TPP, the catalyst can be easily dispersed onto the surface of the polymer particles and TPP may bind to the catalyst. TPP has a strong affinity to the Rh complex catalyst and is soluble in the organic phase. Therefore, the water soluble catalyst's concentration close to the interface of aqueous/organic phase can be increased, and the latex hydrogenation relies on the transfer of the Rh catalytic species from the aqueous phase into the polymer particles with the help of TPP. The water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst was used with TPP in the following NBR latex hydrogenation experiments to test this idea.

## 6.2 Experimental

Catalyst:  $\text{RhCl}(\text{TPPMS})_3$  was synthesized by mixing Wilkinson's catalyst with the TPPMS ligand with 40ml THF and 1ml water according to the synthetic procedure reported by Borowski and Wilkinson et al <sup>[102]</sup>.

NBR Latex: Perbunan latex was the only latex used with the water soluble catalysts (obtained from LANXESS).

For biphasic hydrogenation of NBR, 3 g of VPKA polymer solid dissolved in 20 ml of MCB was mixed with 80 ml of de-ionized water, and then the resulting emulsion was added into a 300 ml Parr reactor with 0.35 g of TPP. The 0.03 g of  $\text{RhCl}(\text{TPPMS})_3$  catalyst was put into a glass bucket and loaded into a catalyst addition device in the reactor. Then, the hydrogenation was carried out like the solution hydrogenation process described in Chapter 3. Samples containing water and solvent were

taken during the reaction. The solvent part of the samples was dried to obtain hydrogenated rubber in order to determine the degree of hydrogenation using FT-IR.

The latex hydrogenation reaction using  $\text{RhCl}(\text{TPPMS})_3$  was carried out in a 300 ml Parr reactor. A measured volume of NBR latex was mixed with a certain amount of additional water in order to adjust the solid content of the latex system. A weighed amount of  $\text{RhCl}(\text{TPPMS})_3$  catalyst was put into a glass bucket and loaded into a catalyst addition device in the reactor. Some other chemicals, such as TPP as the co-catalyst ligand, may be added into this latex as desired, and then the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The mixture was purged by bubbling nitrogen gas at low pressure through the latex system for 20 minutes at room temperature. Subsequently, the system was heated to the desired reaction temperature with agitation. When the temperature of the reactor was stabilized for 30 minutes, the catalyst solid powder was pressurized into the reaction system by high pressure hydrogen gas. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to obtain the final product and to clean the reactor.

Other relevant experimental information has already been provided in Chapter 3.

## **6.3 Results and discussion**

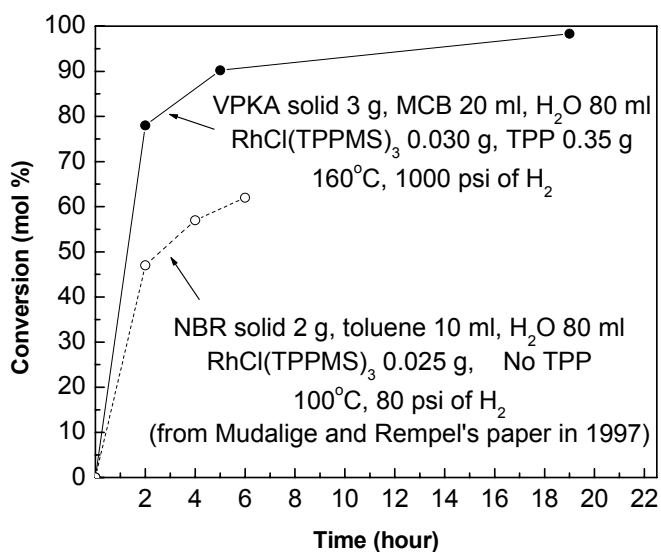
Using TPP with the water-soluble catalyst was initially tested in a biphasic hydrogenation process in order to verify the catalytic activity of such a catalyst system. Then, the combination of TPP and the water-soluble catalyst was used for latex hydrogenation. Effects of other additives on latex hydrogenation were also studied in some experiments.

### **6.3.1 Biphasic hydrogenation of NBR solution using the $\text{RhCl}(\text{TPPMS})_3$ catalyst**

When no TPP was used for the biphasic hydrogenation of NBR solution using water-soluble catalysts, the catalyst remained in the aqueous layer as evidenced by the pale orange aqueous phase and the colorless organic phase obtained after the reaction. It appears that NBR hydrogenation occurred at the interface or in the aqueous media <sup>[103]</sup>. For the experiment using TPP with the water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst, it was carried out at 160°C and under 1000 psi of  $\text{H}_2$  with 600 rpm of

agitation. Experimental conditions and results for experiments with and without TPP are compared below in Figure 6-1.

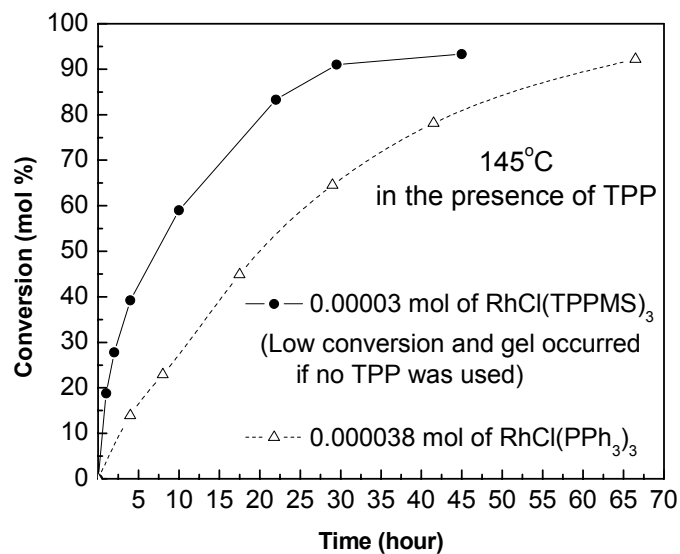
It can be seen from Figure 6-1 that the biphasic hydrogenation in the presence of TPP can reach more than a 98% degree of hydrogenation. The final product from the solvent phase can be totally dissolved in MEK at room temperature, so it has no gel problem. After the hydrogenation, the biphasic reaction system contains a colorless aqueous phase on the top of a dark brown solvent phase. It suggests that Rh was extracted into the solvent phase possibly by forming the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst in the polymer phase after the interaction of  $\text{RhCl}(\text{TPPMS})_3$  with TPP. This experimental result paved the way to use the TPP with water-soluble Rh catalysts for NBR latex hydrogenation.



**Figure 6-1 Bi-phasic hydrogenation of NBR solution**

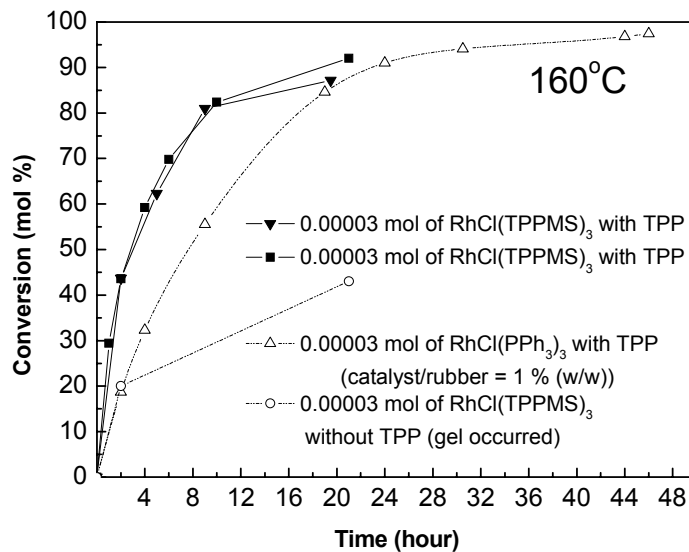
### 6.3.2 Perbunan latex hydrogenation using the $\text{RhCl}(\text{TPPMS})_3$ catalyst

Experimental conditions and results using the  $\text{RhCl}(\text{TPPMS})_3$  catalyst for latex hydrogenation are listed below in Figure 6-2 and Figure 6-3 (compared with experiments using Wilkinson's catalyst).



**Figure 6-2 Latex hydrogenation using  $\text{RhCl(TPPMS)}_3$  and  $\text{RhCl(PPh}_3)_3$  at 145°C**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w), 145°C, 1000psi of  $\text{H}_2$ )



**Figure 6-3 Latex hydrogenation using  $\text{RhCl(TPPMS)}_3$  and  $\text{RhCl(PPh}_3)_3$  at 160°C**

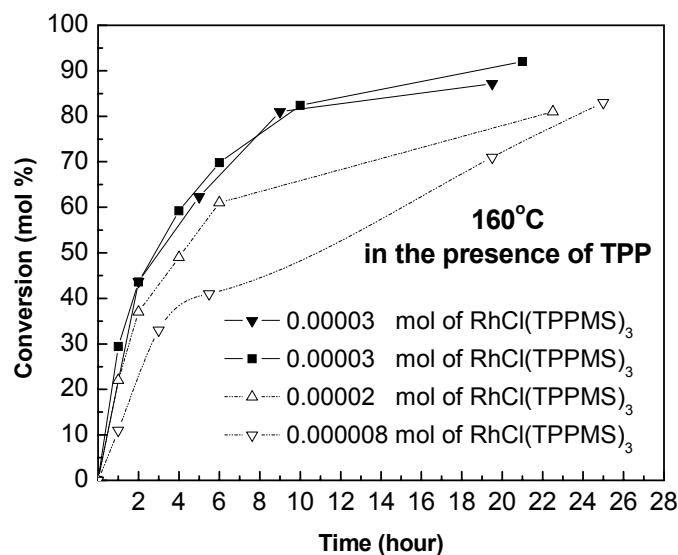
(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w), 160°C, 1000psi of  $\text{H}_2$ )

It was known that if the water soluble catalyst was used without the addition of TPP at 145°C, there was gel formation, and only a low degree of hydrogenation could be achieved. Figure 6-3 confirms that the situation is the same at 160°C. As expected, it was found from Figure 6-2 and Figure 6-3 that the latex hydrogenation rate increased a lot when the  $\text{RhCl}(\text{TPPMS})_3$  catalyst was used with TPP. The final product is a stable polymer latex which contains hydrogenated rubber that can be totally dissolved in MEK at room temperature.

These experimental results clearly show that using water-soluble Rh catalyst with TPP is better than using the Wilkinson's catalyst with TPP. The good solubility of  $\text{RhCl}(\text{TPPMS})_3$  in water provides the catalyst much greater mobility than that of Wilkinson's catalyst in the aqueous phase, which ensures that all the Rh complex molecules can have the chance to have contact with the latex particle interface. Therefore,  $[\text{Rh}]$  at the surface of polymer particles should be higher even if the same number moles of  $\text{RhCl}(\text{TPPMS})_3$  and  $\text{RhCl}(\text{PPh}_3)_3$  were used. When no TPP was used, the  $\text{RhCl}(\text{TPPMS})_3$  can only hydrogenate the C=C bonds at the surface of the polymer particles; it may dissociate the water-soluble TPPMS ligand, and the hydrogen present may cause formation of Rh metal at the polymer phase which promotes the cross-linking. However, if TPP was used with the water-soluble Rh catalyst, once the Rh complex molecule comes to the interface between the water and rubber phase, the interaction between TPP and the Rh-TPPMS complex at the interface may form the  $\text{RhCl}(\text{PPh}_3)_3$  catalytic species; the so formed Wilkinson's catalyst in TPP diffuses into polymer phase with access to all C=C bonds. Therefore, a high degree of hydrogenation without gel formation for NBR latex can only be achieved when TPP was used together with the water-soluble catalyst.

It can also be seen from Figure 6-2 and Figure 6-3 that when TPP was used with  $\text{RhCl}(\text{TPPMS})_3$ , the initial hydrogenation rate increased significantly compared to the results using Wilkinson's catalyst; when the degree of hydrogenation was higher than about 80%, the hydrogenation rate decreased, and the time when more than 90% of conversion was achieved is close to the time needed for latex hydrogenation using Wilkinson's catalyst.

The above results suggest that the initial higher hydrogenation rate enhancement with the water soluble Rh complex is due to the higher catalyst concentration at the outer layers of polymer particles. The hydrogenation rate decreased at high conversion, because the hydrogenation rate of remaining C=C bonds in the inner layers of NBR particles is controlled by the catalyst mass transfer inside the polymer particles. This explanation is confirmed by the hydrogenation results using less  $\text{RhCl}(\text{TPPMS})_3$  catalyst at similar experimental conditions as shown in Figure 6-4.



**Figure 6-4 Latex hydrogenation using less  $\text{RhCl}(\text{TPPMS})_3$  at  $160^\circ\text{C}$**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w),  $160^\circ\text{C}$ , 1000psi of  $\text{H}_2$ )

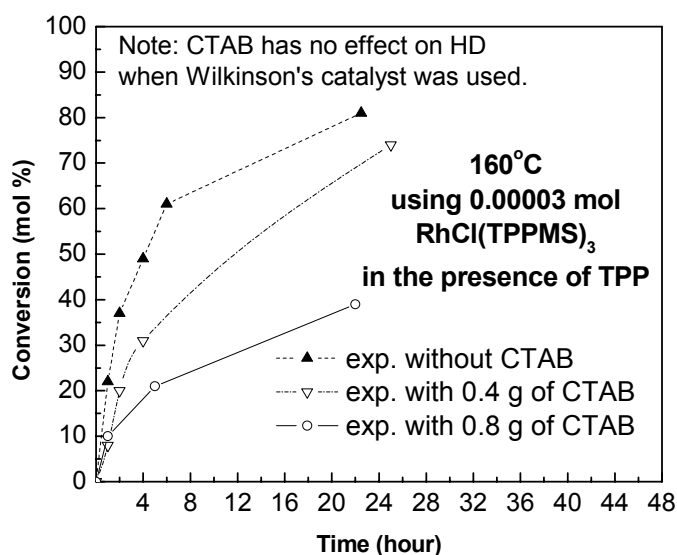
From Figure 6-4, it can be seen that the degree of hydrogenation still reached more than 70% after 22 hours even if a very little amount ( $0.000008 \text{ mol}$ ) of  $\text{RhCl}(\text{TPPMS})_3$  was used, which was similar to the hydrogenation results when a higher amount ( $0.00002 \text{ mol}$ ) of the catalyst was used. Hydrogenation reactions took similar reaction time to achieve similar high hydrogenation degrees, because the hydrogenation rate for  $\text{C}=\text{C}$  bonds in the inner layers of NBR particles mainly depends on how many catalyst molecules can successfully pass outer layers and transfer into the core parts of these particles, rather than depending on the initial amount or concentration of catalyst used. Therefore, it is anticipated that NBR latex with smaller polymer particle size may benefit the hydrogenation process.

### 6.3.3 Latex hydrogenation in the presence of cetyl trimethyl ammonium bromide

There are many papers reporting on the promotion effect of cationic surface-active agents, such as cetyl trimethyl ammonium bromide/chloride (CTAB or CTAC), for biphasic hydroformylation

reactions <sup>[104]</sup>. Cationic surfactants have proven to be the most effective additives for the Rh/sulfonated phosphine system as the positively charged moiety is directed towards the aqueous phase and favors the approach of the anionic Rh-sulfonated phosphine complex to the interface of the water/organic inter phase where the substrate can coordinate to the catalyst.

Experiments using the water-soluble Rh catalysts in the presence of cetyl trimethyl ammonium bromide (CTAB) for latex hydrogenation were conducted in the hope of gathering more water soluble catalyst molecules to the interface between the rubber particle phase and the aqueous phase as shown in Figure 6-5.



**Figure 6-5 Latex hydrogenation using  $\text{RhCl(TPPMS)}_3$  with CTAB**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w), 160°C, 1000psi of  $\text{H}_2$ )

It was found that the use of CTAB actually decreased the reaction rate, and the reaction rate decreased with the increasing of the concentration of CTAB. This could be explained by taking into account the greater steric effects exerted by the higher concentration of all surfactant molecules which are accumulated at the interface.

## 6.4 Summary

It was known from previous latex hydrogenation experiments that the latex hydrogenation rate depends on the amount of catalyst which can successfully diffuse into the polymer particles. In order to improve the catalyst transfer from bulk water phase onto the particle surface, the water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst was tried for the latex hydrogenation in this chapter, and much better hydrogenation results were achieved.

When the water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst was used alone without the TPP, the higher  $[\text{Rh}]$ , probably in the form of Rh metal, at the interface between the aqueous phase and polymer particle phase caused gel formation in polymer particles, and the high degree of hydrogenation could not be realized.

In the presence of TPP, the water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst has much better chances to reach the water-polymer interface, to permeate membrane-like array of surfactant molecules at the interface, and to cross into the polymer particles. The latex hydrogenation can reach more than a 90% degree of hydrogenation after 20 hours at 160°C under 1000 psi of  $\text{H}_2$  using 0.00003 mol of the catalyst with TPP.

It was found that the higher concentration of surfactants at the polymer particle surface can cause more catalyst mass transfer resistance and decrease the hydrogenation rate. Also, the catalyst mass transfer within polymer particles was found to be the rate controlling step for the latex hydrogenation.



## Chapter 7

### Hydrogenation of NBR Latex Using Rh Salts

Inspired by the success of using water-soluble Rh catalysts for the latex hydrogenation in the presence of TPP, latex hydrogenation using water-soluble Rh salts directly as the catalyst precursor was studied, and experimental results are shown in this chapter.

#### 7.1 Introduction

$\text{RhCl}_3$  is the commonly used Rh salt for the synthesis of many different oil-soluble Rh complex homogeneous catalysts. Actually, Wilkinson's catalyst  $[\text{RhCl}(\text{PPh}_3)_3]$  is prepared by refluxing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with recrystallized triphenylphosphine (TPP) in ethanol according to the procedures of Osborn and Ahmad et al. <sup>[99, 100]</sup>. Then the water soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst can be formed by the reaction of Wilkinson's catalyst with TPPMS ligand in THF and water <sup>[102]</sup>.

Also,  $\text{RhCl}_3$  and other Rh salts can be used to directly synthesize water-soluble catalysts. Larpent et al reported the formation of  $\text{RhCl}(\text{TPPTS})_3$  from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with TPPTS in the absence of  $\text{H}_2$ , where TPPTS acts both as a ligand and reducing agent for rhodium(III) chloride to afford  $\text{RhCl}(\text{TPPTS})_3$  <sup>[105]</sup>. Auvray claimed that a water-soluble phosphine complex of Rh perchlorate can be synthesized by mixing tris(3-sulfophenyl)phosphine with the  $\text{Rh}(\text{ClO}_4)_3$  salt <sup>[106]</sup>.

Usually, catalysts are carefully generated before they are used for catalytic reactions. However, it could be even more advantageous if the catalyst can be produced in situ in the catalytic system, because the time and effort for the catalyst synthesis could be saved. One successful example is the Rh/TPPTS complex generated in situ from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and TPPTS, which was used for the aqueous hydrogenation of polybutadiene-1,4-block-poly(ethylene oxide) <sup>[56]</sup>. So, if an active Rh catalytic complex can be obtained in situ directly from  $\text{RhCl}_3$  to hydrogenate NBR latex, a better catalytic latex hydrogenation system can be developed, compared to the latex hydrogenation system using water-soluble catalysts. This idea was tested in this chapter, and good results were obtained.

Another important type of hydrogenation catalysts are transition metal colloid catalysts. These colloid catalysts have a size of a few nano meters and such catalytic species should be transferred into

polymer particles easily. Patin's group synthesized suspensions of Rh(0) nanoparticles by reducing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with sodium borohydride and stabilizing the resulting Rh species with surfactant hydroxyalkylammonium salts. These nanoparticles were used as catalysts in the hydrogenation of various benzene derivatives in aqueous/organic biphasic systems <sup>[107, 108, 109]</sup>. The use of  $\text{RhCl}_3$  to produce a Rh colloid catalysts and the NBR hydrogenation using this colloid catalyst were also carried out in this research.

## 7.2 Experimental

Catalyst was synthesized in situ by mixing  $\text{RhCl}_3$  with the NBR latex in the presence of TPP and then reducing with  $\text{H}_2$ . Perbunan latex was the only latex used for experiments in this chapter.

**NBR Latex:** Perbunan latex was the only latex used with the water soluble Rh salts (obtained from LANXESS).

The latex hydrogenation reaction using  $\text{RhCl}_3$  was carried out in a 300 ml Parr reactor. A measured volume of NBR latex was mixed with a certain amount of additional water in order to adjust the solid content of the latex system. The weighed amount of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (or other Rh salt) and TPP were mixed into the latex in the reactor; then, the reactor was sealed and the reaction system was assembled for the hydrogenation reaction. The system was purged by bubbling nitrogen gas at low pressure through the latex system for 20 minutes at room temperature, and the system was heated to 100°C with agitation. The latex system was kept at 100°C for several hours in order to provide time for the in situ synthesis of active catalytic species for the latex hydrogenation. Subsequently, the temperature was adjusted to the reaction temperature before introducing the high pressure hydrogen gas to initiate the reaction. The counting of the reaction time began once  $\text{H}_2$  was introduced into the latex system. Hydrogenation pressure and reaction temperature were maintained constant throughout the reaction period. Time sampling of the reaction was carried out during the hydrogenation reaction. After a given reaction time, the system was cooled to room temperature and depressurized in order to open the reactor to obtain the final product and to clean the reactor.

For the latex hydrogenation using Rh colloid catalyst, the catalyst was prepared by first dissolving weighted rhodium chloride with certain amount of polyvinyl pyrrolidone (PVP, Mw = 36,000) in water at 90°C for 2 hours and then reducing the mixture with hydrogen according to literature <sup>[110]</sup>.

The obtained catalyst in aqueous solution was directly mixed with latex, and then the hydrogenation was carried out in the same way as the experiments using the  $\text{RhCl}_3$ .

Further information on general experimental procedures has already been reported in Chapter 3.

## 7.3 Results and discussion

### 7.3.1 Effect of mixing $\text{RhCl}_3$ with latex

In order to synthesize catalyst in situ from  $\text{RhCl}_3$ , the  $\text{RhCl}_3$  must first be mixed with the NBR latex system. Therefore, the effect of adding  $\text{RhCl}_3$  on the stability of NBR latex has to be studied. Singha's group in India reported the effect of adding  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  into NBR latex in 1995 <sup>[53]</sup>. According to their paper,  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  caused gelation of the NBR rubber when it was added to the latex at  $75^\circ\text{C}$  and 1 atmosphere of  $\text{N}_2$  pressure. Using Perbunan NBR latex, such experiments were carried out and compared with their result as shown in Table 7-1.

**Table 7-1 Effect of mixing  $\text{RhCl}_3$  with polymer latex**

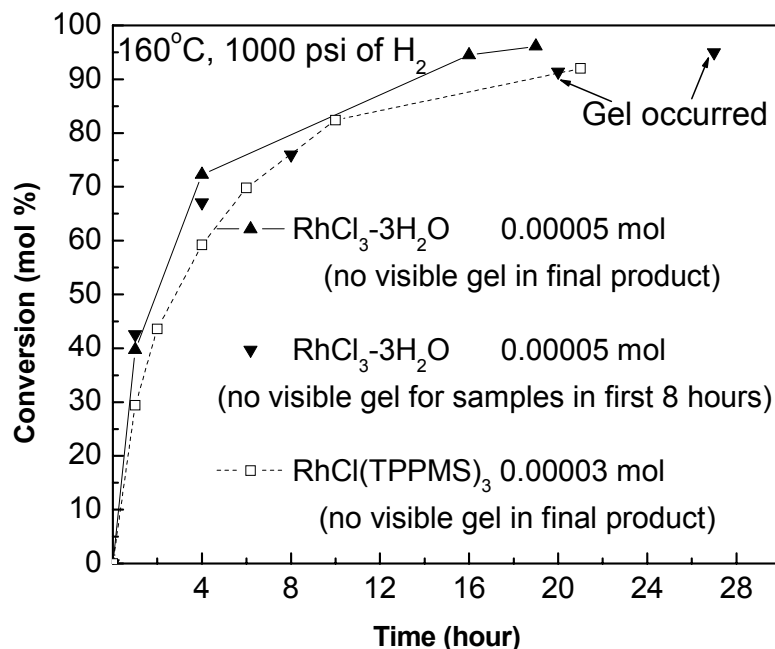
Add $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ into NBR latex	Added TPP (g)	Operation conditions	Latex gel information
Singha's observation <sup>[53]</sup>	None	$\text{N}_2$ 1 atm, $75^\circ\text{C}$	Gel occurred
Experiment using Perbunan latex (Perbunan latex 25 ml, $\text{H}_2\text{O}$ 75 ml, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ 0.012 g)	None	$\text{N}_2$ 200 psi, $100^\circ\text{C}$ (4 hr with agitation)	Gel occurred
	0.353	$\text{N}_2$ 100 psi, $100^\circ\text{C}$ (4 hr with agitation)	No visible gel

One experiment without using TPP was tried, and a result similar to Singha's report was obtained. However, in the presence of TPP, there was no gel observed after 4 hours at  $100^\circ\text{C}$  and under 100 psi of  $\text{N}_2$  pressure.

So it seems that TPP is a gel inhibitor (the role of TPP is discussed in more details in Chapter 9). In the presence of TPP, it is possible to synthesize the active Rh complexes in situ from  $\text{RhCl}_3$  in the latex system without any gel problem.

### 7.3.2 Latex hydrogenation using $\text{RhCl}_3$ directly

Based on the successful experiments of latex hydrogenation using the water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst with TPP, the water-soluble  $\text{RhCl}_3\text{H}_2\text{O}$  was also directly used with TPP for NBR hydrogenation. Experimental conditions and results are shown in Figure 7-1.



**Figure 7-1 Latex hydrogenation using  $\text{RhCl}_3$  directly with TPP**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w), 160°C, 1000psi of  $\text{H}_2$ )

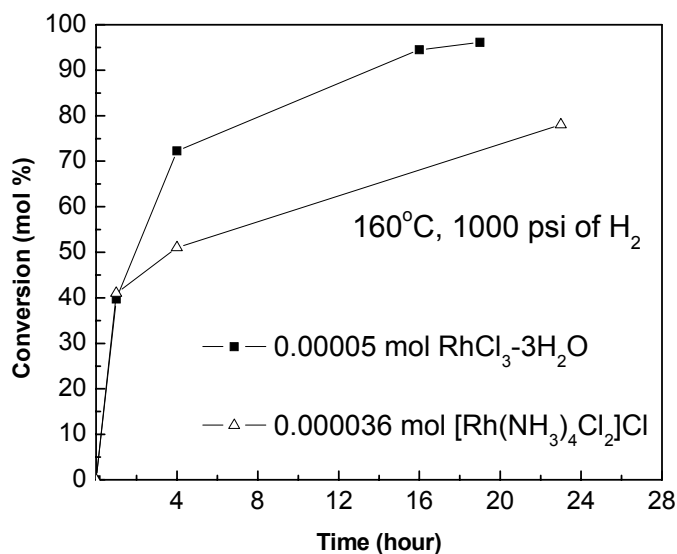
The  $\text{RhCl}_3\text{H}_2\text{O}$  in solid powder form was directly added into the latex in Parr reactor under  $\text{N}_2$  pressure with agitation, and then high pressure  $\text{H}_2$  was introduced to initiate the hydrogenation reaction at the reaction temperature. The final product after 19 hours of reaction is the stable polymer latex with 96% degree of hydrogenation without any gel problem. One repeat experiment was carried out for more than 20 hours, and it was found that gel occurred after 20 hours of hydrogenation under those experiment conditions.

These experiments confirmed that  $\text{RhCl}_3$  can be directly used as an excellent catalyst precursor for the in situ synthesis of an active Rh catalytic complex, and the catalytic performance of the complex for the latex hydrogenation is similar to that of  $\text{RhCl}(\text{TPPMS})_3$  in the presence of TPP.

The  $\text{RhCl}_3$  itself has no catalytic activity for hydrogenation. The successful hydrogenation of NBR latex suggests that a catalyst synthesis process occurs between Rh(III), TPP and  $\text{H}_2$  in water or the polymer phase; so, the Rh(III) in  $\text{RhCl}_3$  may be reduced into Rh(I) by the reduction of TPP to form the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst. Further investigation and more discussion about the catalytic mechanism can be found in Section 9.3.4.

### 7.3.3 Latex hydrogenation using other Rh salts

$[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , another Rh(III) salt synthesized according to literature <sup>[111]</sup>, was also used with TPP for latex hydrogenation as shown in Figure 7-2.



**Figure 7-2 Latex hydrogenation using  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  directly with TPP**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP/rubber is 10% (w/w), 160°C, 1000psi of  $\text{H}_2$ )

It was found that more than 75% degree of hydrogenation was achieved after 23 hours when the  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  was directly used with TPP for latex hydrogenation. The hydrogenation result using  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  as a catalyst precursor is not as good as the result of the experiment using  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  for the latex hydrogenation of NBR. This may be caused by the lower  $[\text{Rh}]$  or by the interaction between dissociated  $\text{NH}_3$  ligand and CN group within the polymer chain.

### 7.3.4 Latex hydrogenation using Rh colloids

Rh colloid catalysts were prepared by initially dissolving weighted rhodium tri-chloride with polyvinyl pyrrolidone (PVP) in water at  $90^\circ\text{C}$  for 2 hours and then reducing the mixture with  $\text{H}_2$ . The obtained Rh colloid catalysts were used in the following experiments as shown in Table 7-2 and Figure 7-3.

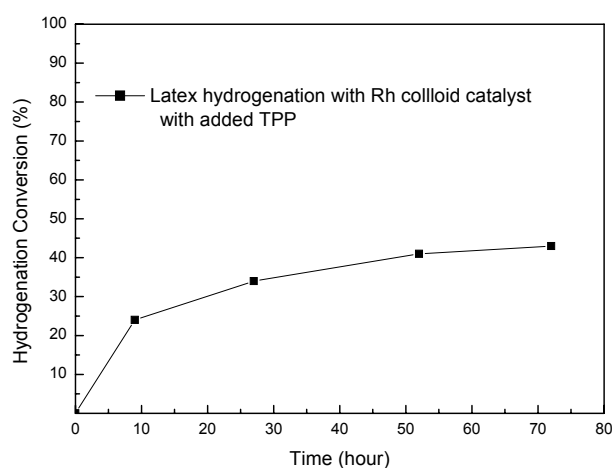
**Table 7-2 Latex hydrogenation using the Rh colloid catalyst**

<i>Exp</i>	Colloid solution	<i>VPKA latex</i> (ml)	<i>Added</i> <i>water (ml)</i>	<i>T</i> ( $^\circ\text{C}$ )	<i>H<sub>2</sub></i> <i>pressure</i>	<i>Conversion</i> (time)
#1	40ml <sup>A</sup> (reduced with $\text{H}_2$ then added into latex)	100	0	80	Purge with $\text{H}_2$	No HD (4h, gel)
#2	40ml <sup>A</sup> (mixed with latex for 42hr then reduced with $\text{H}_2$ )	100	0	80	Purge with $\text{H}_2$	No HD (6h, gel)
#3	15ml <sup>B</sup> (mixed with latex for 23hr then reduced with $\text{H}_2$ )	35	105	80	Purge with $\text{H}_2$	30% (7h, no gel)
#4	13ml <sup>B</sup> (mixed with latex for 24hr then reduced with $\text{H}_2$ )	35	105	70	600psi	25% (47hr, no gel)
#5	12ml <sup>B</sup> (mixed with latex for 20hr then reduced with $\text{H}_2$ )	35	105	145	600psi	18% (25hr, no gel)
#6	15ml <sup>C</sup> (mixed with latex for 17hr then reduced with $\text{H}_2$ , <b>added 0.45152g TPP</b> )	35	85	70	500psi	43% (72hr, no gel)

Colloid solution A:  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  0.03146g + 0.20452g PVP + 40ml water; stir 2 hours at  $90^\circ\text{C}$ ;  
Colloid solution B:  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  0.03101g + 0.20127g PVP + 40ml water; stir 2 hours at  $90^\circ\text{C}$ ;  
Colloid solution C:  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  0.03103g + 0.20198g PVP + 40ml water; stir 2 hours at  $90^\circ\text{C}$ .

It seems that the Rh colloid catalyst obtained in this method (reduced with  $H_2$ ) may not be suitable for the hydrogenation of NBR latex.

From Figure 7-3, it was found that the added TPP has positive effect on the latex hydrogenation (the conversion was below 30% when no TPP was used), but the final conversion after 72 hours was still less than 45%. After all of those experiments, no aggregation or coagulation of colloidal particles was found in the NBR latex.



**Figure 7-3**      **hydrogenation result for latex hydrogenation using Rh colloid catalyst with TPP**  
(Reaction conditions are listed in Table 7-2)

## 7.4 Summary

Active catalytic complexes have been generated in situ from Rh salts for latex hydrogenation. A high degree of hydrogenation can be achieved by using Rh salts directly with TPP. Compared to the use of Wilkinson's catalyst or water-soluble Rh catalysts, the use of Rh salts as the catalyst precursor for latex hydrogenation is better since there is no need to synthesize the catalytic species in advance.

Without the presence of TPP, the addition of  $\text{RhCl}_3$  into NBR latex causes cross-linking of polymer chains. In the presence of TPP, there was no gel problem when  $\text{RhCl}_3$  was added into the latex system.

The hydrogenation of NBR latex by directly using  $\text{RhCl}_3$  powder with TPP produced a stable polymer latex with 96% degree of hydrogenation without gel problem after 19 hours. More than 75% degree of hydrogenation was achieved after 23 hours when the  $[\text{Rh}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  was directly used with TPP for latex hydrogenation. These experimental results suggest that the Rh(III) in these Rh salts may be reduced into Rh(I) and then the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst may be formed within polymer particles in the presence of the TPP ligand.

Rh colloid catalysts obtained by reducing  $\text{RhCl}_3$  with  $\text{H}_2$  in the presence of PVP were also used for latex hydrogenation. Such colloid catalysts were found to be unsuitable for the hydrogenation of NBR latex. Even when such colloid catalysts were used in the presence of TPP, the final conversion after 72 hours was still less than 45%.



## **Chapter 8**

### **Other Studies Related to the Development of the Latex Hydrogenation Process**

Based on the above experimental results using the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst and Rh based catalysts, the direct catalytic hydrogenation of NBR in latex form has been realized. At the same time, technical challenges for the latex hydrogenation process were observed in several aspects other than the development of catalysts with high catalytic activity. Efforts were made to solve these problems in order to establish an efficient direct catalytic latex hydrogenation process.

The research work related to the study of polymer latex properties, improving catalyst performance in the presence of impurities, and preventing the cross-linking is presented in this chapter.

#### **8.1 Latex hydrogenation process development considerations**

Based on the research progress using the Os and the Rh catalyst, the direct catalytic hydrogenation of acrylonitrile-butadiene rubber latex has been successfully realized with a conversion of higher than 95%. However, it was also found that many problems accompany the latex hydrogenation, mainly including:

- Latex problem, which includes the choice of different latices, the stability of the latex before and after hydrogenation, and the change of latex properties with time;
- Impurity problem, which lowers the activities of catalysts and/or decreases the mass transfer rate of the catalysts;
- Gel problem, which increases the final product's viscosity significantly and deteriorates the product's physical properties and processibility.

These challenges are considered for the further development of the NBR latex hydrogenation process, and suitable solutions are explored through the following studies.

## 8.2 Experimental

Solution hydrogenation experiments using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and  $\text{RhCl}(\text{PPh}_3)_3$  catalysts in this chapter were carried out according to the procedures described in Chapter 3.

Latex hydrogenation experiments using  $\text{RhCl}(\text{PPh}_3)_3$  in this chapter was carried out according to the procedures described in Chapter 5.

$\text{CaCl}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and other chemicals used for the impurity study were obtained from Sigma-Aldrich Ltd.

Other relevant experimental information was provided in Chapter 3.

## 8.3 Studies related to NBR latex

### 8.3.1 Comparison of two grades of NBR latices

Two grades of NBR latices have been used for latex hydrogenation in this research project. Table 8-1 shows a comparison of the properties of those two latices.

**Table 8-1 Comparison of VPKA latex with Perbunan latex**

Solid content (g/100ml)	12	12	15
pH	9	About 8	9
Mean particle size (nm)	72	74	78
CN content (%)	38	38	38
Heat stability (heated up to 130°C for 6 hours)	Stable	Phase separated	Stable

\*: VPKA latex arrived in March, 2003.

\*\* : Experiments had good reproducibility up to Nov., 2004. No good hydrogenation results were obtained using VPKA latex after that period.

VPKA 8817 latex was initially used for the direct catalytic hydrogenation. However, those experimental results using the latex could not be repeated in 2005 due to the change of VPKA latex over that period of time. A new batch of latex with the grade name of “Perbunan” was obtained in

June, 2005. Perbunan latex is supposed to have similar properties to those of the previously used VPKA 8817 latex.

### **8.3.2 Stability of NBR latex**

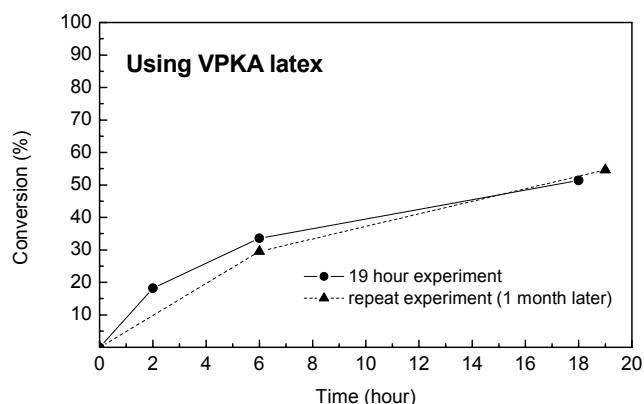
The stability of NBR latex before hydrogenation was tested, and the results can be seen in Table 8-1. The stability of Perbunan latex was further tested by using a new reactor with even higher agitation speeds at higher temperature. The Perbunan latex was found to be stable after two hours at a high temperature up to 177°C and with an agitation speed of 1500 rpm.

Also, according to the research goal for this project, the polymer latex should be stable both before and after the hydrogenation reaction. It is required that the NBR polymer particles can be maintained after hydrogenation and the emulsion breaking of NBR latex should not occur.

When the Os catalyst was used for latex hydrogenation, the degree of hydrogenation was very low if no organic solvent is used. It was found that high hydrogenation conversion could be achieved when a limited amount of MCB was used with the catalyst. However, the NBR emulsion may be broken and a layer of the catalyst solution may be formed at the bottom of the reactor when high hydrogenation conversion was achieved. The final product can be as a stable latex form only when the MCB/latex volume ratio was within a suitable range. Although hydrogenation still proceeded if MCB is used in proportions beyond the upper limit of suitable range, use of the MCB in such an excess proportion leads to the break down of the latex, promoting its separation into a solvent phase and an aqueous phase. Therefore, the stability of polymer latex after hydrogenation is a big challenge when the Os catalyst was used <sup>[112]</sup>. When Wilkinson's catalyst was used for latex hydrogenation, there was no such problem since it is an organic solvent-free hydrogenation process <sup>[113]</sup>.

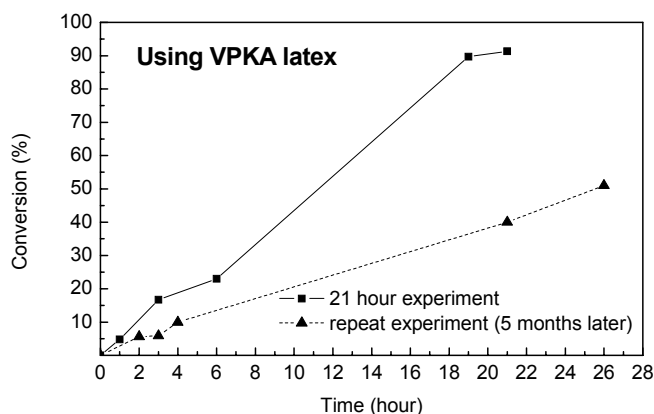
### **8.3.3 Effect of latex change on the latex hydrogenation**

NBR latex (aqueous emulsion of NBR) has limited time as a stable dispersion system; so some properties of latex change with time are shown in Table 8-1. The effects of these changes on latex hydrogenation using the Os catalyst and Wilkinson's catalyst were investigated and are shown in Figure 8-1, Figure 8-2 and Figure 8-3.



**Figure 8-1 Effect of latex change on latex hydrogenation using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  (1)**

(VPKA latex 50ml (rubber content is 12g/100ml),  $\text{H}_2\text{O}$  50ml, MCB 20ml,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  0.02g, 800 psi of  $\text{H}_2$ ,  $100^\circ\text{C}$ )

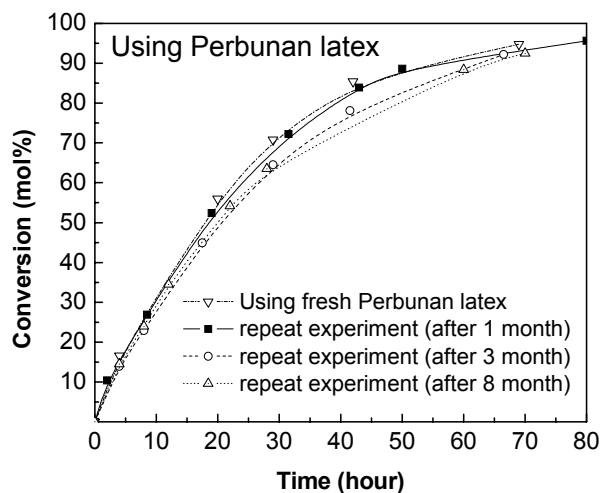


**Figure 8-2 Effect of latex change on latex hydrogenation using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  (2)**

(VPKA latex 20ml (rubber content is 12g/100ml),  $\text{H}_2\text{O}$  50ml, MCB 5ml,  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  0.04g, 800 psi of  $\text{H}_2$ ,  $100^\circ\text{C}$ )

From Figure 8-1 and Figure 8-2, it can be seen that the repeated experiment which was conducted one month later had good reproducibility, while the hydrogenation result of the repeated experiment after five months changed significantly from the original run. This is caused by the change of latex. After stored over a period of time, the morphology of the latex particles may change a lot since some

rubber particles aggregated together (but still suspended in the emulsion) and the remaining particles became denser. Therefore, the transport of the Os catalyst into the polymer particles may become more difficult, and higher conversion can not be achieved after the same period of reaction time.



**Figure 8-3 Effect of latex change on latex hydrogenation using  $\text{RhCl}(\text{PPh}_3)_3$**   
 (Perbunan latex 25ml (rubber content is 15g/100ml),  $\text{H}_2\text{O}$  75ml,  
 $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1%(w/w), TPP/rubber is 10%(w/w), 1000 psi of  $\text{H}_2$ , 145°C)

Repeated hydrogenation results using Perbunan latex are shown in Figure 8-3. It was found that the repeated experiments with  $\text{RhCl}(\text{PPh}_3)_3$  showed good reproducibility, which indicates that the Perbunan latex has better stability for the latex hydrogenation. Another possible explanation is that the Os catalyst is more sensitive to the change of the NBR latex with time.

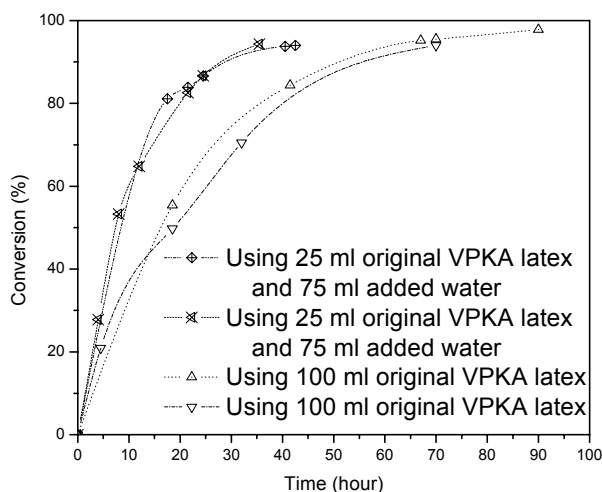
#### 8.4 Studies related to impurity issue

Based on previous latex hydrogenation experiments using the Os and Rh catalysts, it has been observed that there maybe certain chemical(s) inside the NBR latex which can negatively affect the catalytic hydrogenation. Emulsifiers, chain transfer agents, stabilizers and other chemicals used in the synthesis of NBR often remain in undefined amounts within the latex. These residual carboxylates, mercaptans and/or alcohols may adversely affect the catalyst. Consequently, a meaningful evaluation

of the latex hydrogenation technology must involve studies of the latex impurity problem. Some effects have been done to identify the chemicals and minimize the bad influences of such chemicals.

#### 8.4.1 Identify the NBR latex impurity problem

From the effects of system composition and temperature on the latex hydrogenation (see Section 4.3.3 and Section 4.3.4), it was suspected that there are impurities within the latex which cause unusual conversion-time curves when the Os catalyst was used. Also, the effect of Wilkinson's catalyst to rubber ratio on the latex hydrogenation (see Section 5.3.5) confirms the impurity problem. More latex hydrogenation experiments using Wilkinson's catalyst were conducted to identify the impurity issue as shown in Figure 8-4.



**Figure 8-4 Hydrogenation of original and diluted VPKA latex**

(Solid content of VPKA latex is 12g rubber solid/100ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1% (w/w), TPP/rubber is 10% (w/w), 145°C, 1000 psi of  $\text{H}_2$ )

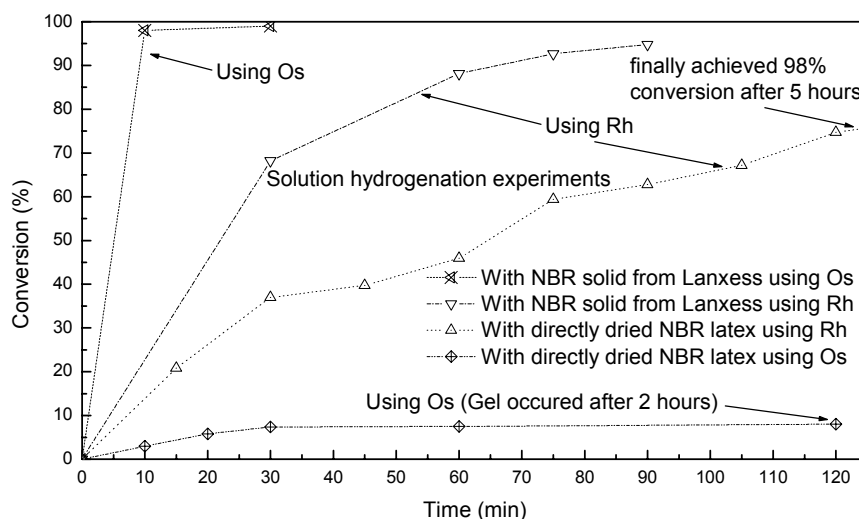
From Figure 8-4, it was also found that the hydrogenation rate increased significantly when the original latex was diluted by mixing 25ml of original latex with 75ml of deionized water. Using the same catalyst/rubber ratio (1 wt%), the hydrogenation of diluted latex can reach more than 90% conversion within 50 hours while the hydrogenation of the original undiluted VPKA latex requires

more than 70 hours. This result further confirms that there are certain impurities within the latex which have negative effects on catalyst activity for hydrogenation. By simply adding water to dilute the original latex, their negative influence on hydrogenation can be decreased (i.e., impurities are now at a lower concentration).

Given all those results, it can be concluded that those impurities should be water-soluble, and they may stay in the water phase or at the surface of the polymer particles. The impurities seem to be non-rubber components such as the remaining initiator, surfactants, stabilizer etc. from the emulsion polymerization, and are most probably some surfactants used in the emulsion polymerization process.

#### 8.4.2 Investigation of latex impurity problem by solution hydrogenation

It is quite possible that impurity in the latex may form an inactive complex species with the catalyst, or the impurity may just interfere with the mass transfer process of the catalyst. In order to investigate the impurity problem without the effect of mass transfer, experiments of NBR solution hydrogenation were carried out. Solution hydrogenation results using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  and Wilkinson's catalyst are compared in Figure 8-5.



**Figure 8-5 Effect of impurities on activities of catalysts for hydrogenation of NBR solution**

(For using the Os catalyst:  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  0.011g, NBR solid 3.578g, MCB 150ml, 600psi of  $\text{H}_2$ , 130°C; For using the Rh catalyst:  $\text{RhCl}(\text{PPh}_3)_3$  0.0113g, added  $\text{PPh}_3$  1.08g, NBR solid 3.579g, MCB 150ml, 600psi of  $\text{H}_2$ , 130°C)

It can be seen that for hydrogenation of those NBR solids which contain impurities (from original NBR latex), Wilkinson's catalyst is much better than the Os catalyst. Thus it appears that it is better to use the Rh catalyst for hydrogenation of NBR latex. The successful latex hydrogenation using Wilkinson's catalyst has already proven this idea.

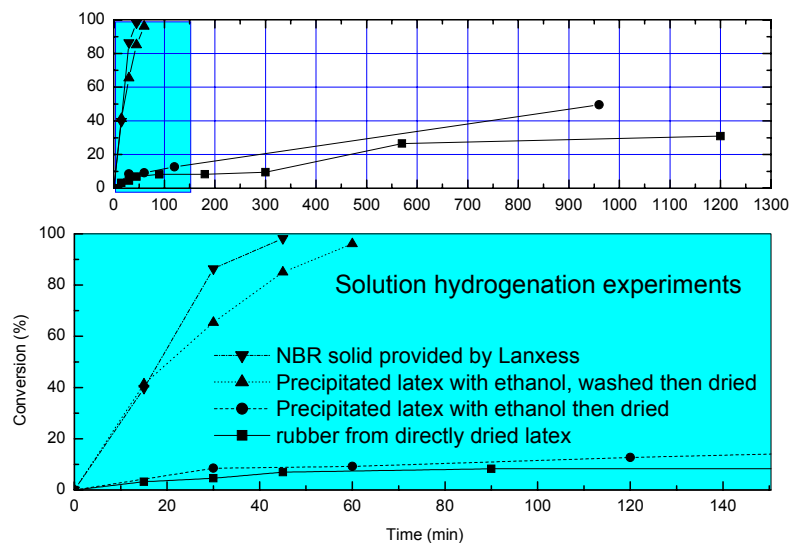
However, for the investigation of impurity problem, the using of the more sensitive Os catalyst should be better. So, more solution hydrogenation experiments have been carried out using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  to investigate the impurity problem. In those experiments, different NBR solids have been prepared by different methods, and then such NBR solids were dissolved in MCB to prepare a NBR solution which was finally used for solution hydrogenation. Reaction conditions and results are shown in Table 8-2, Figure 8-6 and Figure 8-7.

**Table 8-2 Hydrogenation results of different NBR solutions using  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$**

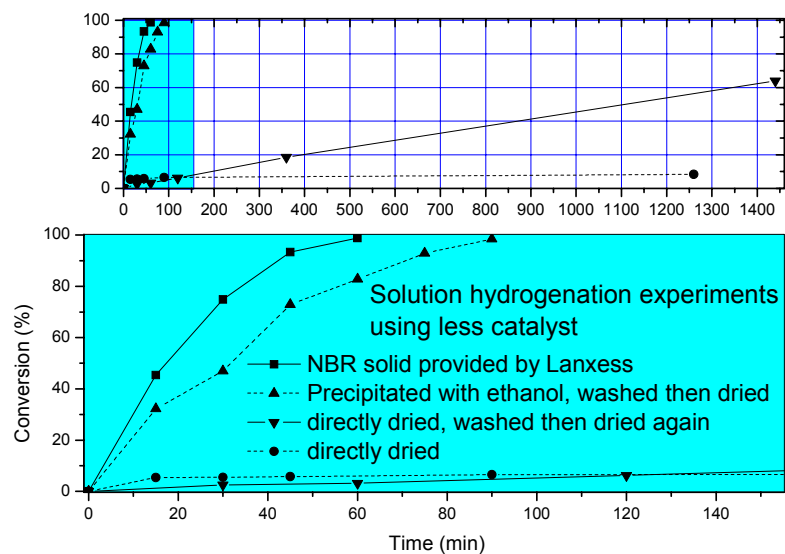
(MCB 150ml, 130°C, 600psi of  $\text{H}_2$ ; VPKA latex was used to make NBR solids and water was used to wash NBR solid in some experiments)

#	Sources of NBR solid	NBR (g)	Os cat. (g)	Conversion (%)
1	Krynac 3850 provided by LANXESS	3.578	0.011	98% (0.75hr)
2	Directly dry VPKA latex in vacuum	3.578	0.011	27% (9hr)
3	Precipitate latex with ethanol then dry precipitated rubber in vacuum	3.579	0.011	49% (16hr)
4	Precipitate latex with ethanol, wash the precipitated rubber, then dry in vacuum	3.579	0.011	96% (1hr)
5	Precipitate latex with $\text{H}_2\text{SO}_4$ , wash the precipitated rubber, then dry in vacuum	3.578	0.011	92% (0.5hr)
6	Precipitate latex with $\text{CaCl}_2$ , wash the precipitated rubber, then dry in vacuum	3.577	0.011	98% (0.5hr)
7	Precipitate latex with $\text{CaCl}_2$ , wash the precipitated rubber, then dry in vacuum	3.579	0.011	99% (0.5hr)
8	Krynac 3850 provided by LANXESS	3.577	0.0039	99% (1hr)
9	Directly dry VPKA latex in vacuum	3.579	0.0039	8% (21hr)
10	Directly dried latex was washed with water, and dry again in vacuum	3.592	0.0048	64% (24hr)
11	Precipitate latex with ethanol, wash the precipitated rubber, then dry in vacuum	3.574	0.0039	98% (1.5hr)
12	Precipitate latex with $\text{H}_2\text{SO}_4$ , wash the precipitated rubber, then dry in vacuum	3.578	0.0039	99% (1.5hr)
13	Precipitate latex with $\text{CaCl}_2$ , wash the precipitated rubber, then dry in vacuum	3.578	0.0039	79% (0.5%)





**Figure 8-6** Solution hydrogenation results of different NBR solids (1)  
( $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  0.011g, other reaction conditions are listed in Table 8-2)



**Figure 8-7** Solution hydrogenation results of different NBR solids (2)  
(Less  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was used, reaction conditions are listed in Table 8-2)

It can be seen that NBR solids provided by LANXESS have the best hydrogenation performance. It is possible that LANXESS has a special process to precipitate and dry the latex to obtain the NBR solid, so any chemicals which have a detrimental effect on the hydrogenation are removed during such a process.

NBR solid directly dried from latex can not be hydrogenated (conversion is below 30% even after 20 hours). Better results can be achieved by using NBR solids from ethanol-precipitated latex or by using NBR solids which were washed with water. Based on the above results, it is proposed that this hazardous chemical is water-soluble and can be washed out using water or ethanol. So the impurities may be some surfactant/emulsifier(s) but we do not exactly know what those chemicals are.

Also, it was found that the best way to obtain good rubber for hydrogenation is to precipitate the NBR latex by adding  $\text{CaCl}_2$  or  $\text{H}_2\text{SO}_4$  solution into it as shown in Table 8-2.

#### **8.4.3 Effect of different latex treatments on hydrogenation**

From the previous latex hydrogenation and solution hydrogenation experiments, it is known that there are water-soluble impurities within the latex which lower the activity of catalysts. Different methods have been tried to treat the Perbunan latex in order to remove those impurities or to overcome their negative influences as shown in Table 8-3. In this way, the direct hydrogenation of NBR latex should take much less time and gel formation may not occur. The hydrogenation results from these studies are shown in Figure 8-8 and Figure 8-9.

It can be seen from Table 8-3 that the stability of the Perbunan latex decreased after it was treated with Dowex resins or silica gel beads. So the resin and silica gel are not suitable for treatment of the latex.

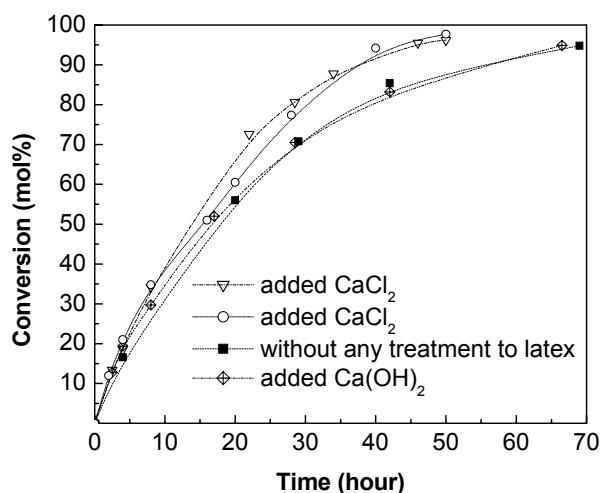
**Table 8-3 Hydrogenation of treated Perbunan latex at 145°C**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1%(w/w), TPP/rubber is 10%(w/w), 1000psi of  $\text{H}_2$ )

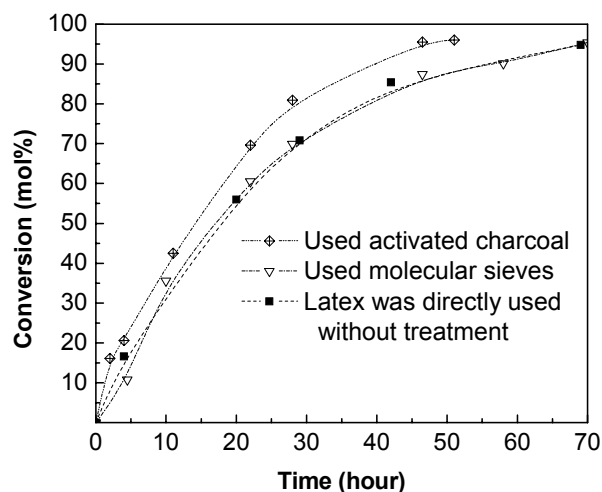
Latex treatment	Hydrogenation results
Added $\text{CaCl}_2$ into the diluted latex* (added 0.1ml of 10 wt% solution)	98% (50hr)
Added $\text{CaCl}_2$ into the diluted latex* (added 0.1ml of 10 wt% solution)	96% (50hr)
Added $\text{Ca}(\text{OH})_2$ into the diluted latex (added 0.01258g solid)	95% (66hr)
Added activated charcoals into diluted latex, stirred for 3 days then remove it before hydrogenation	96% (51hr)
Added molecular sieve into diluted latex, stirred for 3 days then remove it before hydrogenation	95% (70hr)
Added Dowex® resins into diluted latex, stirred for 3 days then remove them before hydrogenation**	Latex phase separated
Added silica gel beads into diluted latex, stirred for 3 days then remove them before hydrogenation**	Latex phase separated

\*: The latex system was destroyed after 1ml to 10ml of the  $\text{CaCl}_2$  solution (10 wt%) was added into the system. The latex system was stable after 0.1ml of the  $\text{CaCl}_2$  solution was added.

\*\*: The stability of latex was decreased and latex separated into clear water phase and rubber sediment phase after 4 hours of reaction.

**Figure 8-8 Hydrogenation of treated Perbunan latex at 145°C**

(Reaction conditions are listed in Table 8-3)



**Figure 8-9 Hydrogenation of purified Perbunan latex at 145°C**

(Reaction conditions are listed in Table 8-3)

From Figure 8-8 and Figure 8-9, it was found that the latex treated with molecular sieve and the latex treated with added  $\text{Ca}(\text{OH})_2$  have similar hydrogenation performance as the un-treated latex. However, the latex shows better hydrogenation performance if the latex was treated with activated charcoal or when a little  $\text{CaCl}_2$  was added into the latex <sup>[114]</sup>. Reproducible experimental results in Figure 8-8 confirm that the  $\text{CaCl}_2$  may capture some impurities within the latex and benefit the hydrogenation process.

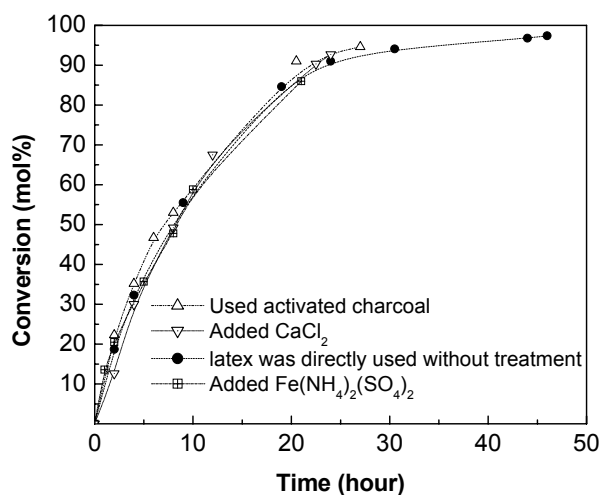
The addition of  $\text{CaCl}_2$  and activated charcoal has been shown to improve the hydrogenation rate at 145°C. More experiments have been carried out to test the effect of different additives at 160°C. Experimental details and results are shown in Table 8-4, Figure 8-10 and Figure 8-11.

**Table 8-4 Hydrogenation of treated Perbunan latex at 160°C**

(Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  $\text{RhCl}(\text{PPh}_3)_3/\text{NBR}$  is 1%(w/w), TPP/rubber is 10%(w/w), 1000psi of  $\text{H}_2$ )

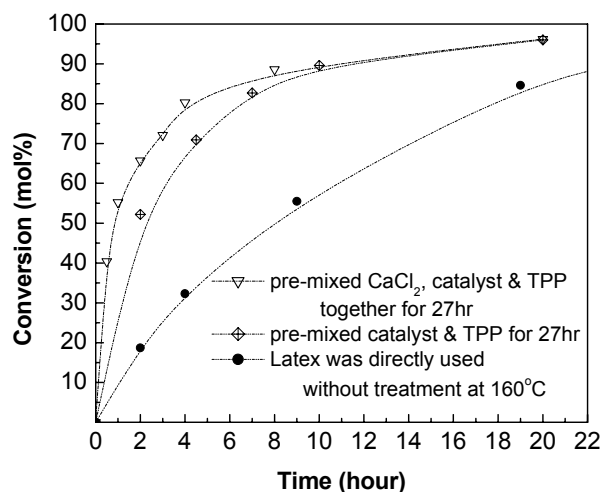
Latex treatment	Hydrogenation results
Added 0.01g $\text{CaCl}_2$ into the <b>diluted</b> latex*	93% (24hr)
Added 0.01g $\text{CaCl}_2$ into the <b>diluted</b> latex*; pre-mixed the catalyst and TPP with latex for 27 hr	96% (20hr)
Added 0.22g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ into the <b>diluted</b> latex under $\text{N}_2$ before hydrogenation	86% (23hr)
Added activated charcoal into 25ml Perbunan <b>original</b> latex, stirred for 3 days then remove it; then diluted the latex with 75ml water before hydrogenation	95% (27hr)

\*: The latex system was stable after this amount of  $\text{CaCl}_2$  solid was added.



**Figure 8-10 Hydrogenation of treated Perbunan latex at 160°C (1)**

(Reaction conditions are listed in Table 8-4; experiment at the same reaction conditions using the untreated latex is listed for comparison)



**Figure 8-11 Hydrogenation of treated Perbunan latex at 160°C (2)**

(Reaction conditions are listed in Table 8-4; experiment at the same reaction conditions using the untreated latex is listed for comparison)

From Figure 8-10, it can be concluded that at higher temperature (160°C), the use of activated charcoal,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  and  $\text{CaCl}_2$  did not result in an increase in the hydrogenation rate as observed at 145°C. This may be a result in that the mass transfer of catalyst into the latex particle was already improved at 160°C. However, when the  $\text{CaCl}_2$  was mixed with the original latex for a long enough time (27hours) prior to hydrogenation, the benefit of using it for hydrogenation at 160°C can still be seen as shown in Figure 8-11.

## 8.5 Gel formation problem

There is a gel formation problem for direct hydrogenation of NBR latex when  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  was used as the catalyst as shown in Table 4-3. The gel content was tested according to ASTM D3616-95. The cross-linking occurring during latex hydrogenation probably involves residual  $\text{C}=\text{C}$  reactivity and possibly is influenced by the presence of the CN group. The underlying mechanism of cross-linking and the kinetics of the gel formation are so far not clearly understood.

When Wilkinson's catalyst was used for latex hydrogenation, TPP was always added with Wilkinson's catalyst and there was no gel formation problem except for experiments in which the catalyst was pre-dispersed with the latex for 72 hours.

When the water-soluble  $\text{RhCl}(\text{TPPMS})_3$  or  $\text{RhCl}_3$  was added into NBR latex in the absence of TPP, gel occurred. However, in the presence of TPP, the latex hydrogenation using  $\text{RhCl}(\text{TPPMS})_3$  or  $\text{RhCl}_3$  can achieve high conversion without the gel formation.

Therefore, TPP is a key component for the latex hydrogenation process using Rh based catalysts in order to avoid the gel formation.

## 8.6 Summary

The present chapter begins with the analysis of problems which emerged from the research results previously presented in early chapters. These problems are related to the NBR latex, impurity issue and gel formation.

The properties of two grades of latices, the stability of latex before and after hydrogenation and the effect of latex change on hydrogenation were studied. Actually, research progress on this project has severely been affected by the aging problems of the NBR latex.

Observations from many latex hydrogenation results confirm that there are impurities within the polymer latex which decrease the latex hydrogenation rate, and the  $\text{OsHCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_2$  catalyst is more sensitive towards the impurity than Wilkinson's catalyst. Research regarding this harmful chemical inside the latex has shown that the impurity can be easily washed out using water or ethanol, suggesting that it maybe a surfactant used for emulsion polymerization. It was found that the latex hydrogenation rate can be increased if the latex is treated with activated charcoal or little amount of  $\text{CaCl}_2$  was added into the latex.

Also, experimental results using Rh based catalysts show that gel formation can be avoided by using the catalyst in the presence of TPP.

## Chapter 9

### Transport Processes in Latex Hydrogenation

An understanding of the mass transport processes occurring in the latex system during hydrogenation is essential in order to optimize the reaction conditions, to control the reaction systems, and to design commercial production processes. The latex hydrogenation is a complicated process which involves the mass transfer of hydrogen and the catalyst to the C=C bonds inside the polymer particles. Due to the high viscosity inside the polymer particles, mass transfer can be critical for the success of latex hydrogenation. Also, the apparent hydrogenation rate is a combination of the intrinsic reaction rate and the mass transfer rates in the latex hydrogenation system. This Chapter presents preliminary mass transport and kinetic studies for the catalytic latex hydrogenation process using Rh based catalysts.

#### 9.1 Introduction

The mass transport processes and kinetic study for the homogeneous solution hydrogenation of NBR have been studied in detail <sup>[3, 115]</sup>. The NBR polymer chains and the catalyst can move freely in the solution hydrogenation process, therefore mass transfer resistance can be minimized for such homogeneous processes.

The mass transport within the latex system during hydrogenation has only been reported for the non-catalytic latex hydrogenation process using diimide <sup>[71, 116]</sup>. A comprehensive simulation of the diimide hydrogenation process confirmed that the diimide diffusion interferes with the hydrogenation of the NBR latex, even though the average particle diameter is as small as 72 nm <sup>[71]</sup>.

For the catalytic latex hydrogenation process, the catalyst must be transferred from outside into the inside of the polymer particles. The catalyst can be distributed at three different locations in the polymer latex: in the bulk water phase, at the polymer particle surface (in the membrane-like surfactant molecule layer and at the surface of particles), and inside of the particles. If the catalyst only stayed in the water phase, no hydrogenation would happen because there are no C=C bonds in the aqueous phase. If the catalyst is only located at the surfaces of the latex particles, a high degree of hydrogenation can not be achieved since the catalyst has no chance to contact C=C bonds within the



inner layers of the latex particles. To fully hydrogenate the latex particles, the catalyst should be able to move inside of the latex particles. The hydrogenation reaction occurs radially from the particle surface inward.

Compared to diimide ( $N_2H_2$ ), the transition metal catalyst complexes have a bigger size. It can be expected that the mass transfer limitations for the transition metal catalyst complex with large dimension is even more severe due to the limited mobility of the catalyst molecules within the polymer particles.

## 9.2 Experimental

The following experiments were conducted in order to investigate the mass transfer of the catalyst from the bulk aqueous phase into the polymer particle phase: A certain amount of different catalysts or catalyst precursors were dispersed or dissolved into 50 or 100ml of de-ionized water in a 200ml three-neck round bottom flask. The aqueous system was agitated by a magnetic stir bar under  $N_2$ , and was heated by using an oil bath at 90 °C and using a condenser to reflux the water vapor. After one hour at 90°C, a certain amount of TPP was also added into the system. The system was kept at 90°C for one more hour with agitation and under  $N_2$ , and then was cooled down to room temperature. The changes of the system's appearance, such as color and phase distribution, were recorded in order to analyze the catalyst mass transfer.

To investigate the catalyst concentration inside the polymer particles, rubber samples were prepared and sent to LANXESS Inc. for Inductively Coupled Plasma (ICP) spectrometry analysis, which can provide information about Rh metal inside the polymer phase (weight of Rh metal in rubber to the weight of total rubber). These rubber samples were prepared in the following way: first, ethanol were added drop by drop into the obtained NBR latex sample until the latex was precipitated; then, after the precipitated rubber agglomerated into small crumbs, the crumbs were placed on a piece of wire gauze and rinsed using a large amount of water; after that, the crumbs were rinsed using a large amount of ethanol followed by water-rinsing again to make sure that all materials which were not inside the polymer network were removed; finally, the crumbs were compacted and dried in vacuum to obtain the solid rubber for analysis.

Further information on general experimental procedures has already been reported in Chapter 3.

## 9.3 Results and discussion

### 9.3.1 Mass transfer steps in the latex hydrogenation system

The latex hydrogenation of NBR is in a particle-water-gas ( $H_2$ ) three phase system. The unique character of this latex hydrogenation system is that the catalyst and  $H_2$  have to be transferred into the polymer particles surrounded by various surfactant molecules to access the C=C bonds.

The mass transfer steps of  $H_2$  in the latex hydrogenation include:

1. Transport of  $H_2$  from the bulk gas phase or the gas bubbles to the gas-water interface;
2. Mass transfer of  $H_2$  from the gas-water interface to the bulk of the aqueous phase;
3. Mass transfer from the bulk water phase or directly from the gas phase to the surface of polymer particles;
4. Intraparticle diffusion of  $H_2$  inside the polymer particles to access all C=C bonds;
5. Participation in the catalysis process for the hydrogenation of C=C bonds in the presence of the catalyst.

Step 1, 2 and 3 belong to the external diffusion while step 4 is internal diffusion. Based on the knowledge in the latex hydrogenation field accumulated <sup>[71]</sup> and from previous chapters in this thesis, the external or internal diffusion of the  $H_2$  should not be the rate limiting step for the overall hydrogenation process. The main concern for the whole process should be the catalyst mass transfer.

The mass transfer steps of the catalyst in the latex hydrogenation include:

- A. Transport of the catalyst from the bulk water phase to the polymer particle surface area;
- B. The catalyst permeates the membrane-like array of the surfactant molecules at the surface area of the polymer particles and contacts the polymer chains which are at the outer layer of the particles;
- C. Intraparticle diffusion of the catalyst within the polymer particles;
- D. At Step B or Step C, the hydrogenation reaction happens as soon as the catalyst contacts C=C bonds with a preferred confirmation (steric factors) in the presence of hydrogen (the catalysis mechanism of Wilkinson's catalyst is shown in Figure 5-1).

It can be seen from the above steps that transport processes in the latex hydrogenation are quite different from the normal homogeneous hydrogenation or heterogeneous hydrogenation processes. The main difference is that the catalyst diffuses into the polymer particles, contacts with the C=C bonds, and then hydrogenation happens in the presence of H<sub>2</sub>. Due to the surfactant molecule layer at the surface of polymer particles, and the long polymer chains entangled within the nano-size particle phase (high viscosity inside the particle), the slow catalyst diffusion rates cause the slow hydrogenation rate compared to those in the typical solution hydrogenation processes.

Also, the movement of the NBR chains, i.e., the moving of C=C bonds, inside of the particles should be considered. The latex hydrogenation reactions were conducted at the temperature over the T<sub>g</sub> (about -40~ -30°C for Perbunan NBR) and below the T<sub>m</sub> of the polymer, which means that the polymer chains coiled in the nano polymer particles can not move freely. Therefore, the chain conformational rearrangement is limited and the movements of C=C bonds are confined to their own local positions due to the inter-penetration and entanglement between polymer chains. The contact of C=C bonds with the catalyst should mainly depend on the diffusion of the catalyst.

Based on the above discussion, the reaction rate limiting step for latex hydrogenation should be the mass transfer of the catalyst, and the observed apparent hydrogenation rate is possibly determined by the catalyst mass transfer rate. More detailed study and analysis of the catalyst mass transport process in latex hydrogenation are listed below.

### **9.3.2 Catalyst mass transport process in latex hydrogenation using RhCl(PPh<sub>3</sub>)<sub>3</sub>**

When TPP was used for the solution hydrogenation of NBR, it only worked as the required free ligand to maintain the high catalytic activity of Wilkinson's catalyst. This was the only known role of free TPP for the polymer hydrogenation system before this latex hydrogenation research project was conducted. Actually, as we shall show later, the most important role of TPP for the latex hydrogenation system is that TPP is a "catalyst mass transfer promoter"; free TPP acts as the reagent (solvent) to facilitate phase boundary crossing of the catalyst dissolved in it.

Initially, the presence of TPP was believed to be beneficial for the catalyst mass transfer because the TPP may act as the plasticizer to swell the polymer; therefore, higher intraparticle diffusion rate of the catalyst could be achieved. However, from the experiment only pre-mixing TPP with the latex (see Figure 5-17), it seems that even if TPP may swell NBR particles (internal mass transfer can be

improved), the catalyst mass transfer from outside into the inside of polymer particles still exists as the key problem. So, the correct explanation for the role of TPP in the catalyst mass transport process should be: Wilkinson's catalyst was dissolved in the melted TPP phase at the reaction temperature of 130~170°C (the melting point of TPP is about 80°C), and then the catalyst was brought into the polymer particles together with the liquid TPP, because the hydrophobic liquid TPP tends to stay within the polymer particle phase.

This proposed role of TPP for catalyst mass transfer agent is consistent with the fact that the degree of latex hydrogenation was very low when no TPP was used with Wilkinson's catalyst (see Figure 5-4). Wilkinson's catalyst was suspended in bulk water phase as catalyst solid powder when no TPP was used. The contact of solid catalyst with the C=C bonds is extremely difficult due to the great mass transfer resistance to the solid catalyst. The high degree of hydrogenation can be achieved only when TPP was present in the latex system, since the solid catalyst was dissolved in liquid TPP which can be easily transferred into the polymer phase in liquid form. This suggests that the successful mass transfer of the catalyst from the bulk water phase to the polymer particle phase with the help of liquid TPP is the key factor to successfully realize the latex hydrogenation.

To further confirm the mass transport process of Wilkinson's catalyst in latex hydrogenation, more experiments are needed to find evidence for the transfer of Wilkinson's catalyst into the TPP phase and the presence of TPP with catalyst inside the polymer particles.

The following experiment was conducted in order to investigate the mass transfer of the catalyst from the bulk aqueous phase into the melt TPP phase (shown in Table 9-1).

**Table 9-1 Study of the catalyst transportation into TPP phase (System A)**

(Melting point of TPP is about 80°C, experiment was carried out under N<sub>2</sub>)

<i>Name for the system using Wilkinson's catalyst</i>	System A
<i>Dispersed catalyst into de-ionized water</i>	Added 0.03359 g of RhCl(PPh <sub>3</sub> ) <sub>3</sub> red solid powder into 100 ml H <sub>2</sub> O
<i>Agitation at room temperature</i>	Red solid particles suspended in H <sub>2</sub> O
<i>Heated to 90 °C for 1 hour before the addition of TPP</i>	Red solid particles suspended in H <sub>2</sub> O
<i>Kept at 90 °C for 1 hour after the addition of 0.35g of white crystal TPP solid (TPP was melt into small droplets)</i>	TPP droplets changed from colorless to brown; red solid particles suspended in H <sub>2</sub> O
<i>Cooled down to room temperature</i>	White TPP crystals contain red spots inside; red solid particles suspended in H <sub>2</sub> O

It was observed that soon after TPP was added at 90°C, it melted into liquid form and was dispersed as small droplets suspended in the aqueous phase due to the agitation in the system. From the color change of the TPP droplets at 90°C and the red spots (indication of the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst) embedded inside TPP solid after cooling down to room temperature, it is confirmed that the catalyst can be transferred from the aqueous phase into the TPP droplet phase.

From the FT-IR spectra for hydrogenated polymer samples, two characteristic peaks for TPP were found (see Appendix A). The absorption band at  $720\text{ cm}^{-1}$  corresponding to the saturated long  $-\text{CH}_2-$  chains was overlapped with that of the TPP. This confirms the presence of the TPP inside NBR polymer particles, which is caused by the diffusion of TPP with catalyst into the polymer particle phase.

The amount of Rh metal inside the polymer particles was analyzed by using Inductively Coupled Plasma (ICP) spectrometry method. The analysis results for these samples from the latex hydrogenation using  $\text{RhCl}(\text{PPh}_3)_3$  are listed in Table 9-2.

**Table 9-2 Analysis of Rh metal resided in polymer phase when  $\text{RhCl}(\text{PPh}_3)_3$  was used**

(Reaction conditions: Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml,  $\text{RhCl}(\text{PPh}_3)_3$  0.0357g, added TPP 0.357g, 1000psi of  $\text{H}_2$ )

T (°C)	Time (hour)	Degree of hydrogenation (mol%)	[Rh metal] in polymer phase (ppm)	Rh metal in polymer phase (g)*	Weight of Rh metal in polymer / total weigh of Rh metal added (%)*
160	0.5	11	56	0.000210	5.3
	1	13	77	0.000289	7.3
	5	49	130	0.000488	12.3
	24	93	240	0.000900	22.7
152	27	91	210	0.000788	19.8

\*: calculated values based on the weight of total polymer solid and the initial amount of Rh metal added into the system in the form of  $\text{RhCl}(\text{PPh}_3)_3$ .

It can be seen from Table 9-2 that more and more catalyst diffused into polymer particles with the increase in reaction time, and only a small percent of the total added catalyst diffused inside the

polymer particles even when a high degree of hydrogenation was achieved. Also, more catalyst can be found inside the polymer particles at 160°C within a similar reaction time due to the increased catalyst diffusion rate at higher temperature.

These results indicate that the hydrogenation rate should be increased if more catalyst could be transferred into the polymer particles rather than stay outside the polymer phase (suspend in water phase or attach to the reactor wall). The latex hydrogenation reaction was catalyst diffusion controlled. This idea is substantiated by experimental results shown in the following sections.

### **9.3.3 Catalyst mass transport process in latex hydrogenation using $\text{RhCl}(\text{TPPMS})_3$**

The mass transport process of the  $\text{RhCl}(\text{TPPMS})_3$  catalyst in latex hydrogenation was more complicated than that of Wilkinson's catalyst, because  $\text{RhCl}(\text{TPPMS})_3$  is water soluble but not oil soluble.

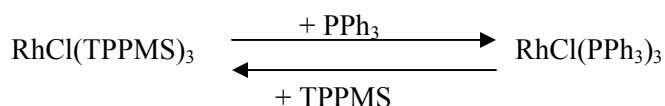
When water soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst was used for latex hydrogenation without TPP, the latex hydrogenation resulted in a gel problem or no hydrogenation occurred (see Table 6-1). When the water soluble Rh catalyst was used in the presence of TPP, a high degree of latex hydrogenation could be achieved with a higher reaction rate and without gel problem (see Figure 6-3). TPP seemed to be the gel inhibitor. However, as we found out later, the possible gel formation was alleviated because there was a transformation of the catalyst mass transfer process when  $\text{RhCl}(\text{TPPMS})_3$  was used in the presence of TPP.

The using of water soluble  $\text{RhCl}(\text{TPPMS})_3$  firstly makes the catalyst mass transfer from the bulk water phase to the polymer particle surface area much easier due to the fact that the water solubility of the  $\text{RhCl}(\text{TPPMS})_3$  provides better chances for the catalyst dissolved in water to contact the particle surface. Therefore, compared to the experiments using Wilkinson's catalyst, the initial hydrogenation rate increased significantly when water soluble  $\text{RhCl}(\text{TPPMS})_3$  was used (see Figure 6-2 and Figure 6-3). The initial hydrogenation rate is determined by the concentration of the Rh complex at the particle surface. Much higher  $\text{RhCl}(\text{TPPMS})_3$  concentration at the polymer particle surface caused the higher initial hydrogenation rate at the beginning of the whole reaction.

As discussed in Chapter 6, the water soluble catalyst dissociated at the particle surface, because those water-soluble TPPMS ligands have to stay out of the polymer phase while the Rh metal center of  $\text{RhCl}(\text{TPPMS})_3$  trends to diffuse into the polymer particles. The dissociation of  $\text{RhCl}(\text{TPPMS})_3$

provided active Rh metal species which can promote the polymer crosslinking. Also, the diffusion of the active Rh metal species into the polymer particles is very difficult. Therefore, high [Rh] was built up at the polymer particle surface when  $\text{RhCl}(\text{TPPMS})_3$  was used without TPP. This is why the initial hydrogenation rate was increased with gel formation while a high degree of hydrogenation could not be achieved.

The interesting question is why these problems no longer exist when TPP was used with  $\text{RhCl}(\text{TPPMS})_3$ . Actually, the  $\text{RhCl}(\text{TPPMS})_3$  catalyst can be formed by the reaction of Wilkinson's catalyst with TPPMS ligand. Ligand exchange reactions can happen between the two catalysts:



Based on this fact, if the water soluble  $\text{RhCl}(\text{TPPMS})_3$  is used in the presence of a large amount of TPP, TPP may replace the TPPMS ligand and cause formation of  $\text{RhCl}(\text{PPh}_3)_3$ . Therefore, the  $\text{RhCl}(\text{TPPMS})_3$  may contact with TPP droplets directly to form Wilkinson's catalyst; also, when the  $\text{RhCl}(\text{TPPMS})_3$  contacts the surface of polymer particles in the presence of TPP, the catalyst can transform into Wilkinson's catalyst rather than dissociate to promote gel. So, in the presence of TPP, there should be no dissociated Rh at the polymer particle surface or the concentration of such dissociated Rh species should be very low, which is why there was no gel formation any more.

This explanation is supported by the following experiment conducted in order to investigate the transfer of the Rh metal from the water soluble  $\text{RhCl}(\text{TPPMS})_3$  into the melt TPP phase (shown in Table 9-3).

It was found that the light yellow aqueous solution of  $\text{RhCl}(\text{TPPMS})_3$  faded into colorless solution at 90°C. After TPP was added, the Rh metal must be transferred into the liquid TPP phase. After the system was cooled down, the aqueous phase was colorless at room temperature, which means that no Rh metal coordinated with TPPMS in the aqueous phase or the concentration of  $\text{RhCl}(\text{TPPMS})_3$  in aqueous phase became very low. Combined with the color change of TPP crystals, it confirmed that Rh metal was transferred from  $\text{RhCl}(\text{TPPMS})_3$  into the TPP phase. This observation suggests that  $\text{RhCl}(\text{TPPMS})_3$  catalyst was transformed into Wilkinson's catalyst in the presence of TPP.

**Table 9-3 Study of the catalyst transportation into TPP phase (System B)**(Melting point of TPP is about 80°C, experiment was carried out under N<sub>2</sub>)

<i>Name for the system using RhCl(TPPMS)<sub>3</sub></i>	System B
<i>Dispersed catalyst into de-ionized water</i>	Dissolved 0.020g of RhCl(TPPMS) <sub>3</sub> white solid powder into 100ml H <sub>2</sub> O
<i>Agitation at room temperature</i>	Light yellow aqueous solution*
<i>Heated to 90°C for 1 hour before the addition of TPP</i>	Colorless aqueous solution
<i>Kept at 90°C for 1 hour after the addition of 0.35g of white crystal TPP solid (TPP was melt into small droplets)</i>	TPP droplets remained colorless; colorless aqueous phase
<i>Cooled down to room temperature</i>	Light yellow TPP crystals; colorless aqueous phase*

\*: The aqueous solution containing only TPPMS ligand is colorless. The color of aqueous solution containing RhCl(TPPMS)<sub>3</sub> depends on the concentration of the catalyst.

The amount of Rh metal inside the polymer particles was also analyzed for the samples from the hydrogenation using RhCl(TPPMS)<sub>3</sub> with TPP. The ICP spectrometry analysis results for these samples are listed in Table 9-4.

**Table 9-4 Analysis of Rh metal resided in polymer phase when RhCl(TPPMS)<sub>3</sub> was used**(Reaction conditions: Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, 160°C, 1000psi of H<sub>2</sub>)

RhCl(TPPMS) <sub>3</sub>	TPP	Time	Degree of hydrogenation	[Rh metal] in polymer phase	Rh metal in polymer phase	Weight of Rh metal in polymer / total weigh of Rh metal added
( g )	( g )	(hour)	(mol%)	(ppm)	(g)*	(%)*
0.0375	0	21	43 (gel)	190	0.000713	22.9
0.0375	0.358	45	92	260	0.000975	31.2
0.0251	0.358	23	81	170	0.000638	30.4

\*: calculated values based on the weight of total polymer solid and the initial amount of Rh metal added into the system in the form of RhCl(TPPMS)<sub>3</sub>.



It can be seen from Table 9-4 that more Rh metal can diffuse into the polymer particles when  $\text{RhCl}(\text{TPPMS})_3$  was used (compare to Table 9-2). When TPP was not used, 22.95% of added Rh metal initially in the form of  $\text{RhCl}(\text{TPPMS})_3$  was transferred into the polymer phase and caused gel (high [Rh] in the outer layer of particles), while when TPP was used together with  $\text{RhCl}(\text{TPPMS})_3$ , the percentage of Rh metal diffused into the polymer phase in the form of  $\text{RhCl}(\text{PPh}_3)_3$  was more than 30% of the total Rh metal input and caused no gel formation. These Rh metal residue analysis results also support the proposed catalyst mass transport process in latex hydrogenation using  $\text{RhCl}(\text{TPPMS})_3$ .

#### 9.3.4 Catalyst mass transport process in latex hydrogenation using $\text{RhCl}_3$

Compared to the use of Wilkinson's catalyst or water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalysts, the use of  $\text{RhCl}_3$  as the catalyst precursor for latex hydrogenation is better since the active catalytic species can be generated in situ. However, the mass transport process for the latex hydrogenation using  $\text{RhCl}_3$  is complicated. The study about the mass transport process in latex hydrogenation using  $\text{RhCl}_3$  is based on the discussion about the mass transfer of  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{RhCl}(\text{TPPMS})_3$  in the latex system.

The normal experimental process for latex hydrogenation using  $\text{RhCl}_3$  includes two steps: firstly the  $\text{RhCl}_3$  and TPP were mixed with the latex under  $\text{N}_2$  at  $100^\circ\text{C}$  for several hours in order to provide time for the in situ synthesis of active catalytic species for the latex hydrogenation; the second step was to increase the temperature to reaction temperature, and then  $\text{H}_2$  was introduced to initiate the hydrogenation.

As described in Chapter 7 (Table 7-1), when  $\text{RhCl}_3$  was mixed with latex without TPP, the latex formed gel before hydrogenation; when the  $\text{RhCl}_3$  catalyst was mixed with latex in the presence of TPP, no gel was found. So, TPP seemed to be the gel inhibitor.

Actually, as reported by Wilkinson<sup>[99]</sup>, Wilkinson's catalyst [ $\text{RhCl}(\text{PPh}_3)_3$ ] is prepared by refluxing  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with recrystallized triphenylphosphine (TPP) in ethanol, and TPP is the reducing agent. In our experiments, an excess of TPP can also act as the reducing agent which reduces the Rh(III) species generated from the dissociation of  $\text{RhCl}_3$  to synthesize  $\text{RhCl}(\text{PPh}_3)_3$  in situ for the latex hydrogenation. Like in the latex system using  $\text{RhCl}(\text{TPPMS})_3$ , the possible gel formation was alleviated because Rh metal was transformed into Wilkinson's catalyst in the presence of TPP.

Therefore, when  $\text{RhCl}_3$  was added into the latex with TPP under  $\text{N}_2$ , the water solubility of  $\text{RhCl}_3$  ensures that the dissociated  $\text{Rh(III)}$  can contact with TPP droplets and polymer particles swollen by TPP. The  $\text{Rh(III)}$  was transformed into Wilkinson's catalyst, and the catalyst was finally transferred into polymer particles for hydrogenation of  $\text{C}=\text{C}$  bonds inside the polymer particles.

However, not all of the Rh metal in  $\text{RhCl}_3$  can be transformed into Wilkinson's catalyst. Aggregated black metal particles were found at the bottom of the latex sample vials for these samples obtained from latex hydrogenation using  $\text{RhCl}_3$ . The observed black metal means that part of  $\text{RhCl}_3$  was not transformed into  $\text{RhCl(PPh}_3)_3$ , and therefore was not transferred into polymer particles. So this part of  $\text{RhCl}_3$  was reduced into Rh metal particles, suspended in aqueous phase, and finally settled to the bottom of the latex system.

This proposed mass transfer process for latex hydrogenation using  $\text{RhCl}_3$  is supported by the following experiments conducted in order to investigate the transfer of the Rh metal from the water soluble  $\text{RhCl}_3$  into the melt TPP phase (shown in Table 9-5).

It can be seen from the color change of System C in Table 9-5 that the concentration of  $\text{RhCl}_3$  decreased and some Rh metal was transferred into TPP, which suggests that Rh metal originally in the form of  $\text{Rh(III)}$  in water phase was transformed into  $\text{Rh(I)}$  metal center of the Wilkinson's catalyst in TPP phase. The same thing happened in System D and System E.

With the increased  $[\text{Rh}]$  and higher agitation speed, a more interesting phenomenon was observed in System D and System E: the final water phase changed into a yellow emulsion, and some red solid particles were found on the glass wall of the flask. These particles could be dried to obtain light brown solid powder. The light brown solid powder could not be dissolved in water at room temperature; however, it could be dissolved into MCB and form a light yellow solution at room temperature. It seems that the red solid particles on the glass wall should be Wilkinson's catalyst which was not inside the TPP phase. When the initial  $[\text{Rh}]$  was low, all of the produced Wilkinson's catalyst should reside inside the TPP phase, so no such red solid particles were found in System C. When the agitation speed was increased into 1200 rpm, the TPP might act as the surfactant and emulsify the system, so the clear aqueous phase became an emulsion state.

**Table 9-5 Study of the catalyst transportation into TPP phase (System C, D and E)**(Melting point of TPP is about 80°C, experiments were carried out under N<sub>2</sub>)

<i>Name for these systems</i>	System C (low [Rh])	System D (high [Rh])	System E (high [Rh])*
<i>Dispersed catalyst into de-ionized water</i>	Dissolved <b>0.014 g</b> of RhCl <sub>3</sub> ·3H <sub>2</sub> O dark red crystals into <b>100ml H<sub>2</sub>O</b>	Dissolved <b>0.028 g</b> of RhCl <sub>3</sub> ·3H <sub>2</sub> O dark red crystals into <b>50ml H<sub>2</sub>O</b>	Dissolved <b>0.028 g</b> of RhCl <sub>3</sub> ·3H <sub>2</sub> O dark red crystals into <b>50ml H<sub>2</sub>O</b>
<i>Agitation speed</i>	<b>600 rpm</b>	<b>1200 rpm</b>	<b>1200 rpm</b>
<i>Agitation at room temperature</i>	Reddish aqueous solution	Reddish aqueous solution	Reddish aqueous solution
<i>Heated to 90°C for 1 hour without TPP</i>	Colorless aqueous solution	Light yellow aqueous solution	Light yellow aqueous solution
<i>Kept at 90°C for 1 hour after the addition of 0.35g of white crystal TPP solid (TPP was melt into small droplets)</i>	TPP droplets changed from colorless to yellow; light yellow aqueous phase	TPP droplets changed from colorless to red; yellow aqueous <b>emulsion</b> phase	TPP droplets changed from colorless to orange; yellow aqueous <b>emulsion</b> phase
<i>Cooled down to room temperature</i>	Light yellow TPP crystals; light yellow clear aqueous phase	Red TPP crystals; yellow aqueous <b>emulsion</b> phase; Red solid particles on the glass wall**	Red TPP crystals; yellow aqueous <b>emulsion</b> phase; Red solid particles on the glass wall**

\*: System E repeated the System D and obtained the same result. The final aqueous phase in System D and System E appears to be in an emulsion form, which is quite different from the aqueous phase in System C.

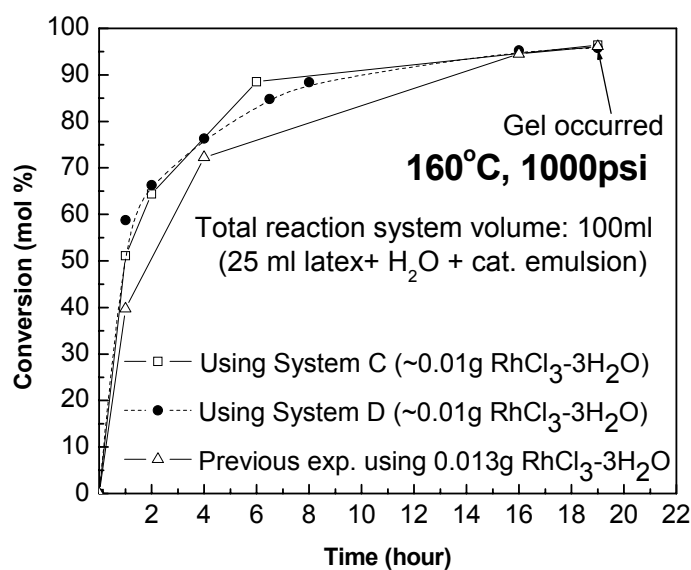
\*\* : Light brown solid powder was obtained by drying these particles.

System C, D, and E were used to conduct further latex hydrogenation experiments. The experimental details and results are listed below in Table 9-6, Figure 9-1 and Figure 9-2.

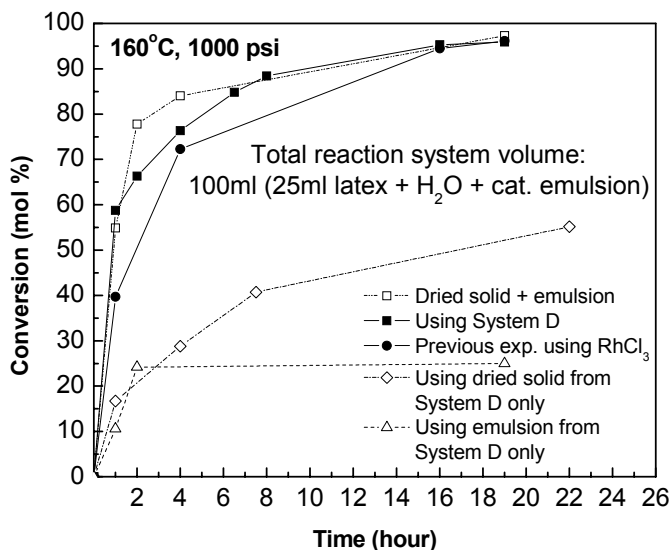
**Table 9-6      Latex hydrogenation using catalyst systems obtained from  $\text{RhCl}_3$**   
(Reaction temperature is  $160^\circ\text{C}$ ,  $\text{H}_2$  pressure is 1000 psi)

Experiment #	Experiment procedure
#1: Using System C	Mixed 75ml of System C (solution and TPP crystals) with 25ml latex under 150 psi of $\text{N}_2$ ;
#2: Using System D	Mixed 20ml of System D (yellow emulsion and TPP crystals) with (25ml latex+55ml $\text{H}_2\text{O}$ ) under 150 psi of $\text{N}_2$ ;
#3: Using <b>emulsion</b> from System D	Mixed 20ml of yellow emulsion from System D (containing no dried solid*) with (25ml latex+55ml $\text{H}_2\text{O}$ ) under 150 psi of $\text{N}_2$ ;
#4: Using dried solid* from System D	Mixed 0.01154g dried solid* from System D with (25ml latex+75ml $\text{H}_2\text{O}$ ) under 150 psi of $\text{N}_2$ ;
#5: Using dried solid* from System D and <b>emulsion</b> from System E	Mixed 0.01141g dried solid* from System D and 20ml emulsion from System E with (25ml latex+55ml $\text{H}_2\text{O}$ ) under 150 psi of $\text{N}_2$ ;

\*: the aqueous phase of System D was filtered to obtain some insoluble particles, and the particles attached to glass wall were also taken out. All of these particles are dried together to obtain the so called “dried solid”, which actually contains all insoluble materials from System D.



**Figure 9-1      Latex hydrogenation using catalyst systems obtained from  $\text{RhCl}_3$  (1)**  
(Reaction conditions are listed in Table 9-6)



**Figure 9-2 Latex hydrogenation using catalyst systems obtained from  $\text{RhCl}_3$  (2)**

(Reaction conditions are listed in Table 9-6)

It was found that all experiments in which  $\text{RhCl}_3$  was mixed with TPP before contacting with latex can achieve higher conversion with shorter reaction time. More catalyst can be transferred into the TPP phase when pre-mixing  $\text{RhCl}_3$  with TPP without the interaction of NBR latex. Then, when latex was added into the catalyst emulsion, more catalyst can be successfully transported into the rubber particles, as TPP tends to diffuse into the polymer phase and bring catalyst with itself. This confirms that the catalyst needs the help of TPP for transferring into the polymer particles. Also, a gel problem occurred when the concentration of the Rh metal in the polymer phase is high.

Also, from Table 9-5, it can be seen that the Rh metal which initially was present in the form of  $\text{RhCl}_3$  had a distribution equilibrium between the aqueous emulsion phase and the TPP phase. So, if the aqueous emulsion or the dried solid was used separately, the amount of Rh metal is not enough for latex hydrogenation. However, if they were used together (as they were in their original system), the hydrogenation reaction had a high reaction rate.

These experimental results which used catalyst emulsions obtained from mixing  $\text{RhCl}_3$  with TPP indicate that one active catalytic species can be directly synthesized from  $\text{RhCl}_3$  with TPP in the

absence of ethanol; therefore, it is better to directly use  $\text{RhCl}_3$  with TPP than use Wilkinson's catalyst or  $\text{RhCl}(\text{TPPMS})_3$  for the latex hydrogenation. The hydrogenation rate can be increased if the catalyst is already inside the TPP phase before the reaction begins.

The amount of Rh metal inside the polymer particles was also analyzed for the samples from the hydrogenation using  $\text{RhCl}_3$  with TPP. The ICP spectrometry analysis results for these samples are listed in Table 9-7.

**Table 9-7 Analysis of Rh metal resided in polymer phase when  $\text{RhCl}_3$  was used**

(Reaction conditions: Perbunan latex 25ml (solid content is 15g/100ml), added water 75ml, TPP 0.35g, 160°C, 1000psi of  $\text{H}_2$ )

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (g)	Time (hour)	Degree of hydrogenation (mol%)	[Rh metal] in polymer phase (ppm)	Rh metal in polymer phase (g)*	Weight of Rh metal in polymer / total weigh of Rh metal added (%)*
0.0127	19	96	770	0.002888	58.2
0.0128	27	96 (gel)	650	0.002438	48.6

\*: calculated values based on the weight of total polymer solid and the initial amount of Rh metal added into the system in the form of  $\text{RhCl}_3$ .

It can be seen from Table 9-7 that much more Rh metal can diffuse into polymer particles when  $\text{RhCl}_3$  was used with TPP (compare Table 9-2 and Table 9-4); the percentage of Rh metal diffused into the polymer phase in the form of  $\text{RhCl}(\text{PPh}_3)_3$  was about half of the total Rh metal input. The increased [Rh] inside the polymer particle caused gel formation, when the reaction time was more than 20 hours (also see in Figure 7-1). These Rh metal residue analysis results indicated that the active Rh species generated in situ from the reaction of  $\text{RhCl}_3$  and TPP in the latex system have much better chances to diffuse into the polymer particles.

### 9.3.5 Improve the mass transport for latex hydrogenation using $\text{RhCl}_3$

Based on the previous discussion about the mass transport process for different Rh based catalysts in latex hydrogenation, it was shown that the hydrogenation rate can be increased if the catalyst is already inside the TPP phase before the reaction begins.

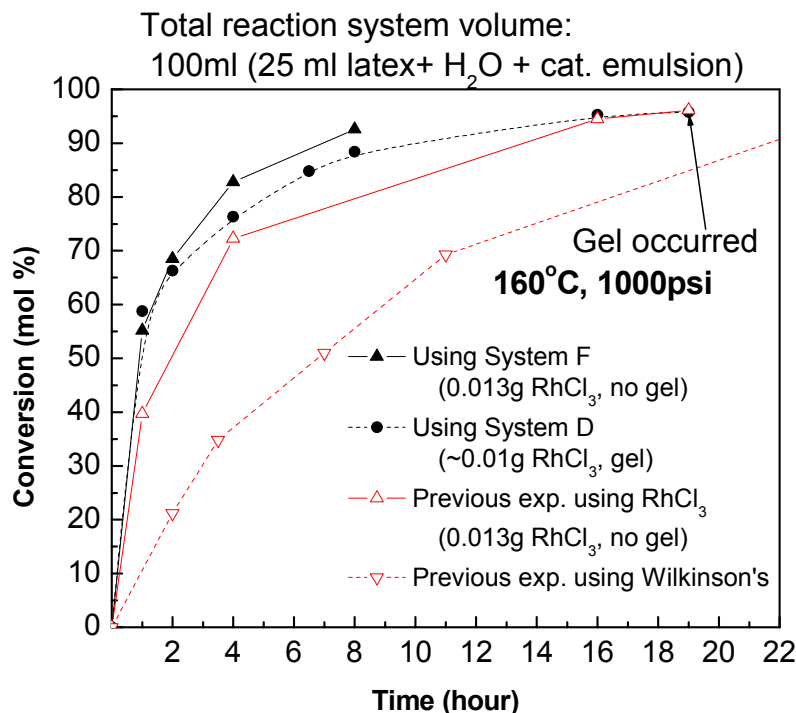
To prove this idea, the following method was used to generate catalyst in situ and transfer the catalyst into TPP before mixing with the latex; also, the catalyst within such a system was pre-dispersed with latex before introducing hydrogen to initiate the latex hydrogenation (experimental process and results are listed in Table 9-8 and Figure 9-3).

**Table 9-8 Study of the catalyst transportation into TPP phase (System F)**

(Melting point of TPP is about 80°C, experiments were carried out under N<sub>2</sub>)

<i>Name for the system using RhCl<sub>3</sub></i>	System F
<i>Dispersed catalyst into de-ionized water</i>	Dissolved <b>0.014 g</b> of RhCl <sub>3</sub> ·3H <sub>2</sub> O dark red crystals into <b>50ml H<sub>2</sub>O</b>
<i>Agitation at room temperature (1200 rpm)</i>	Reddish aqueous solution
<i>Heated to 90°C for 1 hour before the addition of TPP</i>	Colorless aqueous solution
<i>Kept at 90°C for 1 hour after the addition of 0.35g of white crystal TPP solid (TPP was melt into small droplets)</i>	Orange TPP droplets suspended in a yellow aqueous <b>emulsion</b>
<i>Added latex into the system after the in situ synthesis of active catalytic species</i>	Added (25ml latex + 25ml H <sub>2</sub> O) at 90°C and stirred 1 hour; then cooled down to room temperature and transferred the latex system into a high pressure Parr reactor for hydrogenation

It was found that **92% degree of hydrogenation could be achieved in 8 hours without gel formation**, which is the best solvent-free latex hydrogenation result reported so far.



**Figure 9-3 Latex hydrogenation using RhCl<sub>3</sub> with improved mass transfer**

(Reaction conditions are listed in Table 9-8, other experimental results are listed for comparison)

## 9.4 Summary

For latex hydrogenation, the catalyst must diffuse into the polymer particles and contact C=C bonds in the presence of hydrogen. During this mass transfer process, TPP acts as a “catalyst mass transfer promoter”, which is the key to the success of the latex hydrogenation. In the presence of TPP, it facilitates the phase boundary crossing of the catalyst dissolved in it, so the latex hydrogenation becomes possible.

From Chapter 5 to Chapter 7, three types of Rh based catalysts were used. The proposed roles of TPP for mass transport of these different catalysts are classified into the following three situations:

Situation A (when Wilkinson’s catalyst is used): the role of TPP in the catalyst mass transport aspect is simply the catalyst “carrier”;



Situation B (when water soluble Rh catalysts, such as  $\text{RhCl}(\text{TPPMS})_3$ , are used): TPP takes the positions of the water soluble ligands, and therefore transfers the water soluble catalyst into the Wilkinson's catalyst; then, like the last runner in a relay race team, TPP carries Wilkinson's catalyst into the polymer phase to access C=C bonds as in Situation A;

Situation C (when  $\text{RhCl}_3$  is used): TPP firstly acts as the reducing agent to reduce the Rh(III) to Rh(I), and then forms Wilkinson's catalyst in situ for the latex hydrogenation;

With an understanding of the catalyst mass transport process in the latex system, a 92% degree of hydrogenation was achieved within 8 hours without gel formation by using the optimized process for the latex hydrogenation.

## Chapter 10

### Conclusions and Recommendations for Future Research

#### 10.1 Conclusions

##### 10.1.1 Comparison of catalysts for latex hydrogenation

Many different catalysts were used in this research, which are listed below in Table 10-1.

**Table 10-1**      **Comparison of different catalysts for latex hydrogenation**

	<i>Require solvent ?</i>	<i>Degree of hydrogenation</i>	<i>Gel formation</i>	<i>Note</i>
$\text{OsCl}(\text{CO})(\text{O}_2)(\text{PCy}_3)_3$	Yes	> 95%	Easy to form gel	Sensitive to impurities
$\text{RhCl}(\text{PPh}_3)_3$	No	> 98%	No gel	Good for latex hydrogenation
$\text{RhCl}(\text{TPPMS})_3$	No	> 92%	No gel if TPP is used	Higher reaction rate
$\text{RhCl}_3$	No	> 96%	No gel if TPP is used and reaction time is not too long	Highest reaction rate
Rh colloid	No	< 50%	No gel if TPP is used	/

It can be seen that a series of Rh based catalysts are suitable catalysts for the latex hydrogenation of NBR. The addition of triphenylphosphine (TPP) as the co-catalyst ligand for these Rh based catalysts is crucial for the hydrogenation of NBR latex to attain a high degree of hydrogenation, without gel formation.

More than 90% degree of hydrogenation could be achieved by using the Os catalyst within a suitable range of system compositions (volume ratio of latex/added water/MCB is 20/50/5~10) and experiment conditions ( $T=100^{\circ}\text{C}$ ).

In the presence of TPP, NBR latex could be hydrogenated to more than 90% degree without solvent after about 80 hours at  $145^{\circ}\text{C}$  when using Wilkinson's catalyst at a catalyst to NBR rubber ratio of 1 wt%. The final product was a stable HNBR latex without gel formation. It was found that higher latex hydrogenation rates could be obtained, especially before reaching 80% conversion, if the  $\text{RhCl}(\text{PPh}_3)_3$  catalyst was pre-mixed into the latex with TPP before introducing hydrogen gas to initiate the reaction. More than 92% degree of hydrogenation could be achieved within 22 hours by using this catalyst pre-dispersion method at  $160^{\circ}\text{C}$ .

When water-soluble  $\text{RhCl}(\text{TPPMS})_3$  catalyst was used in the presence of TPP, the Rh complex had a much better chance to reach the water-polymer interface and to cross into the polymer particles. The latex hydrogenation could reach more than 90% degree of hydrogenation after 20 hours at  $160^{\circ}\text{C}$  under 1000 psi of  $\text{H}_2$  using 0.00003 mol of the catalyst with TPP.

The experiments using  $\text{RhCl}_3$  as the catalyst precursor showed the overall best performance for latex hydrogenation of NBR. More than a 96% degree of hydrogenation could be achieved without any gel problem after 19 hours when  $\text{RhCl}_3$  was used with TPP.

### **10.1.2 Optimization of the latex hydrogenation system**

The optimization of the latex hydrogenation system includes the screening of catalysts, overcoming the impurity issue, and improving the catalyst mass transfer. A 92% degree of hydrogenation was achieved within 8 hours without gel formation by using the optimized experimental operation for the latex hydrogenation using  $\text{RhCl}_3$  with TPP.

Observations from many latex hydrogenation results confirmed that there are impurities within the polymer latex which decreased the latex hydrogenation rate. Research regarding this harmful chemical inside the latex was carried out. It was shown that the impurity could be easily washed out using water or ethanol, suggesting that it maybe a surfactant used for emulsion polymerization. It was found that the latex hydrogenation rate could be increased if the latex was treated with activated charcoal or a small amount of  $\text{CaCl}_2$  was added into the latex.

The transfer of the catalyst from outside of the polymer particles into the polymer particles and the transfer of the catalyst within the particles are the rate limiting steps for the latex hydrogenation process. TPP was found to be the carrier for different Rh based catalysts, which dissolves and transforms these catalysts into active catalyst species to facilitate the catalyst mass transportation and to prevent the gel formation.

### **10.1.3 Milestones and contributions**

As a result of this research project, new latex hydrogenation technologies including highly efficient catalytic systems, suitable methods to treat latex before hydrogenation and operations to improve hydrogenation rates were successfully developed.

Using these technologies, the direct catalytic hydrogenation of NBR latex was successfully realized with a degree of hydrogenation higher than 95% without gel formation. This new NBR latex hydrogenation process fulfills all major requirements for developing a solvent-free polymer latex hydrogenation route, which is a significant milestone for the improvement of this polymer modification technology.

With the progress of this research project, more knowledge was accumulated for the scientific field of diene-based polymer modification. This research project proved that the catalytic ability of homogenous Rh based catalysts for polymer hydrogenation does not depend on the presence of solvent, and latex hydrogenation can be achieved by solving the catalyst mass transfer problem. Also, the finding of TPP's role as the "catalyst mass transfer promoter" is a breakthrough and an important milestone for the research field related to the hydrogenation of unsaturated diene-based polymers in latex form. The idea of using suitable chemical(s) as "catalyst carriers" to facilitate the phase boundary crossing of catalysts may contribute to solve mass transfer problems in other multi-phase systems.

## **10.2 Recommendations for further research**

### **10.2.1 Further investigation of the catalytic system**

There are still many issues needed to be investigated for the development of latex hydrogenation process:

- Find the minimum amount of TPP needed for successful latex hydrogenation. The TPP which remains in the polymer particles may affect the properties of the final HNBR products, so optimization of the TPP/rubber ratio is required;
- Try to use the water soluble  $\text{RhCl}(\text{TPPTS})_3$  catalyst for latex hydrogenation and compare its performance with  $\text{RhCl}(\text{TPPMS})_3$ ;
- Try more experiments using Rh colloid and TPP. There are other ways in which to make colloid solutions <sup>[117]</sup>, so more study is needed;
- Screen more catalysts for the latex hydrogenation. Based on Gilliom's report about the bulk hydrogenation of olefinic polymers using Ir based Crabtree catalysts <sup>[46]</sup>, Ir based catalysts might be another promising group of catalysts for latex hydrogenation;
- Carry out a more fundamental study about the TPP, Rh(III), Rh(I) exchange relationship, using TEM to study the metal distribution inside the polymer particles, and use NMR to analyze the structure of the active Rh species for latex hydrogenation;
- Conduct a systematic kinetic and mechanism study for the latex hydrogenation system in order to further optimize the latex hydrogenation.

### **10.2.2 Modify NBR latex and synthesize special latex for catalytic hydrogenation**

The negative effect resulting from harmful impurities within the latex may be overcome by adding some additives to the NBR latex. Besides those that have been attempted as shown in Chapter 8, more experiments are needed to modify NBR latex for obtaining better hydrogenation rate:

- Adjust the pH value of the latex system to find suitable aqueous environment for these water soluble catalysts;

- Different NBR latices are needed in order to compare the effect of different surfactants, solid content and [CN] on hydrogenation;
- As discussed in Section 6.3.2, NBR latex with smaller polymer particle size may benefit the hydrogenation process. Therefore, the synthesis of NBR latex with smaller polymer particle size should be considered.

### 10.2.3 Catalyst separation study

After latex hydrogenation, the catalyst was left in the final product. An important concern of the direct catalytic latex hydrogenation is the metal residues in the resulting polymer.

There are no research reports directly dealing with separation of catalyst from polymer emulsions, but there are a few patents for removing catalysts even from polymer solutions. For solution hydrogenation, two main methods are used for the removal of metal catalysts: the first method is to precipitate the catalyst from the solution and then to separate it by filtration or gravity settling; the other one is to adsorb the catalyst from the polymer solution by ion-exchange resins or other absorbents which have an affinity for the metal catalyst. Nguyen et al patented a process for the removal of iron- and rhodium-containing residues from a solution of hydrogenated nitrile rubber by using a macro-porous, mono-dispersed ion-exchange resin <sup>[118]</sup>. Fuji Sumiichi et al <sup>[119]</sup> reported a method for efficiently recovering a rhodium catalyst for a hydroformylation reaction. They added water to mix with the obtained reaction liquid to form an emulsion and the separation of the catalyst component was accelerated by a coalescing agent. Wilkey patented a process to remove hydrogenation catalysts from polymer solutions by the treatment with ammonia and carbon dioxide <sup>[86]</sup>.

The levels of the Rh residue inside the polymer phase were found to be more than 500 ppm for some experiments. The level of Rh residue should be less than a few ppms. Studies about the possibility of transfer of the Rh back to the water phase by adding TPPMS or TPPTS after reaction are needed. The catalyst separation study is the focus of further latex hydrogenation work.

#### **10.2.4 Exploration of the potential application for other latex systems**

Before the success of solvent-free NBR latex hydrogenation, a polymer hydrogenation process usually includes dissolution of polymer, hydrogenation, separation and drying. The extra cost for hydrogenation is always a major factor that inhibits the application of hydrogenated polymers. As a result, the hydrogenation of polymer is utilized in an industrial process only when polymer with a particular structure is difficult to synthesize by polymerization alone. With the development of latex hydrogenation technology, the polymer hydrogenation process should become more and more commercially viable due to the reduction of production cost and the demand for high performance polymeric materials.

The Rh based catalysts were found to be excellent catalysts that can be used in a NBR latex hydrogenation system. It is worthy of exploring its application for other latex systems, such as SBR latex and natural rubber latex.

## Nomenclature

ACN:	acrylonitrile
ABS:	acrylonitrile-butadiene-styrene
ASTM:	American standard test method
COD:	1,5-cyclooctadiene
DPM:	diphenyl phosphino benzene <i>m</i> -sulphonate
FTIR:	Fourier transform infrared
HEXNa:	$\text{Ph}_2\text{P}-(\text{CH}_2)_5-\text{CO}_2\text{Na}$
HNBR:	hydrogenated nitrile butadiene rubber
KOH:	potassium hydrate
MCB:	monochlorobenzene
MEK:	methyl ethyl ketone
NBR:	nitrile butadiene rubber
NR:	natural rubber
PBD:	polybutadiene
PCy <sub>3</sub> :	tricyclohexylphosphine
PETPP:	polyether-substituted triphenylphosphine
PPh <sub>3</sub> :	triphenylphosphine (TPP), i.e., $\text{P}(\text{C}_6\text{H}_5)_3$
psi:	$\text{lb}_f/\text{in}^2$
PVP:	polyvinyl pyrrolidone
rpm:	rotation per minute
SBR:	styrene-butadiene rubber
SBS:	styrene-butadiene-styrene block copolymer
SDS:	sodium dodecyl sulfate
THF:	tetrahydrofuran
TPPMS:	monosulphonated-triphenylphosphine
TRPTC:	thermo regulated phase transfer catalyst
TPPTS:	trisulphonated-triphenylphosphine



## Appendix A

### Determination of the Degree of Hydrogenation Using the Raw Spectroscopic Data

In order to investigate the degree of hydrogenation for samples periodically obtained at time intervals during reactions, a Bio-Rad FTS 3000MX spectrometer was used for Fourier transform infrared (FTIR) analysis of these samples.

A standard test method for the determination of residual unsaturation in HNBR by infrared spectrophotometry was already established and described in the American Standard Test Method (ASTM) D5670-95, which is based on infrared examination of rubber films cast from HNBR solution. The degree of hydrogenation was calculated based on the peak strength from the IR spectrum. The FTIR peak assignments for NBR and HNBR are listed in Table A-1.

**Table A-1 Characteristic peaks for NBR and HNBR FTIR spectrum\***

Wave number (cm <sup>-1</sup> )	Peak assigned to	Note
<i>Around 3500</i>	<i>Primary or secondary amines</i>	<i>Peaks appear if the -CN in NBR polymer chains is reduced by hydrogenation</i>
2236	-CN	This peak is used as the internal standard for the calculation of degree of hydrogenation
970	=CH- in 1,4-trans unit	This peak decreases in strength and disappears during the hydrogenation
920	=CH- in 1,2 unit	This peak decreases in strength and disappears during the hydrogenation
750	=CH- in 1,4-cis unit	This peak decreases in strength and disappears during the hydrogenation
723	Saturated -[CH <sub>2</sub> ] <sub>n</sub> - unit (n>4) in HNBR	This peak appears and increases in strength during the hydrogenation

\*: based on the information given in ASTM D5670-95 and from one paper published by S. Bhattacharjee, A. K. Bhowmick and B. N. Avasthi (*Ind. Eng. Chem. Res.* **1991**, 30, 1086-1092)

According to ASTM D5670-95, the calculation of the degree of hydrogenation is based on corresponding absorbances of the important peaks at 2236, 970 and 723  $\text{cm}^{-1}$  from the IR-spectrum:

(A723 from peak at 723  $\text{cm}^{-1}$ , A970 from peak at 970  $\text{cm}^{-1}$ , and A2236 from peak at 2236  $\text{cm}^{-1}$ )

Let  $A(723) = A_{723}/A_{2236}$ ;

$A(970) = A_{970}/A_{2236}$ ;

$K(723) = 0.255$ , which is a constant specific to peak at 723  $\text{cm}^{-1}$ ;

$K(970) = 2.3$ , which is a constant specific to peak at 970  $\text{cm}^{-1}$ ;

$F = 1 + A(970)/K(970) + A(723)/K(723)$ ;

Then, the relative amount of C=C remaining in HNBR is:

$$C(BR) = A(970)/[K(970)F],$$

and the relative amount of methylene groups formed through hydrogenation of C=C in NBR is:

$$C(HBR) = A(723)/[K(723)F].$$

Finally, the degree of hydrogenation can be calculated as:

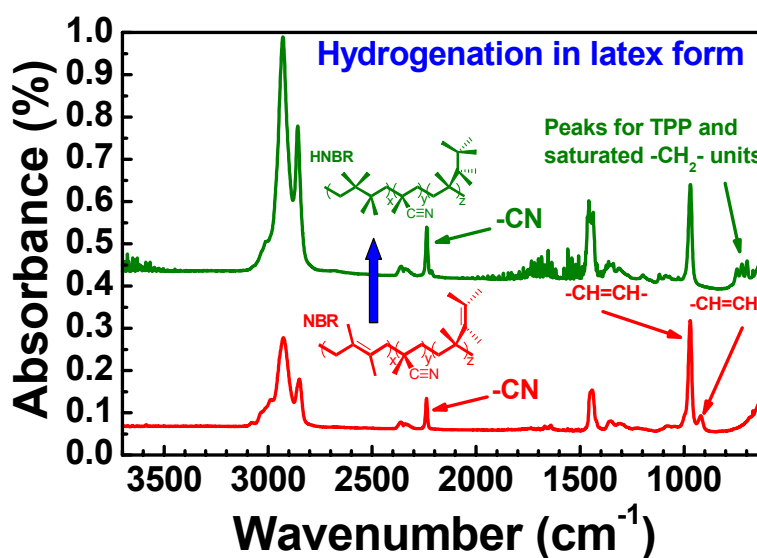
$$\text{Degree of hydrogenation (mol \%)} = 100 - \frac{C(BR)}{C(BR) + C(HBR)} \times 100$$

It can be seen from the above process that the accuracy of the calculated degree of hydrogenation depends on how to prepare the polymer samples in order to acquire good IR spectrum in which the absorbances for the peaks at 2236, 970 and 723  $\text{cm}^{-1}$  can be precisely measured.

In this research, samples were obtained in latex form. So, these samples were firstly used in latex form for FTIR analysis with the following procedures: One drop of the latex was placed on the face of a Zn-Se plate (transmission range of the Zn-Se plate is 20,000 ~ 450  $\text{cm}^{-1}$ ); then the latex on the plate was dried in vacuum to obtain a thin polymer film on the plate; finally the plate was mounted onto the sample holder for the FTIR analysis. Unfortunately, the thickness of the polymer film was hard to control in this way. Therefore, the IR spectra obtained by directly casting latex onto Zn-Se plate are not good.

Then, the latex samples were precipitated to obtain rubber solid which was dissolved in solvent in the following steps to prepare the samples for FTIR analysis: the sample in latex form was

precipitated by slowly dropping 50 ml of methanol from a dropping funnel into the latex sample under agitation with a magnetic stirrer; after the water and solvent were decanted, the precipitated rubber in the form of agglomerated small crumbs was washed with 50 ml of methanol; then, the crumbs were compacted and dried under vacuum to obtain solid rubber; finally, the dried solid rubber was dissolved in 10 ml of methyl ethyl ketone (MEK), and a polymer film was cast onto a potassium bromide disc for FT-IR analysis. The IR spectrum for one latex sample prepared in this way is shown in Figure A-1.

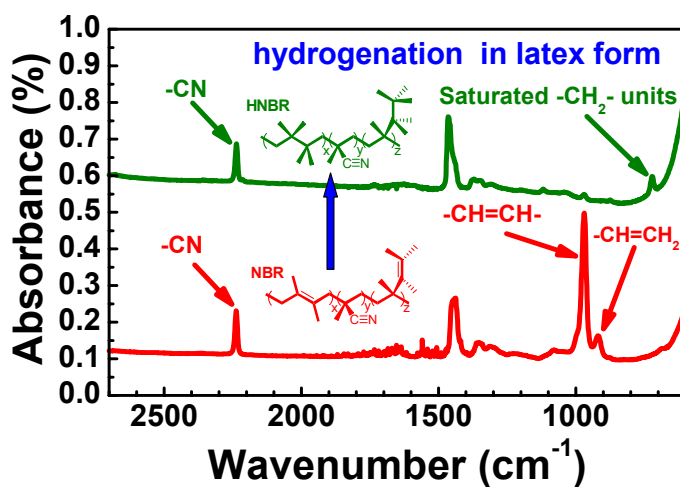


**Figure A-1 IR spectra for NBR and HNBR in the presence of TPP peaks**

It was found from Figure A-1 that two characteristic peaks for TPP appeared around  $720\text{ cm}^{-1}$  in the IR spectrum for the hydrogenated polymer sample. When methanol was used to precipitate the latex and wash the agglomerated small polymer crumbs, methanol could dissolve these TPP molecules which were not within the polymer network; therefore, the TPP remained with final rubber solid must originally reside within the polymer particles when NBR was still in latex form. The absorption band at  $723\text{ cm}^{-1}$  corresponding to the saturated long  $-\text{CH}_2-$  chains was overlapped with

the peaks of TPP, which caused difficulties to measure the real absorbance of the  $723\text{ cm}^{-1}$  peak for saturated  $-\text{CH}_2-$  unit.

In order to solve this problem, the latex samples were treated in the following process to remove all TPP: the sample in latex form was precipitated by slowly dropping 50 ml of methanol from a dropping funnel into the latex sample under agitation with a magnetic stirrer; after the water and solvent were decanted, the precipitated rubber in the form of agglomerated small crumbs was dissolved in 20 ml of MEK; then, the rubber solution was precipitated by slowly dropping methanol into the solution under agitation until enough rubber crumbs were obtained again; after decanted the solvents which contain all TPP, the crumbs were washed with methanol again, and then dried under vacuum to obtain solid rubber; finally, the dried solid rubber was redissolved in 10 ml of MEK, and a polymer film was cast onto a potassium bromide disc for FT-IR analysis. The IR spectra obtained by using this sample preparation method is shown in Figure A-2.



**Figure A-2** IR spectra for NBR and HNBR obtained after removing TPP peaks

It can be concluded from Figure A-2 that TPP was totally removed from rubber by using this special sample preparation method. Therefore, all samples were finally prepared according to this method, and the absorbance data for the peaks at  $2236$ ,  $970$  and  $723\text{ cm}^{-1}$  collected by the Bio-Rad FTS 3000MX spectrometer was used to calculate the degree of hydrogenation.

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